

Cosmetic and Processing

1. Introduction

Cosmetics are broadly classified into basic cosmetics such as lotions, creams, emulsions, packs, and the like; makeup cosmetics such as foundations, lipsticks, rouges, eyeliners, mascaras, eyeshadows, eyebrow pencils, manicures, face powders, and the like; and hair cosmetics. The cosmetic should exhibit aesthetic qualities which are reflected by greater homogeneity in the color and a color which is both transparent and more intense, without deterioration in the qualities over time.

Cosmetic composition mainly includes pigment, fatty binder and filler. Cosmetics products must be homogeneous and stable during the application. Basically, the pigment raw material has the relative large and irregular particle. The pigment is usually ground in aqueous medium in regular ball mill to reduce the pigment particle size. In this step, the pigment can go down to about 10-15 micron. However, a reagglomeration of the various particles is observed after the above grinding and drying. Due to the agglomeration, the compositions are visually appealing, often poorly stable and cover poorly. Therefore, pigments and other ingredients in the cosmetic need to be further ground through some specific milling apparatus to form a homogeneous and fine particle dispersed paste like products (**the ideal pigment particle size should be in 10-30 nm**).

2. Dispersion equipment

Generally, the mixture of the raw materials is processed by the shearing stress apparatus for the homogeneous kneading. The applied shearing apparatus could be a three roll mill, a colloid mill, a sand grinder mill, a Gaulin homogenizer and so on. A three-roll mill is used to the greatest advantage. [1]

Sand mills, vertical cylinders filled with grinding media, operate on the principle that small mill media stir rapidly in the presence of the pigment slurry. Dispersion takes place as a result of pigment shearing as it rises through shaft impeller (Fig. 1). Dispersion of the pigment depends strongly on the media size. Therefore, sand mills is hard to decrease the particle size to the nano range. [2]

