CHAPTER – 1

1.0 INTRODUCTION

Surface coatings will deal with coatings, will provide considerable benefits to both the scientists and technologist in industries like paints and especially epoxy and polyurethane based coatings. Novel messages have been reflected the greater movement from polymer to solvent based coating systems. It has been added in response to current concerns about the commercial point of view. The surface coating industry is one of the oldest industries dating back some 20,000 years.

The world wide coatings industry today is a $ 40 Billion business consisting of architecture, industrial, special-purpose, product-finish and maintenance coatings. The growth rate for the next decade is expected to average 7 percent annually. Although, this is now under a cloud of uncertainty because the oil situation is driving prices up to a point where manufacturers are having difficulty in maintaining margins and passing on a cost increases to their customer. This introductory chapter explains all the basics of coating industry and the significant advances of performance coatings like epoxy and polyurethane in the coating industry.
1.1 Surface coatings and its classifications

A coating is a barrier used to separate two highly reactive materials. A coating must be a completely continuous film in order to fulfill its function. Any imperfection becomes a focal point for corrosion and the breakdown of the structure. Paint can be defined as a fluid material which can spread over a surface in the form of a thin layer, forms a solid, adherent and cohesive film\(^1\). Paints can be classified as decorative/architectural paints and industrial paints. As the names suggest, decorative paints are mainly used for household and construction purposes while industrial paints are used for the coatings of industrial products. On the basis of thinners, paints in turn classified into two types namely solvent based paints and water based paints. The fluid paints consist of the following ingredients:

- Pigments and extenders
- Binders
- Solvents
- Additives

Most of the coatings are described as solvent solutions or dispersion of some sort of binding medium. Usually called as resin in which is dispersed the solid inorganic, organic discrete phase known as the pigment. Depend upon the proportions of these resources can be obtained films with any desired physical and variety of application characteristics.
Among the various types of coatings, epoxy and polyurethane surface coatings are employed for the protection of metals and woods due to their best performance.

1.1.1 Pigments and extenders

Pigments are solid particles, insoluble in the resin, solvents used in the paints and capable of being dispersed in the paint constituents to give utmost benefits in terms of the required properties. The physical properties of the pigments such as refractive index and color have profound effects on the aesthetic properties of paint films. Some pigments like Zinc chrome, zinc phosphate etc., are incorporated in the primers for the corrosion protection purpose. Extenders are mainly used in the primers for a wide range of purposes including opacity /obliteration to facilitate sanding. Pigments can be classified into two major classes. The main pigments are added to the formulation, whereas, auxiliary pigments may be added to the paints to provide economic and also modify the reflectance of the coated film (called Gloss). Based on the origin of pigments, it has been further classified as inorganic and organic pigments. The pigments are generally synthetic. Pigments appear in a variety of shapes, including spherical, nodular (rounded but not necessarily spherical), platy (flat or lamellar), acicular (needle-like), fibrous (stringy) or cubic (chunky, block-like lumps). This wide variety of shapes provides the paint formulator with an abundant source of engineering materials for designing or optimizing specific attributes of performance or aesthetics.
1.1.2 Resins

A resin (binder, vehicle, film former, medium, polymers are the other names used for resin in the industry) must get rehabilitated to an impenetrable, solid, adherent film with each and every one of substrates. It provides uniformity and coherence to any coating system. The binder's ability to form a dense, packed film is directly related to its molecular size and complexity. Except color, the physical properties are based on the binder's performance. The molecular structure of the polymer can also affect the water permeability and absorption. Spadafora noted that, binders exhibiting primary valency bonds with a metal substrate (Eg., epoxy) have much greater resistance to disbondment under wet conditions than do binders bearing only secondary valence attractions for the surface (Eg., silicone).

A variety of resins / binders are used in the paint formulation. These are natural and synthetic. Synthetic resins and many of the natural resins are polymeric in nature. Hence, knowledge of polymer science is necessary to understand the binder chemistry. Some of the examples of polymeric natural resins include cotton, ether, cellulose, rubber, silk, starch etc. The synthetic resins used as a binder in coating formulations could be macro molecular or low molecular weight compounds. Low molecular weight polymeric molecules are usually referred as oligomers. Oligomers undergo curing or cross linking reactions on application and forming macromolecules of three dimensional networks.
Binders are classified according to their molecular weights. Thus low molecular weight will not form solid films normally without further chemical reaction form on first class. High molecular weight polymers would form useful films without further chemical reaction form in the second class.

