

รายงานวิจัยแบบสมบูรณ์
เรื่อง

การศึกษาผลกระทบของปริมาณน้ำในเซลล์โลสไนเตรตต่อคุณสมบัติของน้ำยาทาเล็บ
ที่มีดินเหนียวเป็นสารปรับสภาพการไหล

โดย

ศาสตราจารย์ ดร. วิวัฒน์ ตัณฑะพานิชกุล และคณะฯ
จุฬาลงกรณ์มหาวิทยาลัย

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

รายงานวิจัยนี้ได้รับเงินทุนสนับสนุนจากโครงการวิจัยร่วมภาครัฐ-เอกชน
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บทคัดย่อ

เซลลูโลสไนเตรดเป็นพอลิเมอร์กึ่งสังเคราะห์ที่มีความโปร่งใสดีเยี่ยมสามารถต้านทานน้ำได้ดี ใช้แพร่หลายในอุตสาหกรรมเคลือบผิว เรซินที่ได้จากกระบวนการผลิตมีผลิตภัณฑ์ร่วมที่เป็นน้ำและไอโซโพรพิลแอลกอฮอล์ไม่เกิน 3 และ 30 เปอร์เซ็นต์โดยน้ำหนักตามลำดับ ในงานวิจัยนี้ศึกษาหาปริมาณน้ำที่ยอมรับได้ในผงเซลลูโลสไนเตรดเพื่อประยุกต์ใช้ในงานนำยาทาเล็บ โดยศึกษาการเกิดฟิล์มที่มีคุณสมบัติดี และผลกระทบของการเติมอนุภาคดินประเภทแผ่นซิลิเกตเป็นสารปรับสภาพการไหลในนำยาทาเล็บ ปริมาณน้ำในผงเซลลูโลสไนเตรดมีการปรับเปลี่ยนสัดส่วนตั้งแต่ 1, 2, 3, 4, 6, 8, และ 10 เปอร์เซ็นต์โดยน้ำหนัก เมื่อศึกษาผลกระทบของน้ำที่มีผลต่อคุณภาพฟิล์มซึ่งพบว่าปริมาณน้ำมีผลต่อความหนืดและระยะเวลาการแห้งตัวแต่ละอย่างไม่มีผลกระทบมากนักต่อฟิล์มแข็ง ตามที่เซลลูโลสไนเตรดมีความสามารถในการยึดเกาะค้างต้องศึกษาเรซินชนิดอื่นเพื่อช่วยความสามารถในการยึดเกาะของเซลลูโลสไนเตรด พบว่าเรซินที่เหมาะสมคืออีพอกซีและมาเล-อิกเรซินซึ่งเป็นของเหลวและของแข็งที่อุณหภูมิห้องตามลำดับ โดยจะทำการปรับสัดส่วนระหว่างเรซินทั้งสอง 10:0, 8:2, 5:5, 2:8, และ 0:10 ซึ่งสัดส่วนที่ 5:5 ให้ฟิล์มที่ค่อนข้างดี ทนดี การเตรียมสารปรับสภาพการไหลได้เปรียบเทียบการเตรียมแบบมอเตอร์สเตอร์เรอร์ที่ความเร็วรอบ 650 รอบต่อนาทีเป็นเวลา 4, 8, 14, 24, และ 48 ชั่วโมง การเตรียมแบบไฮโมจิโนเซอร์ที่ความเร็วรอบ 6.5×10^3 , 9.5×10^3 , 13.5×10^3 , 21.5×10^3 , และ 24×10^3 รอบต่อนาที พบว่าสารปรับสภาพการไหลที่เตรียมด้วยไฮโมจิโนเซอร์จะมีความหนืดสูงกว่าและมีสามารถเกิดเจลในในเวลาอันสั้น ฟิล์มที่ได้มีความละเอียดเรียบและให้ค่าความมันวาวสูงกว่าการเตรียมแบบมอเตอร์สเตอร์เรอร์ ออร์แกนอเคลย์ที่ใช้เป็นสารแขวนลอยในโทลูอินในงานวิจัยนี้มี 3 ชนิดคือ ไคเมทิลไดออกตะติซิลแอมโมเนียมเฮกโตไรท์, ไคเมทิลเบนซิลไดคิซิลเฮกโตไรท์, และไคเมทิลไดออกตะติซิลแอมโมเนียมเบนโตไนด์ โดยจะปรับสัดส่วน 1, 3, 4, และ 5 เปอร์เซ็นต์โดยน้ำหนัก พบว่าที่สัดส่วน 5 เปอร์เซ็นต์โดยน้ำหนักสามารถแขวนลอยเม็ดสีได้โดยไม่ตกตะกอน

Abstract

Cellulose nitrate (CN) 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 CN has water and isopropyl alcohol by-product at maximum content of approximately 3 and 30 wt%, respectively. The tolerance water level in the CN powder for a potential application as nail polish is investigated in order to produce good film-forming properties. The effect of adding layered silicate clay particles as thixotropic agent in the nail enamel is also examined. The water content was varied at different weight percent i.e. 1, 2, 3, 4, 6, 8 and 10 wt%. It was found that the increase in water content affected the solution properties of CN by reducing its viscosity and drying time but it has no more effect to the dried films. According to poor adhesion of CN, adhesion promoter types were investigated for CN adhesion improvement. The suitable adhesion promoters are epoxy and maleic resin which is liquid and solid at room temperature, respectively. The compositions of maleic-epoxy mixture were investigated by varying resin ratio 10:0, 8:2, 5:5, 2:8, and 0:10 wt%. At composition 5:5 provides relatively good durable film. Thixotropic suspension preparation was compared mechanical stirrer preparation at 650 r.p.m. for 4, 8, 14, 24, and 48 hr. with homogenizer at 6.5×10^3 , 9.5×10^3 , 13.5×10^3 , 21.5×10^3 , and 24×10^3 r.p.m. for 5 minutes. The suspension preparing by homogenizer furnishes higher viscosity and produces gel in short time, dried film also show fined texture which is higher gloss than motor stirrer preparation. Three kinds of organoclay using as suspension in toluene were dimethyl dioctadecyl ammonium hectorite, dimethyl benzyl dodecyl ammonium bentonite, and dimethyl dioctadecyl ammonium bentonite varying contents from 1-5 wt%. The suitable content is about 5 wt% where able to suspend pigment without hard packed settling.

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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. In this investigation, we will utilize cellulose nitrate resin which is produced locally by nitration. Raw cellulose nitrate from the production plant in Thailand of Nitrochemical Co., Ltd. has a water residue at maximum content of approximately 3% by weight. Commercial cellulose nitrate is also wetted with an isopropyl alcohol at 30% by weight in order to decrease the threat of fire hazard which dry cellulose nitrate poses. Though the resin is widely used in the coating industry, the price of the material must be kept to be relatively low due to the severe global market competition. Therefore, adding the 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 a main ingredient, therefore, so it can be a new potential product for entering the highly competitive market. Due to the presence of water in cellulose nitrate resin which is immiscible with cellulose nitrate solution, it will give rise to the phase separation in the resulting solution. Thus tolerance water content in cellulose nitrate resin will be investigated in this study for types of adhesion good film formation characteristics. In addition, since cellulose nitrate film has poor adhesion to the nail, promoters will be examined enhance its surface bonding.

Generally, polymer solution such as cellulose nitrate solution shows shear thinning flow behaviors, which is time independent behavior, nail enamel system requires time-dependent behavior i.e. thixotropic flow to provide recoverable viscosity with lapse of time. Cellulose nitrate solution can be made thixotropic by adding the thixotropic agent such as organoclay which is not only improve the flow behavior but also suspend pigment in the solution. 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 innocuous to the skin and nails, easy and convenient to apply, stable on storage as regards homogeneity separation, sedimentation, color

and interaction of ingredients, and satisfactory characteristics film. The characteristics of a desirable film that can be accomplished by the proper formulation of essential constituents of nail enamel are as follow [1-2]:

1. Level 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.

1.2 Nail lacquer formulation

Nail lacquer formulation has six major components including a film former, solvent, a 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 that is suitable for coating application. However, using solitary cellulose nitrate has some drawbacks such as poor gloss, tendency to shrink, become brittle and moderate adhesion. This has resulted in the use of modifying resins to impart adhesion, to improve gloss, and adding plasticizers to impart flexibility, and to reduce shrinkage.

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, however, 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].

1.2.3 Plasticizers

Cellulose nitrate is too brittle to applied 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. Plasticizer has two groups providing as follow:

1. Solvent plasticizers, 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 be miscible in all proportions with the solvent including the cellulose nitrate and the resins used. There should be dermatological innocuous and free from any sensitizing properties. Low volatility, being stable, and odorless are required attribution to improve the flexibility and lacquer adhesion in contact with the nail. Also no showing any discoloration of the finished product, that is, it must have moderately good transparency. Main group of plasticizers used in nail varnishes constitute phthalates, phosphates, phthalyl glycollates, sulphonamides and citrates while one of most widely used in nail enamel application is dibutyl phthalates. [2].

1.2.4 Solvents

True solvents of a cellulose nitrate typed nail enamel 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 such as ketones, and esters. Couplers are generally alcohols. They are not solvents for cellulose nitrate, however using 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].

1.2.5 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.

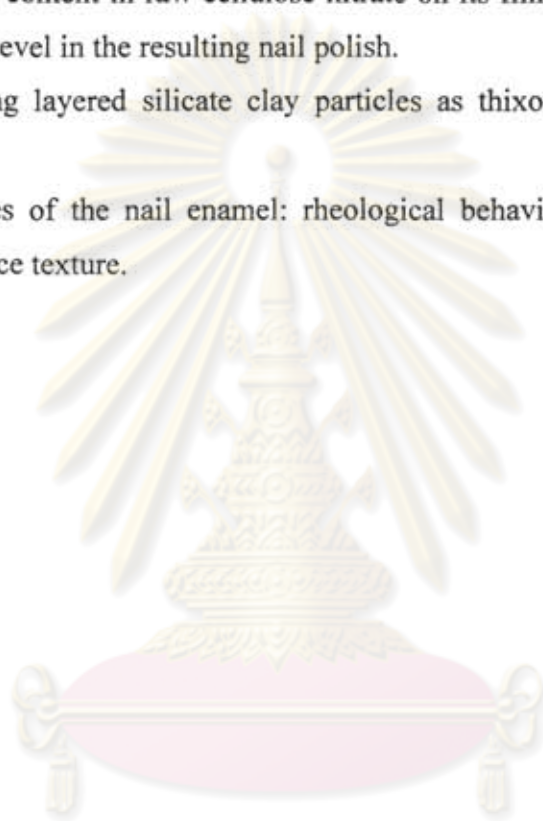
1.2.6 Suspension or thixotropic Agents

The modern trend towards highly pigmented and pearlescent nail lacquers has led to a critical assessment of the ability of traditional nail lacquer formula 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.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER II

THEORY

2.1 Anatomy of nail

The human nail covering of the upper surface of the tip of each finger and toe is a set of complex structures that can most accurately be called the nail unit. The visible nail plate is the ultimate product of the continuous pathway of maturation that occurs in this very active, specialized keratinizing unit. The nail unit can be observed by microscopic observation along longitudinal through the nail axis of the finger. It was described in Figure 2.1 that the nail unit consists of the proximal nail fold, the matrix, the nail bed, and the hyponychium.

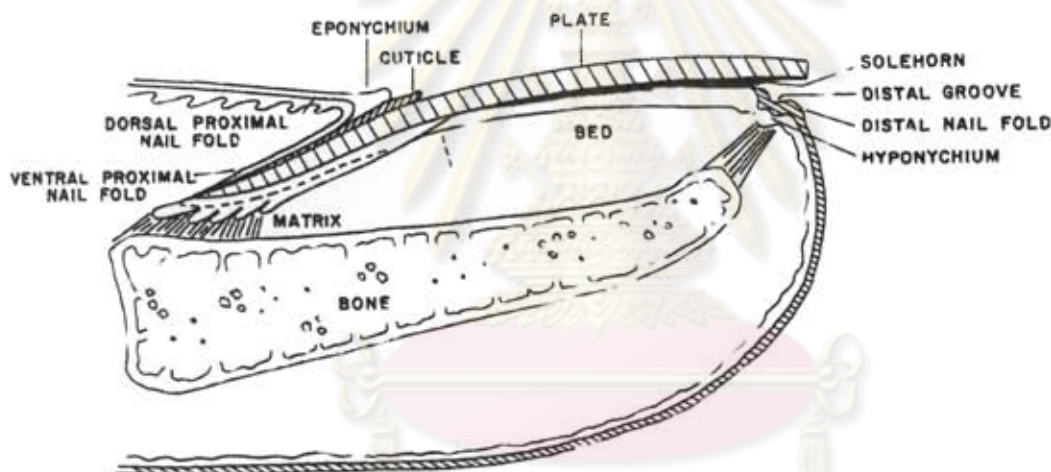


Figure 2.1 Sagittal view of nail unit [8].

The nail plate consists of close-packed, adherent, interdigitating cells that lack nuclei or organelles. Cells in the plate are very flat, lying with the smallest diameter perpendicular to the plane of the nail plate surface. Scanning electron microscopy reveals that the dorsal surface of the nail plate is smooth. The nail plate is approximately 0.5 millimeters thick in women and 0.6 millimeters thick in men. The rate of nail plate growth varies from less than 1.8 to more than 4.5 millimeters per month. Beneath the nail plate, we can see nail bed where is the beginning of hyponychium. The hyponychium is the first site of keratinization in the nail unit. It can make

waterproof area where the nail plate lifts off the nail bed. The hyponychium also is the initial site of invasion by dermatophyte in the most common type of onychomycosis.

Biophysical properties of the nail plate can be studied by x-ray diffraction showing the fibrous proteins (keratins). Transmission of x-ray is directly correlated with the nail plate thickness, generally normal thickness transmit approximately 85 percent of x-rays. The keratins are oriented in the plane of the plate, perpendicular to the longitudinal of growth. Furthermore, nail plate contains normal water content at 18 per cent and varies from 10-30 per cent. The nail plate hydration is related to its hardness. When the water content decreases below 16 per cent, the brittle nail is appeared in dry environment. In contrast, softness of the nail plate occurs in humid environments when the water content of nail plate is greater than 25 per cent. The evaporation of water from the nail plate can be slower by applying a layer of nail polish on the plate. If the nail enamel is used, it should not be removed and reapplied more often than once a week. Formaldehyde-containing nail enamel is the cause of onycholysis, therefore, it is banned nowadays.

2.2 Cellulose nitrate

Cellulose nitrate is the oldest and most important inorganic ester of cellulose. It is a white, odorless, and tasteless substance. It has found uses in plastics, lacquers, and explosives. Cellulose nitrate manufacture is treating cellulose with nitric acid in the presence of sulfuric acid and water as shown in Figure 2.2.

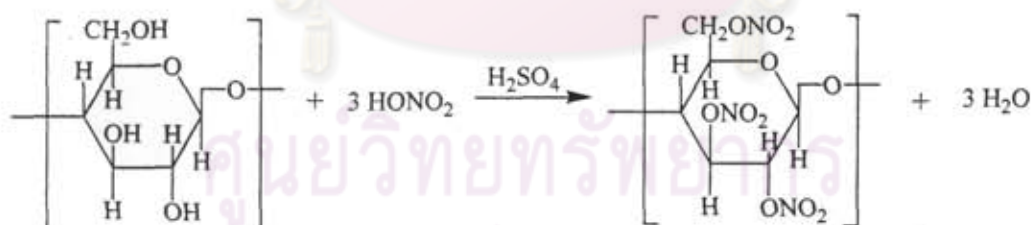


Figure 2.2 The reaction of cellulose nitrate formation [5].

The amount of water present determines the concentration of NO_2^+ . The reaction completion can be forced by removal of water with sulfuric acid. The maximum commercial DS is around 2.9, which corresponds to 13.8% N. Products over 14%N have been obtained by special processes. The viscosity range of cellulose nitrate is from 0.25 to 5000 mPa.s, depending on application. The final viscosity of the cellulose nitrate is adjusted in the digestion or pressure boiling step. The slurry of 6-8wt% of cellulose nitrate is heated, under pressure, to 130-150°C. This process can be achieved

batch wise in autoclaves and continuously by pumping the slurry through long coils of piping (1200-1500 m). During this step, viscosity can be reduced 10-fold in three hours at 132°C. This viscosity reduction allows the production of cellulose nitrate suitable for higher solids and protective lacquers. Additional washing is necessary to remove any decomposition products generated during this step.

Dry cellulose nitrate is extremely flammable; cellulose nitrate with high nitrogen content may explode when heated or subjected to rapid shock. Therefore, it is necessary to transport and handle cellulose nitrate wet with water or an alcohol. After the digestion process and centrifugation, a wet cellulose nitrate containing 25-35wt% water remains. This may be packed as is and shipped. More frequently, the water is displaced with an alcohol, typically ethanol or 2-propanol, by displacement presses or displacement centrifuges. Continuous processes prevail here also. The alcohol-wet cellulose nitrate is pressed to 30-35 wt % alcohol and shredded before packaging and shipping. Alcohol-wet cellulose nitrate fibers are more readily soluble in organic lacquer solvents than dry cellulose nitrate. From the manufacture, cellulose nitrate has four type application which classified by nitrogen content as shown in Table 2.1. For the lacquer industrial, ester-soluble cellulose nitrate is mainly applied as raw material. Physical properties of cellulose nitrate are disclosed in Table 2.2. The water-wet cellulose nitrate can be gelatinized with softeners such as phthalates and dried on drums or band driers for the manufacture of cellulose nitrate chips. For cellulose nitrate typed nail enamel application, most of ingredients are solvents that their properties were revealed in Table 2.3.

Table 2.1 Applications of cellulose nitrate of varying nitrogen content and degree of substitution [5].

CN type	N (%)	DS
Celluloid	10.5-11.0	1.8-2.0
Alcohol-soluble CN	10.9-11.3	1.9-2.1
Ester-soluble CN	11.8-12.2	2.2-2.3
Gun cotton	13.0-13.6	2.6-2.8

Table 2.2 Physical properties of cellulose nitrate [9-10].

Formula	$(C_6H_7N_3O_{11})_n$
Formula mass	297.01
Specific gravity or density (g/cm^3)	1.35-1.40
Boiling point ($^{\circ}C$)	100-110
Melting point ($^{\circ}C$)	271
Glass transition temperature ($^{\circ}C$)	56
Refractive index	1.49-1.51
Tensile modulus (MPa)	1,310-1,520
Tensile strength (MPa)	48.3-55.2
Elongation (%)	40-45
Hardness (Rockwell, R scale)	95-115
Water adsorption (wt%) (294 K, 24 hr, 80%RH)	1-2
Surface tension (mN/m)	38
Solvent	Ketone, esters, amides, and nitroparafins
Solubility parameter range of CN solvents	
- Poor H-bonding	11.1-12.7
- Moderate H-bonding	7.8-14.7
- Strong H-bonding	14.5

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Table 2.3 Properties of solvents in nail enamel [11, 12-13].

Name	Formula	Solvent type	Boiling Point (°C)	Flash Point (°C)	Solubility Parameter (δ)	H-bonding	Evaporation No. (Ethyl ether = 1)	Evaporation No. (Butyl acetate = 100)	Heat of evaporation (ΔH _v , cal/g)
IPA	CH ₃ CHOHCH ₃	Latent	80.4-82.4	15	11.5	High	21	230	159.35
Ethyl alcohol	C ₂ H ₅ OH	Latent	78.3	12.2	12.7	High	8.3	230	204.26
Butyl acetate	CH ₃ COO(CH ₂) ₃ CH ₃	Active	123-127	24	8.5	Med	12.1	100	73.82
Ethyl acetate	CH ₃ COOCH ₂ CH ₃	Active	75-77	-2	9.1	Med	2.8	615	102.01
Toluene	C ₆ H ₅ CH ₃	Diluent	109.5-111	4	8.9	Low	6.1	210	86.8
DBP	C ₆ H ₄ (COOC ₄ H ₉) ₂	Plasticizer	335	165	9.3	Med	-	-	-
Water	H ₂ O	-	100	-	23.4	High	-	-	539

2.3 Montmorillonite

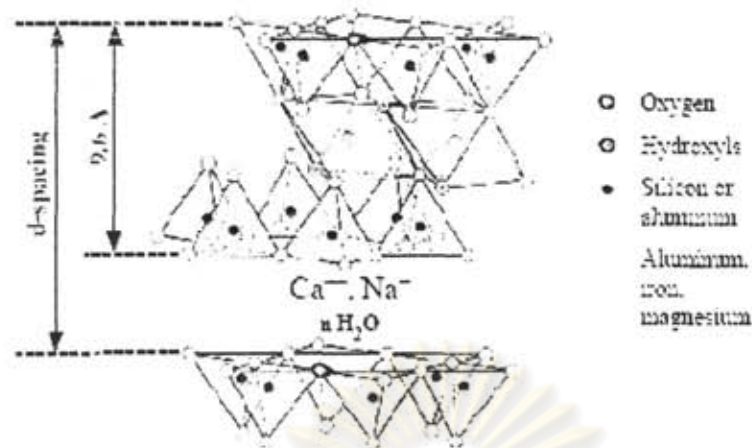


Figure 2.3 Idealized structure for montmorillonite [14].

