

CHAPTER II

THEORY

2.1 Nail lacquer base formulation [2]

There are generally three classes of nail lacquers; first is base coat which often contain a larger amount of resin for increased adhesion; it dries more rapidly and give a harder film than the normal lacquer film. Films built on a base coat are far less liable to crack than ordinary nail enamel. Second is clear or pigmented lacquer formulations which are available with a lower solid content and, lower viscosity than normal lacquer formulations. Third is top coat which is usually clear lacquer film which is applied over the pigmented lacquer film in order to increase film thickness and thus resistance to abrasion and wear, and also to improve gloss. It has a higher cellulose nitrate and plasticizer content and a lower resin content than normal nail enamel and it also has a relatively high diluent content and tend to dry rapidly. Formula for a base coat, a clear or pigmented lacquer and a top coat, originally can be modified by the typical nail lacquer base formula as shown in Table 2.1.

Table 2.1 Typical nail lacquer base [2]

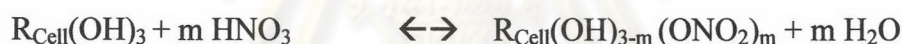
| Ingredients | Percent (weight) |
|---|------------------|
| Cellulose nitrate RS1/2 second (film former) | 10 |
| Santolite MHP (resin) | 10 |
| Santicizer 8 or 160 (plasticizer) | 5 |
| Ethyl alcohol (coupling agent) | 5 |
| Ethyl acetate (active solvent: drying speed up agent) | 20 |
| Butyl acetate (active solvent) | 15 |
| Toluene (diluent) | 35 |

2.2 Ingredients of nail lacquer

In practical terms, the main essentials for the manufacture of nail lacquer are a lacquer base with suspending properties and a color system. These two components can be broken down into necessary constituents, and these are described before manufacture of the product is considered.

2.2.1 Cellulose nitrate [5]

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 is manufactured by treating cellulose with nitric acid in the presence of sulfuric acid and water. The amount of water determines the degree of substitution (DS) attained



The nitration can be considered a typical esterification equilibrium. The removal of water with sulfuric acid forces the reaction to completion. It is believed the nitrating species is NO_2^+ , the nitronium ion.



In Figure 2.1, the $\text{HNO}_3 - \text{H}_2\text{SO}_4$ reaction competes with ordinary dissociation because of water. Therefore, the amount of water present determines the concentration of NO_2^+ and hence the extent of nitration. The degree of cellulose nitration is designated by the nitrogen content. The maximum commercial DS is around 2.9, which corresponds to 13.8% N. Products over 14%N have been obtained by special processes [5].

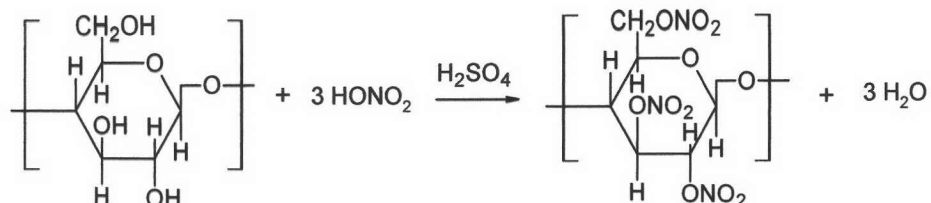


Figure 2.1 The reaction of cellulose nitrate formation

There are two manufacturing methods of cellulose nitrate. Industrial-scale nitration is still regularly carried out using a batch process which shown in Figure 2.2. A preferably small quantity of cellulose is vigorously agitated in a vessel containing a large excess of $\text{HNO}_3\text{-H}_2\text{SO}_4$ nitrating mixture that ratio about 1:20 to 1:50. The proper $\text{HNO}_3\text{:H}_2\text{SO}_4$ ratio as shown in Table 2.2 is chosen to yield the desired degree of nitration and to help maintain fibrous structure by removing heat from the reaction. After 20-30 minutes of nitration, the mixture is centrifuged to remove excess acid, which is recycled. The cellulose nitrate is then immediately placed in a large excess of water to displace the adhering acid. The water slurry that include cellulose nitrate approximately 1wt% is pumped to the purification area where it is centrifuged to remove spent acids for reconstitution and recycling. The yield of common cellulose nitrate, which DS reveals around 1.8-2.7, is about 125 to 150%, with respect to starting cellulose. The losses arise from decomposition of cellulose and from mechanical losses in the ensuing separation steps.

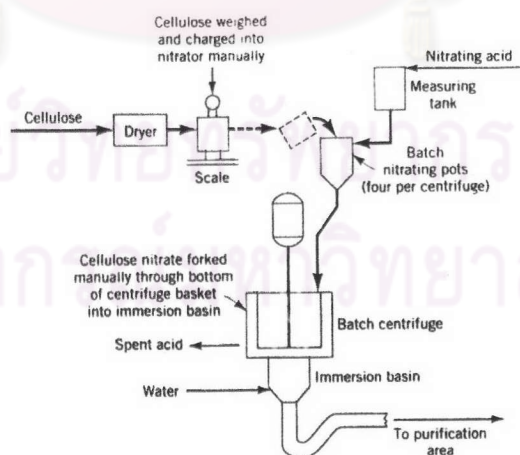


Figure 2.2 Flow diagram of nitration by batch process [5]

Table 2.2 Variation of ester nitrogen content with water content of nitrating bath [5].

