

‘Synthetic Resins & Leather Finishing

Sumant Chatterjee

Leather Technology Department, Harcourt Butler Technological Institute, Nawabganj,
Kanpur- 208002, India

Abstract: Surface of the leather needs a closing and sealing of the Porous surface against humidity, dust, dirt, chemical stability and to make, an attractive appearance. Wax, proteins like blood, milk & Egg., oils like linseed, shellac are used since old times. Since thirties many leathers are finished with coating based on synthetic binders and pigment. Development of polymer technology makes it possible of changing leather surface in many ways. Films produced by natural binders develop cracks slowly during ageing and fungal development. Abrasive resistance of the synthetic binder were comparatively poor and films need to be protected by top coat film of nitrocellulose. Lacqour plasticized with solid synthetic soft resins like alkyd resins. Most of the materials do not posses all the properties. Modern synthetic resins are essentially polymers containing large molecules built up from normal molecules. Alkyd resins form the largest group of synthetic resins. Unsaturated polyesters give hard, Non resistant films with good chemical & solvent resistance. Amino resins are derived by reaction between formaldehyde and either urea or melamine. Epoxy resins can be crosslinked by cold curing or stoving with a range of materials. Polyurethanes are two pack materials, one containing the active hydrogen and the isocyanate packed in separate containers and mixed together immediately before use. Vinyl resins are straight chain thermoplastic polymers principal types being polyvinyl acetate, polyvinyl alcohol, polyvinyl butyral, polyvinylchloride. Polymers of methyl methacrylate and other ester containing alkyl side chains are hard brittle solids but from “straight” esters are soft and flexible.

Silicone resins are semi-inorganic high polymers containing both silicone & carbon synthetic coating materials in use has been discussed.

Key words: Alkyd, Polyester, Amino, Polyurethane, Vinyl, Acrylic, Resins.

Introduction

The surface of the leather in the over most cases the grain, was treated in ancient times with a protective season. Leather needs a closing and sealing of the porous surface against humidity, dust, dirt and to make the surface an attractive appearance.

Wax, proteins like blood, milk and egg, oils like linseed oil, shellac are used since old times. This substances are rubbed into the surface and polished. Often thicker sheets can be detected on the surface containing pigments.

Since the thirties of this century many leathers are finished with coatings based on Synthetic binders and pigments

Leather finishing has to respect the high flexibility and stretchability of leather articles. Casein finishing is known since long and followed by using pigmented nitrocellulose finishes. The first polymer dispersions were presented in 1935.

The finish of a leather can greatly vary mainly depending on the purpose of the leather. Leather for shoes like wear under heavy weather needs a thick, water and scuff resistant coating. Shoes in warm countries to wear in towns and mainly in rooms need only thin coatings. Leather for car upholstery

to be used in sunny parts need special coating resistant to high UV radiation in the polymers and pigments used. The fastness properties determine greatly the character of the finish.

Visual and palpable evaluation of leather depends on its surface treated by which it emphasizes its natural beauty concealing its minor defects.

Development of polymer chemistry and technology makes it possible of changing leather surface in many ways. Apart from chemical stability i.e. resistance to damaging factors like air, oxygen, water and its impurities, it has to be firmly attached to the substrate. The surface tension existing at the ground coat interface during applying i.e. when the coat is liquid affects effectiveness of coat applying. The capability of joining the two substances (adhesion) and internal coherence (cohesion) are responsible for the stability of the coat, together with reactions occurring between the coat layers.

Coats are to protect leather against damage, increase its stability against for instance mud, humidity, and sharp edges, to give a desirable look, consisting of color, gloss and texture. However they should not be made tight and impermeable for gases.

Films produced by binders like casein, shellac, albumin, nitrocellulose, or, pigment finished leathers develop cracks slowly during ageing due to migration of plasticizers from finish film to leather making impermeable bottom coat on leather surface necessary. Froth formation in the season solution during finishing requires suitable synthetic resins. The natural binders shows fungus development on surface during rainy season.

Abrasive resistance of these synthetic binders were comparatively poor and so films needs to be protected by top coat film of nitrocellulose lacquer plasticised with solid synthetic soft resins like alkyd resins to avoid cracking.

Synthetic resins finish films could not be glazed because temperature of glazing was high to melt resins used.

Most of the materials do not possess all the properties, thus two or three materials are mixed and necessary properties are imparted by the addition of suitable substances.

Modern synthetic resins are essentially polymers i.e. they contain large molecules built up from normal molecules or monomers. In a resin there is a range of polymer sizes or molecular weights found to be distributed round a mean value in much the same way as the particles in a pigment.