In Figure 2.3, clays such as montmorillonites have a remarkable ability to exchange ions. Their structure consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet. The isomorphic substitutions of Si^{4+} for Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet cause an excess of negative charges within metal oxide layers. These negative charges are counterbalanced by cations namely Ca^{2+} and Na^{+} situated between the clay layers. As the forces that hold the stacks together are relatively weak, the intercalation of small molecules between the layers is easy [15]. Montmorillonite is the best known member of the smectite group which structure is classified as dioctahedral, having two thirds of the octahedral sites occupied by trivalent cations. Dioctahedral montmorillonite has its structural charge originating from the substitution of Mg^{2+} for Al^{3+} in the octahedral sheet. The idealized structural formula of montmorillonite is $\text{M}_y^+ n\text{H}_2\text{O}(\text{Al}_{2y}\text{Mg}_y)\text{Si}_4\text{O}_{10}(\text{OH})_2$. The negative charge at surface of clay layers are balanced by cations intercalated between the structural units and these cations may be alkaline earth ions or the alkali metal such as Ca^{2+} , Mg^{2+} and Na^{+} . When Na^{+} cations are exclusively in exchange with the montmorillonite surface, the clay is known as Na-montmorillonite is otherwise known as Bentonite especially in drilling fluid literature. The expanding lattice may provide the clay with a specific area of as high as $760 \text{ m}^2/\text{g}$. The chemical formula for Na-montmorillonite is $\text{Na}_{0.33}[(\text{Al}_{1.67}\text{Mg}_{0.33})(\text{O}(\text{OH}))_2(\text{SiO}_2)_4]$. Montmorillonite(MMT) is typically applied to polymer nanocomposites because of its have suitable layer charge density, low thermal expansion coefficient, and a high gas barrier property. On a larger scale of MMT, each layer can be seen as a

high aspect ratio lamella about 100-200 nm in diameter and 1 nm in thickness, this is illustrated in Figure 2.4.

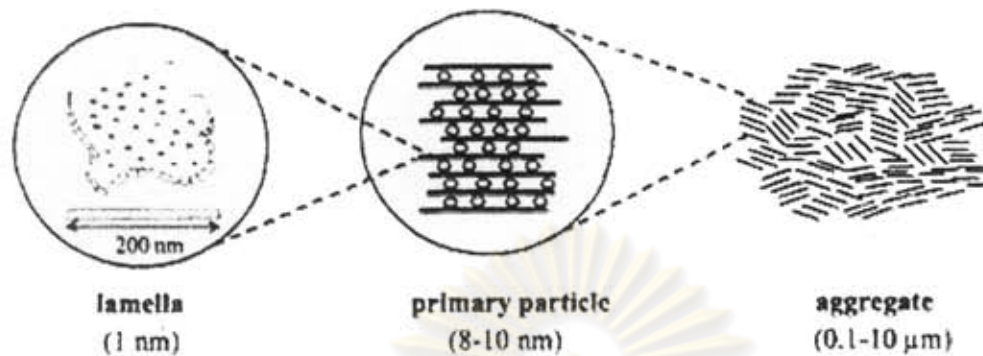


Figure 2.4 Microstructure of montmorillinite [14].

Five to ten lamellae are associated by interlayer ions in primary particles (8-10 nm in the “transverse” direction which, in turn, form larger irregular aggregates (0.1 – 10 μm in diameter) giving to the clay its turbostatic structure. Due to this special characteristic, MMT can be easily dispersed in water resulting in a stable colloid. Typically, the natural MMT is too hydrophilic to disperse in an organic matrix. Its dispersibility can be improved to make it useful by several ways [16]; (1) adsorption, (2) ion exchange with inorganic cations and cationic complexes, (3) ion exchange with organic cations, (4) binding of inorganic and organic anions, mainly at the edges, (5) grafting of organic compounds, (6) reaction with acids, (7) pillaring by different types of poly(hydroxo metal) cations, (8) interlamellar or intraparticle and interparticle polymerization, (9) dehydroxylation and calcinations, (10) delamination and reaggregation of smectitic clay minerals, and (11) physical treatment such as lyophilization, ultrasound, and plasma. Ion Exchange with organic cations is the principle reaction to convert clay mineral to organophilic clay or organoclay.

2.4 Organoclay

The property of clay surface can be modified from hydrophilic to organophilic by (a) an adsorption of the organic molecule into an interlayer, (b) a covalently bonding of the surfactant to a free hydroxyl group on the clay surface and (c) an exchanging of an interlayer cation with a cation surfactant. This is resulting in a more compatible between organic molecule and the clay. The adsorption of the organic molecule often occurs via a complex formation between the organic

molecule and the interlayer cation. The amount of the adsorbed molecule changes as a vapor pressure or temperature changes. The covalent bonded organoclay can be prepared by a condensation of a functionalized organo siloxane. Replacing an exchangeable interlayer cation by the cationic surfactant can carry out the exchange reaction. The intercalation causes an increased in the height of the clay's gallery. Several models were proposed in order to explain the packing of the alkylammonium salt within the clay layer. Dr. John W. Jordan, father of organoclay technology, introduced Organophilic clay or organoclay in 1941. NL Industry sponsored his research. He tries to develop the high value added product from bentonite. Normally, bentonite uses as a gallant for water system but not simplify for organic system. Organoclay was exchange the inorganic cations in the interlayer with organic cations to convert the clay into organophilic compound as shown in Figure 2.5 which suitable for use in organic system [17].

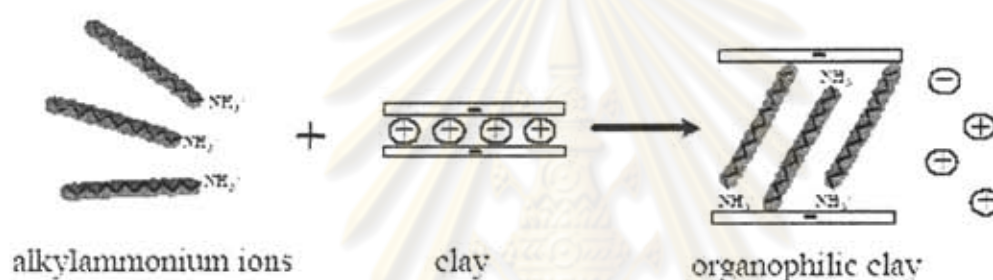


Figure 2.5 The cation-exchange process between alkylammonium ions and cations initially intercalated between clay layers [14].

Since 1941 the numerous researches in organophilic clay, such as the preparation technique, characterization technique, thermal property, has been report. There still a lack of an understanding in controlling the intercalation process and rheological property in organic system. The application of organoclay depending on the grades, which there are many different type on the market. It usually use as a gallant or viscosifying agent in paint, printing ink, grease and cosmetic industry [17]. In this research, nail enamel application, the modified montmorillonite clays act as anti-settling agents for systems generally reducing gloss and specular reflection without markedly altering the transparency of such films. Modified montmorillonite clays of this study are commercially available from Rheox, Inc. under the trade designation “Bentone 38”, “Bentone 27”, and “Bentone 34”. These three kinds of commercial organic montmorillonite (OMMT) are similar in composition but different in quarternary ammonium:

Bentone 38 = dimethyl dioctadecyl ammonium hectorite

Bentone 27 = dimethyl benzyl dodecyl ammonium hectorite

Bentone 34 = dimethyl dioctadecyl ammonium bentonite

2.5 Type of rheological behavior

The behavior of fluids in experiments which conducted at constant temperature and pressure as shown in Figure 2.6 is well known as newtonian. The viscosity is constant with respect to the time of shearing and the stress in liquid drops to zero immediately the shearing is stopped. However, the fluids which their viscosity change as varying shear rate is known as non-newtonian viscous liquid. Their relationship of shear stress and shear rate is not constant. There are several types of non-Newtonian flow behavior, characterized by changing of fluid viscosity in response to variations in shear rate: a) pseudoplastic is fluid behavior which its viscosity decrease with an increasing shear rate, some examples include paints and emulsions. b) dilatant is fluid behavior which is characterized by an increasing viscosity with an increasing shear rate, some examples include clay slurries, candy compounds, corn starch in water, and sand/water mixtures. c) bingham is fluid behavior which behaves like solid under static conditions. A certain amount of force calling yield value must be applied to the fluid before any flow is induced. Tomato catsup is an example of such fluid. Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudoplastic or dilatant flow characteristics. However, some kind of behaviors is depend on the lapse of time such as thixotropic which is the flow of material undergoes decreasing shear stress and apparent viscosity over time at a fixed rate of shear as shown in Figure2.6. Another type of time-dependent rheology is rheopectic which is the behavior of material exhibits increasing shear stress and apparent viscosity over time at a fixed rate of shear as shown in Figure2.7.

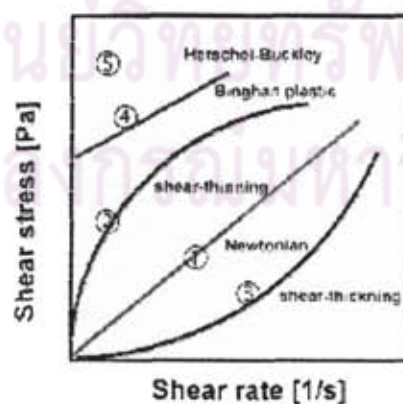


Figure 2.6 Diagram summary of Newtonian and non-Newtonian time independent fluids [18].

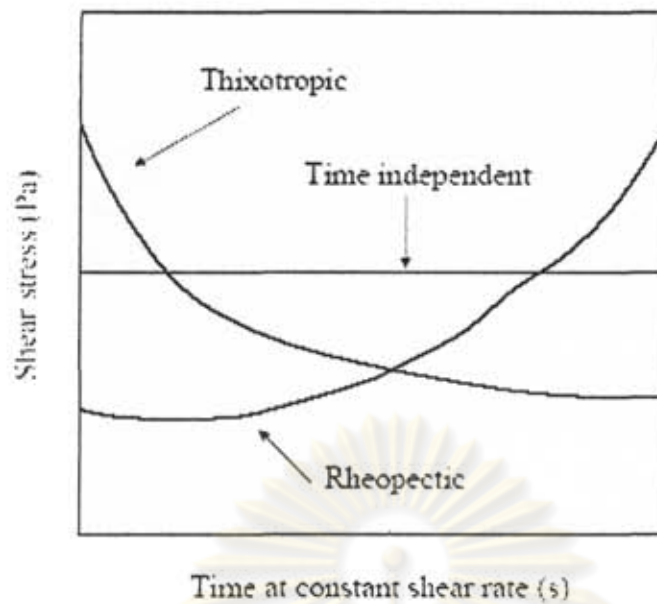


Figure 2.7 Diagram summary of non-Newtonian time dependent fluids [19].

2.6 Characterization of thixotropic flow [20-22]

In research of nail enamel application, thixotropic behavior is a valuable asset, since the lower viscosity at high shear rates (during application) facilitates paint flow and ease of application, whereas the higher viscosity at low shear rates (before and after application) prevents settling and sagging. The practical range of shear rate using in paints industry versus viscosity is revealed in Figure 2.8 and showing optimum regions for yield value, viscosity before brushing, viscosity for paint pick up, and brushing viscosity. In the thixotropic curve, the down curve falls above the up curve.

The technology of thixotropic behavior is quite complex. Therefore, the methods characterization of time-dependent flow behavior is concerned with the experimental techniques for such fluids are far more difficult than for time-independent fluids. One method frequently used to characterize thixotropic behavior is the hysteresis loop, as shown in Figure 2.9. Such a loop is obtained by the technique consists of starting at the lowest shear rate available and obtaining an initial stress measurement. After a given time the shear rate is increased to the next higher shear rate setting and the stress measured again. The procedure is repeated until the highest shear rate is reached and the system is then sheared to its equilibrium stress. After reaching equilibrium the shear rate is reduced stepwise and the shear stress is remeasured at each point until the lowest shear rate is reached. The shear stress is then plotted versus the shear rate. The area of the loop is a measure of the thixotropic breakdown due to mechanical working. Therefore, Thixotropy is defined as the

ability of the system to exhibit lower viscosity as a function of shearing and its ability to have its structure reformed over a period of time. In some cases, thixotropy is confused with the shear thinning index of the system. This index is defined as the ratio of the viscosities of the material at two different constant shear rate at least 10 times.

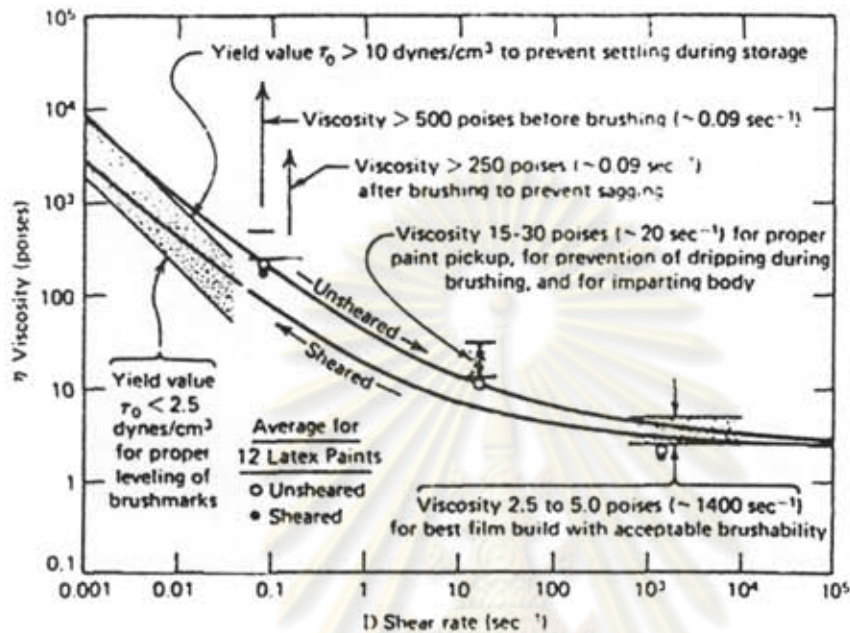


Figure 2.8 Typical shear rates of coating application in thixotropic systems[21].

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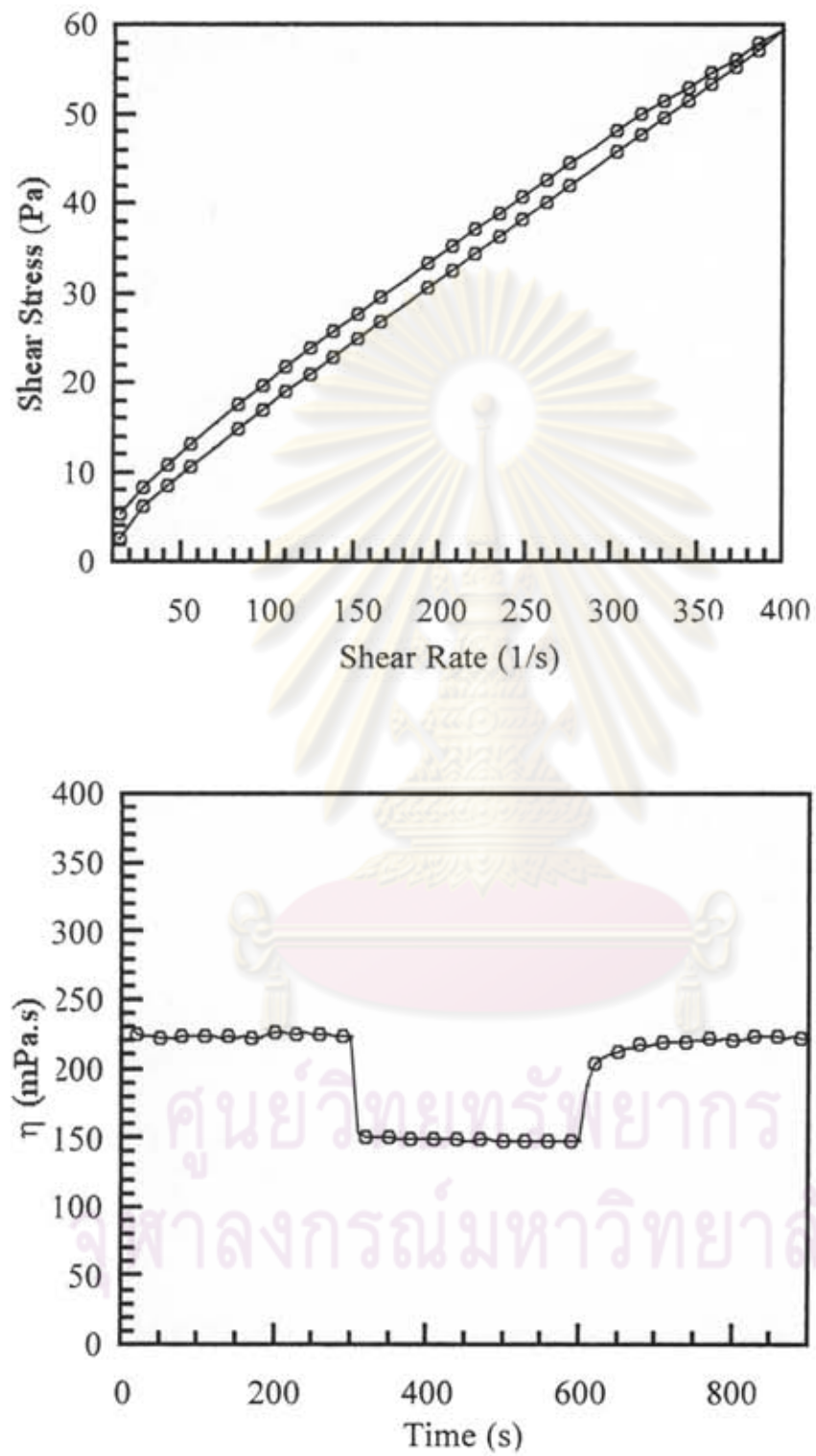


Figure 2.9 Thixotropic characterization of commercial nail enamel.

CHAPTER III

LITERATURE REVIEWS

R. L. Socci, and A. Ismailer [23] had disclosed that nail enamel compositions containing cellulose nitrate as a primary film former should possess a molecular weight of greater than 56,000 for good film-forming characteristics. Cellulose nitrate exists in many grades such as nitrocellulose RS1/2 sec. having a molecular weight of approximately 56,000, nitrocellulose RS5-6 sec. having a molecular weight of 112,000, nitrocellulose RS15 sec. having a molecular weight of 130,000, nitrocellulose RS60-80 sec. having a molecular weight of 175,000, and nitrocellulose RS150 sec. having a molecular weight of about 190,000 etc.

The traditional clear nail enamel formulation is shown in Table 3.1. The pigments or colors are not included in this composition. Natural appearance of clear lacquer is unpleasantly yellow that we can improve or cover this drawback by adding colored substances into its solution. In colored nail enamel formulation, pigments and suspending agent are usually incorporated in the solution to prevent solid particle settling. One sample formulation of colored nail enamel can be shown in Table 3.2

Table 3.1 Example of traditional nail enamel formulation reported by Ref. 2.

Ingredients	Wt%
RS ½ second nitrocellulose	10
Santolite MHP (resin)	10
Santicizer 8 or 160 (plasticizer)	5
Ethyl alcohol	5
Ethyl acetate	20
Butyl acetate	15
Toluene	35

Table 3.2 Example of colored nail enamel formulation reported by Ref. 24.

