CHAPTER I

INTRODUCTION

1.1 Background

Cellulose Nitrate, known commercially as nitrocellulose, is the cellulose inorganic ester of commercial importance. It is manufactured by treating cellulose obtained from either wood pulp or cotton linters with nitric acid in the presence of sulfuric acid and water. Cellulose nitrate is a semi-synthetic polymer rendering outstanding film properties such as good transparency and water resistance, thus finds its major utilization in coating industry. Raw cellulose nitrate from a production plant in Thailand (i.e. Nitrochemical Co., Ltd.) has a water by-product at maximum content of approximately 3% by weight. Commercial cellulose nitrate is also sold wetted with an isopropyl alcohol at 30% by weight in order to decrease the significant fire hazard which dry cellulose nitrate poses. Although, cellulose nitrate is highly demanded in coating industrial but its global market competition is moreover important. Therefore, adding value of cellulose nitrate is necessary, so we developed a new highly demanded product which made from cellulose nitrate. Nail lacquer has cellulose nitrate as main ingredient so it will be a new potential product for exportation beside of cellulose nitrate resin. According to the presence of water in cellulose nitrate resin, it is immiscible in cellulose nitrate solution that it provides phase separation in the solution. Thus tolerance water content in cellulose nitrate resin was investigated in this study for providing good film formation. Since cellulose nitrate film has poor adhesion to the nail, resin types were examined to improve cellulose nitrate adhesion. Generally, polymer solution such as cellulose nitrate solution is shear thinning flow which is time independent behavior, nail enamel system require time dependent behavior called thixotropic to provide recovery viscosity with lapse of time. Cellulose nitrate can be thixotropic behavior by applying the thixotropic agent such as organoclay which is not only improve the flow behavior but also suspend pigment in the solution. Nail lacquers are by far the largest and most important group of manicure preparations. Originally, only colorless or pale pink products were acceptable. A nail lacquer, or nail enamel as it is sometime called, is essentially a

solution of a film former in suitable solvents, capable of supporting colorants and pearls and able to form smooth, glossy, continuous coating on the nails. The required properties for an ideal nail lacquer are as follows [1-2]:

(1) It should be innocuous to the skin and nails.

(2) It should be easy and convenient to apply.

(3) It should be stable on storage as regards homogeneity separation, sedimentation, color and interaction of ingredients.

(4) It should give a film with satisfactory characteristics.

The characteristics of a satisfactory film are:

(1) Even thickness which demands a satisfactory viscosity of the lacquer, neither too thin nor too thick, and good wetting and flow properties.

(2) Uniform color, which demands a very finely divided pigment, intimately ground and wetted by the medium.

(3) Good gloss, which implies a very smooth surface and depends upon the properties of the medium.

(4) Good adhesion to the nail.

(5) Sufficient flexibility to avoid brittleness and cracking.

(6) Hard, non-tacky surface, resistant to impact and scratching, which will not adhere to other surfaces nor mark off color on fabrics or paper.

(7) Satisfactory drying properties-drying time of about 1-2 minutes without development of bloom even in humid atmospheres.

These characteristics can be accomplished by the proper formulation of necessary constituents of nail enamel.

1.2 Nail lacquers formulations

Nail lacquer formulation has four major components, film former, solvent, secondary resin and plasticizer. Colored nail lacquer also contains pigments and pearls, to give the desired color effects on the nail, and may contain suspending agents to help stabilize the pigments in the formulation. UV absorbers and other special

additives, such as proteins, are sometimes added in order to make more powerful claims and generate a higher level of consumer appeal.

The types and contribution of each of the major ingredients in a nail lacquer product will now be discussed.