2. Discussion

2.1 Alkyd resins: Alkyd resins form the largest group of synthetic resins whose consumption is greater than that of any other resin. They form part of the larger group of polyesters, which include all products of the esterification of polybasic acids with polyhydric alcohols. Alkyds differ from other polyesters in containing a monobasic fatty acid in the molecule and are often referred to as oil-modified alkyds. The nature amount of the monobasic fatty acid determine the drying characteristics of the resin.

Saturated fatty acids yields non-drying or plasticizing resins while drying properties are conferred by unsaturated acids. When two moles of glycerol and three moles of phthalic anhydride are heated together a syrup is first formed which on heating further is converted into a gel. Continued heating causes the formation of a resin which ultimately becomes an insoluble and infusible mass. It is thought that a linear polymer is first formed and this gradually crosslinks to give a very complex

structure. The polymerization to the very large polymers can be checked by the introduction of a mono functional component into the system.

Dehydrated castor oil alkyds: Raw materials-Raw castor oil, phthalic anhydride and glycerol are heated together slowly at first and then rapidly to 260^o to 270^oC.

Drying alkyds: These contain unsaturated fatty acids which control to a large degree the drying and performance characteristics of the resin.

Alkyd finishes, show good gloss and gloss retention but are sensitive to moisture both during drying and afterwards.

2.2 Polyester resins:

2.2.1 Unsaturated polyester resins: Product obtained from the condensation polymerization of a glycol such as 1:2 propylene glycol or 1:3 butylene glycol with an unsaturated acid such as Maleic or a mixture of Maleic and saturated acid (e.g. phthalic) in the form of anhydrides is a linear polymer containing unsaturation in the chain. This is dissolved in a suitable monomer generally styrene to produce the final resin.

Unsaturated polyesters give hard mar- resistant films with good chemical and solvent resistance. The films are characterized by depth of gloss.

Saturated polyester resins: Main use of these resins is production of polyurethanes by reaction with isocyanates.

2.3 Amino resins: These are derived by reaction between formaldehyde and either urea or melamine to give urea-formaldehyde or melamine-formaldehyde resins

When urea is heated with formaldehyde solution under slightly alkaline condition, addition takes place to form methylol-urea. Either mono or dimethylol urea is formed according to the ratio of urea to formaldehyde. A water soluble syrup is formed and on continued heating to 200-240 C hardens rapidly to a colour less hard infusible resin valueless as a coating material but if condensation is carried on in the presence of a high boiling primary alcohol like n-butanol the hydroxyl groups are esterified possessing different solubility properties from original hard resin

Alkylated urea resins are water white and compatible with a number of alkyds both drying and non-drying. Combination of urea-resin with non-drying alkyd is used for stoving finish.

2.3.1 Melamine-formaldehyde: A molecule of melamine can react with up to six molecules of formaldehyde to give a series of methylol melamine.

Cross linking reactions occur when amino resins are stoved with one of a number of hydroxyl containing polymers, e.g. alkyds, saturated polyesters, epoxies and acrylics.

Methylated melamines like hexamethoxymethyl-melamine (HMMM) with epoxy resins on stoving yields films of outstanding gloss retention and resistance to heat, detergents, salt solutions and humidity.

2.4 Epoxy resins: Epoxy resins are the product of condensation of epichlorohydrin and diphenylpropane derivatives. Epoxy resins contain hydroxyl and epoxy groups and the epoxy content is the evaluation of these resins. Epoxy resins can be cross linked by cold curing or stoving with a range of materials which include amino and phenolic resins, amines, polyamide resins and isocyanates. Resulting films are very abrasion resistant, resistant to chemical attack and show a high degree of adhesion.

Phenolic and amino resins cross link with epoxy resins. Primary amines react with epoxy resins. The reactive group $-\text{CONH}$ (polyamides) also react with epoxy resins producing flexible and water resistant films. Amines treated films give more chemical resistance.

Curing by isocyanates produces film with high chemical resistance, adhesion, & mechanical properties.

2.5 Polyamide resins: Formed by condensation of polyamines with dimmer (or other polybasic) acids. Dimmer acids are long chain aliphatic dicarboxylic acids containing two or more alkyl side chains. They are used as curing agents for epoxy resins. They react with alkyd resins

2.6 Polyurethane resins: The basis of formation of these polymers is reaction of an isocyanate group ($-\text{NCO}$) with compounds containing an active hydrogen atom which attaches itself to the nitrogen atom of the $-\text{NCO}$ group.

1. Reaction with hydroxyl group: This reaction is used in the formation of surface films. Diisocyanate is reacted with hydroxyl containing polymers such as polyesters, alkyds, epoxies or acrylics.
2. Reaction with carboxyl group-
3. Reaction with amine- polyurethanes are two pack materials, i.e. the material containing the active hydrogen (polyester, alkyd or epoxy) and the isocyanate are packed in separate containers and mixed together immediately before use.

