CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 General knowledge of paint [1,2]

Paint consists of polymeric materials which show adhesive properties on specific types of surface. It is usually made of many raw materials, both organic and inorganic types. Functions of paint are decoration, protection, and substrate coating with opaque color film to change substrate surface to desired properties and other requirements. The main composition of paint can be divided into four types according to nature of raw materials as the following:

(1) Film former or binder [1,2] can be divided by its solubility into 2 groups as: oleoresinous type and water base type binder.

(a) Oleoresinous type is the binder that need specific organic solvent to dilute. Most of the binder are alkyd resins, acrylic resin, epoxy resin and nitrocellulose.

(b) Water base type is the binder which are soluble with water e.g. latex.

Resins are polymer compound which denote a certain group of natural or synthetic film former. To build paint film on substrate, resins bind other components of paint together. Mostly, paint manufacturers use synthetic resin because it generates good quality of film appearance, increases the solid content of paints and improves the gloss and adhesion of coating films. The most two essential functions are to increase hardness and to reduce drying time in oxidative curing system. This effect is said to be the first important finding in oil paint industry and becomes the reason for historical importance of resins.

(2) Pigment [1,2,3] is fine dirt which is insoluble in either binder or solvent. It is dispersed in wet paint or paint film. Pigment can be classified by its functions and sources as the following groups:

(a) Types of pigment classified by function:

1. Colored pigments: such as titanium dioxide, iron oxide, give color, hiding power and anti-corrosion properties.

2. Extended pigments: such as calcium carbonate, china clay, barium sulphate are added into paint to reduce cost of the paint even though. However, extended pigment can decrease gloss and opacity, flow and leveling, durability, film toughness, permeability and rheology.

(b) Types of pigment classified by source and chemical composition:

1. Organic pigment: Organic pigment has bright color and is insoluble in any solvent e.g., dyestuff and toner.

2. Inorganic pigment: It is always non-bright color, light weight and chemicals resistance. It can be synthetic inorganic pigments or metallic pigments e.g., aluminium, titanium dioxide, zinc oxide, calcium carbonate.

Generally pigment has an average particle size between 0.01 to 1 micron. Particle size and size distribution of pigment directly affect color property. Pigment particle can be divided in 3 groups: primary particle, aggregate and agglomerate. Primary particle is extremely small particle size. It is composed of a single crystal structure as show in Figure 2.1.