**TABLE 1.1 Classification of binder based on molecular weight**

<table>
<thead>
<tr>
<th>Low molecular weight</th>
<th>High molecular weight</th>
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</thead>
<tbody>
<tr>
<td>Oleoresinious binders</td>
<td>Nitrocellulose</td>
</tr>
<tr>
<td>Alkyds</td>
<td>Solution vinlys</td>
</tr>
<tr>
<td>Polyurethanes</td>
<td>Solution acrylics</td>
</tr>
<tr>
<td>Urethane oils</td>
<td>Non-Aqueous dispersion polymers(NADs)</td>
</tr>
<tr>
<td>Amino resins</td>
<td>Polyvinylacetate(PVA) Latex</td>
</tr>
<tr>
<td>Phenolic resins</td>
<td>Acrylic Latex</td>
</tr>
<tr>
<td>Epoxide resins</td>
<td>Styrene/Butadiene Latex</td>
</tr>
<tr>
<td>Unsaturated polyesters</td>
<td></td>
</tr>
<tr>
<td>Chlorinated rubbers</td>
<td></td>
</tr>
</tbody>
</table>
Solvents

Solvents are used in paint compositions for two main purposes as they enable the paint to be made and applied to surfaces\textsuperscript{5}. The importance of volatile component of a coating has been rather neglected. But, it is certain that it plays an active role in dissolving the resin, reduce the viscosity of the polymer to the consistency suitable for application, helping in wetting the substrate, controlling the rate of drying or setting of the coating film after application, thus having a profound effect on the durability of the coating. Solvent systems are most often blend of different solvents, designed to facilitate handling and improve the aesthetics of the deposited film.

1.1.4 Additives

In addition to the primary components, there are numerous subcomponents in coatings composition that can vary widely depending on the vehicle type. Paint may contain small quantity of driers, plasticizers, anti-skinning agents, wetting agents, anti-settling agents, anti-fouling agents and fungicides and these additives play an important role in the paint formulations\textsuperscript{6}. Different types of additives are added for different purposes. They are usually in small quantities (1-2\%), of entire formulation. These additives contribute package stability, ease of application, and appearance and corrosion resistance quality to the coating.
The additives in a paint system can be broadly listed as follows\(^7\),

1. **Additives for paint processing**
   a. wetting and dispersing agents (surface active agents)
   b. Viscosity control

2. **Additives for improving paint application properties**
   1. Drier’s
   2. Matting agents
   3. Gloss improvement (leveling and flow control) agent
   4. Wet edge additive
   5. Thixotropic agent
   6. Mar resistance
   7. Anti-Foam
   8. Coalescing agent

3. **Additives to improve storage properties**
   A. Anti settling agent
   B. Anti skinning agent
   C. Desiccants
   D. Anti rust agents
   E. Protective colloids
   F. Biocides

4. **Additives for improvement of performance of the film**
   a. Mar resistance
   b. Biocides
   c. Weathering resistance agents
   d. Adhesion promoters
   e. Surface renewal agents

5. **Additives for special effects**
   * Wrinkle finishes,
   * Hammertone finishes.

Some of the most important additives have been discussed here\(^8,9\),
1.1.4.1 Driers

Driers are the materials that promote or accelerate the curing or hardening of film formers. Driers are metallic soaps that are used in small percentage to catalyze the oxidation and polymerization of drying oils, aldehydes, oil modified epoxies, oil modified urethane and so on. Linseed oil is the one of the most widely used drying oils in paint formulations. The catalytic activity depends on the ability of the metal cation to be readily oxidized from a stable lower balance to a less high valence; metals commonly used are soaps of cobalt, manganese, lead, zinc, calcium, cerium, zirconium, and iron. Dosage of the driers based on the percentage of the metal which is supplied in the market for example as 6% cobalt and 24% lead. The octoate driers are generally consider most desirable in paints.

1.1.4.2 Plasticizers

Plasticizers are introduced into the paints to provide elasticity and flexibility. The introduction of plasticizers makes paint film less brittle and not permitted the tendency to crack. Tri-cresyl phosphate, I-butyl phosphate and di-octyl / di-n-butyl phathalate are some of the frequently used plasticizers. Modified castor oil is also used as plasticizers in nitrile rubber formulations.
1.1.4.3 Anti-Skinning agents

Skinning is the formation of films when paints are exposed in a container. This is due to the oxidation of the surface layer of paints. To avoid the oxidation some catalyst is added, they are called anti-skinning agents (Anti-oxidants). The function of anti-skinning agents is to retard oxidation. During the process of oxidation there is a formation of free radicals and hydroperoxides. Anti-skinning agents check these as free radicals, inhibit initiation and further oxidation and thereby prolongs the induction period. The increase in induction period will result in delayed skin formation. Anti-oxidants used as anti-skinning agents

