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## REVIEW ARTICLE

### A STUDY ON NATURAL OIL BASED GREEN POLYMERS

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# A Study on Natural Oil Based Green Polymers

**Yogita Maheshwary**

Assistant Professor, Chemistry Govt. Rajindra College

Paints have been used for decorative purpose for many centuries. The cavemen were probably the first to use the paint to record their legacy. They used the paints as the means of communication and decoration. Paint making and paint application were more art than science. But after industrial revolution the whole scenario has been changed which leads sciences to emphasize 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 of paint making into science which led to discoveries of new materials and new ways of application of paints, to meet the stringent requirements of protection coupled with decoration in certain instances under diverse service conditions.

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 depends on the nature of binder to a large extent, but nature and quantity of pigments also effect the property of paint film.

Pigments generally give aesthetic appearance and indicate color and opacity to paint film and some pigments also provide 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.

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

Additives are included in a paint system for many different reasons. Though they are present in relatively small quantities, they can significantly influence properties of the liquid paint and/or the dry 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 to date, additives play a major role in formulation and functioning paint system. The present thesis work is in the context of modification of

alkyd resin. Hence, more details about the review on resin have been given.

## **RESINS (I.E. BINDERS) FOR COATING INDUSTRIES**

A wide range of binders are commercially available for coating industries now a days but earlier chemists had to depend on natural products like, natural resin oil until the attempts were made to modify 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 Baekeland in earlier 1900s. After this, there came the new resin called alkyd 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 number 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 system 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 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 of any sort is involved in the film formation. The resin used is of sufficiently high molecular weight to provide better performance properties but the dry paint film remains 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.

## 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.

## RESEARCH

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 and other industries.

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.

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

## ALKYD RESINS

Alkyd resins form the largest group of the synthetic resins available to the paint industries and consumption is greater than that of the any other resin for wide variety of application due to their low cost and versatility. 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. 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 acid s. 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.

## POLYESTER RESINS

The product obtained from the condensation polymerization of a polyhydric alcohol and polyfunctional acid is known as polyester resin and widely used in surface coating industries. The most commonly used polyfunctional acids are maleic anhydride, Phthalic anhydride, Adipic acid, sebacic 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. 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.

## **EPOXY RESINS**

Epoxy resins 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).

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 isocyanates 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 .

## **POLYURETHANE RESINS**

The basis of formation of these polymers 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 and exhibit excellent weather resistance. Other film properties are good resistance to moisture. Chemical attack and many solvents.

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.

## **OILS/ OILS DERIVED FATTY ACIDS**

The oils used in paint industries are derived mainly from vegetable and to a much lesser extent animals sources. They are esters of glycerol and fatty acid, non-volatile and unstable at higher temperature. These oils vary 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.

\_ Drying oils E.g. Linseed oil, Tung oil etc.

\_ Semi drying oil E.g. Soyabean oil, tobacco seeds oil etc.

\_ Nondrying oils E.g. Castor 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.

## **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 mono-glyceride 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 oC-260 oC 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.

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