| Composition of nitrating bath | | | Cellulose nitrate ester | |
|-------------------------------|-------------------------|------------------------|-------------------------|-----|
| Water (wt %) | Sulfuric acid (wt %) | Nitric acid (wt %) | Nitrogen Content (%) | DS |
| 8.5 | 66.5 | 25 | 13.4 | 2.7 |
| 12.0 | 66.0 | 22 | 13.2 | 2.6 |
| 15.2 | 59.8 | 25 | 12.6 | 2.4 |
| 16.0 | 64.0 | 20 | 12.5 | 2.4 |
| 18.4 | 56.6 | 25 | 11.3 | 2.1 |
| 19.3 | 55.7 | 25 | 10.7 | 1.9 |
| 21.0 | 60.0 | 21 | 10.7 | 1.9 |

In Figure 2.3 show continuous nitration processes, which were developed in the 1960s, are more economical and provide a more uniform product as shown in Figure 2.3. Cellulose and the nitrating acids are provided simultaneously into a vessel where nitration occurs. There it remains for 30-55 minutes. A novel process utilizing a continuous loop formed pressure reactor reduces the hold-up time to 6-12 minutes. The nitration mixture is continually withdrawn from the final zone of the reaction vessel and fed to a centrifuge. The centrifuge separates the spent acids and the cellulose nitrate is washed in stages with progressively weaker aqueous acids. Finally, the resulting water slurry of cellulose nitrate is pumped to the purification area. Cellulose strips have been continuously nitrated by drawing them through a bath of nitric acid, phosphoric acid, and water. A process using $Mg(NO_3)_2$ as the dehydrating agent, instead of H_2SO_4 , has also been developed. This nitrating system is also appropriate for a continuous process.

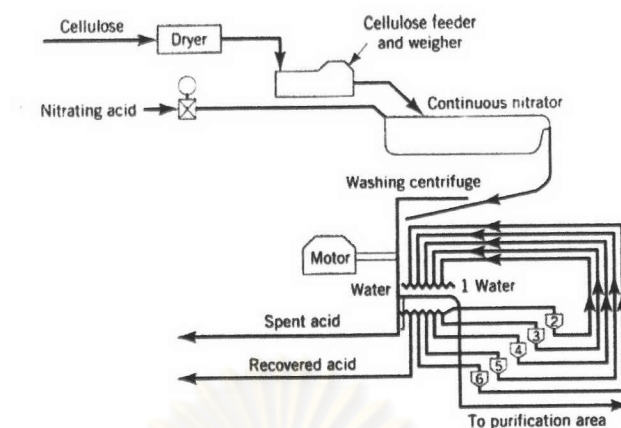


Figure 2.3 Flow diagram of nitration of cellulose by Hercules continuous process [5]

Stabilization and Digestion: Following the initial washing steps, the stabilization of cellulose nitrate occurs. This involves removal of any remaining sulfuric acid since it would catalyze the decomposition of cellulose nitrate. The sulfuric acid present is both physically entrained in the product and chemically bonded to the cellulose chain. Cellulose nitrate can contain 0.2-3 wt% esterified H_2SO_4 , depending on the DS of nitration. The sulfonate ester can be easily removed by saponification in boiling water with 0.5-1 wt% acid residue. Boiling time can vary from 6-40 hours for batch processes.

Cellulose nitrate is manufactured over a viscosity range of 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.

Further stabilization against thermal and photochemical degradation may be necessary in some end uses. Certain organic acids such as citric, tartaric, stearic, and oxalic have been used to stabilize cellulose nitrate against thermal degradation and discoloration during aging. Heat stabilization can be aided by incorporating diphenylamine and epoxy compounds. It is believed these stabilizers act as acid

scavengers. Discoloration by exposure to light can be reduced by addition of small amounts of dibenzoylmethane.

Dehydration: Dry cellulose nitrate is extremely flammable; cellulose nitrate with high N content may explode when heated or subjected to sudden shock. Therefore, it is necessary to ship 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 4 type application which classified by nitrogen content as shown in Table 2.3. For the lacquer industrial, ester-soluble cellulose nitrate is mainly applied as raw material. Physical properties of cellulose nitrate are disclosed in Table 2.4.

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. These cellulose nitrate chips can be colored with pigments so that colored enamels can be produced without using ball or roller mills.

Table 2.3 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 2.4 Physical properties of cellulose nitrate [12, 14]

| | |
|--|---|
| 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 |

2.2.2 Resins [1]

The main function of secondary resins is to overcome some of the inadequacies of cellulose nitrate films. Although several different types of secondary resin have been tried in the past, the most commonly accepted nowadays is the condensation product of p-toluenesulfonamide and formaldehyde, sold under the trade name of Santolite MHP (Monsanto Chemicals). This resin, when included at levels of between 5 and 10 wt%, gives good gloss, good adhesion and improves the hardness of cellulose nitrate film. In addition Santolite MHP confers other benefits to the formulation. It has negligible water solubility and produces a continuous transparent

film with good detergent resistance. It also has good light stability and is totally compatible with nail lacquer pigments.

The only major disadvantage with Santolite MHP is that it causes an allergy in some people. In this case, or if a hypoallergenic product claim is required, the Santolite MHP can be substituted with a polyester resin or oil-free alkyd resin, based on polyol dibasic acid ester. The resin which is chosen to be ingredient of nail enamel should modify the characteristics of cellulose nitrate to impart sufficient hardness, resistance to chipping, and adhesive characteristics to the dried film.