These are generally volatile compounds which evaporate on application along with a solvent and permit the oxidation of paint film to occur causing the drying of paint film. The important anti-oxidants are quinines, hydroquinones, phenols, amines and oximes. The quinines,hydroquinones,phenols and amines which will retard the oxidation of the paint, but they do not evaporate completely from the film and they can extend the drying time of the film. The most widely used anti-oxidants are oximes, which will inhibit oxidation so long as paint is inside the container. After the application of the paint, these oximes evaporate out very fast and do not delay the drying time of the coated film and its subsequent coats. Mainly used oximes are methylethyl ketoxime, butyraldoxime and cyclohexanone oxime.
1.1.4.4 Anti-settling agents, wetting and dispersing agents

Pigment and extenders tends to settle down and form sediment with their particles held tightly together it is often difficult to re-disperse this sediment. The paint contains barytes (a type of extender) a solution of sodium oleate is added to the extent of 1% to avoid settling. With other pigments Turkey red oil is added to check excess settling. The calcium linoleate and napthenate is effective in preventing the causing of rapid settling of pigments. Soyalecithin is added as suspension agent. Zinc and calcium octoates (or) napthenates are a useful wetting and dispersing aid for pigment grinding. Wetting and dispersion agent is used in the range of 0.20 % to 0.50 % on total pigment weight of the paint formulation.

1.1.4.5 Leveling and flow control agents

Leveling is the ability of the wet film to give a uniform smooth finish on drying. Paint with good leveling and sagging resistance could be formulated, if it has a low viscosity during application and after application. Nevertheless high viscosity of the medium is required to reduce or prevent sagging. Especially, zinc benzoate, zinc oxide and benzoic acid have good effect on leveling. In lacquers the films with good leveling is produced by high boiling solvents and liquid plasticizers methyl cyclohexanol stearate and chloroparaffin.
1.2 Need for surface coatings

The main role of a coating whether it is used as a primer, intermediate coating or top coat is to protect the substrate to which it is applied and in some cases its appearance. Because of colorful world can be created as a result of applying coatings like paints. To be considered effective it must give the desired protection level for as long as possible against environmental and mechanical damage. In order to achieve this level of performance good adhesion to the surface and a resistance to moisture and sunlight (Ultra light) are essential. The highly strengthened material like metal is getting corrosion and so we want to give protection against this type of loss.

Corrosion is a major factor in commerce, resulting in the loss of billions of dollars in damage to bridges and other metal-supported structures. Wicks and Lleidhiser et al have studied the corrosion process and developed theories and electrochemical methods to study the process. The protection of metals by surface coating is regarded as one of the most cost effective and largely adopted process. These are used as a fence to avoid the get in touch with the corrosive ions to the metal surface. There are three recognized ways that coatings can protect steel: barrier protection, inhibition, and sacrificial action. A coating protects as a barrier by blocking moisture, oxygen, and other chemicals from the steel substrate.
All coatings are permeable to some degree, but those coatings that protect through a barrier mechanism have relatively low moisture permeability. Coatings that protect by inhibition contain special pigments to inhibit or interfere with the corrosion reactions on the steel surface. The moisture passes through the coating film, the anti-corrosive pigments slowly dissolve and aid in stopping corrosion. Finally, sacrificial action is the method used by zinc- and aluminum-rich coatings.

1.3 Properties of aesthetic and performance coatings

Choice of vehicle is more difficult than the selection of pigment. We have to select the resins, solvents, driers and other additives that might enter into the formulation. Depending upon the environmental condition, we have to select the vehicles. The properties desired in the film and the method of drying will determine the type of vehicle used.

1.3.1 Primer coat

The primer coat may contain rust inhibitive pigments such as zinc chromate, zinc dust, zinc phosphate etc and thereby providing another function in addition to acting as barriers. The major role of a primer is to provide strong bonding to substrate, high order of internal power and also well-built battle to corrosion and chemicals. It must provide appropriate and well-suited base for the top coats. Hence, primer has dual necessities, i.e., adhesion to the substrate and prevention of a surface which will allow proper adhesion of the following coats.
1.3.2 Intermediate coat

Intermediate coats are typically used in coating systems, which are designed for precise purposes. The primary purpose of an intermediate coat is to provide thickness for total coating, strong chemical resistance, increases electrical resistance, strong cohesion and strong bond to primer and top coat. The intermediate coat generally has rather high pigment to vehicle ratio, so that it is a flat coat with superior bond.