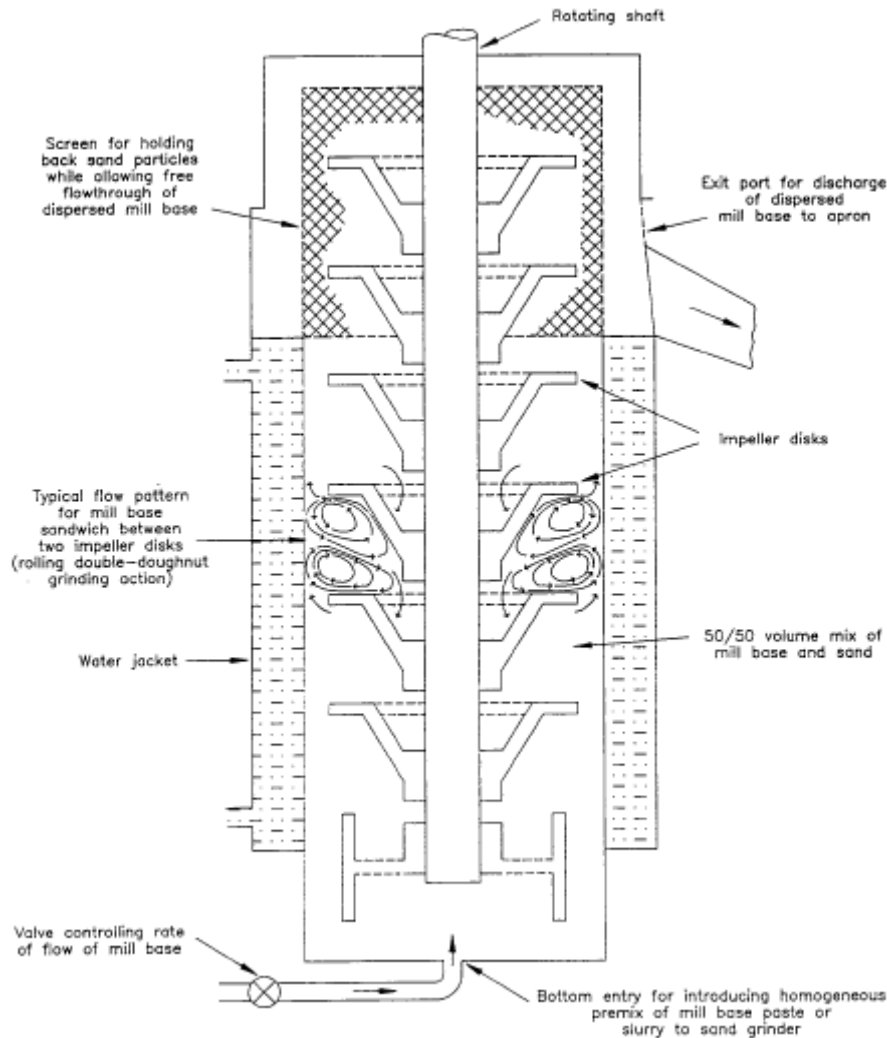


Figure 1 Schematic diagram of sand mill

The colloid mill uses stone grinding discs. The upper stone is stationary and the lower stone is rotating fast at speeds up to 3600 revs per minute. The low viscosity slurry is fed into the center of the static top stone by gravity and is passed between the two stones by centrifugal force, where it is subjected to extreme turbulence and shear forces to affect the dispersion (Figure 2). Colloid mill can reach the very fine particle size. However the limitation is that the colloid mill size is usually small and not suitable to treat a big batch material.

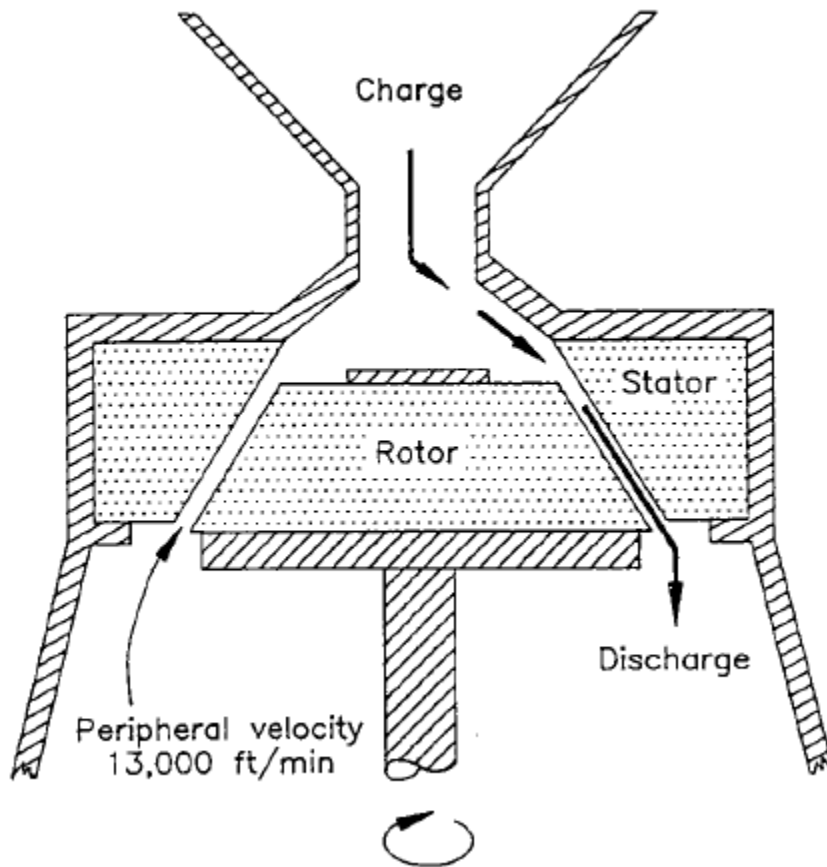


Figure 2 Schematic diagram of colloid mill

Three-roll mill consists of three rollers which are made from chilled steel or granite, run parallel to each other, and each one rotates at a different speed, and each contact face passes in the opposite direction to the adjacent roller. The gap between them, the nip, can be adjusted. The mill base is fed into the nip between rollers one and two and the final product is taken from roller three by means of a scraper bar.

Among these mills, the three-roll mill is preferred since all paste compositions are experienced the shear force when they go through the gap. Therefore the more homogenous structure can be reached by this process. The particle size could go down to nanosize range. The gap between the rolls may be adjusted to control the fines of dispersion. The loading capacity could be easily adjusted through the machine design [3].