2.2.3 Solvents [7, 11]

A solvent is defined as a substance having the power of dissolving or forming solution with something. A solution is described as being dissolved, especially of a solid or gas into a liquid form. In coatings, solvents dissolve resins and polymers to form solutions. These solutions simplify the manufacture and application of paints and, as a result of solvent evaporation, facilitate the formation of the paint film. In essence, solvent convert aggregates of resin and polymer molecules into single molecules or small cluster of molecules in solution. In a solution, molecules of solute and solvent are dispersed one within the other. Forming a solution is simply a process of separating molecules. As the solvent evaporates after application of the paint, the resin or polymer molecules once again form aggregates and become solid. The paint film may be deposited in its final form (non-convertible coatings) or may be modified chemically after deposition (convertible coatings). Oxidation, heating and irradiation are examples of ways in which films may be converted chemically after application. Many properties of solvents influence paint performance such as non-flammable, hazard-free, satisfactory application, but two are most important. These are: solvency, the ability to dissolve the resins that are present; and evaporation rate, the speed with which solvents leave the paint during and after application. The properties of solvents in nail enamel system are shown in Table 2.5. In the nail enamel system require several function of solvents.

2.2.3.1 Dibutyl phthalate

Small proportions of dibutyl phthalate initially increase the elasticity and tensile strength of cellulose nitrate films, the plasticity and tensile strength thereafter diminishes with increasing proportion; maximum gloss is also reached with similar proportion. A somewhat higher proportion is required to cause the ready elimination of residual volatile solvent, while still higher proportions favor adhesion, stability and the ease of application of the lacquer.

2.2.3.2 Ethyl acetate [6]

Ethyl acetate has a low order of toxicity, chronic effect appear to be limited to irritation of the membrane and a tendency to eczema. It can cause transitory pulmonary edema. This solvent is undoubtedly the bat of the low-boiling solvents for the manufacture of cellulose nitrate lacquer and act as drying speed up agent. It has considerable advantages over acetone; its boiling-point is higher and its evaporation rate about one half that of acetone, and it is therefore less likely to cause chilling. Its dilution ratios for cellulose nitrate solutions against dilution with alcohols and parafins are larger than those of acetone, although smaller against aromatic hydrocarbons.

2.2.3.3 Butyl acetate [6]

Butyl acetate known also as butyl ethanoate is the most widely used of all the solvents of cellulose nitrate. It is probably the best true solvent for cold lacquers and cellulose paints, since its volatility is sufficiently high for it to leave the film readily and sufficiently low to render it an excellent blush preventive, especially in conjunction junction with butyl alcohol; the mixture of the two effectively prevents chilling s well as gum and cotton blush. Butyl acetate is non-toxic and has a less pronounced odor than amyl acetate; it gives solutions of cellulose nitrate of somewhat lower viscosity than the latter.

2.2.3.4 Isopropyl alcohol [6]

Isopropyl alcohol is not a solvent for cellulose esters, but has distinct latent solvent properties, the presence of a relatively small quantity of an ester rendering it a solvent for cellulose nitrate. It dissolves cyclohexanone-formaldehyde resin, colophony, shellac, kauri, sandarac, manila and low viscosity silicones; it partly dissolves mastic, elemi, dammar and soft copal, it does not dissolve polyvinyl chloride, acetate or chloracetate. It has the advantage over industrial alcohol in that it is anhydrous and therefore less likely to cause water blush. The fact that no methylation is required is also in its favor, since methylating agents can affect the strength and color of cellulose films.

2.2.3.5 Ethyl alcohol [4]

Ethyl alcohol is not a solvent of cellulose nitrate but when used in conjunction with active solvents, they increase the strength of the latter. Ethyl 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.

2.2.3.6 Toluene [6]

Toluene or toluol is the most widely-used hydrocarbon diluent in cellulose nitrate lacquers, its vapor pressure and power of dissolving resins making it very suitable for this purpose. Its odor is somewhat objectionable; it is narcotic, but not dangerously toxic, being much superior to benzene in this respect. It is not a solvent for cellulose nitrate, but solutions of these in most of the solvents will usually tolerate the addition of a greater proportion of toluene than of any other hydrocarbon diluent.

Table 2.5 Properties of solvents in nail enamel [8, 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 |

2.2.4 Nacreous pigments [2, 7]

There are three classes of nacreous pigments used in nail enamel: natural pearl essence, bismuth oxychloride, and titanium dioxide coated on mica. Natural pearl essence materials known as guanine (2-amino-6-hydroxy Purina), crystalline substance from the scales and body of various fish, has been one of the most frequently suggested. In its pure form it is non-toxic, but there have been references to this material being the cause of dermatitis arising from nail lacquers. This substance has a high refractive index (1.8) and its pearly luster and brilliance are due (i) to the simultaneous reflection of light both from the upper layers of its transparent crystals and from crystal planes at different depths, and (ii) to the alignment of crystals in the same direction, made possible by their shape and dependent on the degree of dispersion of the crystals in the lacquer. Orientation of these crystals takes place when the nail surface is coated with the lacquer containing the pearl pigment and they remain in this alignment when the film hardens.