1.3.3 Top coat

The choice of top coat is very important because it provide the following functions such as

1. Providing a resistant seal for the coating systems
2. Forming the primary wall to the situation
3. Providing a hard and wear resistant exterior
4. Providing nice look

The topcoat is denser than the immediate coat since it is formulated with a lower pigment to vehicle ratio. The paint is generally applied by brush or spray and some special methods such as electro coating, roller coating and fluidized bed methods. The two primary functions of paint are decoration and protection. Decorative effects may be produced by color, gloss, texture or a combination of these. A secondary decorative function of paint is lighting. The color of the surface affects the reflectance. The proportion of light that is reflected by a surface is expressed as a percentage of complete reflectance.
The following are approximate reflectance values for various colors: white 90-80%, very light tints 80-70%, light tints 70-60%, medium to dark tints 60-20%, deep color 20-3%, and black 2-1% \(^{12}\).

### 1.3.4 Acrylic coatings

Unlike other vinyl polymers, thermoplastic acrylics are generally considered inert unless certain functional groups are purposely added to the polymer chain for eventual cross linking. They exhibit good resistance to hydrolysis and ultraviolet degradation, which accounts for their outstanding exterior durability. Other important properties usually associated with thermoplastics acrylics are,

- Transparent water-clear film appearance
- Low pigment reactivity
- Compatibility other film formers
- Chemicals, solvent and water resistance

Thermosetting acrylic polymers differ from thermoplastic polymers, in that they are designed to form films by cross-linking. They are used in a wide and diverse range of industrial coating applications in which the finish is usually baked to achieve maximum film properties.
They offer several advantages over thermoplastic acrylics, such as

- Lower molecular weight, hence higher solids at application viscosity
- Usually formulated on cheaper solvents
- Better gloss and appearance
- Improved chemical, solvent, acid and alkali resistance
- Less softening at higher temperatures and as a consequence, better block resistance

The other examples for aesthetic coatings are alkyd and amine based coatings, which are used only for very good appearance in the interior as well as exterior coatings.

1.4 Performance coatings and its categories

With increased industrialization, the industrial paint requirements are also increased. At this concept, the paint manufacturer should satisfy the customer in the way of quality, service and cost. The coatings that have the property to perform well in the given environment are generally known as performance or specialty coatings. Silicone, epoxy, polyurethane, and phenol formaldehyde coatings are the example for high performance coatings due to their peculiar properties when they contact with different atmosphere.
A silicone is a compound that contains elements silicon, oxygen and organic groups. Silicones may also be thought of as hybrid polymers that is, a cross link between organic and inorganic substances and having some of the characteristics of both parent stocks. They have some of the thermal and chemical stability. They also have their own peculiar chemistry as well, as the Si-C bond, so characteristic as silicones, is not found in any other materials. Silicone resins have been used for more than 30 years by the surface coatings industry. They were used as heat-resistant coating materials in such high temperature areas as ovens, space heaters and chimneys. In more recent years, silicone resins have been used in decorative coatings for improving the weather resistance. Other properties, such as anti-stick effect, water-repellent action and anti-foam properties are often utilized.

The properties of other performance coatings such as epoxy and polyurethane are discussed in detail as follows.

1.4.1 Basics of epoxy coating

The most widely used epoxy resins are the reaction products of BisphenolA (BPA) and epichlorohydrin (EPH). The credit of epoxy synthesis out of BPA & EPH goes to Dr.Pierre castan of Switzerland and Dr.S.O.Greenlee of US. In the plastics industry epoxy resins are classified as thermosetting resins, and they are used in the paint industry as convertible coatings.
Epoxy resins are cured and converted to a thermo set state by chemical reaction between resin and a curing agent. Depending on the curing agent this reaction can take place; either at elevated or at room temperatures. The cured resins are not soluble in solvents and cannot be melted by heating. This property is in direct contrast to thermoplastic products, such as PVC, or polystyrene or non-convertible coatings, such as chlorinated rubber, acrylic or nitrocellulose lacquers which remain soluble in solvents and can be remelted by heating. BPA glycidyl ether resins are produced by reacting BPA & ECH in presence of caustic to form a diglycidyl ether bisphenol – A (DGEBA). The reaction composition of the epoxy resin is given in the following Figure1.1. 80-85% of world production of epoxy resins is based on DGEBA. The varieties of epoxy resins are low molecular weight liquid resins, solid resins, very high molecular weight thermoplastic resins, multi functional reins, radiation curable, special purpose epoxy resins. These uncured resins are characterized by their epoxy content (EpoxyEquivalentWeight-EEW), physical, chemical properties etc.
Figure-1.1 Reaction composition of DGEBA
Epoxies consist of two components that react with each other forming a hard, inert material. At room temperature various methods available for curing the epoxy resin. Curing agents are amines, polyamides, phenolic resins, anhydrides, isocyanates and polymercaptans. Among this, polyamides are more surface tolerant and less troubled by moisture. Epoxy and polyamide curing reaction are given as in the Figure 1.2. Polyamide cure epoxies show better flexibility and water resistance and give longer pot life. Polyamide cure epoxies are low toxicity to handle hence it is used in most of the airdrying epoxy two pack paint formulations.

