

Chapter 2 Leather Finishing Materials

Important finishing materials that mix together in different proportions and suspended in water/solvent & are diluted in required concentration are as follows:

- Finely ground pigments with or without acid dyes of same shade to intensify, brighten or level up the shade.
- Film forming materials having binding power.
- Plasticizers to make the film soft, flexible and stretchy.
- Preservatives to prevent putrefaction.
- Gloss giving materials.

Pigments

Any particulate matter that is insoluble in, and essentially physically and chemically unaffected by, the media into which it is dispersed and also meets desirable factors like_ particle size and shape, nature of surfaces, refractive index, crystal structure.

Function: Imparting specific color; intensify, brighten up and level up the shade; Providing covering power.

Table 1. Differences between organic and inorganic pigments	
Organic pigments	Inorganic pigments
Good brilliancy.	Less brilliancy.
Less covering power.	Good covering power.
Tendency to cause bleeding	No bleeding
Less settling	High settling
Less lightfast	High lightfast
Available in purest form	May contain impurities
Pigment dyestuff (Insoluble), Toner (Undiluted colorant having maximum tinting strength), Lake (more or less definitely combined with inorganic substrate or carrier)	TiO ₂ , Zn-white, CdS, Al ₂ O ₃ , FeO

Reactions for synthesis of organic and inorganic pigments

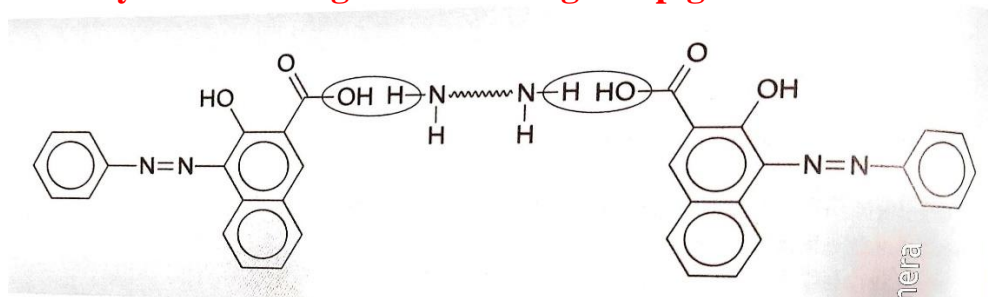


Fig 1. Synthesis of azo condensation pigments (organic)

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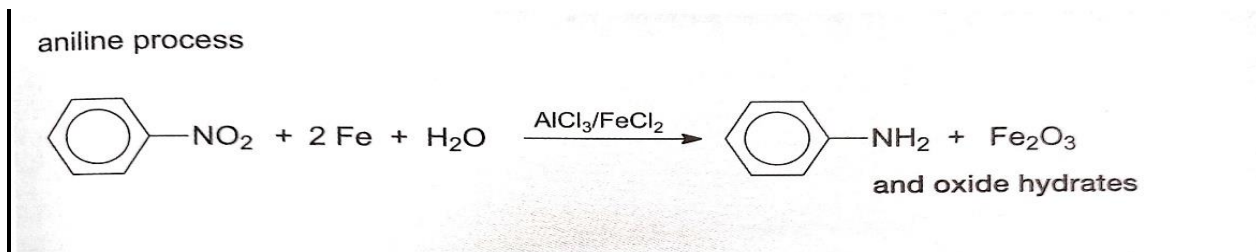


Fig 2. Synthesis of Iron oxide pigments (inorganic)

Covering power of a pigment depends on two factors

The covering power of a pigment can be defined as the area which can be covered, hiding all the defects on the surface, by fixed quantity of pigment. Two factors it is dependent on are:

a) Refractive index of pigment:

Full reflection of light is required to ensure the complete covering by a pigment. The reflection takes place at the interface between Binder-pigment, pigment-air, binder-air provided there are differences in optical densities between two sides of the interface. Refractive indices of inorganic pigments are generally higher than organic pigments, thus the covering power is.

b) Particle size:

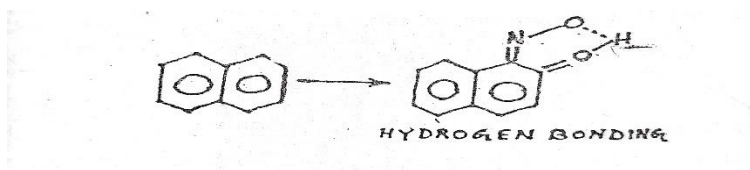
The covering power of pigment is increased if the number of interfaces and total area of interfaces are increased by reducing the particle size of pigment. Inorganic pigments are particulated microfine by repeated grinding. Organic pigments are manufactured by condensation method where insoluble pigments are formed by reaction between dissolved substances.