Synthetic pearl pigments are also available; owing to the high cost and scarcity of guanine, these have become the most predominantly used materials. The most popular is bismuth oxychloride. It crystallizes in platelets, has a high refractive index and produces a high luster and brilliance at low cost. However, the material is denser than guanine and this can lead to problems of settling on standing, within the finished product.

Another type of pearl essence material gaining increasing popularity is mica coated with a thin layer of titanium dioxide which used in this study discloses characteristics in Table 2.7 It is less dense than bismuth oxychloride and therefore can be suspended more easily. However, it is less brilliant and does not have the same covering power as bismuth oxychloride. It is commercially available in cellulose nitrate-solvent suspensions and this method of addition to formulations is preferable to the use of the dry powder, which can be difficult to disperse without the use of specialist mixers. Particle size affects color strength, transparency or opacity, exterior durability, solvent resistance, and other properties of pigments. For any given pigment, the manufacturer selects the most appropriate compromise for the particle size and designs the process to produce that average particle size consistently. Manufacture of most pigments involves precipitation from water; the process

conditions determine the particle size. Many pigments are surface treated during or after precipitation. The precipitated pigment is filtered and the filter cake is dried. During drying, pigment particles become cemented together in aggregates. The coating manufacturer generally receives pigment from the pigment manufacturer as a dry powder of aggregates and must disperse these aggregates to break them up to their original particle size and make a stable dispersion.

Titanium dioxide has greater opacity and tint resistance than any other white pigment and consequently has largely replaced other white pigments in a number of applications. It is non-toxic, resistant to heat and to the media and solvents used in paint manufacture. It also possesses great chemical stability and is dissolved only by hot concentrated sulphuric acid - and this process is slow. The pigment exists in two forms known as anatase and rutile, their characteristics disclose in Table 2.6. Both forms fall into the tetragonal system, but anatase has the lower density arising from a greater distance between the titanium and oxygen atoms. When exposed to ultraviolet radiation both forms absorb strongly. Anatase becomes highly “excited” and exhibits intense surface catalytic activity. Excitation and catalytic activation of rutile is very much less, most of the absorbed energy being dissipated as heat. The ultraviolet absorption band of rutile overlaps the far blue end of the visible spectrum (up to about 410 nm) with the result that in daylight the reflected light is deficient in blue and gives rutile the characteristic yellowish cast.

Table 2.6 The physical characteristics of the two grades titanium dioxide are as follow [7].

| Properties | Rutile | Anatase |
|---------------------------------------|---|------------------|
| Color | Slight yellowish cast (chloride types are cleaner and brighter than sulfate process type) | Cold blush-white |
| Specific gravity (g/cm ³) | 4.0-4.1 | 3.7-3.8 |
| Refractive index | 2.71 | 2.55 |
| Oil adsorption (g/100g) | 17-24 | 19-22 |
| Relative tint resistance | 1.2-1.4 | 1.0 |
| Resistance to chalking | Good | Poor |
| Mean particle size range (µm) | 0.2-0.3 | 0.18-0.25 |

Table 2.7 The physical characteristics of used titanium dioxide coated mica in this research.

| | | |
|--------------------------------|---|-------------------------|
| Chemical varieties | Inorganic compound | |
| Chemical components | Mica, Titanium Dioxide. | |
| Appearance | Dry, free-flowing powder | |
| Range of Particle Size | 5-25 μm , 94% of particle size concentrated within the standard range of particle size | |
| TiO ₂ -modification | Anatase | |
| Content (%) | Mica TiO ₂ | 61-65 35-39 |
| Reflected color | Silver | |
| Density (g/cm ³) | 3.00-3.10 | |
| Bulk density (g/100 ml) | 18-22 | |
| Oil absorption (g/100g) | 60-70 | |
| Thermal stability | No change at 800°C. Non-burning and self-ignition. | |
| Solubility | No soluble in water or solvent | |
| Moisture content | ≤ 0.50 % | |
| PH - Value | 6- 9 (10% aqueous suspension) | |
| Chemical resistance | Acid and Alkali resisting | |
| Heavy metal content | Pb < 50 ppm, As < 5 ppm, Hg < 5 ppm | |
| CAS No. | Mica TiO ₂ | 12001-26-2 1317-70-0 |
| CI No. | Mica TiO ₂ | 77019 77891 |

2.2.5 Clay and Clay Mineral

Clay or layered silicate is a natural, earthy, fine-grained material composed largely of a limited group of crystalline minerals known as the clay minerals. Generally, it can be classified into many types according to differences in its structure and composition. The clay minerals are hydrous silicates, which contain tetrahedral silicate sheet and octahedral aluminum or magnesium sheet. The clay minerals were classified by used layer type 1:1 or 2:1, as the main criterion for establishing divisions in Table 2.8 [19].

Clay minerals find almost innumerable applications, and the diversity of uses is still increasing. The reason is the large variety of clays and clay minerals and the ease with which these materials are modified. Swelling behavior, adsorption properties, colloidal and rheological phenomena can be optimized and adjusted to the intended used [20]. In addition to applications well known for a long time, new uses are found and new types of materials are created. Clay minerals and clays are more and more involved in material science studies and are parent materials of organic-inorganic composite. Among several types of clays, the smectite is usually used as additive in polymer composites. The layered silicates are the most attractive because it can intercalate organic molecule.