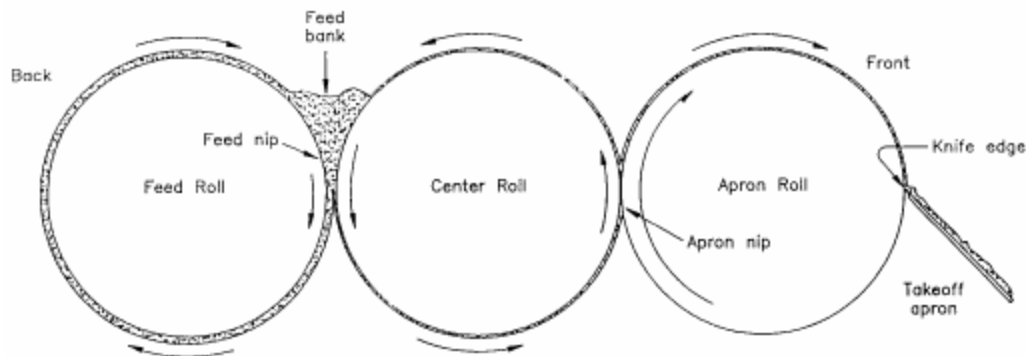


Figure 3 Schematic diagram of three roll mill.

3. Cosmetic Compositions

Cosmetic compositions (dispersions in an oil or water medium or water-in-oil (W/O) or oil-in-water (O/W) emulsions) comprises pigment, essentially titanium dioxide and optionally fillers, and fatty binder. Fillers act as to improve the dispersion of pigment both at the time of preparation of the composition and during its spreading. Fillers also improve the cosmetics stability.

Pigment particle size could be ranging from 0.01 to 0.15 microns and more preferably for 0.01 to 0.03 microns. The pigments can be inorganic pigment or organic pigments. The fillers also have inorganic and organic source materials. The fillers usually are in the size of greater than or equal to 10 microns. The pigments and fillers combinations occupy from 5 to 15% by weight of the composition.

The fatty binder is usually from oils and waxes of animal, vegetable or synthetic origin and their mixtures. The binder presents solid at room temperature. The fatty binder can additionally contain volatile oils (called spreading agents) which facilitate the spreading of the composition during application on the skin. The volatile oils have a saturated vapor pressure at 25 C, at least equal to 0.5 millibar (i.e. 0.5×10^2 pa). The volatile oils is generally less than 10% by weight of the final composition and less than 20% by weight of the fatty binder.

Dispersing agents which contributes better dispersion and better stability of the formula have the molecule formula X-CO-AR, in which A represents a divalent radical, R is a primary, secondary or tertiary amine or the salt of an amine with an acid or a quaternary ammonium and X represents a polyester residue, the X-CO- group being derived from a hydroxycarboxylic acid of formula HOR_1COOH in which R_1 represents a saturated or unsaturated hydrocarbon group. Dispersing agent could be made from derivatives of ricinoleic acid, hydroxystearic acid, or the fatty acid from hydrogenated castor oil.

Polyester residues or salts of a carboxylic acid or hydroxycarboxylic acid can also be the resources for making dispersing agent. The dispersing agent amount is from 5 to 20% by weight with respect to the weight of filler and pigment.

Cosmetic composition also consists of the ingredients such as surfactants, whether non-ionic, cationic, anionic or amphoteric, fragrances or adjuvants such as hydrophilic or lipophilic gelling agents, hydrophilic or lipophilic active principles, preservatives, antioxidants, solvents or coloring materials. The amounts of these various adjuvants are usually from 0.01% to 20% of the total weight of the composition. The detail compositions are listed in Table 1.