Ingredients	% by weight
Cellulose nitrate	11.5
IPA	6.4
Diacetone alcohol	0.5
Butyl acetate	15.8
Ethyl acetate	41.2
Propyl acetate	0.5
Heptane	0.5
DBP	1.7
Camphor	0.2
SAI	5.9
Triphenyl phosphate	2.9
Poly ether modified	0.4
Tosylamide epoxy resin	6.6
Acrylates copolymer	0.7
Polyester	0.6
Dimethicone	0.1
Bentone 38	0.8
Sterakonium hectorite	0.1
Titanium dioxide	2
Red iron oxide	0.1
Lake D&C yellow No. 5	0.1
Black iron oxide	1.3
Benzophenone	0.05
Etocrylene	0.05

Up to present, there exist many proposed nail enamel formulations containing several ingredients depending on a particular purpose or requirement. Each ingredient normally has its own function. In this research, we will develop nail enamel from the traditional formulation as reported in Ref. 2. and will pay attention to the effect of water content on solution and dry film properties, which will be the guideline of water tolerant limit in the production process of CN, as well as the

effect of organoclay as thixotropic agent of the nail enamel. The useful properties of nail enamel had been reported by several inventors in the US patents as summarized in Table 3.2.

Furthermore, an inherent poor adhesion of cellulose nitrate to nail surface leads to the use of many kinds of resins to enhance its adhesion characteristics. A.M. Kuritzkes [25] suggested that arylsulfonamide formaldehyde resin be added into nail enamel for increasing adhesion and gloss of the resulting dry film. However, at present, arylsulfonamide formaldehyde resin has been avoided in the nail enamel formulation due to the potential of releasing free formaldehyde to cause allergy to the users. G. G. Graves, and T. C. Jacks [26] invented a nail lacquer added with vinyl-silicone copolymers in the range of 0.1-5 wt% as an adhesion promotor. The trapped bubbles in the dried film were prevented by incorporating a dimethicone anti-foaming agent in range of 0.02-0.3 wt%. T. Ikeda, and T. Kobayashi [27] reported the use of a secondary film based on various molecular weights of polyethylene glycol ranging from 200-4000 to produce the nail enamel. Leo X. Mallavarapu [28] reported a novel resin to substitute toluenesulfonamide formaldehyde resin and invented a process for the preparation of novel epoxy sulfonamide-based resin. The epoxy polymers are substituted for formaldehyde by reaction with aryl or aliphatic sulfonamides in the presence of a Lewis acid. Example of epoxy resin which may be used in the reaction include diglycidyl ether bisphenol A type, with a molecular weight of up to approximately 20,000, and epoxy resin of the diglycidyl bisphenol F type, with a molecular weight of up to approximately 20,000. It has been determined that the resinous reaction products of this invention perform well in the nail lacquer formulation. Frederick L. Martin [29] disclosed the nail enamel formulation that its composition comprised maleic modified resin. This composition can be applied as a base coat over natural nails to act as a primer for pigmented nail enamels. This base coat dries to the touch in less than two minutes and provides excellent flexibility, excellent initial adhesion to the bare nail as well as excellent adhesion for at least seven days. In our research, secondary film forming substances is investigated chosen from silicone, acrylic polymer, epoxy, and maleic resin.

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Table 3.2: US patent review on desired properties of nail enamel formulation.

Patent No.	Viscosity (cps.)	Drying time (min)	Gloss (G.U)	Adhesion	Hardness	T.I.
4,222,908	1,510-2,000	-	81.7	-	110 vicker	4.2
5,093,108	400-1200	@20°C 37%RH =3 @20°C 70%RH=5	70-95	-	-	-
5,972,095	-	1-4	-	-	-	-
6,177,065	-	<3	-	No squares peeling off of 10x10 squares crosscut film	HB level	-
6,740,314	-	-	81-118	-	-	-

Milan Bohuslav Bednarek [30] reported the solvent system of nail enamel compositions may comprise from 0-30wt% water, based on the weight of the solvent system. For nail enamel compositions comprising a high weight percent of the solvent system, the water content would be at the lower end of this range. It is not to advantage for water to be present in the nail enamel compositions, so the presence of water in the solvent system is to be avoided. One problem in nail enamel processing is the water level in cellulose nitrate resin often presented at the significant amount due to the washing step in the production process. Phase separation might occur as water is immiscible with CN resin and the obtained enamel solution may be cloudy while the resulting dried film may become opaque which is the unpleasant appearance to the customers. Therefore, the appropriate or acceptable water level in the nail enamel formulation will also be systematically studied.

Generally, polymer solution exhibits non-Newtonian flow of a shear-thinning type. In the case of nail enamel solutions or typical coatings, time-dependent flow of a thixotropic type is required. This can be achieved by the incorporation of thixotropic agents. One important group of thixotropic agents are modified natural clays of a layered silicate type. A.M. Kuritzkes [25] reported that the quaternary ammonium ion-modified montmorillonite clays could perform as flattening agents

for lacquer systems. The filler generally reduced gloss and specular reflection without markedly altering the transparency of such films. The quaternary ammonium cation-modified montmorillonite clay is added to nail enamel lacquers at the concentrations varying from about 0.4 to 6% by weight. The commercially available organoclays for nail enamel formulation are Bentone38, Bentone27, and Bentone34 which will be used in this investigation.

T. Ikeda, and, T. Kobayashi [27] revealed that the interlamellar distance (001 face) of dimethylbenzyl dodecyl ammonium montmorillonite powder measured by an X-ray diffraction device (RIGAKU Rota Slex Type RU-3) to be 9.4°A and that D.B.P. , a CN plasticizer, cannot expand the interlaminar distance of the organoclay. The good solvents which can effectively swell Bentone27 should give an expanded interlaminar distance of bentone27 of not less than about 16°A . This convention used about 5 wt% of Bentone27 in total weight of nail enamel solution utilizing roll milling technique i.e. a Banbury mixer, at a temperature of about 40 through 70°C . D.A. Pappas and H.J. Laresen [31] disclosed a gelled nail enamel solution having toluene as a solvent of stearakonium hectorite thixotropic agent. A strong shearing force of a Hoffmeyer industrial mixer is generally applied for a period of about one hour. The preferable content of stearakonium hectorite is about 3wt% of total ingredients. In the final step, one or more pigments were added to the aforementioned gelled mixture under high shear speed to produce colored nail enamel. G. G. Graves, and T. C. Jacks [26] disclosed a nail enamel formula containing stearakonium hectorite and stearakonium bentonite as a preferred thixotropic agent. The fillers were used at the amount ranging from 2-5 wt%.



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CHAPTER IV

EXPERIMENTAL

4.1. Materials

Nitro Chemical Industry Co., Ltd. contributed RS ½ second cellulose nitrate powder and the solvents. Maleic resin, ER-912, was obtained from Eternal Resin Co., Ltd. Epoxy resin, EPON 828, was purchased from Shell Chemicals Co., Ltd. Acrylic resin, SD 603, was taken from Siam Chemicals Co., Ltd. Liquid silicone rubber was obtained from Applied Silicone Corporation. Benzoxazine monomer based on bisphenol, aniline and paraformaldehyde was synthesized. The monomer synthesis was based on the patented solventless synthesis. The organoclays, Bentone 27, Bentone 38, and Bentone 34, were provided by Cornell Brothers Co., Ltd. The pigment, S1120, was supported by Koventure Co., Ltd.

4.2 Sample Preparation

4.2.1 Cellulose nitrate solution

Cellulose nitrate resin as received was treated at 100°C for 1 hour in the oven to remove isopropyl alcohol and moisture then took up water to adjust the water content of cellulose nitrate powder to be 1, 2, 3, 4, 6, 8, and 10 % by weight, the Karl Fisher titrator was used to checked water content in cellulose nitrate resin. Cellulose nitrate solution obtained by mixing 10 gram the CN powder at various water contents using a mixed solvent system as follows: ethyl alcohol 5 gram, butyl acetate 15 gram, ethyl acetate 20 gram, and toluene 45 gram. To study an effect of water content in the cellulose nitrate solution on nail enamel properties, the characteristics of the solution were examined including viscosity, and drying time, and film properties such as adhesion, gloss, hardness, and surface texture.

4.2.2 Clear nail enamel

Nail enamel solution was obtained by mixing 10 grams of resin, 5 grams of a DBP plasticizer, and 50 grams of a cellulose nitrate solution (contained cellulose nitrate of 10 grams,

ethyl alcohol of 5 grams, butyl acetate of 15 grams, and 20 grams of ethyl acetate). The secondary film formers used are acrylic SD603, silicone, benzoxazine, maleic, and epoxy. All of clear nail enamel films were tested adhesion by cross cut showing the suitable resin type for nail enamel. Effect of various epoxy and maleic content also was investigated as illustrated in Figure 4.1.

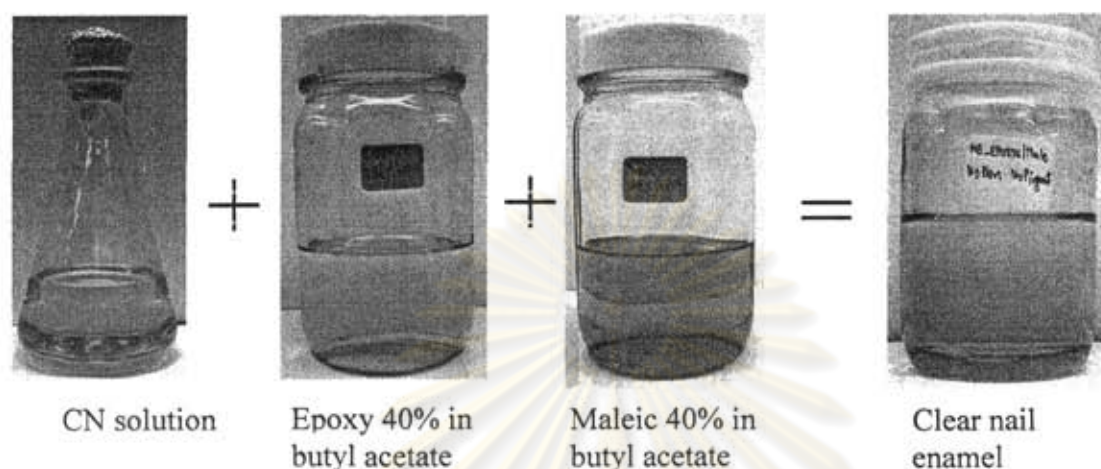


Figure 4.1 Clear enamel preparation.

4.2.3 Suspension gel

The dimethyl dioctadecyl ammonium montmorillonite clay was heated up at 100°C for 1 hour to remove moisture and stored in a desiccator. The clay was dispersed at the amount of 8 gram in 100 gram of toluene using a mechanical stirrer at room temperature for 4, 8, 14, 24 and 48 hours with a constant speed 650 rpm. Another dispersion preparation is by using a homogenizer which was conducted at room temperature at high shear rates of 6500, 9500, 13500, 21500, and 24000 rpm for 5 minutes at each speed. The homogenizing suspension was compared with motor stirring suspension. The other two different organoclays such as dimethyl benzyl dodecyl ammonium hectorite and dimethyl dioctadecyl ammonium bentonite were also prepared suspension gel for nail enamel as shown in Figure 4.2. Three types of organoclays can perform like solid when having no force application.



Figure 4.2 Suspension gels of three organoclays prepared by a homogenizer.

4.2.4 Dry nail enamel film

The polymer/clay nanocomposite film was prepared by mixing clear nail enamel as received from 4.2.2 with organoclays suspension as received from 4.2.3 adjusted the organoclay content in final formula to be 0.35, 1, 3, and 5 wt% by loading in container and mixed for 5 minutes using homogenizer at 9500 rpm. Interlayer spacing of organoclay in nanocomposite was investigated by XRD.

4.2.5. Colored nail enamel

In this process, toluene of 34 grams was used to suspend the bentone38, bentone27, and bentone34, which prepared from 4.2.2. The obtained suspension was then mixed with 65 grams of the clear nail enamel solution. The pigment suspended system was conducted by adding the desired amount of mica coated titanium dioxide pigment at 1 grams in the nail enamel using a mechanical stirrer (at 600 rpm for 1 hour) or a homogenizer (at 9500 rpm for 5 minutes). The solid films were obtained by casting the enamel solution on a clean glass plate followed by evaporating the solvent at ambient conditions to yield films of constant weight. The scanning electron microscope was used to compare surface texture of the two different mixing methods. The finished nail enamels of the three organoclays as illustrated in Figure 4.3 were characterized for their solution properties including flow behavior, drying time, and dry film properties such as gloss, hardness, surface texture etc. The anti-settling system was also investigated by sedimentation experiment. The various organoclays content of 1, 3, 4, and 5wt% were put into volumetric flask of 8 milliliter without shaking for 10 days observed the pigment precipitation. The nail enamels which have superior anti-

settling content of organoclay were tested on 10 women. After those of women applied formulated nail enamels, the satisfactions of women on nail enamel characteristics such as pick up, ease of brushing, drying time, and gloss were investigated in questionnaires. The women were allowed to work in everyday life and prohibited to remove nail enamel films before accomplish the research. After 10 days, the abrasion characteristic was examined again in questionnaires. The data of questionnaires was calculated to be percentage of human satisfaction.



Figure 4.3 Colored nail enamels using the three types of organoclays.

4.3 Characterization Methods

4.3.1 Cellulose nitrate solution flow behaviors

Cellulose nitrate solution at various content were measured flow behavior using a rotational viscometer, Physica Rheolab MC1: Standard measuring system MS-Z3 DIN/MC1 at shear rate 30-1000 s^{-1} for 10 minutes. The volume of measured solution was about 17-20 gram. Temperature was control at 25°C. The raw data was plotted shear rate versus viscosity of the solutions and shear stress.

4.3.2 Thixotropic evaluation

Suspension gel and color nail enamel were measured thixotropic behavior using a rotational viscometer, Physica Rheolab MC1: Standard measuring system MS-Z3 DIN/MC1. Suspension gel was measured at forward shear rate 0.1-1000 s^{-1} for 10 minutes after that sample was backwardly

measured viscosity at shear rate $1000-0.1 \text{ s}^{-1}$ for 10 minutes. The measuring shear rate of nail enamel is from $0.1-400 \text{ s}^{-1}$ for 5 minutes after that reverse action. The volume of measured solution was about 17-20 gram. Temperature was control at 25°C . The raw data of forward and backward testing were plotted shear rate versus viscosity of the solutions and shear stress. The area between up curve and down curve disclosed the thixotropic behavior of those samples. Thixotropic index and recovery time were calculated applying three interval of shear rate. First interval, the sample was applied constant shear rate at 40 s^{-1} for 5 minutes then changed constant shear rate to be 400 s^{-1} for 5 minutes in the second interval and returned back to the shear rate 40 s^{-1} for 5 minutes again in the third interval. The raw data was graphed time versus viscosity of sample. The period of recovery time can be discovered in third interval by checking recovery viscosity that it have to be 90% value of first interval viscosity. The average viscosities of first and second interval were calculated dividing first interval by second interval, thixotropic index was figured out.

4.3.3 Drying time

Drying time of cellulose nitrate solution was conducted following ASTM 1640 at temperature 25°C and $50\pm 5\%$ relative humidity in the humidifier control room. All test specimens were prepared and tested by one operator applying 10 gram of various water content cellulose nitrate solution on the clean glass panels and casting by applicator after that clean fingered touch the film lightly at varying intervals of time. The films are considered dry when no appeared marks are left by the fingerprint on the film in the same area on each observation. The dried films thickness was $12.5\pm 2 \mu\text{m}$.

4.3.4 Adhesion

This experiment was conducted following ASTM 3359. The cellulose nitrate solution at amount 18 gram was applied on the glass plate, which cleaned by hydrochloric acid at 5 wt% concentration, let films dried at room temperature for 24 hours. Dry films thickness was up to and including $50 \mu\text{m}$ space the cuts 1 mm apart and make eleven cuts in horizontal and vertical providing 100 squares of films as illustrate in Figure 4.4. All cuts were about 20 millimeters long by cutting through the film to the substrate in one steady motion using just sufficient pressure on the razor to have the cutting edge reach the substrate, used razor have to use one time for one sample. After making the required cuts brush the film lightly with a soft brush or tissue to remove any

detached flakes or ribbons of coatings. Examine the cutting edge and, if necessary, remove any flat spots or wire-edge by abrading lightly on a fine oil stone. Make the additional number of cuts at 90° to and centered on the original cuts. Brush the area as before and inspect the incisions for reflection of light from the glassplate. Remove two complete laps of tape and discard. Remove an additional length at a steady rate, no jerking, and cut a piece about 75 millimeter long. Place the center of the tape over the grid and in the area of the grid smooth into place by a finger. To ensure good contact with the film rub the tape firmly with the eraser on the end of a pencil. The color under the tape is a useful indication of when good contact has been made. Within 90 ± 30 s of application, remove the tape by seizing the free end and rapidly, not jerked, back upon itself at as close to an angle of 180° as possible. Inspect the grid area for removal of coating from the substrate or from a previous coating using the illuminated magnifier. The percent adhesion was the total adhered squares on the glass plate.

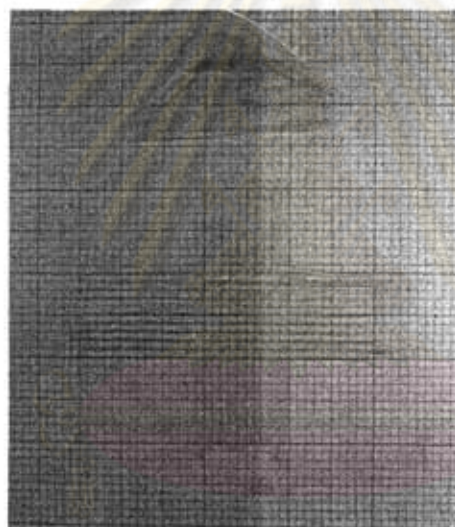


Figure 4.4 Sample of adhesion.

4.3.5 Gloss

This experiment, following ASTM 523, measured the specular gloss of cellulose nitrate and nail enamel films using glossmeter geometries of 60° , 20° , and 85° as shown in Figure 4.5. Gloss meter model is Microsheen 250. The 20 gram of cellulose nitrate solution was applied at dimension 75 by 150 millimeter on the black glass plate and allowed film dried at room temperature, after 24 hours, measuring gloss of film compared with the gloss of standard black glass. Put the geometry sensors of 60° , 20° , and 85° on the dried films, the gloss value of them were shown on the monitor screen.



Figure 4.5 Gloss meter.

4.3.6 Hardness

The cellulose nitrate solutions in amount of 3-5 gram were applied on the slide glass and dried at room temperature for 24 hours, after that they were measured hardness by microhardness tester as depicted in Figure 4.6. The 100 gram force of test load was applied on the films surface for 15 seconds and measured diagonal length by optical microscope and recorded dimension for calculating hardness value in unit of vicker.

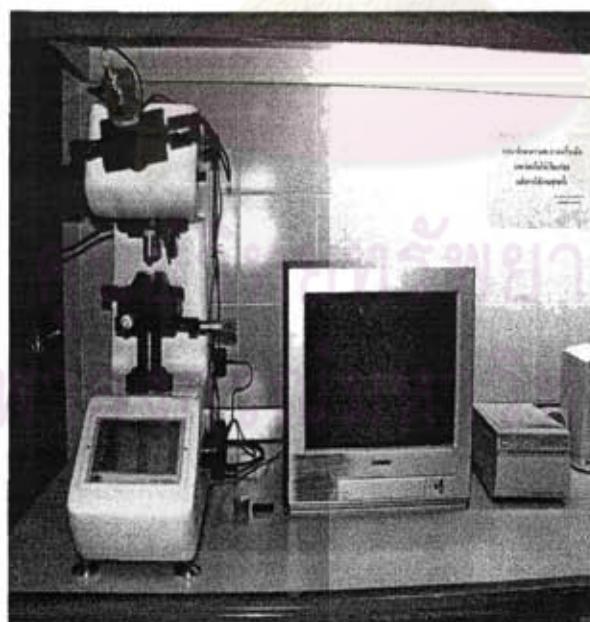


Figure 4.6 Microhardness tester.

4.3.7 Surface texture

The surface texture of dried cellulose nitrate films were investigated with an ISM-5400 scanning electron microscope from JEOL Ltd. at an acceleration voltage of 10 kV. Before obtaining a micrograph, the dried films were coated with a thin film of gold using a JEOL ion sputtering device model JFC-1100E for 4 minutes to obtain a thickness of approximately 300\AA . The micrographs were studied the effect of water content in dried films on their surface property.

4.3.8 X-ray diffraction

Sample was detected by X-ray diffractometer of Bruker model D8 ADVANCE with $\text{CuK } \alpha$ radiation (1.541 \AA). The voltage and the current are 40 kV and 30 mA, respectively. The measurement was scanned at 2θ in range of 1.0 to 15.0 with scan speed 30.0 sec/step and step size $0.05^\circ 2\theta$. The measurements were operated by EVA program.