Table 2.8 Classification of phyllosilicates, emphasis on clay minerals [19]

| Layer type | Group | Subgroup | Species |
|--------------------------|------------------------------|--|---|
| 1:1 | Serpentine-Kaolin (z~0) | Serpentines (Tr) | Chrysotile, antigorite, lizardite, berthierine, odinite |
| | | Kaolins (Di) | Kaolinite, dickite, nacrite, halloysite |
| 2:1 | Talc-pyrophyllite (z~0) | Talc (Tr) | |
| | | Pyrophyllite (Di) | |
| | Smectite (z~0.2-0.6) | Tr smectites | Saponite, hectorite |
| | | Di smectites | Montmorillonite, beidellite, nontronite |
| | Vermiculite (z~0.6-0.9) | Tr vermiculites | |
| | | Di vermiculites | |
| | Illite (0.6>z<0.9) | Tr illite | |
| Di illite | | Illite, glauconite | |
| Mica (z~1.0) | Tr micas | Biotite, phlogopite, lepidolite | |
| | Di micas | Muscovite, paragonite | |
| Brittle mica (z~2.0) | Di brittle micas | Margarite | |
| Chlorite (z variable) | Tr,Tr chlorites ^a | Common name based on Fe ²⁺ , Mg ²⁺ , Mn ²⁺ , Ni ²⁺ | |
| | Di,Di chlorites | Donbassite | |
| | Di,Tr chlorites | Sudoite, cookeite (Li) | |
| | Tr,Di chlorites | No known examples | |
| 2:1 | Sepiolite-palygorskite | | Inverted ribbons (with z variable) |

^a 2:1 layer first in name of chlorite; Tr = trioctahedral and Di = dioctahedral; z = charge per formula unit.

2.2.5.1 Smectites

Smectites are a group of clay minerals, which possess expandability, taking up water or organic molecules between their structural layers, and also marked cation exchange properties. The structure can be either dioctahedral or trioctahedral depending upon a type of substituted center cationic atom. Dioctahedral means two of octahedrons are filled with trivalent cation such as Al^{3+} or Fe^{3+} . Trioctahedral means all their octahedrons were filled with divalent Mg^{2+} or Fe^{2+} .

Table 2.9 Chemical formula of clay in 2:1 phyllosilicates types

| Subgroup | Species | General formula |
|-------------------------|-----------------|--|
| Dioctahedral smectites | Montmorillonite | $M_{x/n}^{n+} \cdot y\text{H}_2\text{O}[\text{Al}_{4.0-x}\text{Mg}_x](\text{Si}_{8.0})\text{O}_{20}(\text{OH})_4$ |
| | Beidellite | $M_{x/n}^{n+} \cdot y\text{H}_2\text{O}[\text{Al}_{4.0}](\text{Si}_{8.0-x}\text{Al}_x)\text{O}_{20}(\text{OH})_4$ |
| | Nontronite | $M_{x/n}^{n+} \cdot y\text{H}_2\text{O}[\text{Fe}_{4.0}](\text{Si}_{8.0-x}\text{Al}_x)\text{O}_{20}(\text{OH})_4$ |
| Trioctahedral smectites | Saponite | $M_{x/n}^{n+} \cdot y\text{H}_2\text{O}[\text{Mg}_{6.0}](\text{Si}_{8.0-x}\text{Al}_x)\text{O}_{20}(\text{OH})_4$ |
| | Hectorite | $M_{x/n}^{n+} \cdot y\text{H}_2\text{O}[\text{Mg}_{6.0-x}\text{Li}_x](\text{Si}_{8.0})\text{O}_{20}(\text{OH}, \text{Fe})_4$ |

The principal smectite are montmorillonite, beidellite and nontronite, all of which are dioctahedral 2:1 layer silicate, and saponite, hectorite and sanconite, which are trioctahedral [21]. Its structure illustrate in Table 2.9.

The smectite clay minerals consist of many layers of octahedral aluminates sheets sandwiched between tetrahedral silicate layers. Oxygen atoms reveal the layer edge of tetrahedral site and octahedral site. Illustration in Figure 2.4 is structure of smectite clay [22].

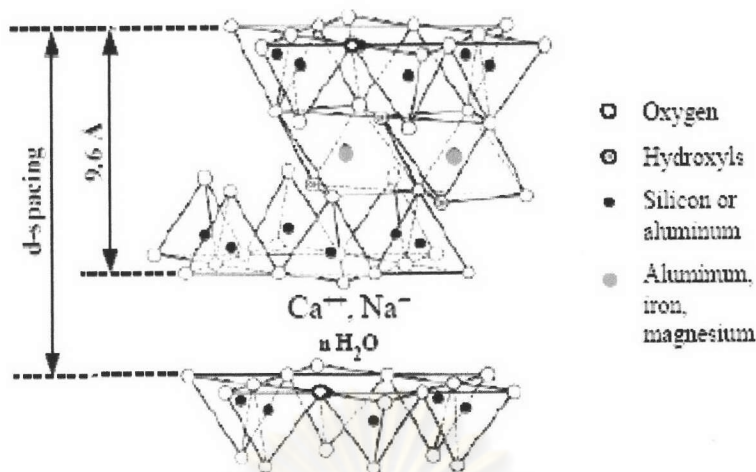


Figure 2.4 Idealized structure for montmorillonite [10]

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 isomorphous 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 [23]. Montmorillonite is the best known member of the smectite group. The montmorillonite 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 classified smectite group normally applied to polymer nanocomposites because of its have suitable layer charge density.

