The science that stands behind nail lacquers

ABSTRACT

Nail lacquers serve two main functions; to protect the nail and to make it look aesthetically pleasing. The chemistry of nail lacquer is closer to industrial coatings than traditional cosmetics. The foundation of nail lacquer is the film-forming polymer; nitrocellulose is the commonly used polymer. Along with the film-forming polymer, a modifier/plasticizer is used to optimize physical and chemical properties of the film-forming polymers. Proper solvent blend is critical for application of the nail lacquer, the length of dry time, appearance, and wear of the nail product. Colorants are used to make the lacquer aesthetically appealing.

INTRODUCTION

Nail lacquer is a product that is very different from other cosmetic products because of its smell, application, and chemistry. Lacquer technology has its roots in the paint and coatings industry. Nail lacquers are flammable because of the solvents used in the formulation. Due to the unique chemistry, fewer cosmetic chemists are familiar with nail lacquer chemistry. The global nail products market is $3.3 billion and 75% of that is nail lacquer (1).

Nail lacquer is sometimes referred to as nail enamel or nail polish but those terms are not scientifically accurate. A lacquer is a coating that consists of a film forming system dissolved in a volatile solvent phase, and the film is formed by evaporation of the volatile solvent phase. No chemical reaction takes place during film formation, while the term enamel is usually used for coatings that undergo a chemical reaction. A varnish is a blend of natural or synthetic resins and drying oil in a solvent that forms a thin film that must be buffed to form a glossy finish.

A typical nail lacquer consists of film-forming polymers, film modifiers, solvents, suspending agents, colorants, and optionally some additives.

FILM-FORMING POLYMERS

The film-forming polymer is the foundation of a nail lacquer formulation; the film has to be robust enough to withstand all the different activities fingers go through. The polymer is required to have good adhesion to nails, toxicological safety, and regulatory compliance with good chemical, mechanical, thermal resistance and ease to removal.

Nitrocellulose is the most common film-former in nail lacquers today. It is also called gun cotton, nitro, cellulose nitrate, pyroxylin, and collodion. It has been used in nail lacquers since the 1920s and still continues to be the film-former of choice today (2, 3). It meets all the requirements mentioned above and is economically favorable. Nitrocellulose is a naturally derived polymer as it is produced by nitration of cellulose, derived from cotton fibers or wood pulp. The structure of nitrocellulose is given below:

![Nitrocellulose structure](image)

The solubility of nitrocellulose depends on the degree of nitration of cellulose. There are three grades of nitrocellulose based on degree of nitration. The SS grade (in Europe called grade A) contains the lowest degree of nitrogen (10.9-11.2%). It is soluble in esters, ketones, and glycol ethers and can tolerate significant amounts of hydrocarbons and lower alcoholic solvents. Due to its higher hydroxyl content, the SS grade is sensitive to moisture. The middle grade of nitration is called AS grade (European grade M) and the RS grade (European grade E) contains the highest degree of nitration (11.8-12.2%). RS grade nitrocellulose is typically used in nail lacquers. RS type nitrocellulose is soluble in esters, ketones, and glycol ethers. It can tolerate small amounts of alcohol and hydrocarbons. Since it contains lower amounts of hydroxyl groups, it is the least water sensitive grade of nitrocellulose.

The molecular weight of nitrocellulose affects solution viscosity, film robustness, chemical resistance, and application of nail lacquer. If nitrocellulose is looked at as a chain of beads, then each anhydroglucose unit is a bead, and the number of beads is referred to as degrees of polymerization (DP). The viscosity of the polymer depends upon DP; the higher the DP, higher the viscosity. The viscosity of a nitrocellulose solution is measured by the "falling ball" method (ASTM D3015, ASTM D1343-56).
The viscosity is measured by the time taken for a steel ball of specific size and density to travel a given distance in a solution of nitrocellulose of known concentration in a specific solvent mixture. Lower viscosity solutions have lower molecular weight and shorter times required for the steel ball to descend. The term "s" second refers to lower molecular weight nitrocellulose as compared to "f" second or 60-80 second nitrocellulose. Generally, / and "f" second nitrocellulose are used in nail lacquers.

Nitrocellulose is an explosion hazard in a dry state; therefore it is mixed with a wetting agent for safe handling and transport. Wetting agents are water and alcohol at 30% concentration, and 70% is nitrocellulose cotton. Generally, isopropanol wet nitrocellulose is used in nail lacquers.