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CHAPTER V

RESULTS AND DISCUSSION

5.1 Characterization of cellulose nitrate solution at various water content

5.1.1. Rheological behavior of cellulose nitrate solution

Viscosity of cellulose nitrate (CN) solution was moderately affected by its water contents such as the systematic decrease of its viscosity as shown in Fig.5.1. Generally, cellulose nitrate resin, industrially produced, contains about 3wt% of water in the resin system. To study the effect of water content on the viscosity of the polymer, water was intentionally added in the range of 1-10wt%, and the shear rate was applied within the range of 30-1000 s^{-1} . At the low shear rate in the range of 34 s^{-1} to 600 s^{-1} , all CN solutions exhibited Newtonian flow pattern. For the high shear rate above 600 s^{-1} , the low water level in the CN solution showed high pronounced deviation from the Newtonian plateau of the shear-thinning type, whereas at the highest water content, i.e. 10 wt%, the flow of the CN solution at this high shear rate range remained near-Newtonian behavior. The viscosity of these cellulose nitrate solutions is ranging from 156 to 242 mPa.s, whereas the required viscosity of commercial nail enamel should be in range of 400-1200 mPa.s [30]. The shear thinning behavior of nail enamel solutions according to Carreau's equation given $R^2 = 0.93266-0.9999$, standard deviation = $9.7898 \times 10^{-4}-0.0015887$, and $n = 0.5588-0.9736$.

$$\eta = \frac{\eta_0 - \eta_f}{(1 + (\lambda\dot{\gamma})^2)^{1-n/2}} + \eta_f$$

where η_0 = a zero shear rate viscosity

η_f = a final shear rate viscosity (its value rarely appear)

λ = characteristic (or relaxation) time

n = dimensionless parameter

The slope of η versus $\dot{\gamma}$ in the power law region is given by $n-1$. In the special case of $n=1$ or $\lambda\dot{\gamma}$ close to zero, this equation simplifies to the Newtonian fluid model. For $n < 1$, this equation predicts shear thinning behavior. Typically commercial nail enamel needs to incorporate a resin to promote adhesion, a plasticizer to enhance flexibility, as well as pigments or other solid

contents to obtain a finish nail enamel product. Those solid ingredients will further raise the nail polish viscosity with even high complicated flow characteristics. Therefore, the viscosity of the CN solution was kept relatively lower than the standard value for further rheological modification.

One major goal of our research is to develop a nail polish solution to exhibit complex non-Newtonian flow pattern with time-dependency of a thixotropic type. The utilization of a layered clay additive was thus necessary to alter the flow behavior of the resulting enamel to achieve a thixotropic flow. From the viscosity measurement as shown in Figure 5.2, it has been confirmed that increasing water content would reduce the viscosity of the cellulose nitrate solution. This curve exhibited exponential decay of the solution viscosity with the amount of the water diluent.

5.1.2 Drying time of cellulose nitrate solution

The drying time of the obtained cellulose nitrate (CN) solution was found to increase as its water content increased as illustrated in Figure 5.3. At 90±5% relative humidity at room temperature, CN solution with 1, 2, 3, 4, 6, 8, and 10 wt% of water contents took about 6, 7, 7, 7.5, 8, 9, and 9 minutes respectively to fully dry and at 50±5% relative humidity at 23±2 °C, which is the standard condition, the CN solution with the same water contents of 1, 2, 3, 4, 6, 8, and 10 wt% took about 3, 3, 3, 3.5, 3.5, 5, and 5 minutes to fully dry in the respective order. The curves show linear trendline which 90%RH fit equation equal to $y=6.0595+0.32599x$ $R^2=0.9679$. At the 50%RH, the fit equation is $y=2.4097+0.25683x$ $R^2=0.91079$.

Our nail polish formula contained ethyl alcohol, butyl acetate, ethyl acetate, and toluene as major liquid components, while the contaminated water was a minor component possessing the highest heat of evaporation or latent heat among those. The latent heat for the phase change at constant temperature may be expressed in terms of the latent heat and the heat capacity of the phase

$$\Delta Q = T_d (S_g - S_l)$$

where ΔQ is evaporation heat or latent heat (cal/g)

T_d is evaporation temperature (°C),

S_g is entropy of gas phase

S_l is entropy of liquid phase

The values of heat of evaporation of solvents are as follows: ethyl alcohol = 855.20 J/g, butyl acetate = 309.01 J/g, ethyl acetate = 427.01 J/g and toluene = 363.41 J/g, while the latent heat of water is 2,256.7 J/g [14]. Therefore, the drying time was high at the presence of water. From this reason, it could be estimated from a linear relationship with the amount of the water. The drying time was also affected by the humidity of the surrounding. Solvent evaporation expectedly occurred at a low rate with the increase of the humidity in the environment. The suitable drying time of commercial nail enamel should be 1-4 minutes at $50 \pm 5\%$ relative humidity (25°C) [30]. Consequently, the obtained cellulose nitrate solution met its application standard even though there was the presence of some water, i.e. less than 6 wt%. In the case of more slowly drying time at high humidity condition, the solvent content needed to be adjusted in order to optimize the heat of evaporation of solvents.

5.1.3 Hardness of cellulose nitrate film

The values of CN film hardness were in the range of 14-17 of Vicker scale as shown in Figure 5.4 implying that water content had no significant effect to CN films. The fit curve is $y=17.633-0.29912x$ $R^2=0.8991$. After solvent evaporation, the water ingredient of each thin film could also evaporate so all of the films were of similar hardness value. From those hardness results, it is essential that CN films are to be modified to improve their flexibility, typically by adding plasticizer such as dibutyl phthalate.

5.1.4 Gloss of cellulose nitrate film

All of CN films were measured by a gloss meter which had been calibrated by a standard black glass as calibration. The samples were evaluated by three geometries of reflection angle. The sensors at 20° , 60° , and 85° were for high gloss, semi-gloss, and low gloss, respectively. Gloss of a black standard glass at 20° , 60° , and 85° were 112.8, 129.7, and 99 G.U, respectively, whereas gloss of CN films at 20° , 60° , and 85° were 101.97-103.41, 122.42-124, and 97.99-99.14 G.U, respectively as depicted in Figure 5.5. Effect of water contents on films surface texture was negligible due to water ingredient of each film could also evaporate. The results indicated that CN films possessed high gloss values close to a standard black glass. This property is required for the good appearance of nail enamel films.

5.2 Effect of adhesion promoter on CN film

In this study, four types of resins were investigated in order to improve adhesion of CN film. From literature review, the resins of silicone, maleic resin, epoxy, and acrylic were used as adhesion promoter of nail enamel formula. Benzoxazine resin, a novel resin that exhibits good adhesion, was also utilized. Table 5.1 shows that silicone, maleic resin (ER-912), epoxy (Epon 828) and benzoxazine resin are useful for improved adhesion of CN film compared with a relatively high-end commercial nail enamel, i.e. Red Earth[™]. These four types of resin provided area of adhesion from 84-100 area%. There is acceptable to use for nail enamel application because the values of Red Earth adhesion are related to 100area%. The poor 5 area% of adhesion shows that the acrylic resin was unable of adhesion improvement in cellulose nitrate. We can arrange the adhesion capability of resins in a consecutive order as follows: SD603 < ER-912 < EPO828 < Benzoxazine = Silicone

Since silicone and benzoxazine resin gave unpleasant appearance and color to the resulting films so these resins were not suitable for utilization as nail enamel composition. The effect of adhesion of mixture between maleic resin and epoxy resin was also studied to find out optimum mixing ratio for adhesive and hardness properties as shown in Table 5.1. The obvious effect of these mixtures was in the film hardness as shown in Figure 5.6. The increase in maleic resin content increased the hardness of films, while epoxy resin acted like plasticizer which decreased the hardness of the CN films as well as maintaining the good adhesion. As the composition of maleic resin in the nail enamel is about 10wt%, the hardness of the nail enamel film is about 4.8 in Vicker scale. The optical microscope depicted deformation of film after loading of 100 g_f for 15 seconds, that its shape was sharp while that of filled epoxy resin of 10wt% showed plastic deformed shape and its hardness value is only about 0.6 Vicker which lower than that of the neat CN i.e. 2.8 in Vicker scale. From this experiment, we can adjust requirement hardness value by selecting the content of maleic-epoxy mixture. For nail enamel application, the CN film needed to be relatively hard but not too hard to avoid brittle fracture. The composition of 5wt% maleic resin and 5wt% of epoxy resin was found to be preferable in nail enamel ingredients with appropriate adhesion and hardness.

5.3 Clay suspension preparation

5.3.1 Mechanical stirring

In Figure 5.7, mixing time of clay suspension was studied by mechanical stirring at a constant shear rate 650 rpm for 4, 8, 14, 24, and 48 hr. The result revealed that all suspensions were shear thinning fluid. Viscosity of clay suspension at the mixing time of 4, 8, and 14 hr. were in the range of 10-13600 mPa.s while the mixing time up to 24, and 48 hr rendered viscosity in a range of 31.6-24800 mPa.s. These results indicated that mixing time expectedly affected clay delamination. The clay layers were sheared by Teflon paddle for long mixing time, the layers were more delaminated and formed the strong three dimension network that obtained high viscosity. The hysteresis loop of the suspension was shown with the wide loop implied great thixotropic behavior. The mixing time of 4, 8, and 14 hr showed unclear thixotropic loop which is required for nail enamel rheological behavior, whereas, the mixing time of 24, and 48 hr. were preferable for suspension preparation in the nail enamel application.

5.3.2 Homogenizing

Bentone38 at 8wt% in toluene was also prepared and tested using a homogenizer at various shear rates of 6500, 9500, 13500, 21500, and 24000 rpm for 5 minutes as shown in Figure 5.8. At the shear rate of 6500 rpm, the relatively low viscosity in range of 37.7-3240 mPa.s was obtained while all other shear rates provided viscosity in range of 97.7-17800 mPa.s showing strong three dimension network. From these results, we can confirm that the effect of high shear rate rendered high clay delamination or high gel viscosity. It was also observed that the viscosity at higher shear rates from 9500-24000 rpm was similar in value. Therefore, the moderate shear rate of 9500 rpm is chosen for the clay suspension preparation for good gel, for energy saving and for safety purpose. This result also showed hysteresis loop of various high shear rates, the graphs depicted that all of high shear rate exhibited thixotropic behavior.

The clay suspension preparation was compared between using motor stirring and homogenizing, we found that at constant shear rate of 650 rpm the motor stirring provided gelation at over 24 hours. while homogenizing contributed good gel network in 5 minutes at 9500 rpm. Therefore, the homogenizing was high efficiency and suitable for suspension preparation.

5.4 X-ray diffraction patterns of organoclays in CN nail enamel films

CN films incorporated various loadings of the organoclay were investigated for the d-spacing of the clay layer by XRD as shown in Figure 5.15. Bentone 38 powder showed a peak at 2θ of 3.39 and d-spacing of 26 Angstroms. The CN films with 1, 3, and 5wt% bentone38 depicted a XRD peak with the 2θ of 2.26, 2.39, and 2.55 respectively. This implied that the layers of montmorillonite were intercalated by the polymer chains and the particle structure still maintained its order.

In Figure 5.9, Bentone27 powder exhibited a x-ray diffraction peak at 2θ of 4.96 with a d-spacing of 18 Angstroms. CN films incorporated with 3, and 5 wt% of Bentone27 possessed a XRD peak of the 2θ at 2.35, and 2.45 ,respectively. This result means that the layer of montmorillonite clay was intercalated by the polymer chains and the particles structure can still maintain their ordered morphology. CN films of 0.35, and 1wt% of Bentone27 showed no peak of diffraction as illustrated in the pattern. That means two cases. First is that the micro-particles of the clay particles were exfoliated by high shear rate when the clay composition was low enough. Therefore, the suspension of 0.35 and 1 wt% of Bentone 27 was capable of forming exfoliated nanocomposite, whereas 3, and 5wt% of Bentone 27 were intercalated in nature. We can confirm this case by using Transmission Electron Microscope (TEM) to observe the polymer-clay nanocomposite. Second case is that the clay concentration in films was too low to absorb x-ray intensity therefore no showing peak of clay d-spacing. The XRD results of the nanocomposites of various Bentone34 contents in CN films were shown in Figure 5.10. Bentone 34 powder revealed a x-ray diffraction peak at 2θ of 3.06 with a d-spacing of 29 Angstroms. The sign of intercalated nanocomposites was disclosed at the contents above 1wt% of Bentone34. The intercalation of Bentone34 content of 1, 3, and 5 wt% exhibited a sharp diffraction peak of their ordered structure at 2θ equal to 2.45, 2.48, and 2.55, respectively. No diffraction peak, however, was observed at lower clay content i.e. 0.35 wt% in our case. This could be explained as some of the clay thixotrope seems to be partially exfoliated whereas most of the clay particles were intercalated during the preparation process. We can confirm this phenomenon by using Transmission Electron Microscope (TEM) to observe the polymer-clay nanocomposite. Other explanation is that the clay concentration in the films was too low therefore the diffraction peak seemed to be hardly observed i.e. too small XRD peak.

In Table 5.3, Δd -spacing of clays was calculated by subtracting d-spacing of clay powder with that of the reference. At clay content of 5wt%, we found that Bentone27 provided broad clay

Δd -spacing that means the great of polymer chain crawled into interlayer presented intercalated nanocomposite and occurred gel forming ability.

5.5 Characterization of resulted nail enamels

5.5.1 Rheology of resulted nail enamels

The fully formulated nail enamel and commercial one were compared in Figure 5.11. That also discloses the shear thinning behavior. The viscosity range of the resulting nail enamel were 266-1082 mPa.s at the shear rate of 13.9-400 1/s. while that of the commercial grade were requirement for the 153.9-310.7 mPa.s at the same shear rate above. The industrial viscosity of nail enamel should be in the range of 400-1200 mPa.s. From the rheological testing, the viscosity of the commercial nail enamel was slightly lower than that of the standard, while our systems achieved that requirement. Bentone27 resulted the highest nail enamel viscosity which corresponds to the widest Δd -spacing.

Furthermore, the hysteresis thixotropic flow of our research nail enamels was also illustrated indicating that all of the suspensions were thixotropic or time-dependent flow. The recovery time of the thixotropic nail enamel was depicted in Figure 5.12 at the third interval of the test while the first and second test intervals provided the thixotropic indices. The thixotropic indices of nail enamels using Bentone 38, Bentone 27, Bentone 34, and commercial nail polish were about 1.4, 1.4, 1.4, and 1.5, respectively. These indices indicated that the obtained nail enamel as these of a commercial one showed similar time-dependent flow behaviors.

The lapse of time of the tested samples using Bentone 38, Bentone 27, Bentone 34, and a commercial specimen were approximately 56.6, 8.13, 19.3, and 18.8 seconds, respectively. The Bentone38 formulated nail enamels might require long somewhat recovery time of its viscosity which tended to cause the dripping flow from the nail during the application. The brushed mark might expose on the Bentone27 formulated nail because of its concise viscosity recovery time. However, the nail enamel based on Bentone 34 was capable of building up its viscosity in the same time as the commercial nail enamel.

5.5.2 Drying time of resulted nail enamels

At $23 \pm 2^\circ\text{C}$ and 50-55%RH, the drying time of resulted nail enamel such as clear nail enamel, Bentone38, Bentone27, Bentone34, and Red Earth were 3.12, 3.80, 3.70, 3.80, and 3.80, respectively. The three types of organoclays showed no effect to the drying time of nail enamel since it depends mainly on the rate of solvent evaporation. The groups of solvents used to make nail enamels based on cellulose nitrate are typically the same; therefore, our formulated nail enamel and the commercial one exhibited similar drying time and all of them showed the drying time of about 1-4 minutes which is required in many industrial standards.

5.5.3 Gloss of resulted nail enamels

The organoclays such as Bentone38, Bentone27, and Bentone34 reduced gloss of clear nail enamel from 122.5 to 56.8, 29.8, 76.7, and 74.2 G.U, respectively. The different types of organoclay and surfactant are significant object of resulted film gloss. Bentone38 and Bentone34 are the same group of clay as well as the same surfactant. However, Bentone38 is of lithium rich whereas Bentone34 is of aluminium rich. Metal in clay structure might effect to light reflection providing different gloss value. Bentone38 and Bentone27 are the same of lithium rich but they are different surfactant which provided different gloss values.

5.5.4 Sedimentation of various clay-suspended nail enamels

Figure 5.13 reveals that the suspension of 1, 3, and 4 wt% of Bentone34 showed some sedimentation at the bottom of the container, while the suspension concentration of 5wt% could maintain its pigment suspension even after 10 days. On account of clay concentration, there was soft gel at low clay content which could not carry the pigment in solution. In contrast to soft gel, strong gel was required to overcome the gravity force which corresponded to the settling of the pigments.

5.6 Evaluation of the formulated nail enamels on human use

The formulated nail enamels as below were blind-tested on human use as shown in Figure 5.14. From the test, films of the resulted nail enamels as well as commercial grade of nail enamel appeared on human nail even after 10 days, but about 20% of the total area of films peeled off from the nail because of everyday life working. All of formulated and commercial films were durable for 10 days after brushing on human nail. The results revealed that our nail enamels showed durability on human nail comparable to the good commercial products, i.e. Red Earth™.

From the data in questionnaire, we found that women of over 50% satisfied the pick up characteristics of nail enamel, which could be settled during transport to nail without enamel dripping which stain women's clothes. As nail enamel was applied on nail, more than 50% of women felt easily brush provided smooth and leveling film on nail. At the ambient condition, the solvents in nail enamel evaporated offering dried enamel film within 1 minute. That made over 70 % of women satisfied. The women satisfied percentage on gloss characteristic is about 90% on the Bentone34 formulated nail enamel, while others two formulated nail enamel need to improve the gloss characteristics. Those women gave us some comments that they were unsatisfied at the gloss appearance which might be reduced gloss value by clay surfactant. We can develop this property by employing more glitter pigment to gain high light scattering. After 10 days, those 70% of women reported that on the enamel surface appeared obvious mark because of abrasion, while some of them expressed no any mark on the film because their work occasionally damage the film.