\[ \text{EPOXIDE} + \text{AMIDE} \rightarrow \text{FINAL PRODUCT} \]

**Figure -1.2 Reaction product of Epoxy polyamide composition**

Epoxy resins became commercially available in Australia in the early 1950’s and since that time have become firmly established in many industries. Most commonly used types are based on epichlorohydrin and diphenol propane and are available in range of molecular weights. The low molecular weight resins are liquid and the high molecular weight resins are solid. Epoxy resins can be cure by using Isocyanates.
1.4.1.1 Properties of Epoxy coatings

The important properties of epoxy based coatings are listed below

1. The chemical structure of epoxy resins gives them high chemical resistance against a wide range of severe corrosive conditions. These properties are derived from the aromatic nature of the backbone and good chemical stability of the phenolic ether linkage.

2. Epoxy resins have good adhesion to a wide range of materials, including metals, wood concrete, glass, ceramic and many plastics. This is due to the presence of polar groups in the cured resin.

3. Low shrinkage during curing results in good dimensional accuracy in construction of structural items and enables manufacture of high strength adhesives with a glue line of low residual stress.

4. Ease of fabrication means that complicated shapes can be reproduced easily using liquid epoxy resins systems, which can be cured at room temperatures.

5. Good physical properties such as toughness, flexibility and abrasion resistance can be obtained.

6. Although there are temperature limitations, epoxy resins are generally superior to almost all thermoplastics in elevated temperature performance.
1.4.2. Properties of polyurethane

Interest in polyurethane coatings is growing rapidly because of their high chemical and abrasion resistance, excellent electrical properties, and very low temperature cure due to the exothermic nature of the polymerization. Polyurethane coatings are capable of being made into soft, elastic materials, as well as into very hard, tough, abrasion-resistant products. Polyurethane coatings have been used for many years, but they are still a relatively new type of surface coating medium. Despite the relative high cost, their excellent durability, corrosion, abrasion, water and resistance to resistance chemicals, vegetables, mineral oils and many solvents. Flexibility and impact resistance make them suitable candidates for many high performance applications.

These properties render the urethane coating system suitable for wide variety of purpose on practically any substrate including metal, wood, rubber, synthetic elastomers and fabrics of various types. They can be applied by dip, spray or brush and adhere well to a wide variety of materials. They are suitable in applications which unusual impact and abrasion resistance is required, such as gymnasium and dance floors and bowling pins, in magnet wire coatings and in a variety of outdoor and marine uses because of their good weather ability.
Polyurethanes cure to a safe, inert product. It has been estimated that the average family owns approximately 25 to 100 pounds of polyurethane present in such areas as insulation for refrigerators, foams for bedding and cushions, and as dashboards and bumper covers in cars. Technically speaking the term epoxy refers to the uncured resin component only (the hardener is usually an amine) whereas polyurethane is the generic term for the cured product, which is formed from a chemical reaction between a polyol resin and a polyisocyanate hardener. When two components are mixed the hydroxyl groups of (-OH) in the resin react with the isocyanate groups (N=C=O) in the hardener and a three dimensional molecular structure is produced.

The simple reaction scheme given in the Figure 1.3.

\[
\begin{align*}
R'\text{O} & \quad + \\
N=\text{C}=O & \quad \rightarrow \\
R\text{O} & \quad \text{Urethane}
\end{align*}
\]

**Figure -1.3 Reaction scheme of urethane product**
Only one isocyanate group can react with one hydroxyl group so there is an ideal ratio of hardener molecules to resin molecules, which will give optimum mechanical properties. Despite this fact, it is possible to vary this ratio slightly either way in order to modify the mechanical properties of the system. This is because the isocyanate hardener is also capable of cross linking with itself in the presence of atmosphere moisture. Generally speaking polyurethane systems cure faster than their epoxy counterparts. They can however, be difficult to use when cured in moist conditions at low temperature, again because of the affinity of the isocyanate for moisture. This may result in an inadequate cure and premature embrittlement.