Table 1 The cosmetic composition and raw materials (Summarized from [4])

Cosmetic Constituents	Source materials for selection	Sub-Classification for Source Materials	Detail Raw Materials Description and Examples
Pigments	Inorganic		iron oxide, titanium dioxide, zinc oxide, bismuth oxychloride, calcium silicate, chromium oxide, chromium hydroxide, ammonium ferric ferrocyanide, ferric ferrocyanide, kaolin, manganese violet, ultramarine or carbon black nanoparticles and their mixtures. Metal oxides like titanium oxides, zinc oxide and iron oxide, which is commonly used in the cosmetic field as screening agents
	Organic		
Filler	Inorganic		talc, silica, mica and boron nitride
	Organic		nylon powder, silicone powder and poly (methyl methacrylate) powder
	Oil		mink oil, turtle oil, soybean oil, grape seed oil, sesame oil, maize oil, rapeseed oil, sunflower oil, cottonseed oil, avocado oil, olive oil, castor oil, jojoba oil, groundnut oil and hydrocarbon oils, such as liquid paraffins, squalane and petroleum jelly; esters, such as isopropyl myristate, isopropyl palmitate, butyl stearate, hexyl laurate, isononyl isononate, 2-ethylhexyl palmitate, 2-hexyldecyl laurate, 2-octyldecyl palmitate, 2-octyldodecyl myristate, di(2-

		ethylhexyl) succinate, diisostearyl malate, 2-octyldodecyl lactate, glyceryl triostearate, and the like; silicone oils, such as polymethylsiloxane, polymethylphenylsiloxanes, polysiloxanes modified with fatty acids, polysiloxanes modified with fatty alcohols, polysiloxanes modified with polyoxyalkylenes, fluorinated silicones, and the like; perfluorinated and organofluorinated oils; higher fatty acids, such as myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, linoleic acid, linolenic acid and isostearic acid, and higher fatty alcohols, such as cetanol, stearyl alcohol, oleyl alcohol, and the like
	Wax	carnauba wax, candelilla wax, beeswax, spermaceti, microcrystalline waxes, lanolins, and the like
	Volatile (Spreading agent)	Silicon Oils hexamethyldisiloxane, cyclopentadimethylsiloxane and cyclotetramethylsiloxane
		Fluorinated Oils the commercial name GALDEN (Montefluos)
		Isoparaffin Oils commercial name ISOPAR (E, G, L or H)
Dispersing Agents		derivatives of ricinoleic acid, hydroxystearic acid, or the fatty acid from hydrogenated castor oil. Polyester residues or salts of a carboxylic acid or hydroxycarboxylic acid.
		Polyester residues or salts of a carboxylic acid or hydroxycarboxylic acid. For example, the alkanolamides can be selected from ethanolamine, propanolamine and aminoethylethanolamine
		polymers or copolymers of acrylic acid and of methacrylic acid, as well as those having an epoxy group in their base constituent. Such as those prepared from ethoxylated phosphate

			esters
Others	Surfactants	silicon-based emulsifiers and lipid emulsifiers,	fatty alcohols, fatty acids, glycerol esters, sorbitan ester, methylglycoside esters and sucrose ester
	Adjuvants	Hydrophilic gelling agent	carboxyvinyl polymers (CABROMER), acrylic copolymers, polyacrylamides, polysaccharides such as hydroxypropyl cellulose or natural gums (xanthan), and clays
		Lipohilic gelling agent	bentones, meal salts of fatty acids (aluminum stearates, hydrophobic silica, polyethylenes and ethyl cellulose).
		Hydrophilic active principles	proteins or protein hydorlysates, amino acides, polyols, urea, allantoin, sugars, and sugar derivatives, water-soluble vitamins, starch, or bacterial or plant extracts (in particular of Aloe vera)
		Lipophilic active principles	of tocopherol (vitamin E) and its derivatives, essential fatty acids, ceramides, or essential oils
	Preservative		
	Antioxidant		
	Solvent		
	Coloring Materials		

4. General steps in three-roll mill

Generally, the raw compositions should go through the three-roll mill several times to reach the desired viscosity since viscosity measurement is the most common technique for assessing the effectiveness of pigment dispersants. This is because the tremendous viscosity reduction provided by a dispersant (wetting agent) affords a very practical indication of its depressive powers [5]. Lower viscosity indicates a better pigment wetting [6]. If the paste is too thick, a little bit of solvent should be added into the formula.

5. Main products, formula and making procedures [7]

5.1 Lipstick

A lipstick should apply easily, give good color coverage, yet look natural. It should feel moist, not dry, and should not bleed (flow) in to the lines around the mouth. It should not change color during wear and should have an acceptable flavor fragrance. It should keep lips from cracking and peeling, and at last minimum of three to four hours.