Ingredients	wt %
Cellulose nitrate	10
Maleic resin	5
Epoxy resin	5
Dibutyl phthalate	5
Ethyl alcohol	5
Butyl acetate	15
Ethyl acetate	20
Toluene	29
Bentone 27	5
Pigment	1

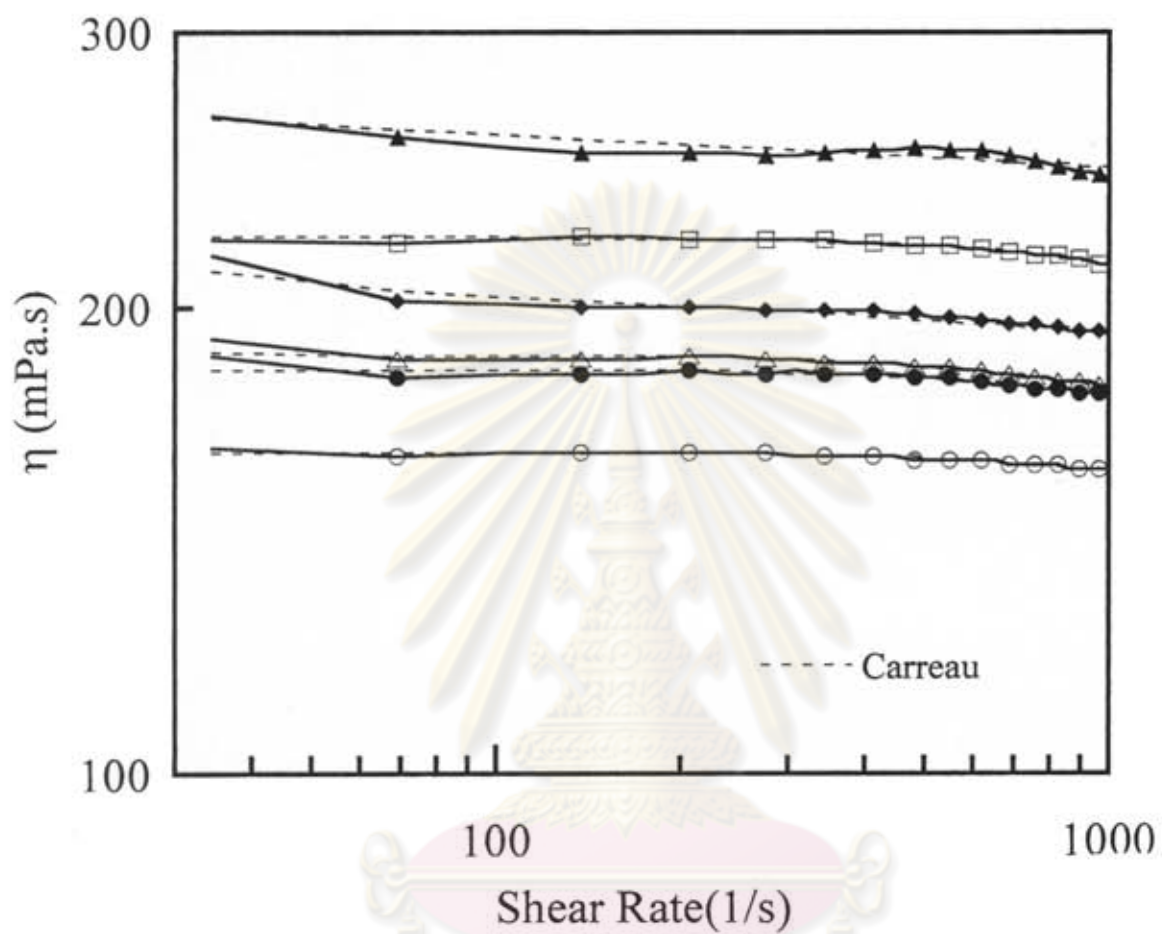


Figure 5.1 Viscosity curves of CN solution at various contents of water:

(▲) 1 wt%, (□) 2 wt%, (◆) 3 wt%, (△) 4 wt%, (●) 6 wt%, (○) 10 wt%

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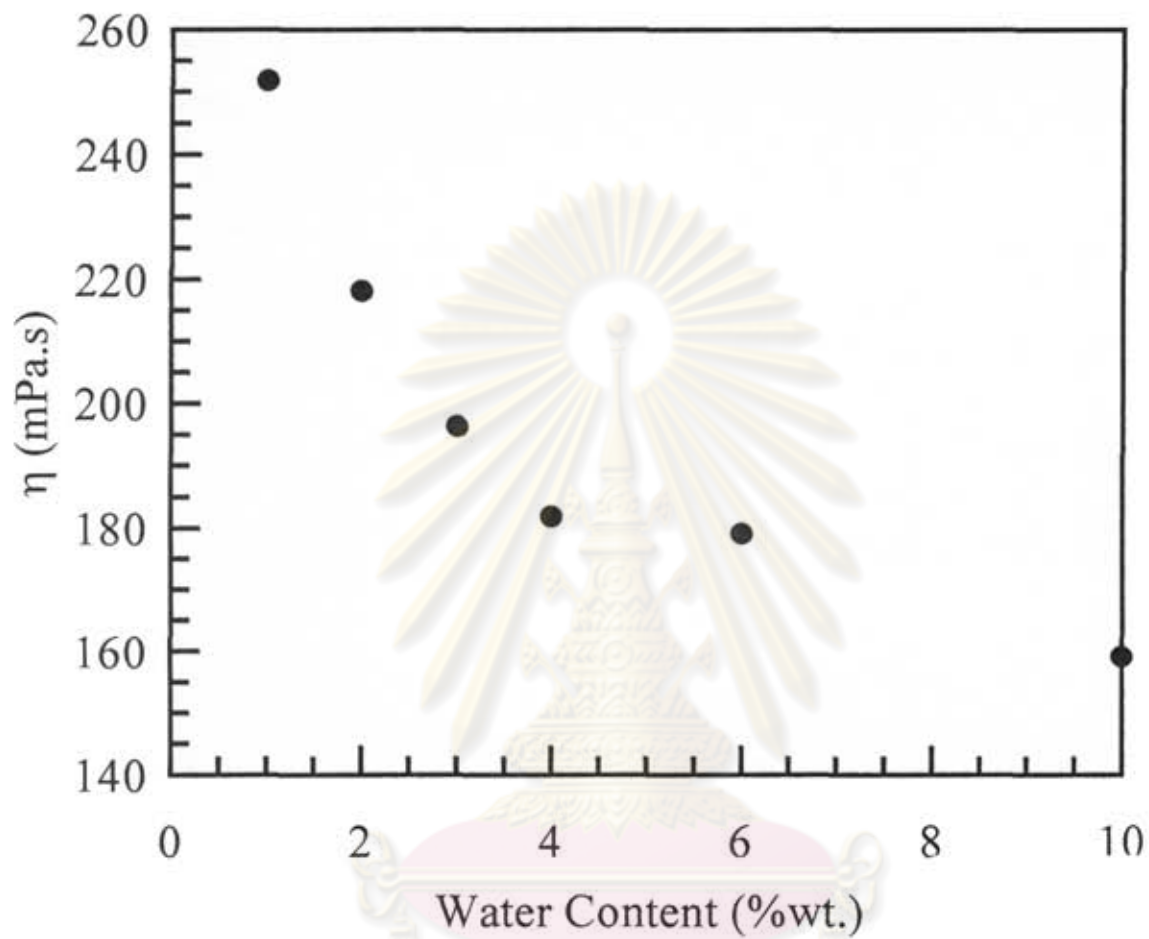


Figure 5.2 Viscosity of CN solution at various water contents at shear rate 620 (1/s).

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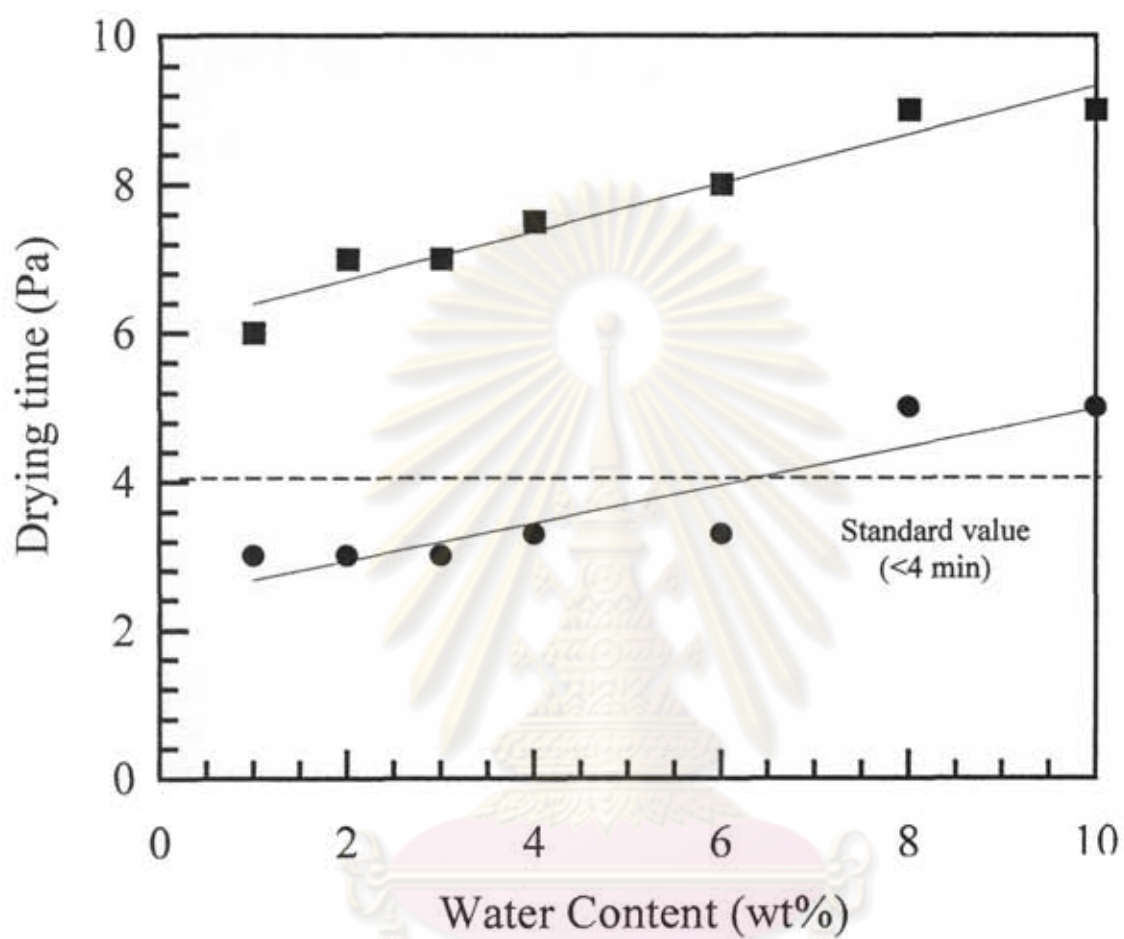


Figure 5.3 Drying time of CN solution at two different relative humidity:

(■) 90%RH, (●) 50%RH

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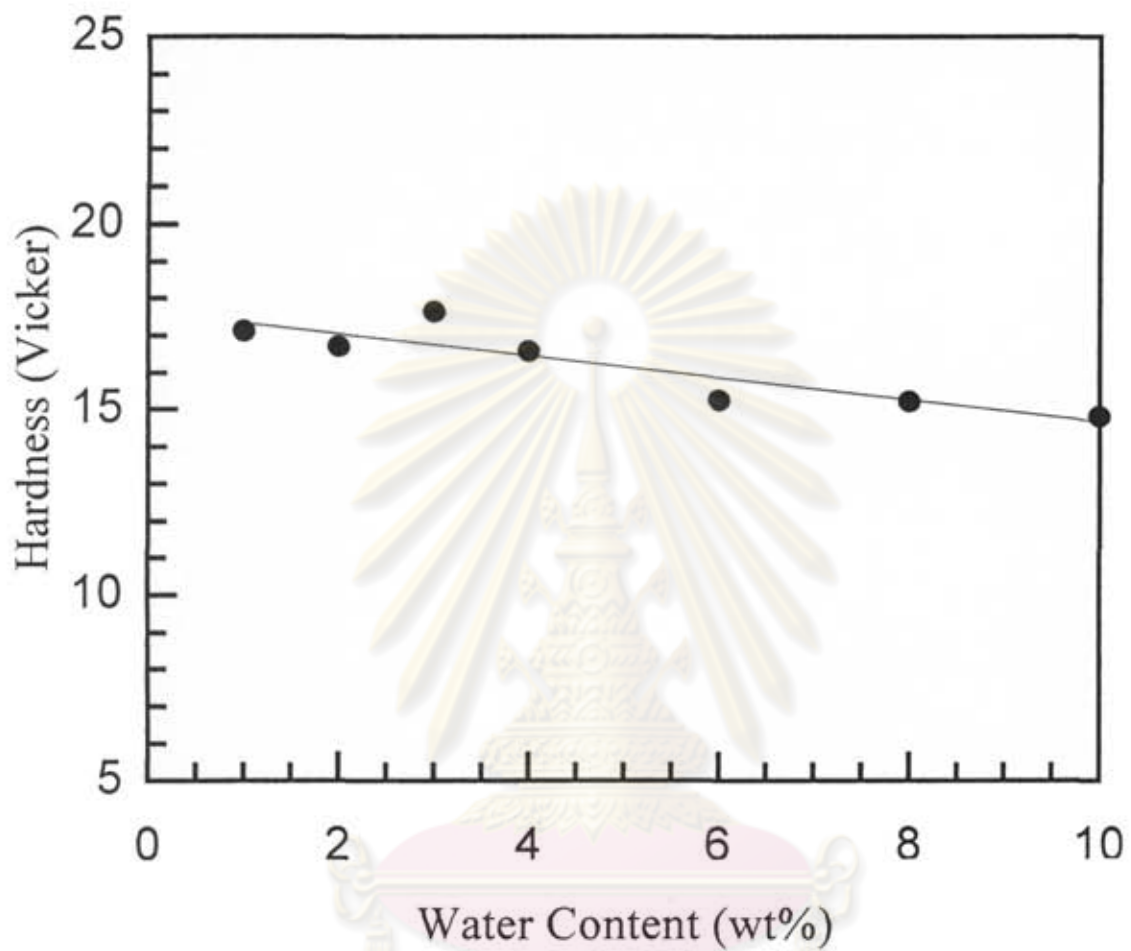


Figure 5.4 Hardness of CN film at various water contents.

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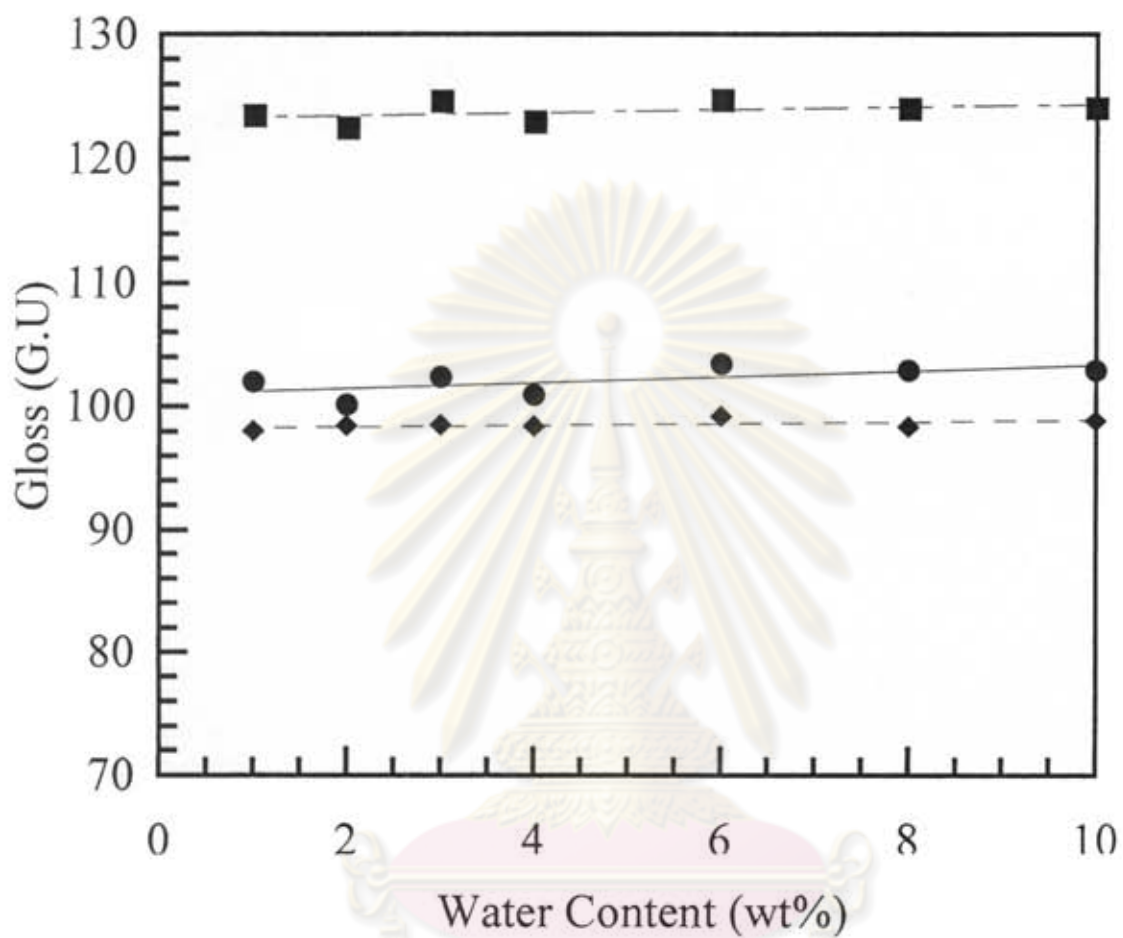


Figure 5.5 Gloss of CN films at different reflection angles:

(■) 60 Geometry, (●) 20 Geometry, (◆) 85 Geometry

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Table 5.1 Effect of various adhesion promoters on CN films.

Resin Type	Area of adhesion (%)			
	% adhered area I	% adhered area II	% adhered area III	Average
SD 603	7	2	6	5
Silicone	100	100	100	100
ER-912	73	83	95	84
EPO 828	85	100	80	88
Benzoxazine	100	95	100	98
Red Earth™	100	100	100	100



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Table 5.2 Effect of maleic resin on adhesion properties of CN films.

Maleic content (wt%.)	Area of adhesion (%)				Hardness (Vicker)
	% adhered area I	% adhered area II	% adhered area III	Average	
10	73	83	95	84	4.8
8	86	93	83	87	4.3
5	91	100	100	97	1.9
2	90	85	100	92	0.9
0	85	100	80	88	0.6



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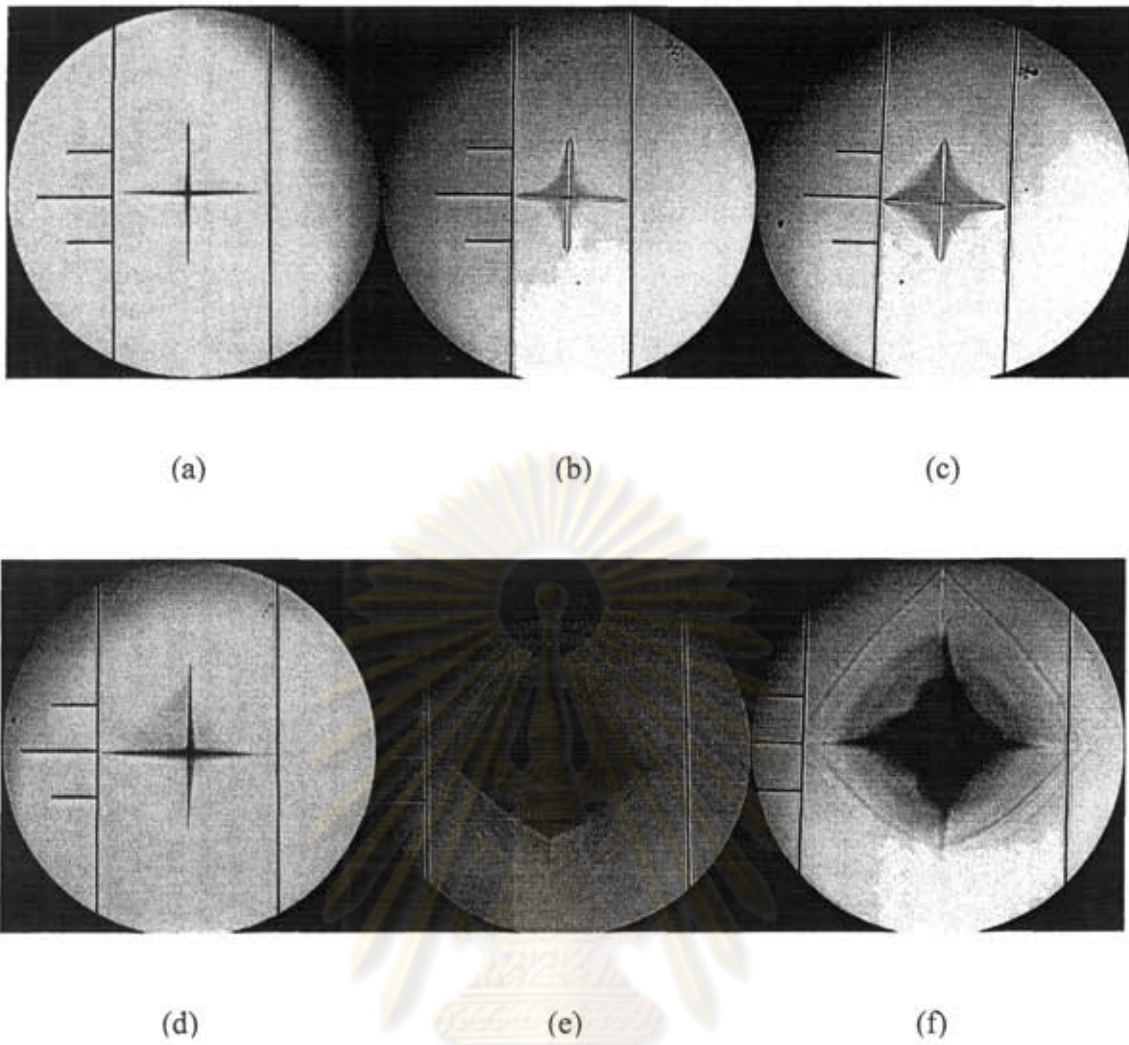


Figure 5.6 Effect of maleic resin content on hardness of CN films:

(a) no adhesion promoter, (b) 10wt%, (c) 8wt%, (d) 5wt%, (e) 2wt%, and
(f) epoxy 10wt%