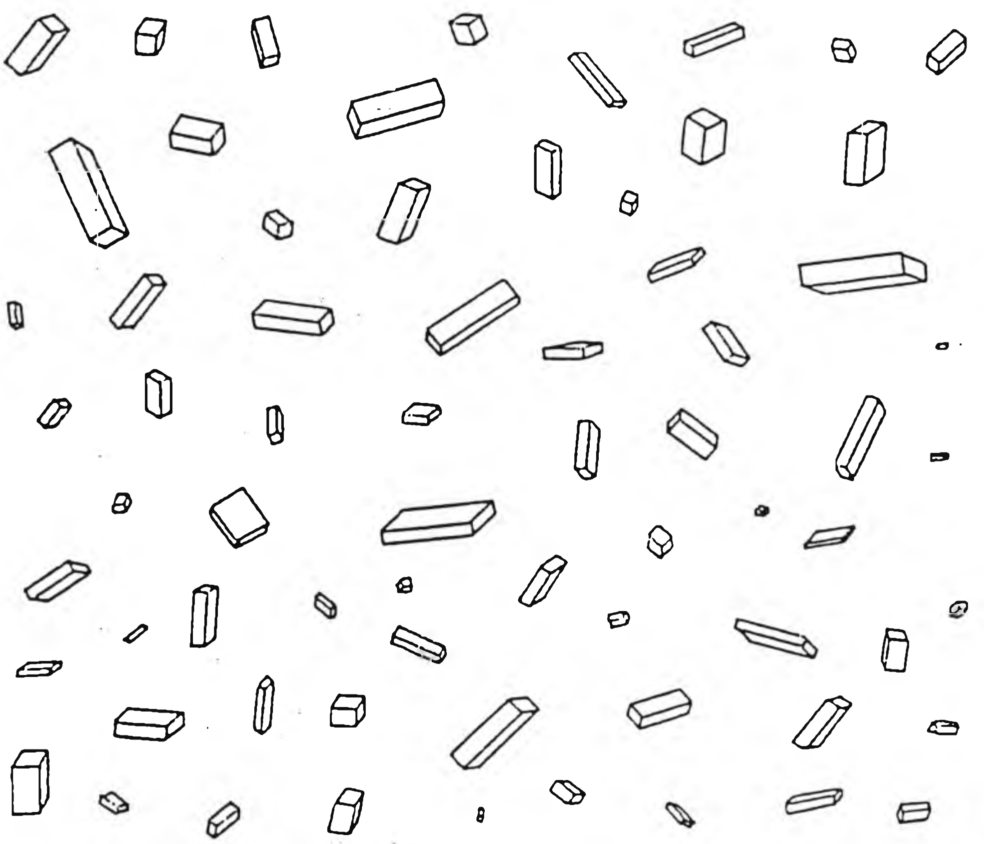

Figure 2.1 Primary particles of a crystalline pigment [7]

Aggregate is the clusters of primary particles which joined together at crystal faces or a single plane. The essential feature is the strength of bonding of the original primary particles into an assembly which behave as a single particle. Figure 2.2 shows aggregates of pigment.

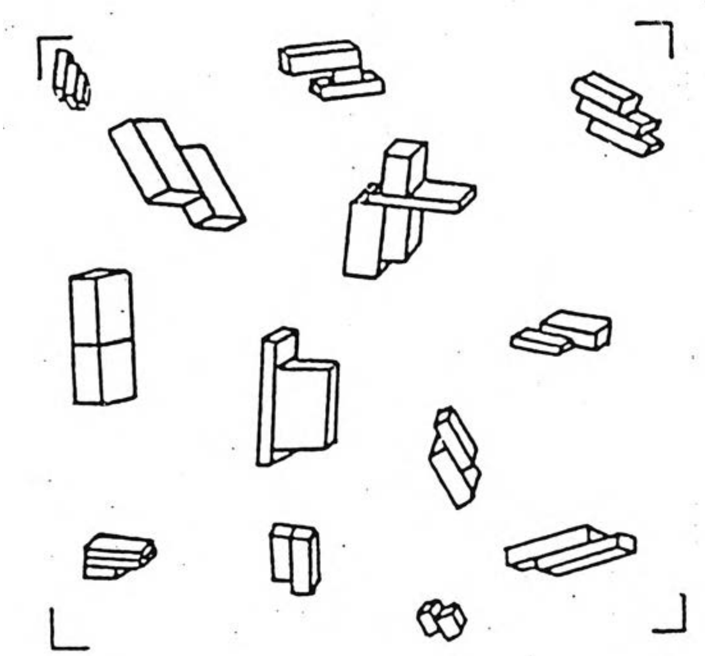

Figure 2.2 Aggregates of primary particles [7]

Agglomerate is primary particles which touch only at edges or corners, forming a looser and more open structure as show in Figure 2.3.

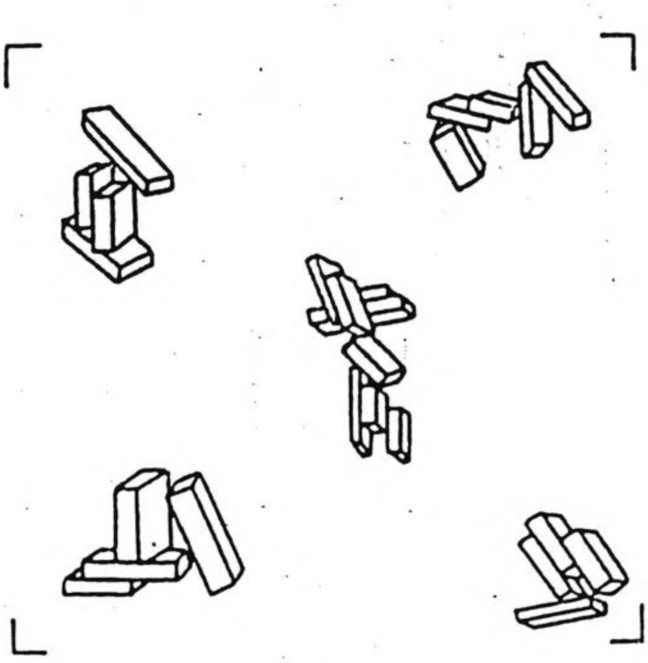

Figure 2.3 Agglomerate of primary particles [7]

(3) Solvent [1,4,5] is volatile fluid that evaporates from the coating during the film-forming process. It is a very important component of liquid paint formulations.