2.2.5.2 Montmorillonite

MMT has a low thermal expansion coefficient and a high gas barrier property. Stacking of this structure leads to a regular weak dipolar or Van der Waals interaction between the layers. Isomorphic substitution in each layer generates negative charges that are counterbalanced by hydrated sodium or potassium ions residing in the interlayer spacing [24]. In aqueous suspension, cations in interlayer may exchange with ions in the bulk solution. They are known as exchangeable cations. The total amount of cations adsorbed in the clay interlayer, expressed in milliequivalents per hundred grams of dry clay, is called the cation exchange capacity (CEC). It is an important characteristic of clay mineral. The cation exchange capacity is high for sodium montmorillonite, comparing it to the other clay minerals.

There are many ways to investigate the CEC values. The principle method suggest by Rhoades in 1982 is displacement of saturating index cation and then displacement the saturating index cation after washing free from saturating salt. The last step, detect the saturating index cation by many technique such as titration, atomic emission spectroscopy depending on the type of index. Methylene blue index is the simple method to detect the CEC values [25]. There is contain in the ASTM C 337-99 for characterize property of clays.

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 2.5.

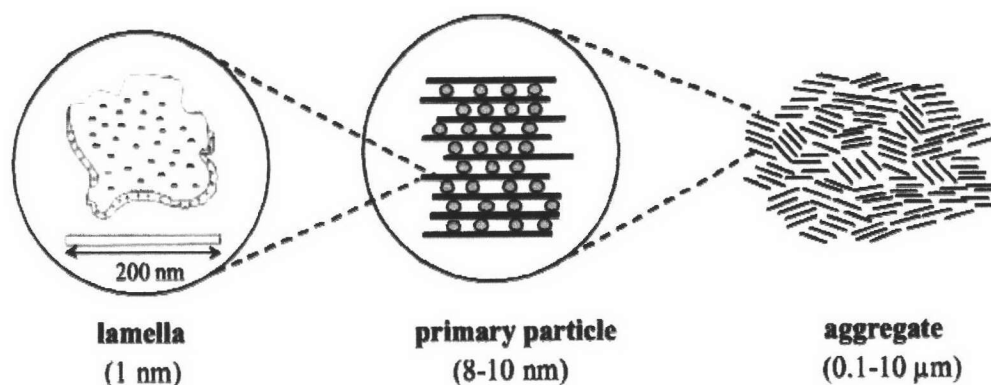


Figure 2.5 Microstructure of montmorillinite [10]

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 [20]; (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 lyophilication, ultrasound, and plasma. Ion Exchange with organic cations is the principle reaction to convert clay mineral to organophilic clay or organoclay.

2.2.5.3 Organoclay

It has long been known that the clay’s surface property can be modified from hydrophilic to organophilic. The modification can be done 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 2.6 which suitable for use in organic system [26].



Figure 2.6 The cation-exchange process between alkylammonium ions and cations initially intercalated between clay layers [10]

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.

2.2.5.4 Application

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 [26]. 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 cation as illustrated in Figure 2.7, and 2.8 [27]:

- Bentone 38 = dimethyl dioctadecyl ammonium hectorite
 Bentone 27 = dimethyl benzyl dodecyl ammonium hectorite
 Bentone 34 = dimethyl dioctadecyl ammonium bentonite

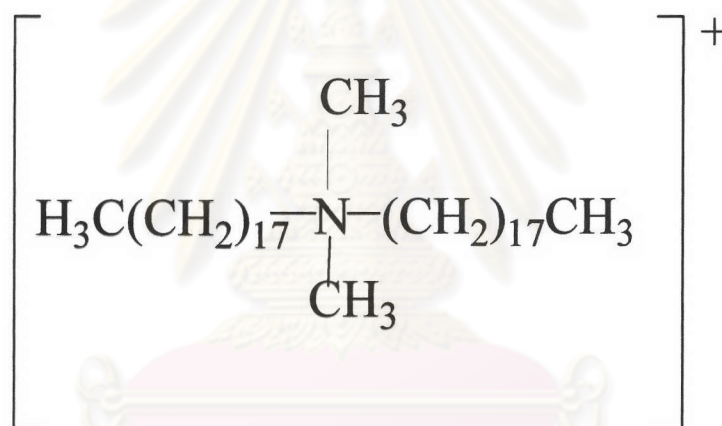


Figure 2.7 Dimethyl dioctadecyl ammonium ion.