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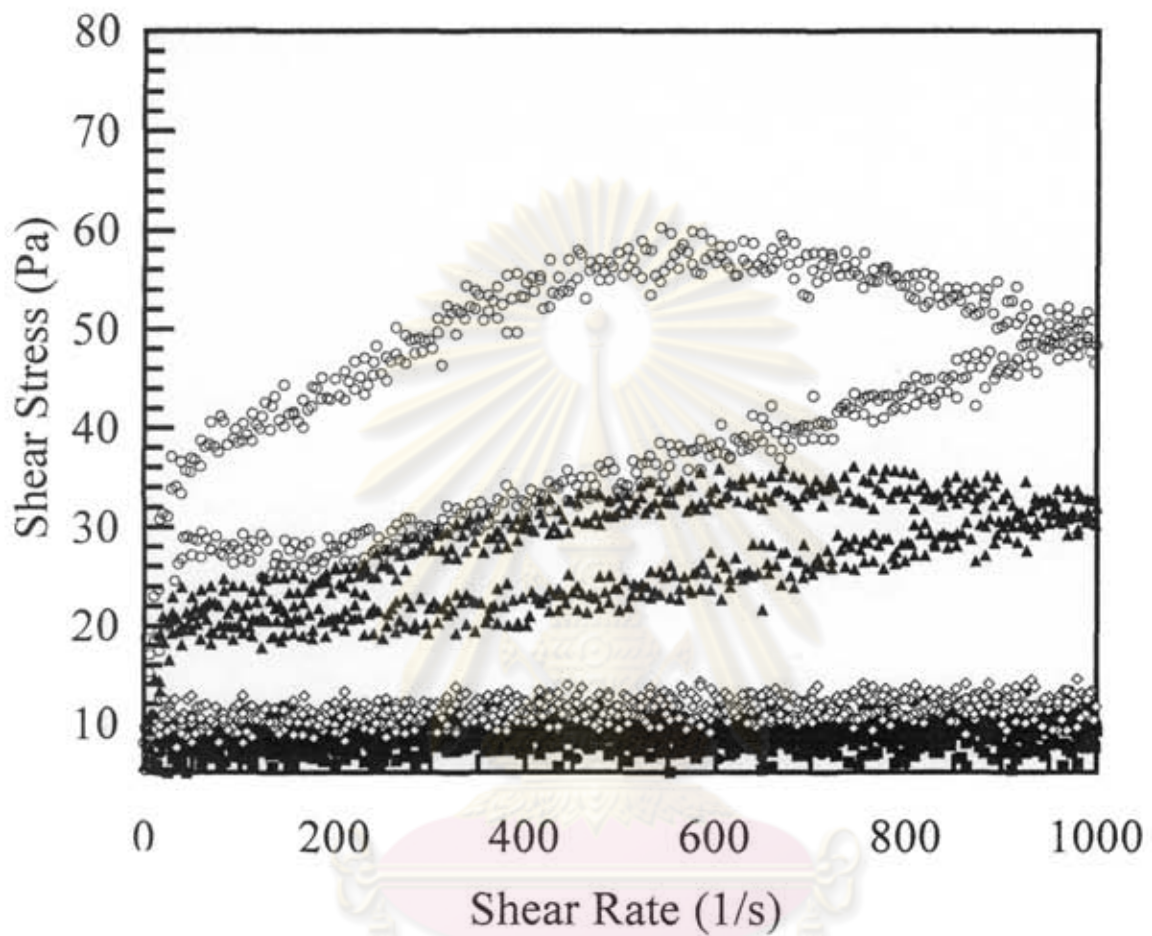


Figure 5.7 Hysteresis of 8wt% bentone38 in toluene at various mixing times using a mechanical stirrer at a speed of 650 rpm:

(○) 48hr, (▲) 24hr, (◇) 14hr, (■) 8hr, and (●) 4hr

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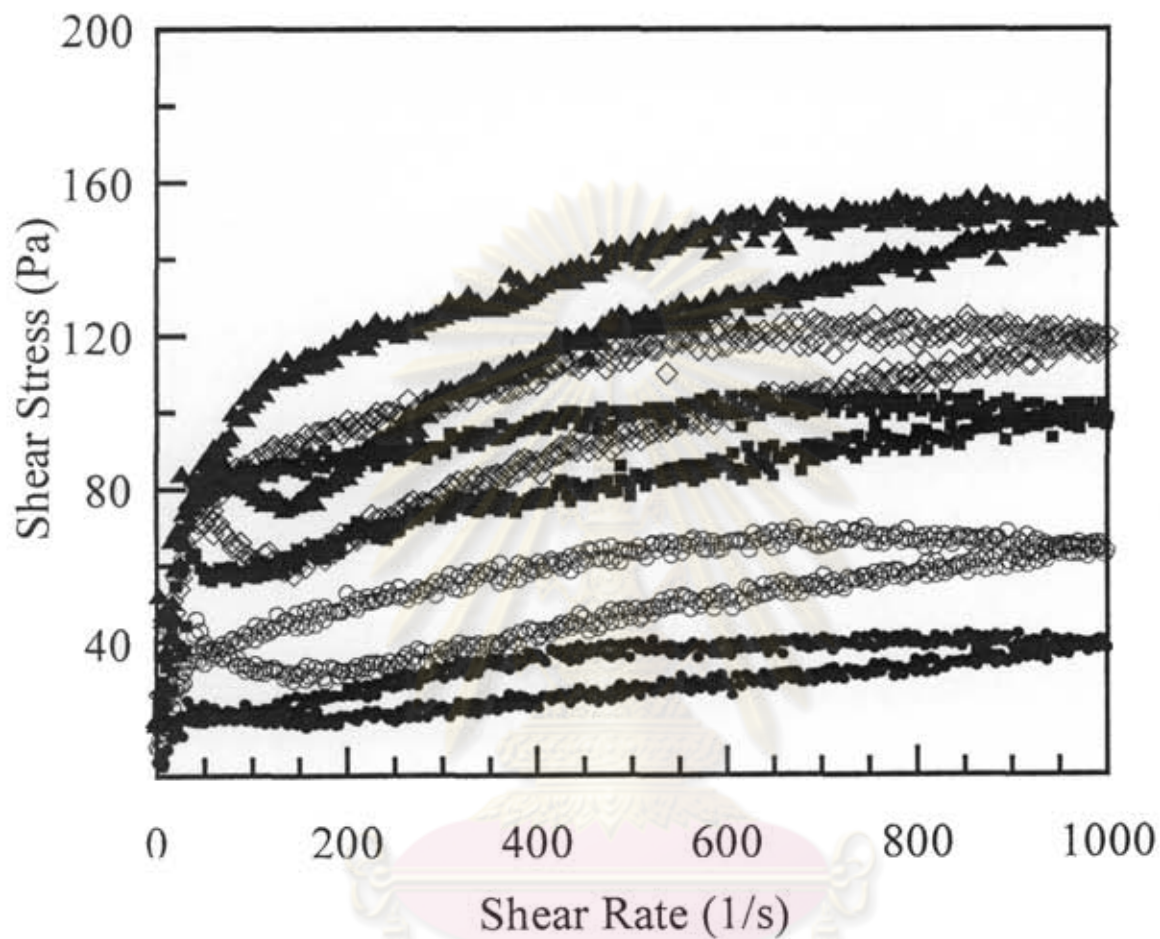


Figure 5.8 Hysteresis of 8wt% bentone38 in toluene at various high speed shear rates using a homogenizer 5 minutes:
 (▲) 24000 rpm, (◇) 21500 rpm, (■) 13500 rpm, (○) 9500 rpm, and
 (●) 6500 rpm

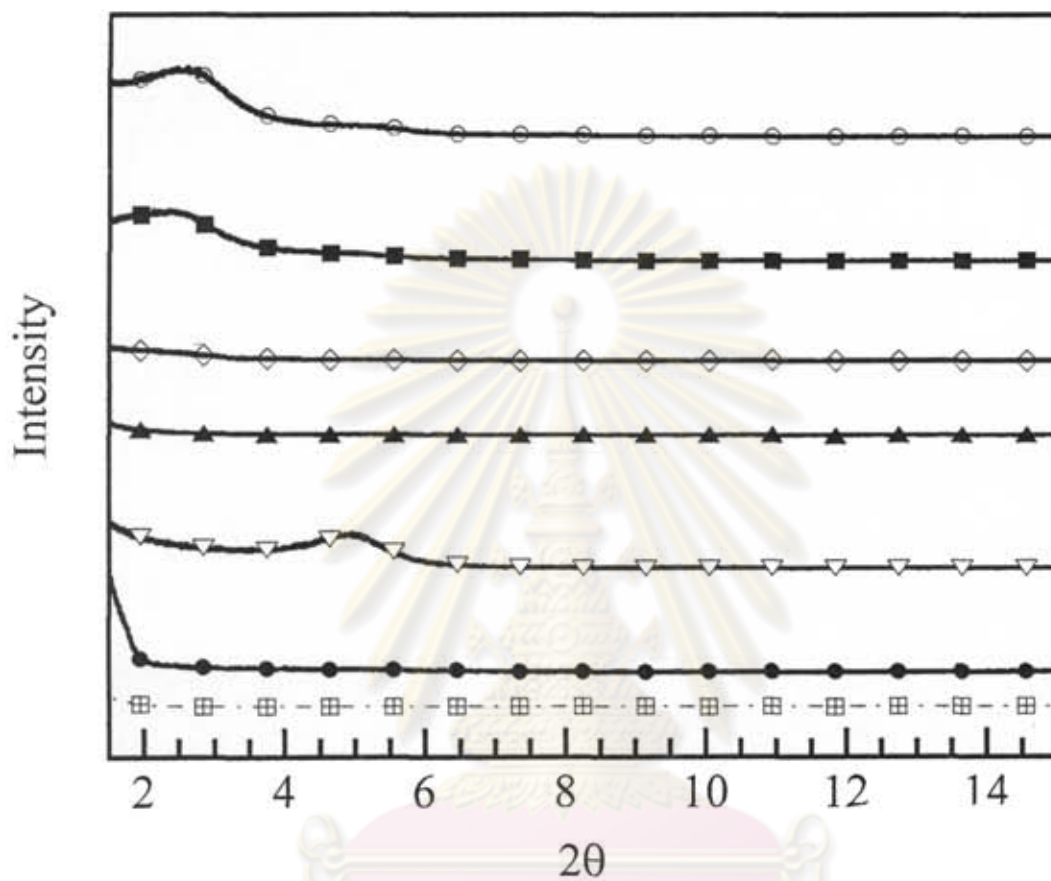


Figure 5.9 XRD patterns of bentonite27 in CN nail enamel films:

(○) 5wt%, (■) 3wt%, (◇) 1wt%, (▲) 0.35wt%, (▽) powder,
 (●) unfilled film, and (⊞) slide glass

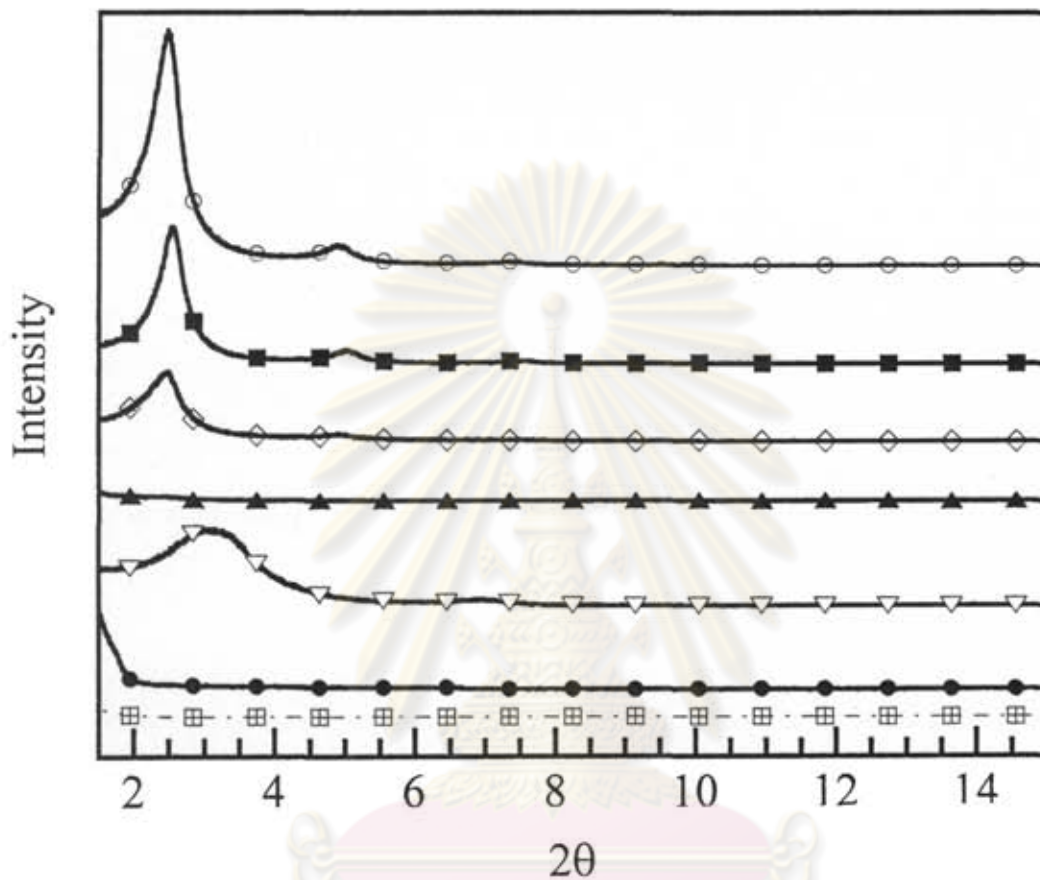


Figure 5.10 XRD patterns of bentone34 in CN nail enamel films:

(○) 5wt%, (■) 3wt%, (◇) 1wt%, (▲) 0.35wt%, (▽) powder, (●) unfilled film, and (⊞) slide glass

Table 5.3 d-Spacing of clay interlayer in CN nail enamel films prepared by homogenizing at high shear rate of 9500 rpm for 5 minutes.

Sample	2 θ	θ	sin (θ)	d-Spacing (Å)	Δ d(Å)
Ben38 powder	3.39	1.70	0.030	26	-
Ben38 5wt%	2.55	1.28	0.022	35	9
Ben38 3wt%	2.39	1.20	0.020	37	11
Ben38 1wt%	2.26	1.13	0.019	39	13
Ben38 0.35wt%	-	-	-	-	Exfoliated
Ben27 powder	4.96	2.48	0.040	18	-
Ben27 5wt%	2.45	1.23	0.020	36	18
Ben27 3wt%	2.35	1.18	0.019	38	20
Ben27 1wt%	-	-	-	-	Exfoliated
Ben27 0.35wt%	-	-	-	-	Exfoliated
Ben34 powder	3.06	1.53	0.030	29	-
Ben34 5wt%	2.55	1.28	0.022	35	6
Ben34 3wt%	2.48	1.24	0.022	36	7
Ben34 1wt%	2.45	1.23	0.020	36	7
Ben34 0.35wt%	-	-	-	-	Exfoliated

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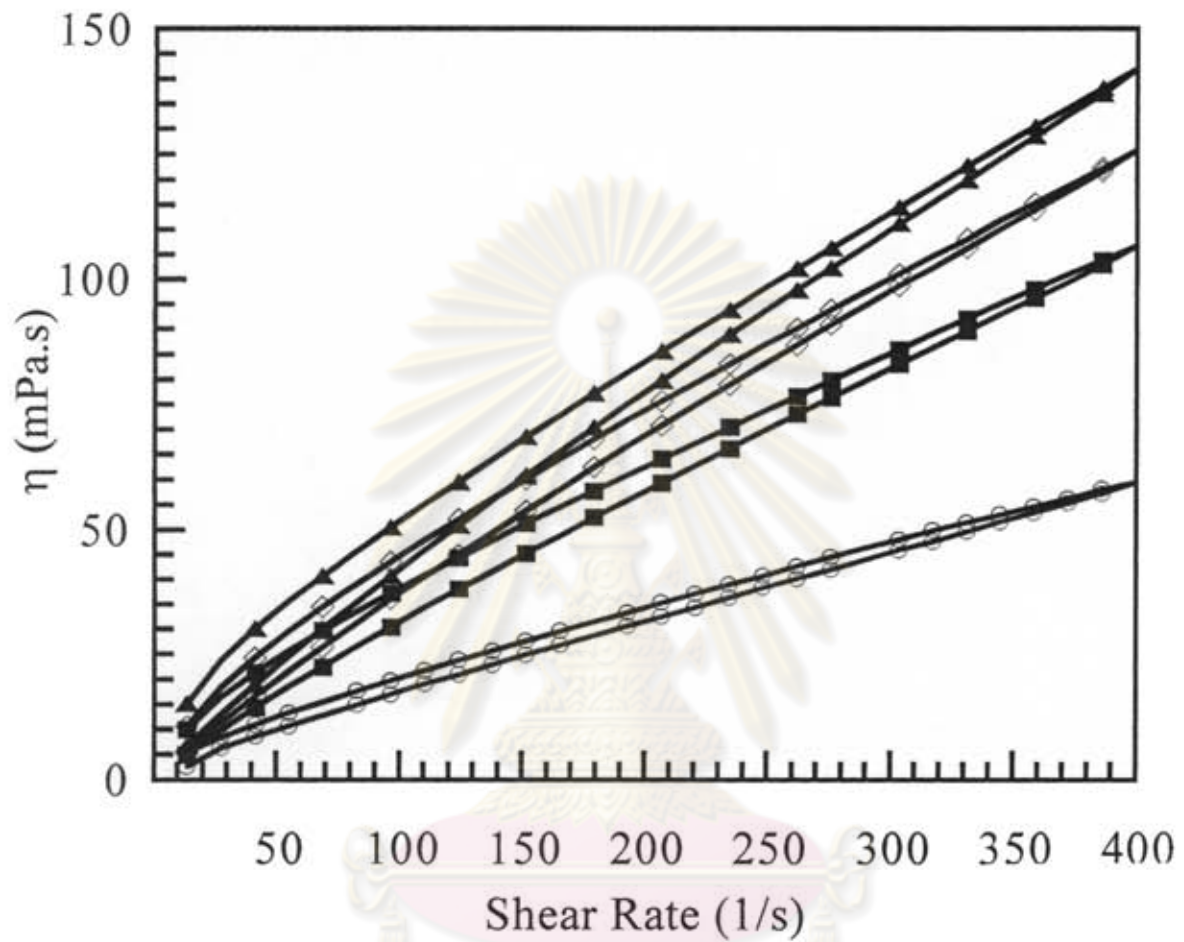


Figure 5.11 Effect of types of clays on thixotropic behaviors of formulated nail enamel at 5wt %:

(▲) bentone27, (◇) bentone34, (■) bentone38, and (○) Red Earth™

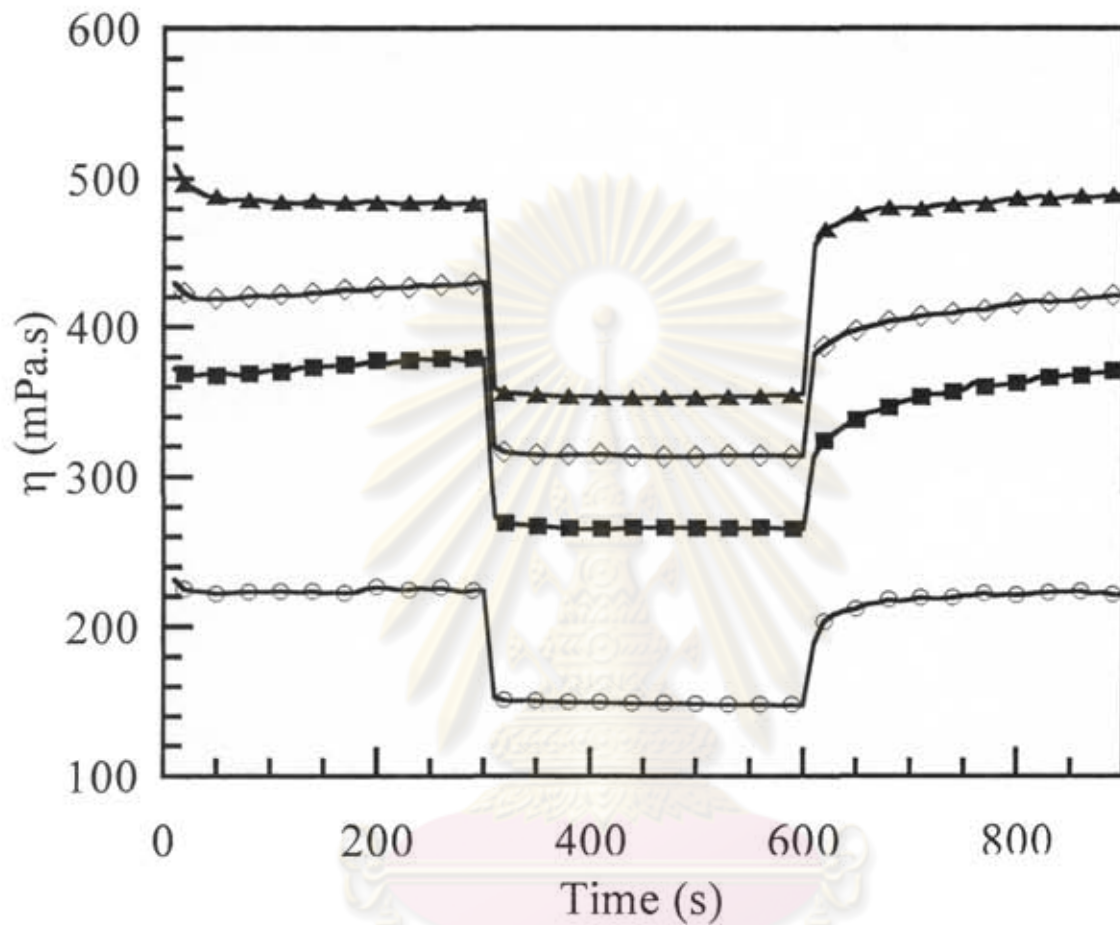


Figure 5.12 Step shearing 4/400/4 (1/s) for thixotropic test of the result nail enamel at 5wt %:

(▲) bentone27, (◇) bentone34, (■) bentone38, and (○) Red Earth™

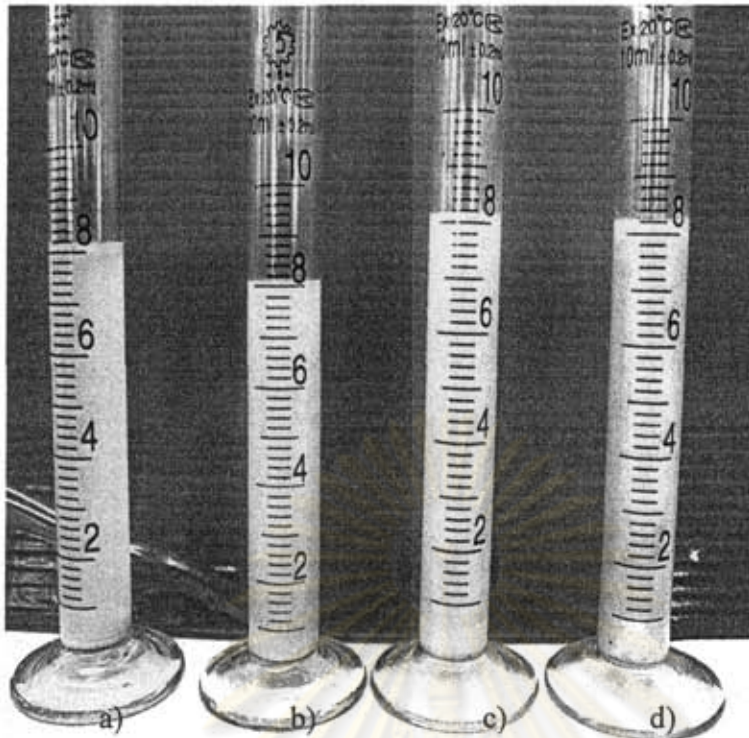


Figure 5.13 Sedimentation of formulated nail enamel at various content of bentone27

(at day 10th):

(a) 1wt%. (b) 3wt%. (c) 4wt%., and (d) 5wt%.

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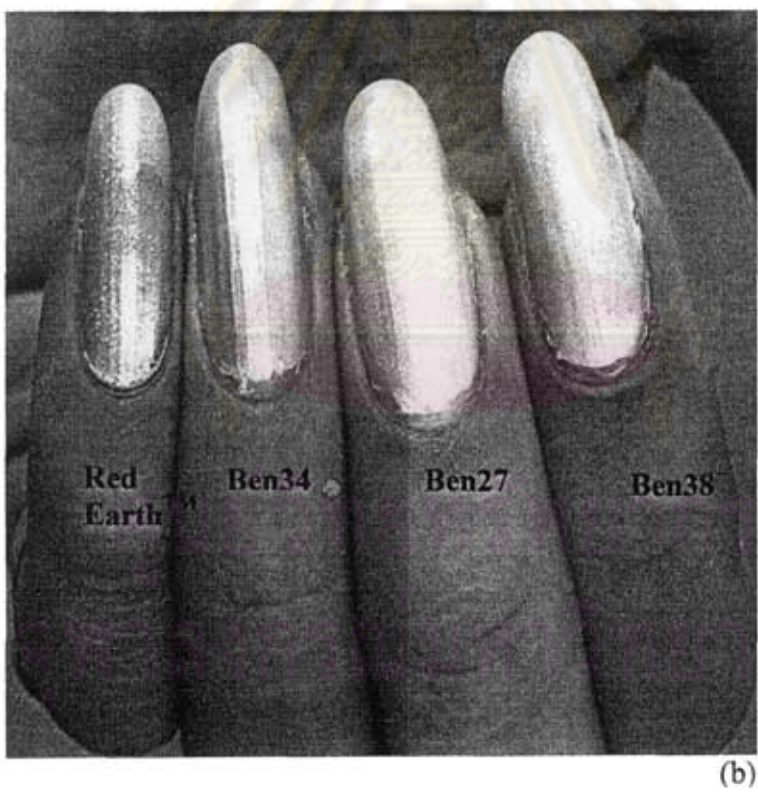
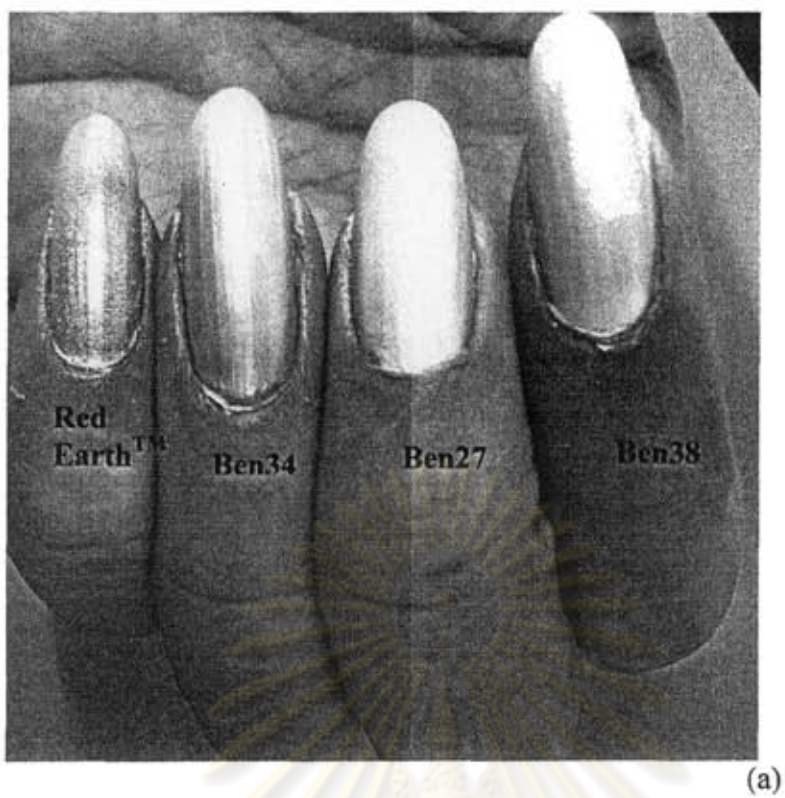


Figure 5.14 Comparative test on human of formulated nail enamels of various suspending agents:
(a) 1 day (b) 10 days

CHAPTER VI

CONCLUSIONS

6.1 Clear nail enamel

In raw cellulose nitrate has water by-product which is immiscible to cellulose nitrate (CN) solution. To evaluate the effect of water content on the CN solution and film properties, the CN powder at various contents were studied in this research to investigate the tolerance water content. The water content of 6wt%, which is generally presented from the CN production, was found to marginally affect the general film properties of the CN based nail enamel similar to those of lower water content and was acceptable to produce nail enamel. The CN poor adhesion was also improved by the acceptable content of maleic-epoxy resin mixtures which is about 5:5 % of total formulated weight provides the relatively good durable nail enamel film.

6.2 Thixotropic suspension preparation and polymer-clay nanocomposite

The thixotropic suspension of nail enamel is necessary to develop shear thinning clear nail enamel to be time-dependent nail enamel. As for thixotropic gelation, the organoclays powder might be activated by their good solvents and required shear force to particles deagglomeration. Therefore, two different methods of gelation were compared. The mixing time of up to 48 hours at a shear rate 650 rpm was found to be enough to prepare a thixotropic flow of the clay solution prepared by a mechanical stirrer. Whereas the much higher shear rate and shorter processing time based on using a homogenizer was resulted in improved thixotropic characteristics of the enamel solution. The high shear rate also provides good clay deagglomeration which can present superb gelation to suspend the solid in nail enamel system. In order to investigate an effect of organoclay deagglomeration, x-ray diffraction was used to observe d-spacing of clay interlayer. Smoother film surface, thus higher degree of reflected light or gloss, was also achieved from the enamel solution prepared by using a homogenizer.

6.3 Color nail enamel

In order to produce color nail enamel, pigment was applied in the clear nail enamel. Nevertheless the pigment precipitated at the bottom of solution container because of gravity force. Anti-settling agent at various contents was employed to figure out this problem. At low concentration thixotropes of nail enamel still appeared the pigment sedimentation and required strong shaking before application. The preferable content of thixotropes to suspend pigment is about of 5wt%, the pigment in thixotropic nail enamel can be uniformly presented its good appearance of luster in solution without precipitation during 10 days. From the blind tests, we found that our formulated nail enamels give women somewhat satisfaction with the similar characteristics to the commercial nail enamel which highly cost import from foreign country.

6.4 Suggestion for future work

1. The hardness of clear nail enamel can be adjusted by the various content of maleic-epoxy resin mixtures.
2. The surfactant of the organoclays can be developed in nail enamel system.
3. The sample can be developed to large scale for industrial manufacture.



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REFERENCES

1. Knowlton, J., and Pearce, S. Handbook of cosmetic science and technology, 1st ed., pp. 160-164. Oxford: Elsevier Advanced Technology, 1993.
2. Harry, R.G. Harry's cosmeticology, 7th ed., pp. 363-388. London: C. Codwin, 1982.
3. Mallavarapu, L.X. Novel epoxy sulfonamide-based resins, a process for their preparation and use of same. US Patent 4, 996, 284. (February 1991).
4. Balsam, M.S., Gershon, S.D., Rieger, M.M., Sagarin, E., and Striance, S.J. Cosmetics: science & technology, vol. 2. 2nd ed., pp. 521-531. Canada: John Wiley & Sans Inc, 1972.
5. Brewer, R.J., and Bogan, R.T. Encyclopedia of polymer science and technology, vol. 5. 2nd ed., pp. 529 –537. New York: Wiley Inter Science, 1985.
6. Durrans, T.H. Solvents, 7th ed. London: Chapman & Hall, 1957.
7. Wicks, Z.W., Jones, F.N., and Pappas, S.P. Organic coatings science and technology, 2nd ed., pp. 306-319, 370. Canada: John Wiley & Sans Inc, 1999.
8. Scher R.K., and Raph, C.R. Nails: therapy, diagonosis, surgery, 2nd ed. Philadelphia: Suanders, 1957.
9. Sward, G.G. Paint testing manual: physical and chemical examination of paints, varnishes, lacquers, and colors, 13th ed., pp. 130-138. Pennsylvania: ASME, 1972.
10. Brewer, R.J., and Bogan, R.T. Encyclopedia of polymer science and technology, vol. 3. 2nd ed., pp. 139 –153. New York: Wiley Inter Science, 1985.
11. Morgans, W.M. Outlines of paint technology, 3rd ed., pp. 54, 220-221. London: Edward Arnold A Division of Hodder&Stoughton, 1990.
12. Sward, G.G. Paint testing manual: physical and chemical examination of paints, varnishes, lacquers, and colors, 13th ed., pp. 130-138. Pennsylvania: ASME, 1972.
13. Stocker, G.N. Thermodynamics and statistical mechanics, p. 41. New York: Springer-Verlag New York, Inc, 1995.
14. Kornmann, X. Synthesis and characterization of thermoset-clay nanocomposites, pp. 5-9. Sweden: Division of Polymer Engineering, Lulea University of Technology, Lulea, 1999.
15. Theng, B.K.G. The chemistry of clay-organic reactions. New York: John Wiley&Sons, 1974.
16. Bergaya, F., and Lagaly, G. Surface modification of clay minerals. Applied Clay Science. 19(2001): 1-3.
17. Clarke, G. Industrial clays (A special review), pp. 78-79, Industrial Minerals Division of Metal Bulletin. 1989.
18. www.mtec.co.th

19. Steffe, J.F. Rheological methods in food process engineering, 2nd ed., pp. 13- 32. Michigan: Freeman Press, 1992.
20. Lambourne, R. Paint and surface coatings: Theory and practice, pp. 557-559. Chichester: Ellis Horwood Limited, 1987.
21. Patton, T.C. Paint flow and pigment dispersion, 2nd ed., pp. 9-10. New York: John Wiley& Sons, 1979.
22. Braun, D.B., and Rosen, M.R. Rheology modifiers handbook: Practical use & application, pp. 27-48. New York: William Andrew Publishing, 2000.
23. Socci, R.L., and Ismailer, A. Nail enamel compositions containing bismuth oxychloride. US Patent 6,740,314. (May 2004).
24. Socci, R.L., and Ismailer, A. Quick drying nail enamel composition. US Patent 5,977,217. (November 1999).
25. Kuritzkes, A.M. Nail enamel composition containing quaternary ammonium cation modified montmorillonite clays. US Patent 3,422,185. (January 1969).
26. Graves, G.G., and Jacks, T. C. Fast drying nail enamel composition and method. US Patent 5,972,095. (October 1999).
27. Ikeda, T., and Kobayashi, T. Thixotropic nail enamel. US Patent 4,222,908. (September 1980).
28. Leo, X.M. Novel epoxy sulfonamide-based resin, a process for their preparation and use of same. US Patent 4,996,284. (February 1991).
29. Frederick, L.M. Nail coating composition free of aromatic and ketone solvents and formaldehyde resins. US Patent 5,662,891. (September 1997).
30. Milan, B.B., and Cristopher, S. Nail polish compositions containing acrylic polymers. US Patent 6,254,878. (July 2001).
31. Pappas, D.A., and Laresen, H.J. Quick-drying nail enamel compositions and method for coating a surface. US Patent 5,093,108. (March 1992).



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Appendix A

Water content in cellulose nitrate

The water and isopropyl alcohol in as received cellulose nitrate was removed by heating at 95-100 °C for 1 hour. After that, checking water content by Karl Fisher Titrator, we found that the rest of water content in dried powder is 1wt% approximately. To adjust water content in dried powder to be 2, 3, 4, 6, 8, and 10wt%, distilled water was added into resin. Cellulose nitrate solution obtained by mixing 20 gram the CN powder at various water contents using a mixed solvent system as follows: ethyl alcohol 10 gram, butyl acetate 30 gram, ethyl acetate 40 gram, and toluene 70 gram. Calculation of water content adjustment in dried cellulose nitrate can be demonstrated as below.

Dried CN water 1wt% 20 gram	+	Distillated water 100wt% x gram	=	Dried CN water 10wt% 20+x gram
---------------------------------------	---	--	---	---

$$(1/100)(20) + (100/100)(x) = (10/100)(20+x)$$

$$0.2 + x = 2 + 0.1x$$

$$0.9x = 1.8$$

$$x = 2$$

Water content in CN (wt%)	Distillated water quantity uptake (gram)	Checking water content in CN solution by Calculation	Checking water content in CN solution by Karl Fisher
1	-	1.18	1.2433
2	0.2	2.35	2.4329
3	0.4	3.53	3.7421
4	0.6	4.71	4.8257
6	1	7.06	7.1465
8	1.5	9.41	9.5432
10	2	11.76	11.8411

Appendix B

d-spacing calculation

The d-spacing of organoclays in cellulose nitrate film were calculated by Bragg's law equation as shown below.

$$n\lambda = 2d\sin\theta$$

where n = integer

λ = wavelength, 1.541°A

d = d-spacing of organoclays interlaminar

θ = diffraction angle

Bentone38 powder was measured diffraction angle by XRD. The value of 2θ is 3.39 angle which we can calculate d-spacing of powder showing as follow.

$$(1)(1.541) = 2d \sin (1.7)$$

$$d = 26 \text{ }^\circ\text{A}$$

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Appendix C

Thixotropic indices

Viscosity of Nail enamel (mPa.s)							
Ben38		Ben27		Ben34		Red Earth™	
at 400 (1/s)	at 4 (1/s)	at 400 (1/s)	at 4 (1/s)	at 400 (1/s)	at 4 (1/s)	at 400 (1/s)	at 4 (1/s)
273.2	372.5	358.9	509	319.7	420.9	152.8	231.2
269	368.9	355.9	496.6	316.3	418	150.5	224.9
268	367.8	355.3	492.2	315.4	418.8	150.1	223.4
267.4	368.5	354.9	488.4	314.8	418.6	150.4	222.7
267	367.4	354.4	487.7	314.5	419	150	221.5
266.6	369.1	354.1	485.2	314.3	418.6	149.6	221.9
265.9	367.4	353.8	485.6	314.3	419.6	149.5	222.3
265.5	368.9	353.6	485.7	314.5	420.2	149.3	223.1
265.2	369.7	353.5	485.2	314.4	421.3	149.2	223
265.2	371	353.5	483.7	314.4	420.2	149.1	223
265.2	370	352.7	484.2	314.9	421.5	149	223.2
265.1	371	352.7	483.6	314.6	420.9	148.9	222.9
265.4	373.3	352.7	483.4	314.2	421.6	148.6	222.4
265.8	372.9	352.5	485.4	313.8	422.8	148.4	223.2
265.9	373.9	352.5	484	313.6	423.1	148.2	221.9
265.9	374.1	352.6	483.4	313.4	423.7	148.1	222.6
266	374.8	352.6	484	313.3	425.2	148.3	222.2
265.8	374.8	352.7	483.5	313.1	424.7	148.3	222.5
265.7	375.8	353	484.7	313.2	424.8	148.1	225.1
265.6	377.8	352.6	483.9	313.4	426.3	147.9	226.1
265.5	375.7	352.9	483.8	313.6	425.9	147.8	225.7
265.6	376.7	353.4	483	313.9	426.3	147.7	224.2
265.5	377.7	353.1	484	314	426.5	147.7	224.1
265.3	378.7	353.4	483.5	314.2	427.9	147.5	225.7
265.6	378.1	353.5	483.9	313.9	427.4	147.5	224.8
265.9	378.9	353.8	484.4	314.1	428.1	147.2	225.4
265.8	379.1	354.3	483	314	427.6	147.3	224.3
265.3	377.6	354.3	483.3	313.9	428.6	147.1	222.8
265.1	378.8	354.6	483	313.7	429	147.3	223.7
265.2	378.6	355.2	484.6	313.6	429.7	147.1	223.8
266.14	373.65	353.77	485.86	314.3	423.56	148.62	223.79
1.4		1.4		1.4		1.5	

Appendix D

Carreau's equation

The shear thinning behavior of nail enamel solutions according to Carreau's equation as below:

$$\eta = \frac{\eta_0 - \eta_r}{(1 + (\lambda\gamma)^2)^{(1-n)/2}} + \eta_r$$

where η_0 = a zero shear rate viscosity

η_r = a final shear rate viscosity (its value rarely appear)