Diluent is volatile liquid which can not dissolve binder by itself but can be homogenous with solvent. Diluent is appropriate for coating application, modifying volatility and costing down.

The main function of solvent is to dissolve solid or highly viscous binder components without chemical reaction; it gives the binders a processable consistency and provides a means for accurate viscosity adjusting for paint application. Appropriate solvent composition improves wetting, dispersing of pigments, degassing of the wet film from occluded air and condensation products, leveling and increasing of gloss.

The main classes of solvent used and typical examples of each class are shown in Table 2.1.

Table 2.1 Main class of solvents [4]

class	solvents
aliphatic hydrocarbon	white spirit, distillate
aromatic hydrocarbon	xylene, toluene
alcohol	methanol, ethanol, propanol, buthanol
ketones	acetone, methyl ethyl ketone, methyl isobutyl ketone
esters	ethyl acetate, butyl acetate
glycol ethers	butyl cellosolve, butyl carbitol
glycol ether esters	butyl cellosolve acetate, butyl carbitol acetate

(4) Additive[1] is the last component of paint in addition to binder(resin), solvent and pigment. The additive content in finished paint is typically between 0.01 and 1%. Although applied in low concentration, additives are used to significantly improve the

properties of paints to prevent defects in the coating film (e.g., foam bubbles, poor leveling, flocculation, sedimentation) and to impart specific properties to paint (e.g., betterslip, flame retardance, UV stability) that are otherwise difficult to achieve. Additives are classified according to their effects such as defoamers, wetting and dispersing additives, surface additives, rheology additives, drier and catalysts, preservatives, light stabilizers and corrosion inhibitors.

2.2 Paint production.

Paint production process has two main steps: mixing and grinding. Raw materials of paint (resin, pigment and solvent) are mixed together in mixing step. Then, raw material ingredients are adjusted to proper particle size in grinding step.

2.2.1 Mixing [6,20,21]

Mixing is a process performing random distribution of many raw materials. The mixing tends to reduce non-uniformities or gradients in composition, and temperature of material in bulk. Mixing is accomplished by shear force which conducts movement of material (fluid movement) between various parts of the whole mass. A single homogeneous material cannot be mixed until some other materials are added into it.

The term "mixing" is applied to a variety of operations differing widely in the degree of homogeneity of the "mixed" material. Mixing applications can be divided into many groups of fluid and solid pairs such as liquid-solid, liquid-gas and emulsions (immiscible liquids).

Mixing process in paint production is the mixing raw materials such as resin, pigment and solvent together in the batch. The main purpose of mixing is only dispersion of the pigment which has homogeneous phase and uniform particle size. Size reduction of pigment cannot be succeeded if the shear force in mixing is not enough. The raw materials which are well mixed to homogeneous phase and uniform particle size can support the efficiency of grinding process.

W. Carr and A. Kelly [8] have studied factors which affect the efficiency of sand grinding of decorative paint stainers by using pigment particle size measurements as the criterion of dispersion level and hence grinding efficiency. According to this large number of possible factors, a statistical approach has been used.

The experiments have used β-phthalocyanine blue and a long oil soya penta alkyd resin as pigment and binder respectively. The type of grinding machine has been sand mill. The factors which might affect the efficiency of the sand grinding process. The list of factors are as follows:

1. speed of rotation of discs
2. diameter of discs
3. number of discs
4. thickness of discs
5. size of vessel
6. order of charging vessel
7. type of grinding media
8. size of grinding media
9. grinding media charge
10. formulation charge
11. pigmentation level
12. pigment/binder ratio
13. pre-mixing stage
14. time of grinding
15. temperature of grinding

The experiment had been divided into four stages, and just only 3 from those 4 stages are relevant to this matter. The results of mixing process from 3 of 4 stages are as follows:

In the first stage, two factors have been fixed, size of grinding media and order of charging vessel, while other factors have been varied at two levels, high and low. The result of the first stage has shown six factors which are significant for efficient sand grinding, and only one factor, the number of disk, is at the border line. The six factors are size of the vessel, diameter of discs, pigmentation level, pigment/binder ratio, pre-mixing stage and type of grinding. Any other factors is insignificant.