The resins most widely used for reaction with diisocyanates are saturated polyesters. The Nature of the film produced will depend on the chemical structures of both polyester & isocyanate. Soft films are formed from polyesters based on aliphatic acids but harder and sometimes brittle films result from the use of alkyds based on phthalic and terephthalic acids. The type of polyol use in the resin also affects film properties. Glycerol and pentaerythritol give hard films by crosslinking but diols such as 1,4-butanediol or ethylene glycol give much softer films.

Depending on the type of polyester or polyol and hardener films can be produced in a wide range of hardeners and flexibility. Blending according to requirements is done.

2.7 Vinyl resins: Vinyl resins are straight-chain thermoplastic polymers produced by addition polymerization of compounds containing the vinyl- group- $\text{CH}_2 = \text{CH}$ - polymers can be made from straight monomers to give homopolymers or from two or more monomers to give copolymers. Two methods are employed (a) solution polymerization in which the monomer is dissolved in a suitable solvent (b) Emulsion polymerization in which the monomer is emulsified in a non-miscible solvent, usually water. In each case a catalyst e.g. benzoyl peroxide is present. Polymerization is catalyzed also by heat, irradiation or light. Emulsions can be produced in any desired particle-size range.

2.7.1 Principal types of vinyl resins are:

Polyvinyl acetate. Colourless resin with low softening point, non-toxic and thermoplastic.

Films produced from solutions of the resin tend to be brittle and lack adhesion on smooth Surfaces. Plasticized with up to 20 percent ester- type plasticizer like Dibutylphthalate

Polyvinyl alcohol: Produced by incomplete hydrolysis of polyvinyl acetate.

Polyvinyl butyrate: Reaction of polyvinyl alcohol with butaraldehyde.

Polyvinyl chloride. Produced from vinyl chloride by bulk, emulsion or suspension polymerization. It is a colorless polymer with a high TG.

Vinyl acetate can be copolymerized with a wide range of other unsaturated monomers to give a variety of products with any desired degree of hardness or flexibility. A range of co-polymers of vinyl chloride and vinyl acetate containing 86-90 percent vinyl -chloride are available which are thermoplastic, non reactive very resistant to moisture and chemical attack.

2.8 Polystyrene resins: Styrene or vinyl benzene is the basic monomer manufactured by reacting Benzene and ethylene at high temperature and pressure in presence of a catalyst. Ethyl Benzene is produced which is then Dehydrogenated to yield styrene. It is a mobile liquid with a characteristic odour and polymerizes readily. Copolymers of styrene and acrylic acid derivatives form the basis of many thermosetting acrylic systems. Copolymers of vinyl toluene and acrylic esters in solution form and copolymers of styrene and vinyl toluene with alkyd resins is important.

2.9 Acrylic resins: The acids acrylic and methacrylic as well as their esters can be polymerized to form long chain thermoplastic resins.

Polymers of methyl methacrylate and other esters containing alkyl side chains are hard brittle solids but from "straight" esters are soft and flexible. By copolymerizing mixtures of the two type it is possible to produce polymers with any desired degree of hardness and flexibility. Acrylic acid, as well the straight and branched esters can be polymerized with other unsaturated compounds like styrene, vinyl-toluene vinyl acetate or vinyl-chloride to give a variety of interesting and useful products.

Generally these are colourless, thermoplastic solids soluble in esters, ketones and aromatic solvents, resistant to water, alkali, mineral oils and greases.

Introduction of reactive groups spaced along the polymer -chain which can be crosslinked with other groups can form three-dimensional structures like carboxyl, hydroxyl, amino & epoxy.

2.10 Silicone resins: These are semi- inorganic high polymers containing both silicon and carbon & from these elements it is possible to prepare a large number of silicone- polymers "tailored" for a great many specific-purposes. The nature of the alkyl and/or aryl groups determines the properties of the resin. The films produced can vary from rubbery to glass-like hardness. Softer types are the more resistant to heat and weathering and blending of two types for necessary mechanical properties.

3. Conclusion

Development of polymer chemistry and technology makes it possible of changing leather surface in many ways. The very wide range of synthetic resins available is the result of systematic investigation into the formation of resinous materials, which are materials of high molecular weight, and their formation is associated with the presence of certain groups in the reacting molecules. Resin formation depended on relative quantities of reactants. Synthetic coating materials in use have been discussed.

Reference:

- [1] WM Morgans, "Outlines of Paint Technology", 3rded, Edward Arnold, Hodder and stoughton limited, U.K., 1990.
- [2] Heidemann, E., "Fundamentals of Leather Manufacture", Edward Roether Ed., Darmstadt (1993).

- [3] Henry Fleming Payne, "Organic Coating Technology", Vol. 1, John Wiley & Sons, Inc., USA, 1954.
- [4] Krzysztof Bienkiewicz, "Physical Chemistry of Leather Making", Robert E. Krieger publishing Company, Florida, 1983.