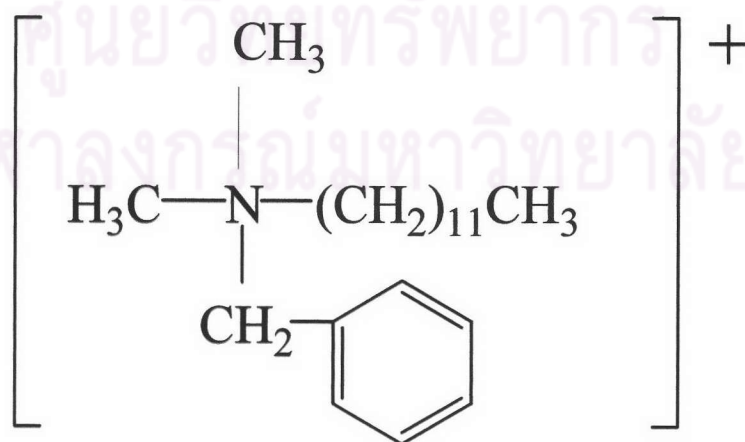
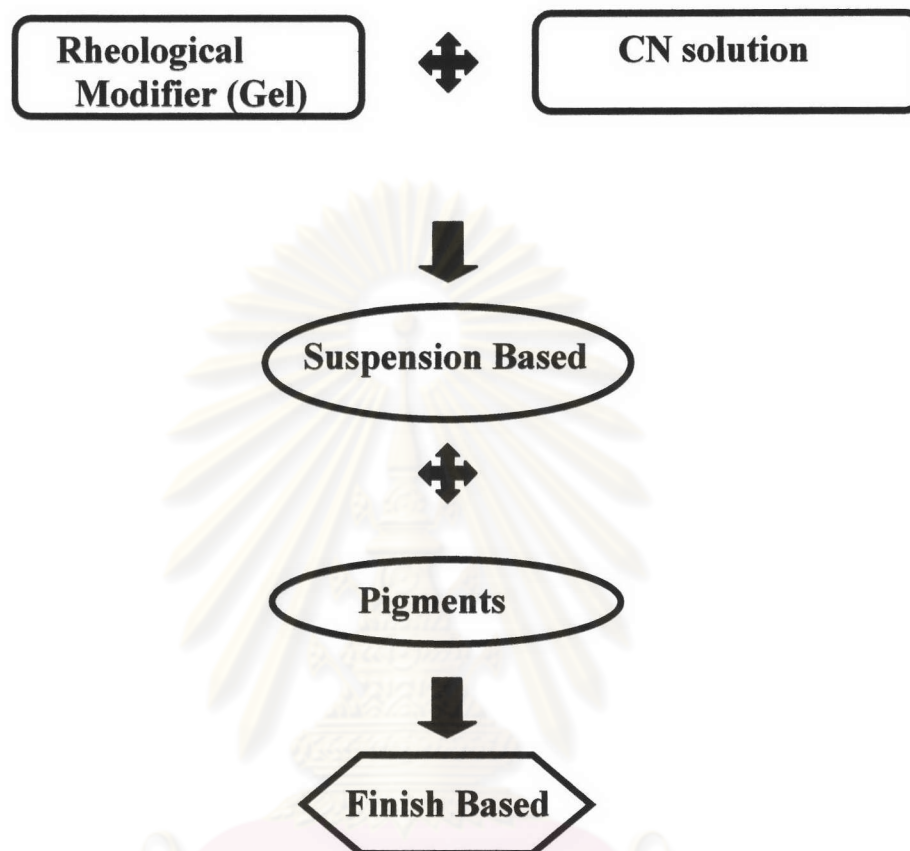


Figure 2.8 Dimethyl benzyl dodecyl ammonium ion.

2.3 The manufacture of nail lacquers



2.4 Type of rheological behavior

2.4.1 Newtonian viscous liquid

The behavior of Newtonian liquids in experiments conducted at constant temperature and pressure has the features as Figure 2.9. The viscosity is constant with respect to the time of shearing and the stress in liquid drops to zero immediately the shearing is stopped.

2.4.2 Non-Newtonian viscous liquid

2.4.2.1 Non-Newtonian fluids - time independent

A non-Newtonian fluid is defined as one for which the relationship shear stress and shear rate is not constant. The viscosity of non-Newtonian fluids changes as the shear rate is varied. There are several types of non-Newtonian flow behavior, characterized by the way a fluid's viscosity changes in response to variations in shear rate.

- Pseudoplastic: Fluid display a decreasing viscosity with an increasing shear rate, some examples include paints and emulsions. This type of behavior is called shear-thinning.
- Dilatant: Fluid is characterized by an increasing viscosity; with an increase in shear rate, some examples include clay slurries, candy compounds, corn starch in water, and sand/water mixtures. Dilatancy is also referred to as shear-thickening.
- Bingham: Fluid behaves like solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced. This force is called yield value. 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.

2.4.2.2 Non-Newtonian fluids – time dependent

- Thixotropic: Thixotropic material undergoes decreasing shear stress and apparent viscosity over time at a fixed rate of shear as shown in Figure 2.10.
- Rheopectic: Rheopectic material exhibits increasing shear stress and apparent viscosity over time at a fixed rate of shear as shown in Figure 2.10.

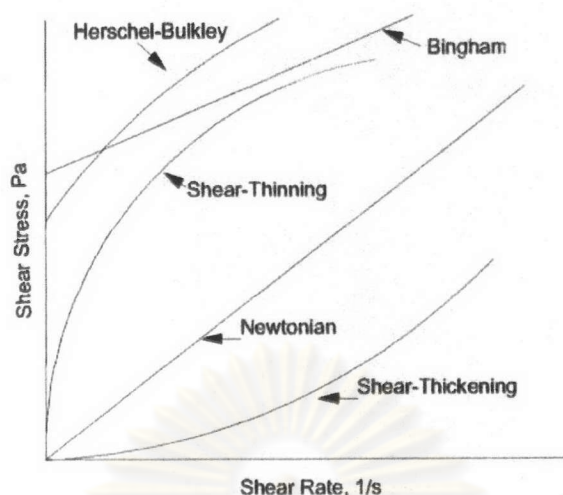


Figure 2.9 Diagram summary of Newtonian and non-Newtonian time independent fluids [15]