The general term ‘Polyurethane’ (PU) has become known for a multitude of polymers are prepared by diisocyanate-polyaddition polymerization. In the polyaddition process, two or polyfunctional hydroxyl or amino group containing compounds are reacted with di or polyisocyanates. Polyurethanes are a wide variety of polymers with quite different compositions and correspondingly different properties. The multitude of building blocks and the possibility of designed polymerization by formation of stable intermediates (pre-polymers) are features, which are unsurpassed by any other polymer. The same is true concerning the adaptability in processing and composition to fulfill the widest variety of product requirements.
The characteristics structural element of almost all of these polymers is the urethane group formed in the course of the polyaddition:

\[-\text{NCO} + \text{-OH} \rightarrow \text{NH-CO-O}\]

Polyisocyanate Polyol Urethane linkage

Figure-1.4 Urethane formation

The linkage is produced by the transfer of the hydrogen atom of the hydroxyl group to the nitrogen atom of the isocyanate group. This is the fundamental reaction in the field of urethane chemistry. The fundamental reaction of an isocyanate with an alcohol to form a urethane was discovered by Wurts in 1848. Polyurethane is the commonly used term for the final product, ex foams or coatings. These products neither contain monomeric isocyanates nor biologically available isocyanate groups.

1.4.2.1 Formation of polyurethane

The reaction of a diisocyanate with a diol is presented in the following equation:

\[\text{HO-R’-OH} + \text{OCN-R-NCO} + \text{HO-R’-OH} + \text{OCN-R-NCO} + \ldots \rightarrow \text{--O-R’-O-C-NH-R-NH-C-O-R’-O-R’-O-C-NH-R-NH-C-\ldots}\]

Figure- 1.5 Urethane formation for polymers
This simple equation is an expression of the principle of the polyaddition reaction, which leads to an exceptional multitude of any imaginable polymer structure. As polyisocyanates, one or multi ring aromatic, aliphatic or cycloaliphatic(modified isocyanates) compounds can be used. Besides polyether and polyester polyols, short chain diols and polyols are used for the polyaddition reactions. Blends can be used not only of the hydroxyl containing reactants but also on the isocyanate side. This means that the chemist has an unlimited variety of building blocks from which to select. If there is a tri or polyl or a tri or polyisocyanate present in the reaction branching and eventually cross linking of the polymer chain occur. The cross link density of such a polymer depends on the amount of higher functional raw materials. This feature leads to the extension of the property spectrum of the final product.

The stochiometric ratio of the isocyanate to the total amount of active hydrogen in the reaction mixture is of significant importance for the formation of polyurethanes and their final properties. Formulation with excess and equivalent amounts of isocyanate as well as with sub-equivalent amounts of isocyanate is used. The ranges of polyurethane coatings available for surface coating applications are:

- Oil modified polyurethanes
- Moisture curing single component polyurethane
- Blocked single component polyurethane system
- Polyurethane based on prepolymers with catalyst system
- **Two component systems based on polyol cured with isocyanate**
- Solvent based urethane lacquers
- Aqueous polyurethane dispersion, known as PUD’s
- Polyurethane based on acrylate urethane oligomers
- Polyurethane based on urethane polyols
- Acrylate urethane oligomers based polyurethanes
- High solid polyurethanes
- Solvent free polyurethanes
- Hybrid polyurethanes based on other polymers
- Polyurethanes powder coatings
- Polyurethane vapour cure system.

**1.4.2.2 Polyols**

Compounds with several hydroxyl functions in the molecule are besides the isocyanates, the essential components for the formation of polyurethanes. Lower molecular weight compounds such as ethylene glycol, glycerine, butanediol, trimethylolpropane etc., act as chain extenders or as cross linkers. Higher molecular weight polyols (With an average molecular weight up to 8000) are the actual basis for the formation of the polyurethanes.
These higher molecular weight polyols are obtained mainly from two classes of the products: the polyethers and the polyesters. They are almost exclusively manufactured by synthetic routes. There are some natural products such as castor oil which is also is used but as of today these play only a minor role. In general the polyol requirement being a high hydroxyl value and an acid value as low as possible to avoid liberation of carbon dioxide. In coating industries three different types of hydroxyl group containing polymers have typically been utilized.

- **Polyester polyol:** in addition to the typical linear and branched polyester, oil modified polyesters are often used in coating applications. The molecular weight weights vary between 500 and 5000. Their hardness ranges from soft to hard and brittle materials.