1.2.1 Primary film former

The basic film-forming material in nail lacquers is cellulose nitrate, a cellulose nitrate obtained by the reaction of mixtures of nitric acid and sulfuric acid with cotton. In this reaction all three of the alcohol groups in the cellulose ring can be esterified. The degree of esterification or substitution determines the intrinsic characteristics of the nitrocellulose and the degree of polymerization of the cellulose chain governs the viscosity of the product. The cellulose nitrate used in nail lacquers has a degree of substitution of approximately two and is known as dinitrocellulose-pyroxylin.

Different grades of cellulose nitrate are characterized by their viscosity in organic solvents, for example 1/2-second or 1/4-second cellulose nitrate, using the US nomenclature based on the falling ball method of determining viscosity. In practice, the grades of nitrocellulose used to manufacture nail lacquers are those which give sufficiently fluid solutions to allow easy application on the nails.

Films produced by cellulose nitrate are waterproof, hard and tough and resist abrasion. However, when used alone cellulose nitrate has some drawbacks, namely, poor gloss and a tendency to shrink and to become brittle and adhesion to most surfaces is only moderate. This has resulted in the use of modifying resins to impart adhesion and to improve gloss, and of plasticizers to impart flexibility and to reduce shrinkage. With the use of solvents and diluents one then has the complete range of ingredients used in nail lacquers.

1.2.2 Secondary film former

In about 1938 resins of the aryl sulfonamide-formaldehyde type were introduced which gave good luster to nail varnish films and improved their resistance in detergent solutions; such resins have been used in many nail lacquers since that time to impart gloss, improve adhesion and often to increase the hardness of resulting

films. During the past several years, there has been a growing concern about the use of any type of aldehyde condensate, particularly, formaldehyde condensates, both in the work place and in the area of consumer product, be it adhesives, coatings, or in the formulation and application of cosmetics, etc. This growing concern, in part, is attributable to research which has determined that formaldehyde is suspected to be a human carcinogen. In an effort to replace the use of sulfonamide formaldehyde resins with less toxic substitutes, rosin esters, acrylic resins, polyester resins, and certain emulsion type resins have been used. The use of such substitutes, how ever, has been less than satisfactory in result. Invariably, the finished formulation would have numerous drawbacks in performance characteristics including, but not limited to, adhesion, gloss, water resistance, brilliance, and clarity of film [2-3].

1.2.2 Plasticizers

Cellulose nitrate is too brittle to be used in lacquers on its own and even the inclusion of a resin will not impart the necessary flexibility to lacquer films. Plasticizers must therefore be included in nail lacquer formulations in order to ensure that the film which remains on the nails after the solvents have evaporated adheres well, is flexible and does not flake off. By virtue of their high boiling point, plasticizers will remain in the film after the solvents present in the formulation have evaporated and render the films pliable. Plasticizers, even at low concentration, will furthermore enhance the gloss of resultant films and will also improve the flow properties of lacquers.

There are two groups of plasticizers:

1. solvent plasticizers which, as the name implies, are solvents for cellulose nitrate. These are true plasticizers, comprises mainly high-molecular-weight esters, with fairly high boiling points and low volatility.
2. non-solvent plasticizers, also referred to as softeners. These are not solvents for cellulose nitrate and are not compatible with it. If they are used in the absence of solvent plasticizers, they will form separate droplets on the film once the solvents have evaporated. They must therefore be used in

conjunction with true plasticizers which will hold them in solution, under those conditions they will impart additional flexibility to the film. The most common representative of this group is castor oil which, when used in combination with a true plasticizer in the proportion 1 : 1, at a level of about 5 per cent, produces a very flexible film.

A good plasticizer must:

1. be miscible in all proportions with the solvent, the cellulose nitrate (applies to true plasticizers) and the resins used;
2. be dermatological innocuous and free from any sensitizing properties;
3. have a low volatility;
4. improve the flexibility and adhesion of the lacquer;
5. not cause any discoloration of the finished product, that is, it must have moderately good transparency;
6. be stable and odorless, or it must have a pleasant odor, since it does not evaporate but remains in contact with the nail.