Formulation: Lipsticks are mixtures of waxes, oils and pigments. Formulation with a high wax, low oil, high pigment formulation generally results in a long-wearing product that sacrifices a varying degree of gloss and texture. Meanwhile formula with a lower wax, higher oil base will apply more smoothly, has greater shine, but no long wear [6]. Caster oil, which acts as pigment dispersing aid and imparts a superb creamy, moisturizing feel on the lip, is the backbone of most lipstick formulations. Oils used include castor oil, mineral oil or petrolatum; waxes include beeswax, carnauba, candelilla, and ozokerite (ceresin). Waxes can be used in either powder, flake, prill pellet or solid form. Silicone compounds are also sometimes used in the base formula. Fragrance/favor is often added (usually at less than 1%) to improve the taste of the product. Typical ratio of oil:wax:pigment would be as follows:

Oil 50 - 70%

Wax 20 - 30%

Pigment 5 - 15%

The lipsticks are generally manufactured in four stages: (1) pigment milling, (2) combination of pigment phase into the base, (3) molding, and (4) flaming. Milling is to break up pigment agglomeration rather than to reduce particle size. **A good rule of thumb of the pigment/oil ratio is to use two parts of oil for one part of pigment.** The resultant paste can be passed through three-roll mill till the satisfactory particle size (usually 20 micron). Combination of pigment phase into the base is a simple procedure. The wax and oil phase are usually melted in a steam-jacketed kettle equipped with a single propeller agitator. Following this, the milled pigment phase is added into part of the oil using a three-roll mill to a satisfactory particle size (usually 20 μ m). Molding is by use of vertical split molds (Figure 4). Most lipstick formulations mold well between 75 and 85 C. Pre-heating the mold be around 35 C avoids the formation of “cold marks” on the stick, and holding the mold at a light angle to the vertical is a technique often used to avoid air entrapment. Rapid cooling after the mass is poured into the mold of important since it leads to a smaller, more uniform crystalline, structure, which, in turn, leads to better stability and gloss. Once cooled, the molds can be spit open and the sticks subjected on to the trays or some other suitable storage container until they are ready for flaming. Flaming is a procedure for passing the molded stick through the flame of a gas burner, or series of burners, to increase the surface gloss. The flames are adjusted to a level just hot enough to just melt the surface of the stick (Figure 5).