The second stage is to determine the order of importance of six (possibly seven including border line factor) significant factors. In this stage, insignificant factors are fixed. Pre-mixing stage at high level (5 hours) has shown better result than that of low level (1 hour) and the stage importance ranks at the fifth.

The third stage is to recheck whether conclusion from using other pigments and resins gives the same result as the earlier experiment. The pigment used were Irgalite red 2GW and red FBL, and binder used was polyurethane resin.

Mixing process of paint production has two important equipments: tank and impellers. The required tank for solvent base paint is made of steel or stainless steel and has shaft to agitate. The required impellers have many types i.e. sawtooth propeller, turbines. The two types of impellers considered here are shown in Figure 2.4 and Figure 2.5 respectively.

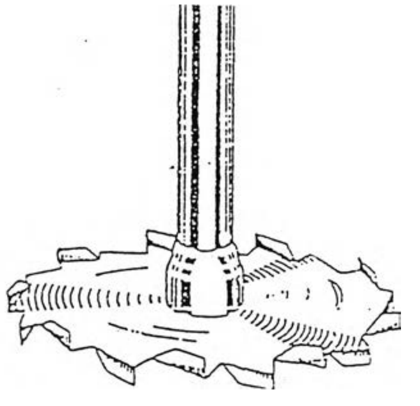

Figure 2.4 The sawtooth propeller [5]

Shown in Figure 2.4, the first type is axial-flow propeller with high-speed impeller for low viscosity liquid. For this type, the disk has been modified with sawtooth design around the rim. Contrary to popular opinion, the modification does not enhance the hydraulic shear characteristic, but simply magnifies circulating capacity of the disk.

The second type as shows in Figure 2.5 is a multi blade turbine ranging from 30 to 50 percent of the diameter of the vessel. The number of blades is not important and can be two or more. Turbines are effective over a very wide range of viscosity. General applications are chemical reaction of liquids and solids, reagent mixing, neutralization reactions and mineral surface conditioning. Figure 2.5 shows the turbine types.

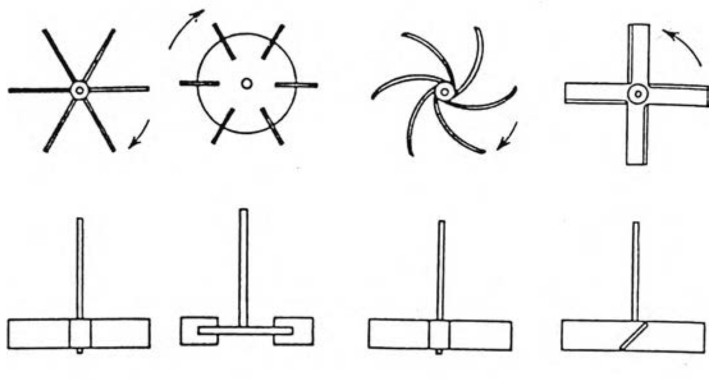

Figure 2.5 Turbine types: a) open straight-blade turbine b) bladed disk turbine c) vertical curved-blade turbine d) pitched-blade turbine [6]

2.2.2 Grinding [11,23]

Grinding process reduces the particle size of in-process paint. The general grinding process has both dry and wet types. Dry grinding is almost comminution of ore. Wet grinding reduces size of the slurry of solid-liquid mixtures. Dry versus wet grinding can be say follow this. Ball mills have a large field of application for wet grinding in closed curcuit with size classifiers. If the presence of liquid with the finished product is not objectable or the feed is moist or wet, wet grinding generally is preferable to dry grinding. In fine dry grinding, surface forces come into action to cause cushioning and ball coating with a less efficient use of energy. Other factors that influence choice are the performance of subsequent dry or wet classification steps, the cost of drying, and the capability of subsequent processing steps for handling a wet product. In practice it is found that finer size can be achieved by wet grinding than by dry grinding. There are many types of grinding machines separated by method of comminution as follows:

-nipping machines e.g., jaw crushers, pan mills.

-impacting machines e.g., ball-loaded mills, autogenous mills.

-cutting machines

-attriting machines e.g., sand mill and ultra-rotor.

In this experiment, sand mill is the selected machine in grinding process. So it is focused further on.