Nitrocellulose degrades when exposed to heat, sunlight, alkaline materials, and some metals, especially iron. Therefore, it is important to store nitrocellulose in a non-ferrous lined container that is sealed well. Sunlight, heat, and exposure to iron will turn nitrocellulose yellow in color.

Nitrocellulose solutions discolor and lower in viscosity with age. To protect nitrocellulose from photo degradation, ultraviolet light absorbers (UV absorbers) are added to nail lacquer formulations. Commonly used UV absorbers are Benzophenone-1, etiorylene, and octocrylene.

Non-nitrated cellulose esters like cellulose acetate propionate (CAP) or cellulose acetate butyrate (CAB) stay clear or water white when exposed to heat or sunlight. Therefore, they are used in non-yellowing formulations. Various grades of CAP and CAB are available on DP, degree of substitution, and amount of ester functionality. They are not explosive and are sold as 100% solids materials. CAP and CAB films are not as glossy or robust as nitrocellulose films.

Acrylic polymers (acrylate and methacrylate polymers) are sometimes used as primary film-formers in nail lacquers. They are homo and copolymers of acrylic, methacrylic acids, and their esters. These polymers have good heat and light stability, and favorable solubility profile for use in nail lacquers. One has to be careful in selecting the acrylic polymer, as some polymers are sensitizers.

**FILM MODIFIERS**

The primary film former used in nail lacquers is nitrocellulose; it forms hard brittle films at room temperature, as its glass transition temperature is 53°C (4). It requires a plasticizer to form flexible films at body temperature. Historically, phthalates (particularly dibutyl phthalate, DBP) were used as plasticizers but due to their toxicological safety they are banned for use in nail lacquers in the European Union.

Castor oil (glyceryl triricinoleate) and its derivatives were used in the past. Citrate esters, benzoate esters, adipate esters, and N-substituted toluenesulfonamides have been used as plasticizers in nail lacquers. Amount of plasticizer is important as too little can make films brittle and too much would make films sticky, soft, and would also increase the drying time of the nail lacquer.

Sometimes, secondary film-formers are added as film modifiers to improve flexibility, adhesion, water-resistance, and gloss of the formulation. Historically, toluenesulfonamide/formaldehyde resin (TSFR) was used but due to potential sensitization potential of formaldehyde, it is not the modifier of choice now. As an alternative to TSFR, toluene sulfonamide/epoxy resin (TSER) is used at present. Polyester resins are also used as film modifiers; they are formed by the reaction of one or more polyhydric alcohols with one or more polycarboxylic acids or acid anhydrides. A commonly used example of this class is adipic acid/neopentyl glycol/trimellitic anhydrides copolymer. Some acrylic copolymers (e.g., copolymer of methyl methacrylate and butyl methacrylate or styrenated acrylics) are used for their color stability.

**SOLVENTS**

The solvent blend in nail lacquer influences viscosity, application, drying time, gloss, film hardness, and long term stability of the product.

The solvents are volatile. The solvency power of a particular solvent depends on its structure and geometry and can be described as solubility parameter or Kauri-Butanol value (KB value) (5). The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from complex thermodynamic calculations that are based on the idea that "like dissolves like". The KB value is determined for hydrocarbon solvents.

It is a numerical value determined by the maximum amount of hydrocarbon solvent that can be added to a kauri resin solution in butyl alcohol without causing turbidity (ASTM method D1133-04).

The boiling point and relative rate of evaporation are important in solvent selection as they affect the length of drying time and initial hardness of the film. The evaporation rate is expressed as a dimensionless numerical value, which is a ratio of the evaporation rate of the solvent relative to the evaporation of standard solvent, normally n-butyl acetate, as measured under standard test conditions. The value of 1 is assigned to the evaporation rate of n-butyl acetate. Therefore, solvents with evaporation rates greater than 1 will evaporate faster than n-butyl acetate and solvents with evaporation rates less than 1 will evaporate slower than n-butyl acetate. Oxygenated solvents have one or more functional groups containing oxygen (e.g., alcohols, ethers, esters, and ketones).

These solvents are referred to as active solvents as they actively dissolve the polar nitrocellulose (the main film-forming polymer) and modifiers used in nail lacquers. Hydrocarbon solvents consist of only carbon and hydrogen and they lack oxygen. They are referred to as diluents as they do not dissolve the film-former or the modifier by themselves but are often added to lower that cost of the formulation.