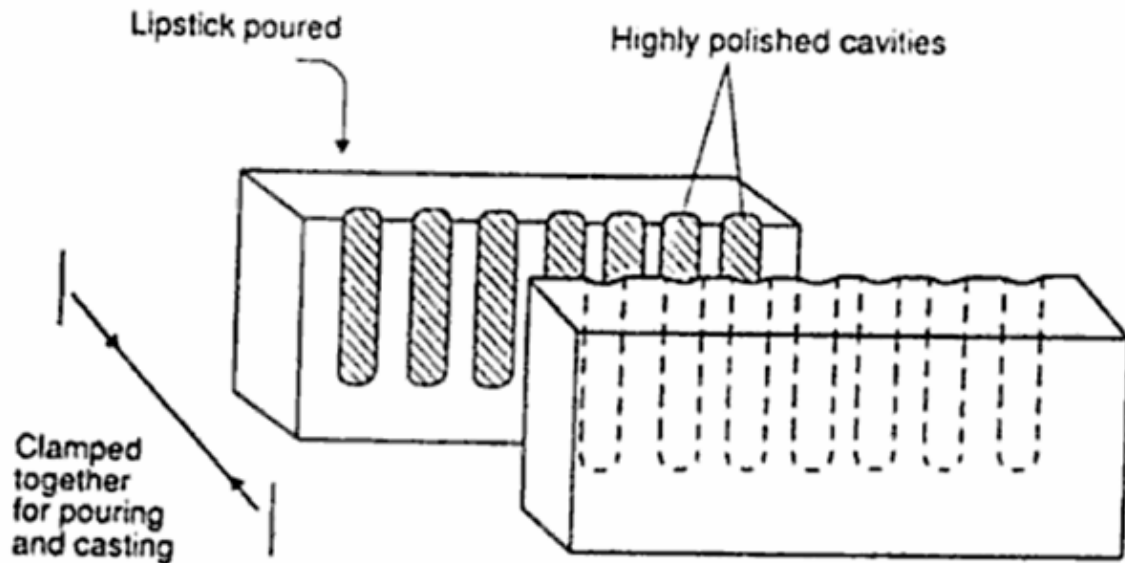


Figure 4 Lipstick split mold

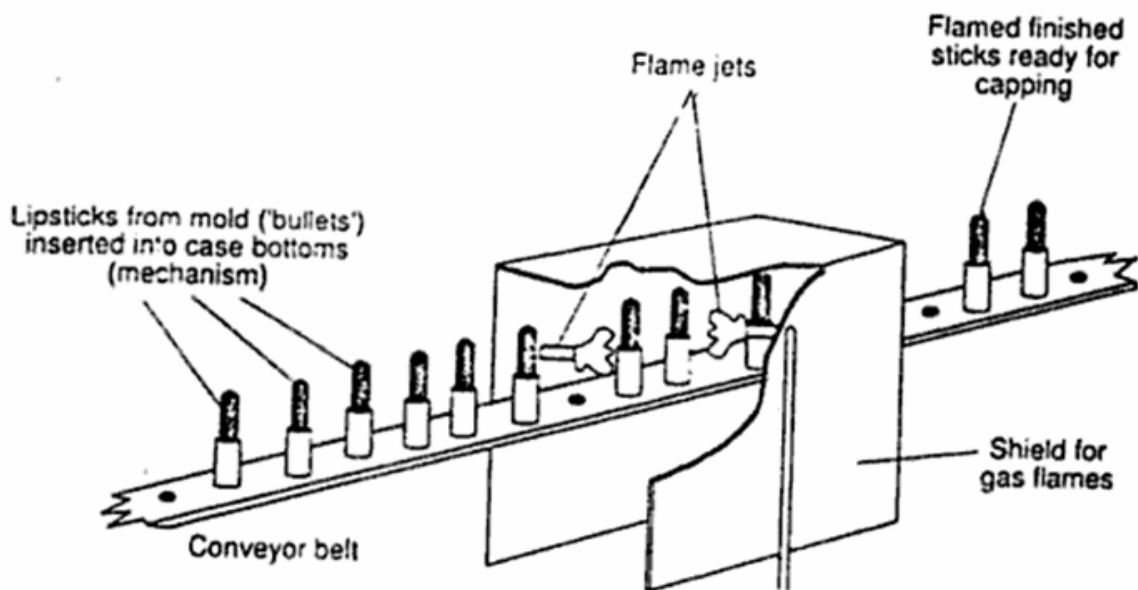


Figure 5 Lipstick flame line

Lip Gloss [8]

Constitutions	Weight percentage
Beeswax	7.0
Ceraphyl 140A	12.7
Propylparaben	0.1
Tenox 4	0.1
Bentone Gel LOI rheological additive	70
Timeron Pearl Sheen MP-30	5.0

Pigment Concentrate*	0.4
Perfume	0.2

* Pigment concentrate

Castor Oil	60.0
Color No.3106 D&C Red No. 6	40.0

Procedure: Weigh dry powder into castor oil using a slow speed Hobart type mixer until uniform and pass through the three-roll mill at room temperature three times.

4.2 Nail polish

Nail polish should be easy to apply, giving a good cover of the nail with two coats, and should not streak or apply unevenly. The polish should dry quickly to the touch and leave a high-shine finish film that will not stain the nail when removed. The film should be sufficiently hard so it will not mar easily and, during the wear cycle should not chip or peel. Durability and wear should last for 4 or 5 days. It is particularly important that nail polish is available in a wide range colors, cream and frost (pearl), transparent and opaque.