- **Acrylate resins:** The hydroxyl group contains acrylate polymers have gained significant importance in the coating area. Their market acceptance is due to their quick physical drying and better weather ability. Another important factor is the reduced isocyanate demand of these products owing to their relatively low hydroxyl content. Polyacrylates usually are very hard resins. They exhibit good resistance against oxidation, good weather ability and good hydrolytic stability.
• Polyether polyol: linear and slightly branched polyethers with molecular weights between 1000 and 2000 are preferably used. In comparison to polyester polyols, the polyethers are more resistant to hydrolysis: however, the resistance to oxidative degradation is lower.

• Other products with reactive hydroxyl groups: preparation of polyols from vegetable oils has been extensively reported by many researchers. Highly reactive epoxy resin can also undergo ring opening reaction to yield polyester polyol and other polyols contains a free hydroxyl group that can be utilized to produce polyurethanes. Interpenetrating Networks (IPN) is the most important concept in the coating industry, which is based in the compatibilization of two components like different polyols involve in the formation of PU’s.

1.4.2.3 Isocyanates

Isocyanates with two or more NCO groups in the molecule are needed for the formation of polyurethanes as outlined in the following sections. Aromatic as well as aliphatic and cyclo aliphatic , di and poly isocyanates are suitable building blocks for polyurethane chemistry, the aromatic types being volume wise more important. Reasons for this are that the aromatically linked isocyanate group is a significantly more reactive group than the aliphatic one and also that, in general terms, the aromatic isocyanates are economically more readily available.
Aliphatic isocyanates are only used if their reactivity fits specifically the polymer formation or if special properties are required regarding the final products. For example light stable coatings can only be obtained with aliphatic isocyanates.

1.4.2.4 Basic reaction of the isocyanate groups

Polyisocyanates have been known since the middle of the last century \(^2^1\). The very high reactivity of isocyanates, especially with nucleophilic co-reactants, has always been of intriguing interest. However, polyisocyanate gained technical importance only through their use in polyaddition chemistry.

\[ R-(\text{N=C=O})_n, \text{n}=2-4. \]

The reactivity of the NCO group is mainly determined by the pronounced positive character of the C-atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen. The positive charge at the C-atom becomes obvious if one looks at the resonance structure, which also indicates how substituents at the radical which bears the NCO group can influence this reactivity (Figure 1.6):

\[ R-N=C=O \leftrightarrow R-N=C-O \leftrightarrow R-N-C=O \leftrightarrow R-N-C-O \]

**Figure 1.6 Resonance structure of isocyanate**
1.4.2.5 Hammett constant

The negative charge can be delocalized into R, if R stands for an aromatic radical. This also explains the distinctly higher reactivity of aromatic isocyanates over aliphatic isocyanates. Substituent’s on the aromatic ring show the known influences on the positive character of the NCO group: electro with drawing substituent’s in para or ortho position increase the reactivity of the NCO group; electro-donating substituents lower its reactivity. A measure of intensity of this influence is the hammett constant.

1.4.2.6 Solvents

The polyols used are soluble in esters and ketones and a balanced mixture of low, medium and high boiling types is generally used. In some cases toluene or xylene is used as diluents. Alcohol must be avoided. The diisocyanates are generally dissolved in esters. All solvents should be dry to avoid reaction between water and the isocyanate group leading to formation of carbon dioxide.

1.4.2.7 Addition of nucleophilic reactants

The most important reaction of isocyanates is in the formation of carbamic acid derivative (Figure 1.7.) by the addition of components with an acidic H-atom across the C-N double bond.
With increasing nucleophilic character of HX, this reaction occurs more easily at lower reaction temperatures. At higher temperatures, isocyanate and reactant can be regenerated. This clearly indicates that the addition reaction is a genuine equilibrium reaction. The regeneration of isocyanates at elevated temperatures is used technically by capping or blocking the isocyanate with nucleophiles with an unblock readily at elevated temperatures (Eg., Phenol, Oxime, Lactam, CH-Acidic compounds, Bisulfite).

The nucleophiles reaction can be strongly influenced by catalysts: Acid compounds (mineral acid, acid halides etc.) prolong the reaction, whereas basic compounds, especially tertiary amines accelerate it. Also metal compounds (Sn, Zn, Fe salts) have an accelerating influence. The catalyst is needed or preferred for certain applications. OH group containing compounds are by far the most important reactants for isocyanates. They are added under mild conditions to the isocyanates, forming carbamic acid esters. Primary alcohol, secondary alcohol, and phenols show a decreasing reactivity in the sequence.
The name Urethane: polyisocyanates and polyols to form polyurethanes. The much more nucleophilic primary and secondary amines react much more vigorously with isocyanates. In the reaction of urea are formed (Figure -1.8)\textsuperscript{22,23}.

\[
\text{R-N=C=O + R'-NH}_2 \rightarrow \text{R-NH-CO-NH-R'}
\]