N-butyl acetate, propyl acetate, and ethyl acetate are the most commonly used ester solvents in typical nail lacquer formulations. Ethyl acetate is considered to be...
a fast evaporating solvent, then comes n-propyl acetate followed by n-butyl acetate; this is related to their boiling points of 77, 101.6, and 126°C respectively.

Occasionally, amyl acetate (BP 142°C) is used as a "tail solvent", the slowest evaporating solvent in a given solvent blend.

Tert-butyl acetate (BP 97.8°C) can also be used but it has a strong odor. Sometimes glycol ethers are used in nail lacquer formulations, they are more common in industrial coatings. Propylene glycol based ethers have favourable toxicological profiles; propylene glycol monomethyl ether (methoxypropanol, BP 118°C) is sometimes used in nail lacquers as a tail solvent.

Ketones are rarely used in nail lacquers due to their fast evaporation rate and odor but acetone is commonly used as the main ingredient in nail lacquer remover. It is considered to be a VOC (volatile organic compound) exempt solvent. The ketone that is seldom used is methyl ethyl ketone (sometimes referred to as MEK, BP 80°C).

Hydrocarbons are sometimes used to lower the cost of the solvent blend. Historically, toluene (BP 110°C) was used in nail lacquers but due to toxicological and environmental issues it was banned by California Air Resource Board (CARB). Xylene (BP 137-140°C) and n-heptane (BP 98.4°C) are occasionally used as diluents.

SUSPENDING AGENT

Suspended pigments are used in nail lacquers to suspend colourants and to provide proper rheology for application. Organically modified montmorillonite clays have been used since 1950's (6).

Hydrophobic silica is used occasionally as a suspending agent. They form a three dimensional structure that prevents colourants from settling down. Stearalkonium hectorite and bentonite are used in pigmented nail lacquers.

The organo-clays impart thixotropy (shear thinning) to the nail lacquer formulation (i.e. nail lacquer is thick when at rest and becomes thin when shaken), which helps in the application of the product.

COLOURANTS

Coloured nail lacquer is 75% of the total nail category and it can be broadly classified into two categories: crème and frost.

Crème nail lacquer consists of organic and inorganic pigments while frost nail lacquer contains pearlescent pigments along with other pigments. The Cosmetics Directive 76/768/EEC contains a list of colouring agents allowed for use in cosmetic products (Annex IV). Pigments are identified by their Colour Index (CI) numbers.

Organic pigments are brightly coloured compared to inorganic pigments.

Lakes are organic dyes (organic colourants soluble in solvents) that are precipitated onto inorganic substrates that are allowed by the Cosmetics Directive (e.g. calcium carbonate, rutinum sulfate). Lakes are insoluble in solvents used in nail lacquers. Red 6 Lake (CI 15850), Red 7 Lake (CI 15850;1), Red 34 Lake (CI 15880), and Yellow 5 Lake (CI 19140) are widely used in nail lacquers. Sometimes, ferric ferrocyanide (CI 77510) is used. The only natural organic pigment used is carmine (CI 75470) which is obtained from the shells of a specific species of beetle.

The majority of inorganic pigments are metal oxides e.g. titanium dioxide (CI 77891), iron oxides (CI 7749, 77492, and 77490).

Titanium dioxide is white in colour while iron oxides come in variety of red, yellow, brown, black and maroon shades. Inorganic pigments have high opacity but they are relatively dull. They are dense and therefore, are difficult to disperse in nail lacquers. To overcome this issue, many times pigments are coated with reactive silicones (silanes) or dimethicone.

Pearlescent pigments are widely used in nail lacquers along with other pigments. They exhibit shimmer or sparkling effects. Some commonly used pearlescent pigments are titanated micas (mica on which layers of titanium have been deposited), synthetic mica (fluorophlogopite), calcium borosilicate, bismuth oxychloride (BiOCl), aluminum powder and guanine (natural pearl obtained from the scales of Atlantic herring).

OPTIONAL ADDITIVES

Sometimes nail lacquers contain slip and mar additives; typically they are silicones, fluoropolymers, micronized waxes, or surfactants.

Promotional ingredients are added in small quantities and include vitamins, minerals, proteins, botanical extracts, fragrance etc.

REFERENCES AND NOTES