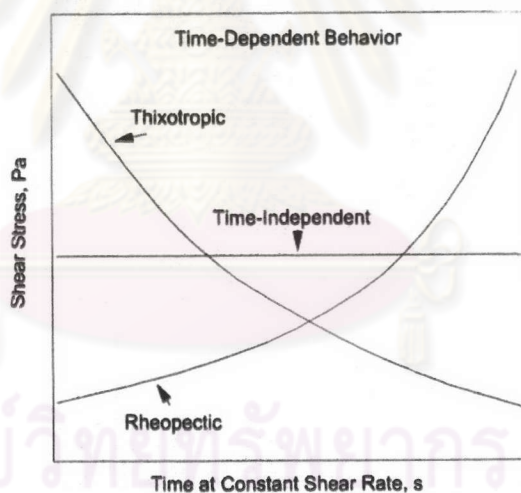


Figure 2.10 Diagram summary of non-Newtonian time dependent fluids [15]

2.4.3 Characterization of thixotropic flow [16-18]

In coating systems, 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 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.

2.4.3.1 Hysteresis loop method

One method frequently used to characterize thixotropic behavior is the hysteresis loop, as shown in Figure 2.11. 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 practical range of shear rate using in paints industry versus viscosity is revealed in Figure 2.12 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 area of the loop is a measure of the thixotropic breakdown due to mechanical working. . The area enclosed by this loop as obtained by this arbitrary procedure is taken as an index to the thixotropy resident in the test coating. 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

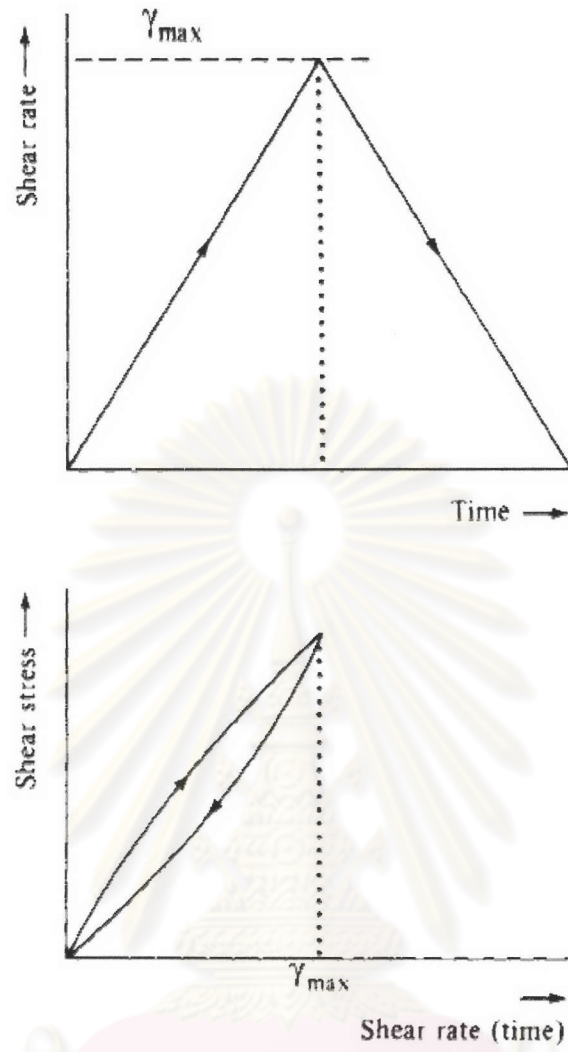


Figure 2.11 Thixotropic behavior [16]

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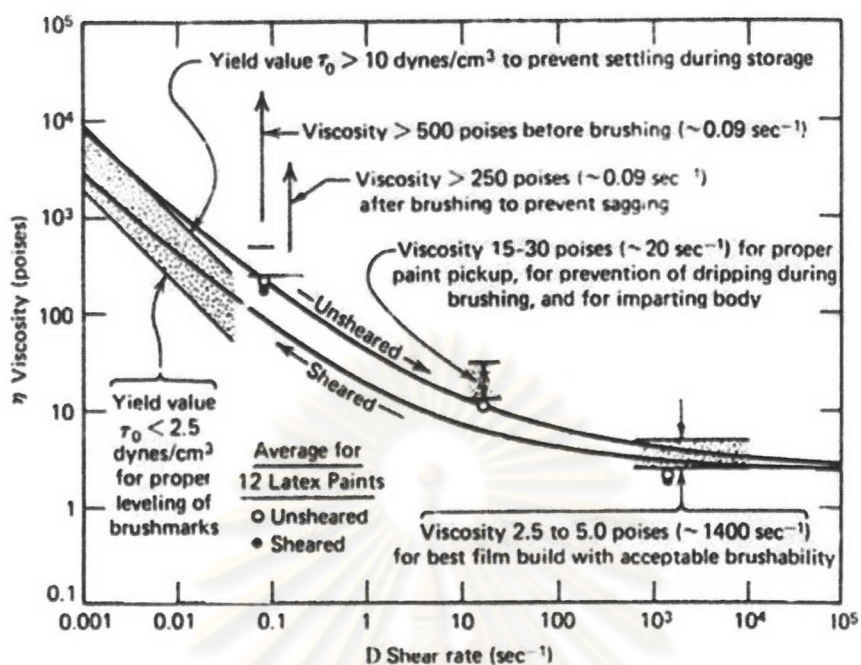


Figure 2.12 Typical shear rates of coating application in thixotropic systems[17]