As far particle size is concerned, the covering powers of organic pigments should be more but due to their very low refractive indices the covering powers of inorganic pigments are more than organic pigments.

Transformation of dyes to pigments

a) Intermolecular hydrogen bond formation:

Dyes become insoluble due to intermolecular hydrogen bond formation between two electronegative atoms present in the nearby groups. Large number of dyestuff pigments have such intermolecular hydrogen bonds for their insolubility.

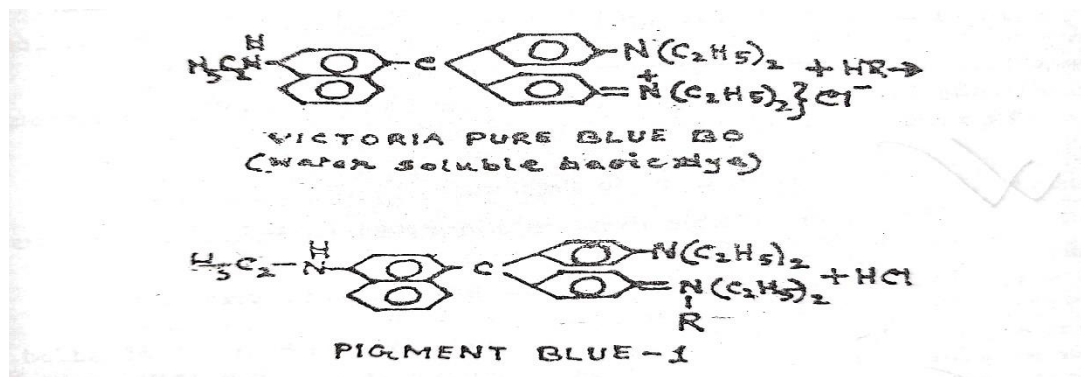


b) Salt formation:

When hetero-poly-acids are added to precipitate the basic dyes, such salt formation takes place.

Similarly, when solutions of acid dyes and basic dyes are mixed, both of them precipitate out as salt.

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c) Complex formation or chelation:

Many acid dyes are converted to pigments with salts of heavy metals. The metals get fixed through both covalent and co-ordinate bonds and thus remains dissolved. Finally, the solvent evaporates out leaving a glossy flexible film on the leather surface. For high degree of gloss, the emulsion is diluted with non-aqueous solvents like acetone, alcohol etc. and for matt finish the diluent is water.

Effects of pigment

- In general, inorganic pigments contribute to the hardness and firmness of coatings. In gloss coatings, the pigment reduces moisture permeability, but high pigment content of flat wall coatings tends to make them more permeable than clear coatings.
- Basic pigments such as ZnO, white-Pb and red-Pb react to the free fatty acids of binder to form metallic soaps. Zn-soaps tend to make coatings hard whereas lead soaps tend to soften the coatings, but both appear to improve water resistance slightly.
- UV from sunlight accelerates the oxidation decomposition of drying oils and degrades nitrocellulose. Pigments such as ZnO absorbs UV ray to protect the surface from degradation.

Film forming materials

Shellac

- Shellac is a natural resin having free carboxyl group and hydroxyl group. The carboxyl groups can react with many alcohols to formation of esters whose viscosity depends upon the alcohol used. The hydroxyl groups can react with fatty acids with the formation of series of compounds of varying properties.
- Due to the melting point of 75°C, shellac cannot be thermo-hardened under pressure & heat. This is the reason why shellac film on leather does not become hard during plating.
- Alkali treated shellac film shows less adhesion and more brittleness than films produced by alcoholic shellac solution.

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- Shellac is a powerful bonding material with low thermal conductivity and small coefficient of expansion. Its thermal plasticity and capacity of absorbing large amounts of fillers like pigments are noteworthy.
- *Shellac is used in leather finish mainly due to waterproofing properties. It is a good insulating material for electricity and it may produce good leather shoes for electricians working on high voltage lines. Unlike plastic or lacquer finishes shellac retains the leather appearance but the main disadvantage is its brittleness and cannot retain the plasticizer for long.*

Protein products

Casein

- Casein is insoluble in neutral water but soluble both in acidic and alkaline waters.
- When casein is dissolved with ammonia, a more or less hard waterproof film results whereas caustic alkali treated casein produces a softer type film. That's why a *common practice is to mix formalin with sealer prepared with casein*. Slight boiling of casein solution increases the adhesive strength.