Nail polish consists of pigments suspended in a volatile solvent in which a film former or film former have been dissolved. On application the solvent evaporated leaving the color and film former on the nail. A standard nail polish formulation is as follow:

Constitutions	Weight percentage
Nitrocellulose ½ sec	15.00
IPA	4.5
Polyester resin	8.0
Ethyl acetate	28.0
Butyl acetate	40.0
Bentone	1.0
Camphor	3.0
Color	0.5

The vast majority of the film former is nitrocellulose since it satisfies a successful product. The reasons are (1) nitrocellulose films are quite hard yet remain flexible for a reasonable amount of time; (2) the films adhere well to the nail surface, which reduces the occurrence of chipping and peeling; (3) nitrocellulose has excellent gloss, which is extremely important to the consumer; and (4) nitrocellulose is not totally occlusive to the passage of water and air, which eliminates the possibility of fungal infections in the nail bed. **Nitrocellulose** is generally shipped 70% active in **isopropyl alcohol (IPA)**. **Butyl and ethyl acetates** are solubilizers for nitrocellulose. By modifying the ratio of the two solvents, the drying time of the film on the nail can also be modified. Since ethyl acetate is approximately four times more volatile than butyl, the higher the level of ethyl, the faster in the film will dry. This is often a delicate balance in nail polish formulations – if the film dries too fast it can cause streaky appearance and low gloss on the nail, while if it dries too slowly it is an obvious inconvenience to the consumer. **Camphor** is a

plasticizer for nitrocellulose. Its inclusion increases the flexibility of the film, reducing brittleness, thus reducing the potential for film chipping. Dibutyl ophthalate is also commonly used as a plasticizer. **Benton** acts as suspending agent. Being thixotropic, its “at rest” viscosity is relatively high, making it ideal for suspending the pigments.

Polyester resin is used as an auxiliary resin nitrocellulose. The addition of this material improves hardness and increases the gloss of the film. The popular resins are as follow: santolite MHP, dammar, sandarac, pontianac, resin and esters, ester gum, hexyl methacrylate-methylmethacrylate copolymer, acrylic ester oligomers, alkyd resin, polytetrahydrofuran, polyamides, lauro lactam-caprolactam-hexamethylene diamine adipate terpolymer, and helamine resin.

The process of nail polish involves the high-shear mixing. Pigment is the most important step. The finer the pigment is ground, the higher the gloss achieved, and the more stable the finished product. The required pigment is blended with nitrocellulose in a mix of bentone solution and plasticizer. The resultant is then ground through a three-roll mill, dried and “chipped” (i.e. split up into solid fragments). The color chips are blended in the desired shades and dissolved in the nitrocellulose solution (lacquer) using a high-shear mixing blade (Cowles) under flame-proof conditions. The temperature must be carefully monitored to avoid a large increase. The other solvents and additives are added when a uniform color has been achieved. Following this, the bentone is added and the viscosity adjusted by addition of lacquer or thinners. Specially, viscosity modifying additives are also required. The viscosity of nail polish is sometimes adjusted by adding small quantities of phosphoric acid or organic acids to modify the gelling system.

4.3 Mascara

A mascara is designed to make the eyelashes look thicker and longer. Coverage should be good, but the mascara should not clump on the lashes, flake during wear, or feel brittle after drying. The mascara should be tear-resistant, water-proof or water-resistant, and must not smear or smudge. Most popular color is black but other dark shades (e.g. blue, green and brown) are also used.

Waterproof mascaras consist of a blend of waxes and pigments in a volatile hydrocarbon solvent. Waterproof mascara is less popular than the water-resistant type because it hard to be removed. A typical formulation is as follows:

Constitutions	Weight percentage
Pigments	5.0-10.0
Beeswax	26.00
Ozokerite	4.0
Lanolin	0.5
Preservative	0.25
Aluminium stearate	2.50
Hydrocarbon solvent	To 100.00

Procedure: Add the aluminium stearate to the solvent with stirring while the mixture is heated to approximately 90 C. Maintain at that temperature until solution and gelation are evident. Melt the waxes together and add to the solvent. Grind the pigment in a portion of the solvent-wax mixture and add to the remainder of the batch. To avoid settling of pigments while the mixture is still warm and fluid, continue stirring until the mixture is cool.