\text{Isocyanate} \quad \text{Amine} \quad \text{Urea}

\textbf{Figure 1.8 Formation of urea}

Besides these two basic reactions for the addition reaction, there is a third fundamental one. This is the reaction of isocyanates with water which is essential for the formation of polyurethane foam (Figure – 1.9). In this reaction, the primary addition product is the carbamic acid. Since the carbamic acid is not stable, it splits off carbon dioxide, forming the corresponding amine. The amine immediately reacts with the isocyanates which are still present in the reaction mixture forming the symmetrical urea.

\[
\text{R-N=C=O + H-O-H} \rightarrow [\text{R-NH-CO-O-H}] \rightarrow \text{R-NH}_2 + \text{CO}_2 (g)
\]

\text{water} \quad \text{carbamic acid} \quad \text{amine}

\textbf{Figure 1.9 Reaction scheme of isocyanate and water}
The carbon dioxide, which is formed, takes over the role of the blowing agent during the formation of the polyurea which leads to the formation of the macromolecular skeleton. The reaction products of alcohol and amine with isocyanates which are urethanes and ureas still possess acidic protons. The reactivity is significantly lower than the one of the starting alcohol, phenol, or amine, but under more rigorous reaction conditions, they are capable of reacting with aliphatic isocyanate. In the case of polyisocyanates, these reactions lead to branching of the polymer as given in Figure 1.10 and Figure 1.11 respectively.

At elevated temperatures, the allophanates and biurets can be split into isocyanate and urethane or the urea respectively.

![Figure 1.10 Formation of allophanates](image-url)
1.4.3 Combination of epoxy and polyurethane coatings:

In order to understand the different film properties and applications of each product, a basic understanding of their chemistry is worthwhile. It is apparent that epoxy systems are particularly suitable for use as primer and intermediate coatings because of their good adhesion and water resistance whereas polyurethanes offer very good color stability and gloss retention and therefore they tend to be used for top coats where a cosmetic finish is required. Where there is a requirement for good adhesion and water resistance as well as high gloss and color stability (i.e. non-yellowing) epoxy and polyurethane systems can be used in combination of the same substrate. The benefits of this combination of materials are clearly illustrated on many of the high performance wooden coating currently racing, where a top quality clear coating is required to enhance the wood work. The present investigation clearly describes about the performance of combination of these two polymers on the metal substrate.
1.4.3.1 Difference between aliphatic and aromatic polyurethane coatings

Aliphatic and aromatic coatings differ in the types of polyols and isocyanates used in the formulation, hence their stability in atmospheric conditions differ significantly. Because they are very stable when exposed to ultraviolet light, weathering, and hydrolysis, aliphatic coatings are the superior choice for exterior protection. Aromatic coatings do not fair as well against atmospheric exposure since the UV light causes yellowing and chalking.

Aliphatic coatings are produced as a result of the reaction between aliphatic isocyanates, such as HDI and IPDI, and polyester or acrylic polyols. In contrast, aromatic coatings are designed from aromatic polyisocyanates and polyether polyols. The raw materials used in formulating aliphatic systems are generally more expensive and have higher viscosities than their aromatic counterparts. The need for solvents to reduce viscosity has been an obstacle in trying to achieve 100% solids aliphatic polyurethane coatings. New developments such as the use of lower molecular weight resins, reactive diluents, and new polyurethane prepolymers have resulted in higher solids systems.
1.4.3.2 Advantages of polyurethane coatings over epoxy coatings

The advantages of polyurethane coatings are:

- Polyurethane coatings can be made to cure at virtually any given time by changing the amount of catalyst or the type of polyol in the formulation\textsuperscript{25}. Thus, fast-setting, one coat polyurethanes have a much faster turnaround time than epoxy systems. Epoxy coatings generally take seven to ten days to fully cure and to allow the solvents to evaporate. Some epoxy systems require force curing.

- One hundred percent polyurethane coatings are solvent free and have lower toxicity levels than the epoxies. Due to solvent content, epoxy coatings are extremely flammable.

- Due to the exothermic nature of the reaction between polyol and isocyanate, polyurethane coatings can cure at almost any ambient temperature. This means that polyurethane coatings can be applied even during the cold months of the year. Epoxy coatings, on the other hand, usually require temperatures above 50°F (10°C).

- One hundred percent polyurethane coatings feature a unique “self-inspecting” property; they fail almost immediately if they are incorrectly applied or if there is a problem with the surface preparation or the mixing ratio. Thus, polyurethane coatings can be inspected immediately after application and any defects in the coating will be visible.
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