Albumins

- Albumins are soluble in water and dilute salt solutions but coagulate by heat, saturated ammonium sulfate and acids.
- It produces a hard film that takes a very good gloss under friction glazing and recommended for top coat finishing.

Lacquers

- This is a colored or clear solution made up of shellac dissolved in alcohol or synthetic substances that dries to form a hard protective coating for finish.
- This is generally used in top coats for protection, non-cracking property on ageing and good film flow characteristics.

NC lacquers

- Nitrocellulose lacquers contain plasticizers, solvents and diluents providing filling effect, flexing endurance, elasticity and alcohol fastness.
- Applied to completely dry base coats since it is very hard yet flexible durable finish.
- Sensitive to prolonged exposure to light, heat, UV radiation, amine vapors which results yellowing, discoloration or embrittlement of the film.

NC emulsion lacquers

- This remains available as lacquer-in-water emulsion and easy to dilute with water. Comparing to NC lacquer, it provides pleasing handle and having low fire hazard.

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- Use of these lacquers depend on absorbing and swelling property of the substrate.

Emulsion bases

- Exists as water-in-lacquer phases without forming any emulsion.
- It provides unlimited stability in storage and resistance to cold as well as pleasing smooth handling.

PU lacquers

- These lacquers are being used due to their superior ageing characteristics, fastness to rubbing, elasticity and flexing endurance especially in the cold light fastness.
- These have negative influence on embossing properties.

Thermoplastic and crosslinking binders

Resin Binders

- Continuous Film formation
- Adhesion to leather
- Inter-coat Adhesion
- Binding capacity – pigments, auxiliaries etc.
- Flexibility over desirable temperature range
- Physical properties – resistance to abrasion and rubbing etc.
- Filling of grain surface
- Plating/embossing properties
- Compatibility with other finishing chemicals

Protein Binders

- Adhesion properties
- Improve plate release, stacking and dry rub properties in base coats
- Polishable ground coats for burnishing (stone, felt or paper polishing wheels)
- Complete glazed finishes
- Classic glazed feel and handle (top coats)

Fillers

- Used in bottom and middle coats, thus reduces the necessity of some pigments, providing less plastic looking films.
- Its drawback is to reduce coating stickiness, giving stacking and plate ability improvements.
- Improved coverage and upgrading
- Gloss and Feel adjustment
- Improved uniformity and filling
- Improved flow out, plating and stacking properties

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- Oil and Wax pull-up effects

Hand Modifiers

- Water or organic solvent carrier.
- May be oils, waxes, resin or silicone based.
- Can be used in all finish coats, but not recognized for film forming.
- Improved surface handle/touch/feel.
- Give special tactile fashion effect
- Improved physical performance

Dullers

- Control/adjust gloss
- Control/adjust feel
- Control/adjust appearance
- Control/adjust fashion effects

Penetrators

- Finish penetration
- Adhesion
- Impregnation
- improve film flow characteristics

Cross-linkers

- Improved physical properties
- Improved adhesion
- Improved Waterproofing

Auxiliaries

- Thinners -Solvent dilutable finishes
 - Ensures optimum finish performance
 - Flow out
 - Inter-coat adhesion
 - Appearance (Physical properties)
- Foaming agents (Improved foaming for foam finishes)
- Defoamers (Reduced foaming –in curtain coaters)
- Levelling / flow agents (Improved levelling and flow out)
- Rheology Modifiers (Control flow and viscosity).

Polymers used for leather finishing

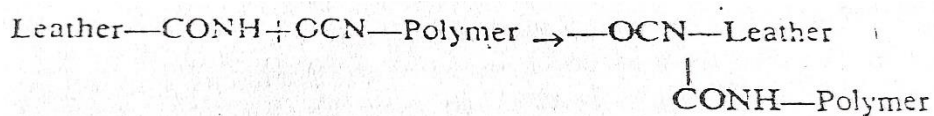
Sometimes acrylates and methacrylates are copolymerized with other types of polymers like polybutadiene, polyacryline, polystyrene et. To produce modified resins suitable for leather finishing.