λ = characteristic (or relaxation) time

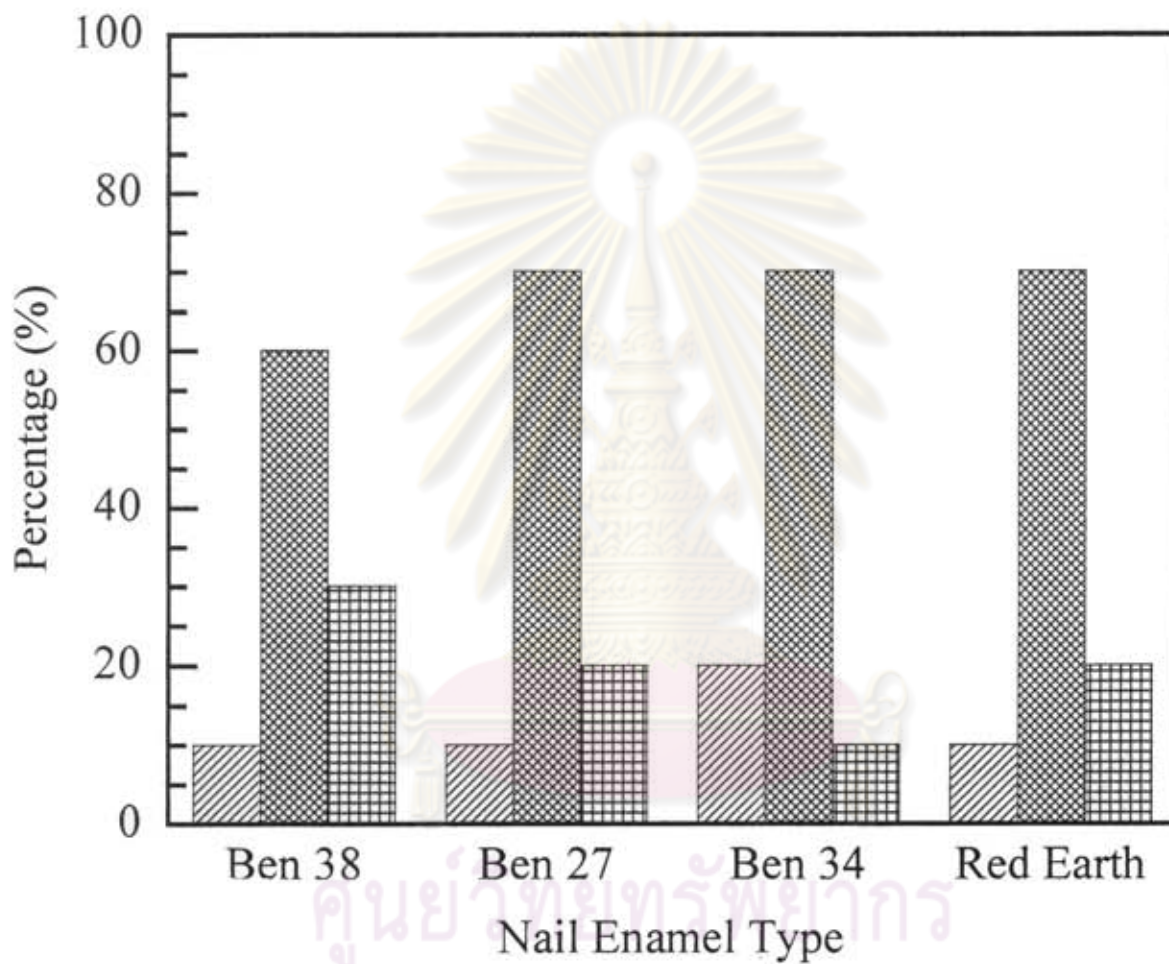
n = dimensionless parameter

The slope of η versus γ in the power law region is given by $n-1$. In the special case of $n=1$ or $\lambda\gamma$ close to zero, this equation simplifies to the Newtonian fluid model. For $n < 1$, this equation predicts shear thinning behavior. All of parameters is calculated by Par Physica software (US200/32 v. 2.30).

Parameter	Water content (wt.%)					
	1	2	3	4	6	10
η_0 (Pa.s)	0.62225	0.22164	0.34849	0.18658	0.1823	0.16133
η_r (Pa.s)	2.75E-8	2.54E-8	2.289E-8	2.114E-8	2.095E-8	1.87E-8
$\eta_0 - \eta_r$	0.62225	0.22164	0.34849	0.18658	0.1823	0.16133
λ	4.4E+10	4.48E-4	5.61E+6	0.0016227	0.001167	0.0017601
$(1-n)/2$	0.015596	0.22058	0.01316	0.03793	0.044703	0.020243
n	0.968	0.5588	0.9736	0.924	0.9106	0.9595
Std.devi.	0.0023522	4.2E-4	0.001589	9.79E-4	8.63E-4	3.233E-4
R^2	0.93972	0.98875	0.93689	0.94802	0.93266	0.97759

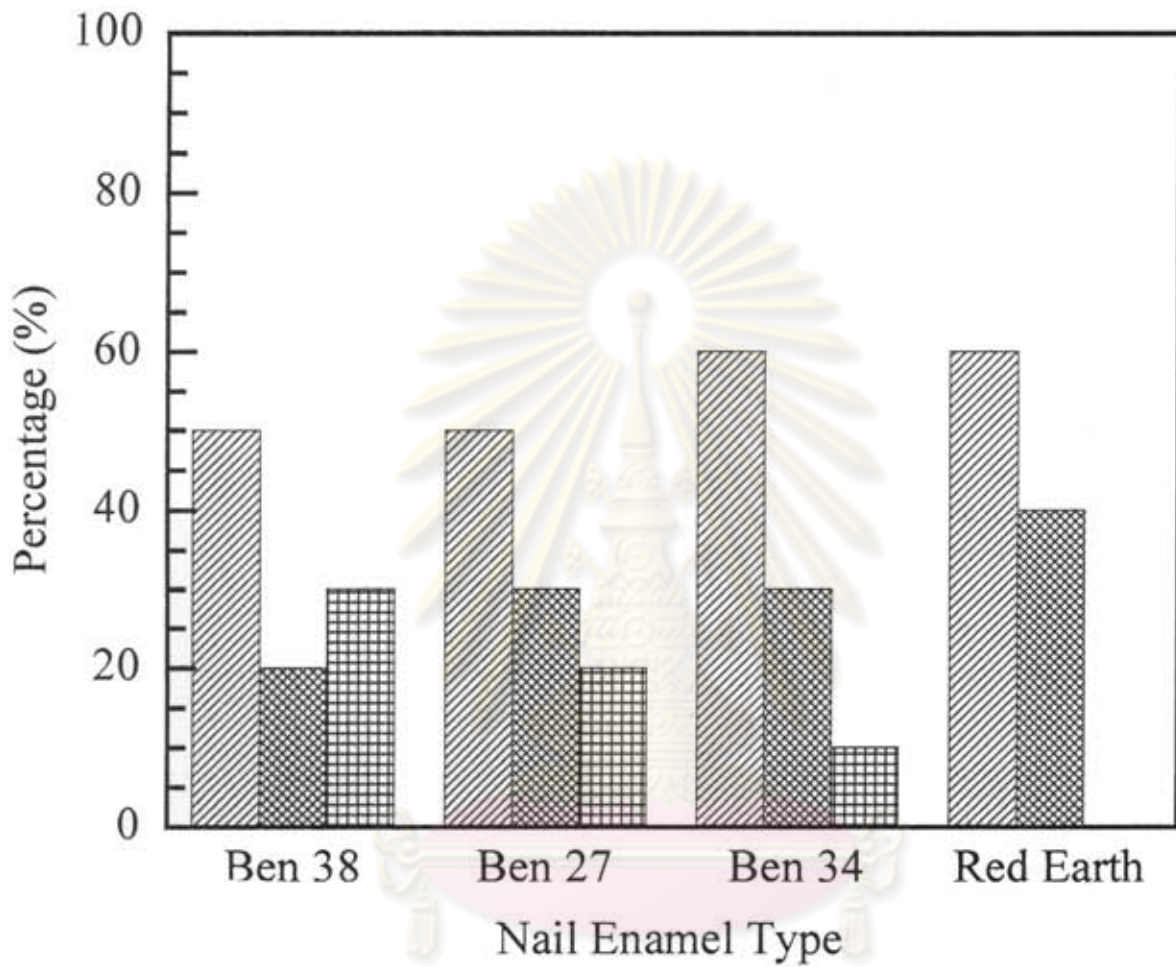
Appendix E

Questionnaire data of human satisfaction



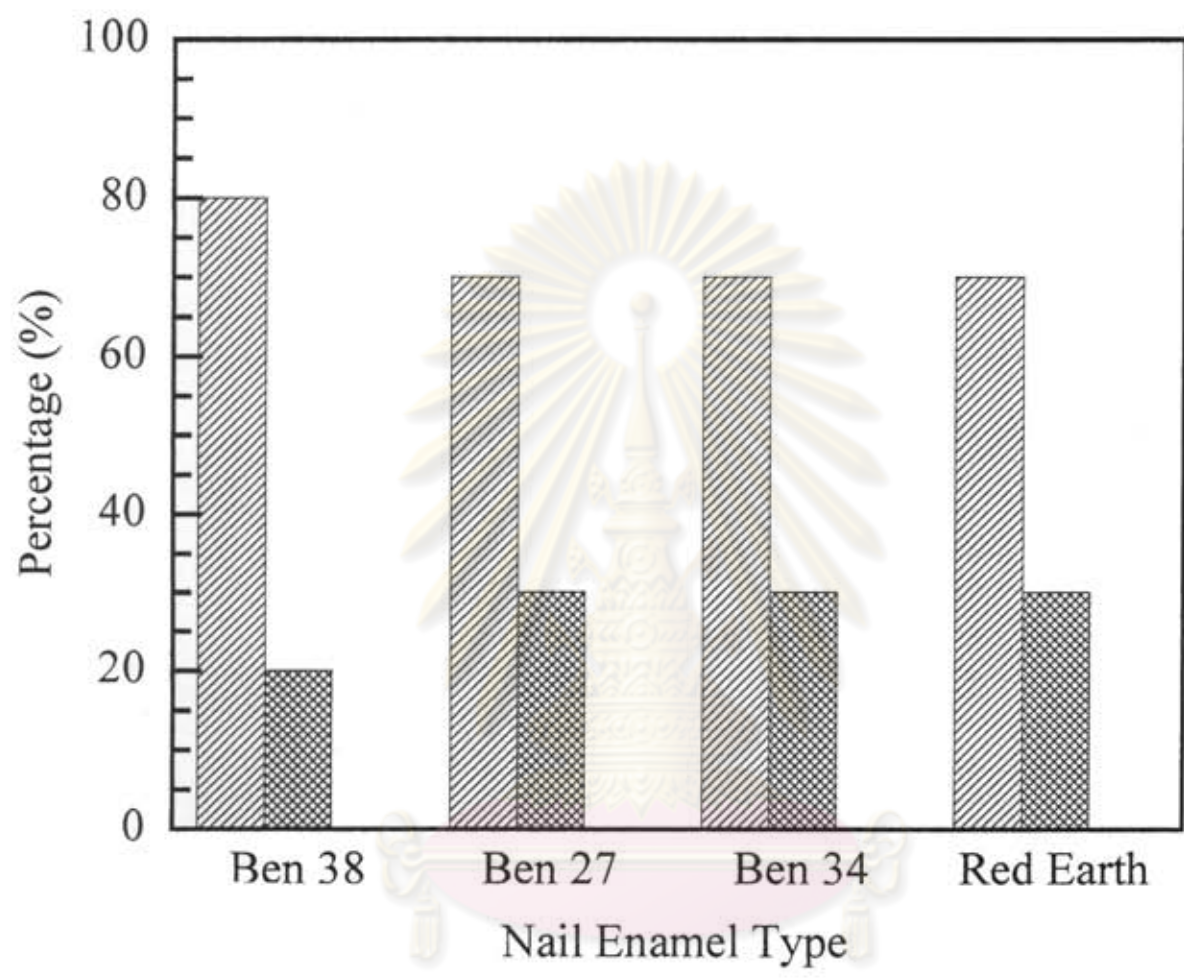
Human satisfaction on pick up characteristic of formulated nail enamel:

(/) dripping, (X) settle, and (■) lump



Human satisfaction on ease of brushing characteristic of formulated nail enamel:

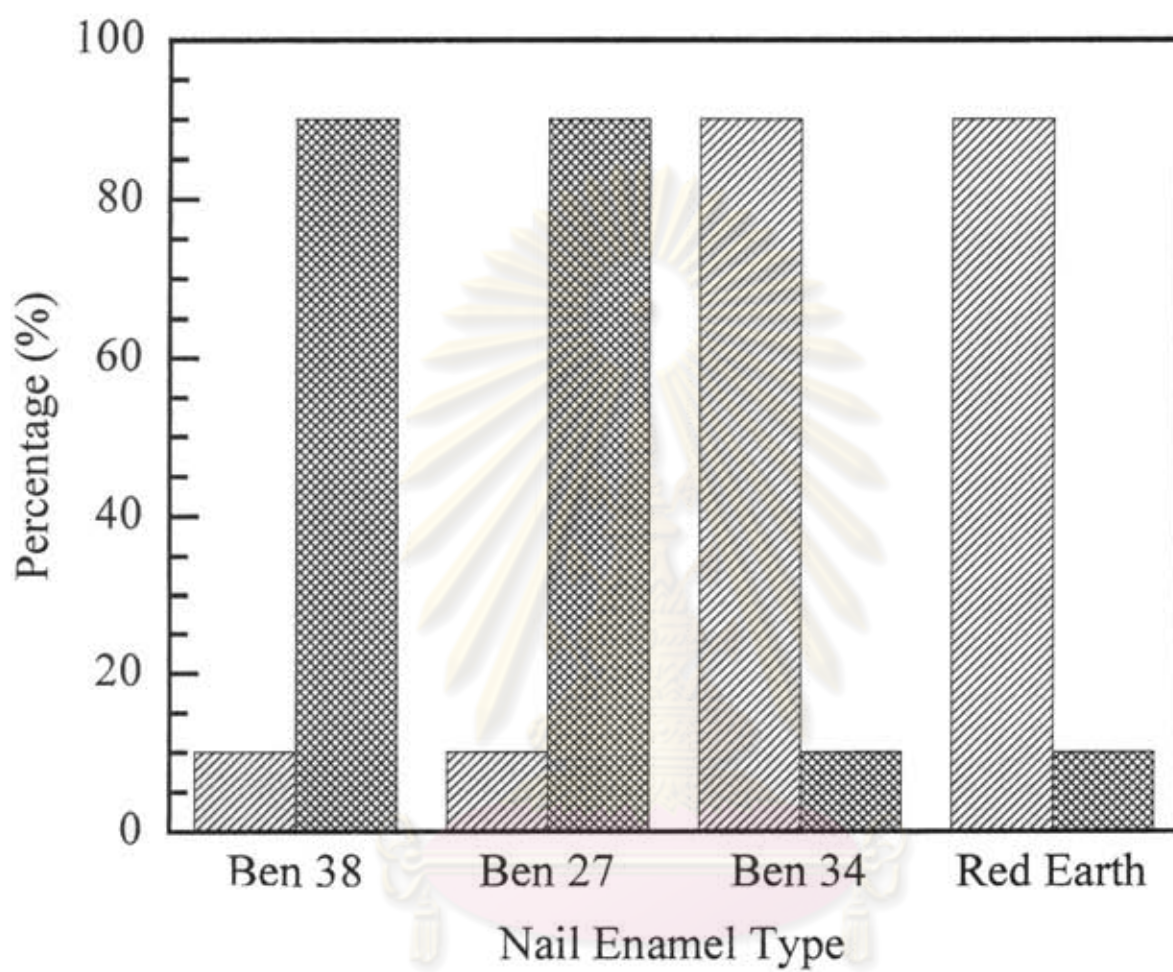
(//) easy, (X) preferable, and (■) difficult



Human satisfaction on drying time characteristic of formulated nail enamel:

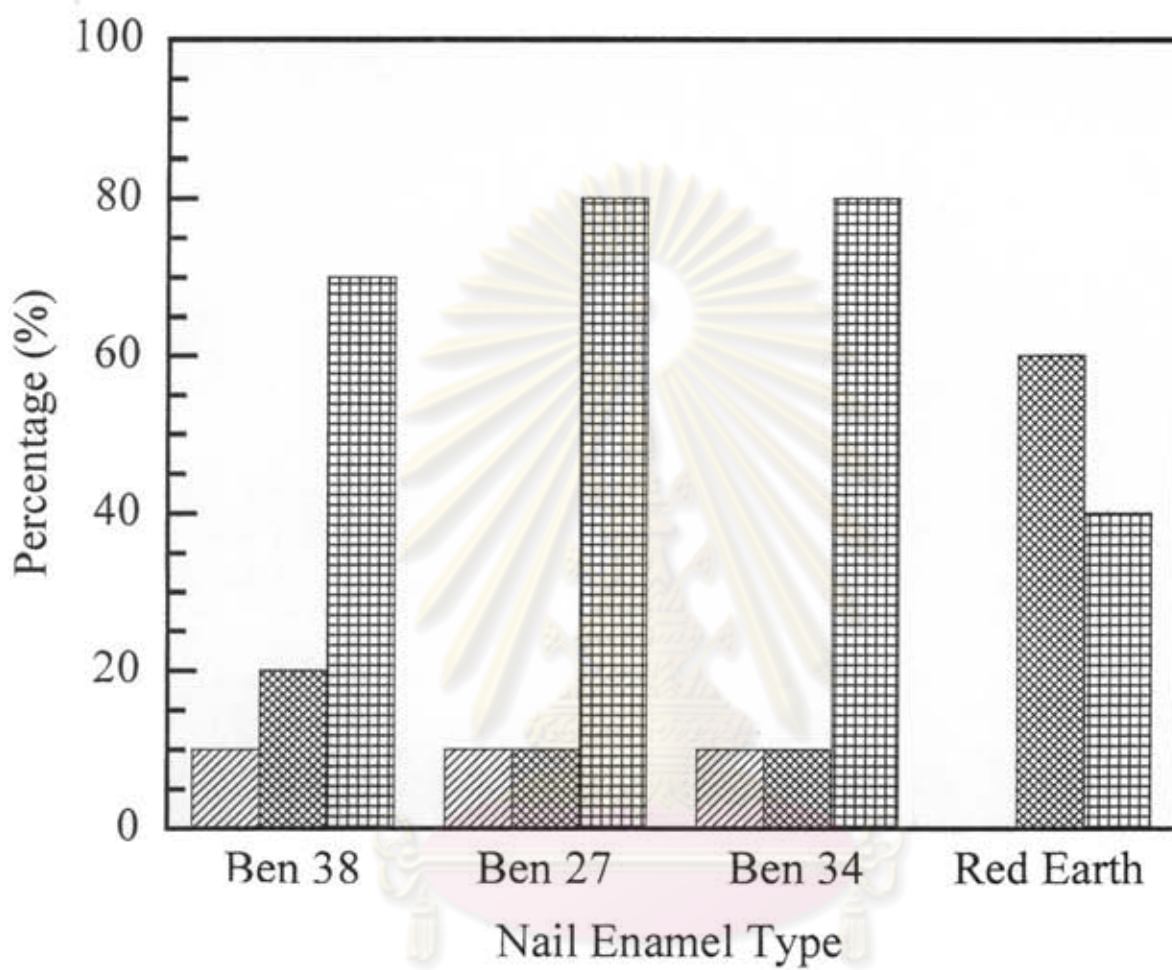
(▨) < 1 min., (▩) 1-4 min., and (▧) > 5 min.

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Human satisfaction on gloss characteristic of formulated nail enamel:

(▨) satisfied, and (▩) unsatisfied



Human satisfaction on abrasion characteristic of formulated nail enamel:

(/) no abrasion, (X) a little bit of abrasion, and (■) obviousness

Appendix F

List of publications

1. Aimon Treewisessorn, Toemsak Srihirin, Wiwut Tanthapanichakoon, and Sarawut Rimdusit “Effects of Water Content in Cellulose Nitrate on the Properties of Nail Enamel with Clay as Thixotropic Agent”, Proceedings of the Third Thailand Materials Science and Technology Conference 2004, National Metal and Materials Technology Center (MTEC), August 10-11, 2004, PP-04, P. 385-387.
2. Aimon Treewisessorn, Toemsak Srihirin, Wiwut Tanthapanichakoon, and Sarawut Rimdusit “Characterization of Cellulose Nitrate Based Nail Enamel Using Clay as Thixotropic Agent”, Proceedings of the Promoting the Growth of Composites in Asia 2004, RP Asia, September 1-2, 2004, P.291-29.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

VITA

Miss Aimon Treewisessorn was born in Bangkok, Thailand on January 11, 1979. She completed senior high school at Suksa Naree School in 1996 and received Bachelor degree from the Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Thailand in 2000. She continued her study for Master degree at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University Bangkok, Thailand.



ศูนย์วิทยทรัพยากร
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