An easy removal formula (form Tevco) is showed as follow:

Constitutions	Weight percentage
Part A	
Petroleum distillate	to 100.00
Beeswax	18.00
PEG-6 sorbitan beeswax	6.00
Ozokerite 170-D	4.00
Carnauba wax	6.00
Propylparaben	0.10
Glyceryoleate (and) propylene glycol	1.50
Part B	
Iron oxide	15.00
Part C	
Petroleum distillate (and) Quaternium-18 hectorite (and) propylene carbonate	12.50
Part D	
Deionized water	15.00
Methylparaben	0.30
Sodium borate	0.60
Quaternium-15	0.10

Procedure: Mill pigment, part B, into part A, which has been heated to 90 C. After part C has been added slowly and heated with part A, emulsify by adding part D at 90 C to the mixture of parts A, B and C. Continue mixing until cool.

The most popular is water-resistant mascaras, which formula based on a triethanolamine state, or oleate, soap system. The Tevco formulation are showed as follow:

Constitutions	Weight percentage
Part A	
Deionized water	43
Hydroxyethyl cellulose	1.00
Methylparaben	0.30

Triethanolamine	1.00
Ammonium hydroxide, 28%	0.50
Preservative	2.00
Part B	
Iron oxide	10.00
Ultramarine blue	2.0
Part C	
Isostearic acid	2.00
Stearic acid	2.00
Glyceryl monostearate	1.00
Beeswax	9.00
Carnauba wax	6.00
Propylparaben	0.10
Part D	
Quaternium-15	0.10
Part E	
30% Acrylic/acrylate copolymer solution in ammonium hydroxide	20.00

Procedure: Mill the pigment of part B in the water phase, part A. Heat to 80 C. Heat the oil phase , part C, to 82 C. Emulsify. Cool to 50 C. Add part D then part E, cool to 30 C.

4.4 Sunscreen

Sunscreen products are simply vehicles for preventing UV radiation from reaching the skin. The products include lotions (o/w emulsions), oils (solutions of sunscreens in mineral oil, vegetable oil, volatile silicones, or esters), gels of water or water/alcohol character, spray, and sticks. Many sunscreens are formulated with the materials that have absorbance in both the UV-A and UV-B range, as well as physical blocks.

For example, the typical formula f suntan lotions are listed as follow:

Constitutions	Weight percentage
Part A	
Ethylhexyl <i>p</i> -methoxycinnamate	2.0
Oxybenzone	1.0
Isopropyl palmitate	6.0
Stearic acid	3.0
Cetyl alcohol	1.0
Glycerol monostearate	1.0
Part B	
Deionized water	71.0
Sorbitol	30
Carbomer 934 (2% dispersion)	10.0

Triethanolamine, 99%	1.2
Prt C	
Fragrance and preservative	q.s

Procedure: Heat parts A and B separately to 70 C. Add part A to part B with good agitation. Mix to 35 C and add part C. Continue mix until dispersion is complete.

Typical waterproof sunblock creams formula:

Constitutions	Weight percentage
Part A	
Stearic acid	4.0
Cetyl alcohol	1.0
DEA cetyl phosphate	.0
PVP eicosene copolymer	3.0
Dimethcone	0.5
Ethylhexyl <i>p</i> -methoxycinnamate	7.5
Oxybenzone	6.0
Octyl salicylate	5.0
Octyldodecyl neopentanoate	10.0
Part B	
Deionized water	53.9
Glycerin	5.0
Carbopol 940	0.1
Prt C	
Deionized water	0.9
Triethanolamine, 99%	0.1
Part D	
Fragrance and preservative	q.s

Procedure: Add part C to part B and mix until uniform. Add ingredients of part A and mix to dissolve evenly. Hold at 85 C. To form the emulsion, add part A to the mixed parts of B and C at 85 C. Mix and cool to 35 C. Add part D.

5. Our three-roll mill products information [9]

Our company provides three-roll mill of ultra precise, top class quality, high capacity production. We have made quite a stir in the industry, and accomplished what many set out to do, but few have achieved. Our three roll mills offer the same excellent performance as brand name ones while cost up to 30% less. They are currently used for high volume production in China, US, Hong Kong, Canada, Mexico, Colombia, Europe and South East Asia.

6. Conclusion

The cosmetic manufacture requires a highly homogeneous and fine dispersed structure as well as the very fine particle size of the pigment. Mills providing high shear force are generally adopted machine in cosmetic industry. Among these, the three-roll mill is the preferred mill since its advantages of uniformly applied shear force on the whole ingredients and adjustable product capacity by different designed size.

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