Through emulsion polymerization method, monomer and necessary additives are emulsified in a dispersing medium permeable resin layer on leather surface. *Comparatively weaker types of emulsifying agents are used during preparation of resin emulsions for the top and intermediate coats.*

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PU

It is an ideal material for the preparation of non-aqueous grain tightening bottoming agent. The isocyanate group of PU binds with CONH group of collagens of leather to show high scuff resistance.



Hybrid resins

As basecoat application

- High Performance Finishes, used alone or in combination with other resins (example: upholstery leathers)
- Foamed Finishes
- Upgrading low grade corrected leather
- High performance splits (example: for steering-wheels)
- Excellent plate release -- deep prints without cut-through
- As a general-purpose binder

As top coat application

- Near-zero VOC
- High mechanical stability
- For both side and upholstery leathers

Production of Casein

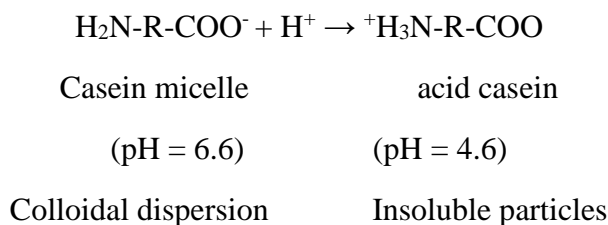
Extraction of casein from milk –

Separation

Whole cow's milk (with a typical fat content of 4.65%) is first separated by means of **centrifuges** that produce cream and **skim milk**. Skim milk can thus be considered as the raw material from which casein products are made.

Precipitation

Precipitation by means of acidification can be considered in terms of simple chemistry as follows, R being the casein protein:



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Wet-processing operations

When the casein has been precipitated, the mixture **is heated**. Heating of the precipitated casein causes the particles to shrink and expel moisture (whey) (rather like a sponge), and also to **agglomerate** together to **form clumps of curd**. The curd is then separated from the whey and washed several times with water in vats prior to mechanical **dewatering by pressing or centrifuging**.

Drying and dry processing of casein

The dewatered curd, with a **moisture content of about 55%**, is **dried by means of hot air** using either fluidized bed driers with multiple decks or pneumatic-conveying ring driers to produce a dry casein having a moisture content **of 10-12%**. The warm, unmilled casein is then subjected to several dry processing steps including **cooling (usually by air conveying), tempering” or conditioning** to ensure that moisture is distributed evenly between large and small particles, **milling, sifting** (to produce coarse, medium and fine mesh particles), **blending** (to ensure uniformity) and **bagging**. The 25 kg bags of casein are placed on pallets and stored ready for shipping.

Production of Acrylic Resin

Selection of monomer

The properties of acrylic and meth-acrylic ester polymers depend mainly on the alcohol used in the preparation of the monomer.

Solution polymerization

Polymerization of acrylic esters are usually carried out in large, agitated, stainless steel cylindrical kettles.

The kettle should be fitted with a jacket for heating or cooling, a reflux condenser

Production of Polyurethane Resin

Chemical Composition of Polyurethane Resin Blends

To make a polyurethane, a polyol is reacted with a diisocyanate. These ingredients may include catalysts, surfactants, colorants (pigments or dyes), blowing agents, and flame retardants.

Blends of Polyurethane Resin

Consists of a diisocyanate and a polyol resin blend. To make polyurethane resin, the user meters the “A-side” and “B-side” in the proper ratio, using a proportioning pump to a mix head or spray gun, where the ingredients are mixed and dispensed.

Polyols

The major ingredient in Polyurethane Resin blends is a polyol or a mixture of several polyols. Polyols typically make up at least 70% by weight of a Polyurethane resin blend.

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Catalysts

It is already incorporated into the Polyurethane resin blend at typically less than 10% by weight. Some amine catalysts and various metal catalysts (e.g., tin, potassium, bismuth) can be strongly basic.

Surfactants

Generally, surfactants are a minor constituent of the polyol resin blend formulation (0 to 2% by weight).

Colorants

Their presence at low levels (typically less than 1% by weight) in the blended polyol resin can minimize the potential for significant exposure.

Blowing Agents

Blowing agents that currently are used include hydrofluorocarbons (HFCs), hydrocarbons (pentanes), liquid carbon dioxide (CO₂), acetone, and water (reacts with di-isocyanate to form CO₂).

Flame Retardants

- Brominated compounds
- Antimony compounds
- Chlorinated phosphorus compounds