Dibutyl phthalate is one of the most widely used. Phthalates, phosphates, phthalyl glycollates, sulphonamides and citrates constitute the main group of plasticizers used in nail varnishes [2].

1.2.3 Solvents

True solvents or volatile portion of a cellulose nitrate nail enamel formulation provides the means for dispersing the film-forming and nonvolatile portion, so that a uniform mixture of these components may be obtained. Solvents for use in cellulose nitrate nail lacquer formulations must be considered in the three general interrelated categories: active solvents, couplers or latent solvents, and diluents.

Active solvents are those liquids that dissolve cellulose nitrate; they include ketones, and esters. Their rates of evaporation are classified as fast, medium, and slow evaporating.

Couplers are generally alcohols. By themselves they are not solvents for cellulose nitrate, but when used in conjunction with active solvents, they increase the

strength of the latter. Because the alcohol couples with the ester solvent, synergism takes place. A solution of cellulose nitrate in an active solvent alone will have a greater viscosity than those similar solutions containing mixtures of the active solvents and the alcohol. Depending on the percentage of alcohol utilized, the flow of the nail enamel can be improved.

Diluents are nonsolvents for cellulose nitrate. They are used to stabilize the viscosity in nail lacquers in order to reduce the number of applications of a base coat, help to carry resins into solution, and lower the overall cost of the lacquer formulations. Aromatic hydrocarbons, notably toluene and xylene, are the most common diluents found in nail lacquers [4].

1.2.4 Pigments [7]

Pigments are insoluble, fine particle size materials used in coatings for one or more of five reasons: to provide color, to hide substrates, to modify the application properties of a coating, to modify the performance properties of films, and/or to reduce cost. Pigments are divided into four broad classes: white, color, inert, and functional pigments. Pigments are insoluble materials used as colloidal dispersions. Dyes are soluble colored substances; they are used only in specialized coatings such as stains for wood furniture. Some pigments are called lakes. The original meaning of lake was a dye that had been converted into a pigment by irreversible adsorption on some insoluble powder. The term lake is now sometimes used when a colored pigment is blended with an inert pigment; when the pigment is essentially all colored pigment, it is sometimes called a toner. However, dyes should not be used for nail enamel owing to they are soluble to the nail and tissue around the nail plate.

1.2.5 Suspension or thixotropic Agents

The modern trend towards highly pigmented and pearlescent nail lacquers has led to a critical assessment of the ability of traditional nail lacquer formular to suspend these materials at high concentration. Additionally, consumers have reacted against products showing 'settled out' materials, and thus systems developed to avoid sedimentation soon showed themselves both to be technically superior and to have

enhanced consumer acceptance. The suspension properties are obtained by creating a thixotropic system with the use of pretreated colloidal clays such as benzyl dimethyl hydrogenated tallow ammonium montmorillonite (Bentone 27), dimethyl dioctadecyl ammonium bentonite (Bentone 34), or dimethyl dioctadecyl ammonium hectorite (Bentone 38). These clays increase the viscosity of the system to such an extent that the heavy oxide pigments remain in suspension. When a shear force is applied to the system by shaking, or by brushing the product across a nail, the viscosity drops sharply allowing a smooth application. On standing the system regains its initial high viscosity. A thixotropic system containing nacreous pigments has been described in a US patent. In modern practice bentone levels range from 0.5 to 2 per cent, since the viscosity of the system can be enhanced even further by adding small quantities of a polyvalent acid, for example, ortho phosphoric acid, which precludes the use of high levels of bentone and makes the system more controllable [2].

1.3 Objectives

1. To study the effect of water content in raw cellulose nitrate on its film forming properties and determine a tolerance water level in the resulting nail polish.
2 To examine effect of adding layered silicate clay particles as thixotropic agent in the nail enamel.
3 To investigate the properties of the nail enamel: rheological behaviors, drying time, gloss, adhesion, hardness and surface texture.