Sand mill [1] is a type of media mills. It can be regarded as slender attritor with a forced product circulation. Actuated by disk impellers, sand mill is made of cylinders with grinding media such as glass beads. A premixed pigment (or other particulate solid) is resin base, or similar. Then, slurry is passed through for being processes. Materials are charged vertically from the bottom upward. Gravity separates the grinding media. A sieve is usually installed to improve separation. The development of sand mill increases both product quality and productivity. However, it is limited by the force of gravity. The viscosity of the paint pastes, therefore, has to be relatively low which cannot create optimum dispersion.

In paint production, wet grinding process is the most important step for adjusting pigment particle size. The adjustment of pigment particle size is very useful in paint application by generating the smooth paint film. The grinding process is a size reduction process which may be called the complete dispersion of pigment in liquid media. The cause of breaking down particles is the homogeneous and uniform particle size of mixed raw materials feeded into sand mills. Then the pigment particles contact with grinding media. The collision is conducted to break particles. The grinding, complete dispersion process, has three stages to disperse dry powder in liquid medium. These three stages are quite distinct in their nature. However, in normal practice, they overlap and can be considered as the following[7,16]:

1. Wetting of the powder: In dry state, the powder usually contains some aggregates of primary particles. It may attach to other aggregates and/or primary particles forming agglomerates. Not only is it necessary for the liquid to wet the external surfaces, but it must also displace air from the internal surfaces between the particles (the pores of agglomerated particles) in the clusters. So that there is direct contact between the liquid medium and the solid surface.

2. Breaking up of the clusters to form colloidal particles (mechanical deagglomeration): Aggregates may require considerably mechanical energy to break

them down completely to the point when the surface of each primary particle is available to the wetting liquid. Presumably agglomerates would normally require less energy than aggregates.

The most difficult part to define the dispersion process concerns breaking down of the aggregates and agglomerates into finer particles after all of the available surfaces have been wetted. Particles which are held together by weak forces in the dry agglomerate state which presumably requires little energy to disperse. Once wetted and charged, surface tension effects would be important.

Mechanical energy is required to destroy aggregates or to break down single crystals into smaller units. In normal practice, the relation between grinding efficiency and the adjustable parameters in any particular dispersion process has usually been established empirically.

A great deal of consideration has been given to this problem by Rehbinder and his colleagues in Moscow[7]. They have established that the fine grinding of solids to create new interfaces is facilitated considerably by the adsorption of surface active agents at structural defects in the surface. These defects are normally presented in the natural state, but they might also appear as microcracks during the milling process. The decrease in surface energy associated with the adsorption may even be so large that the colloidal state becomes more stable than the condensed state, and then the material would break down spontaneously, without external forces, into smaller units.

3. Stabilization: Having wetted the surfaces and broken down the clusters into fine particles, these are then dispersed throughout the medium. The problem is to maintain the dispersed state since the particles have natural tendency to reduce in number with time due to irreversible collisions. An attractive force exists between the particles as their approach decrease which would normally lead to flocculation. The reduction in particle number is here to be termed flocculation. Stabilization occurs as the result of interactions occurring at the solid-liquid interface, such as the adsorption of molecules or ions from solution, which modifies the attraction potential between the particles, or prevents the close approach of particles into region of strong attractive forces.

W. Carr [9] has studied factors which affect the efficiency of ball milling of decorative paint stainers.

Measurement of pigment particle size is used as the criterion of dispersion and grinding efficiency. The pigment particle sizes are measured by indirect technique based on color strength determination.

The experiments are carried out with a β-phthalocyanine blue and a long oil soya penta alkyd resin by using ball milling. Conditions in the experiments are pigment/ binder ratio of 1.59, time of ball milling is 24 hours, the ball mill critical speed at 158 rpm., milling media as steatite balls. The investigating factors and their results are as follows:

Milling time: At any range of time longer than 24 hours, the color strength (k/s) and dispersion improve very slowly with extra time of milling. The data is shown in Table 2.2.

Table 2.2 Effect of milling time [9]

Milling time (hours)	Steatite balls		Steel balls	
	K/S value	Mean particle diameter (μ)	K/S value	Mean particle diameter (μ)
2	1.084	0.430	1.200	0.390
4	1.250	0.375	1.420	0.335
8	1.480	0.320	1.835	0.265
12	1.590	0.305	2.020	0.240
16	1.690	0.285	2.140	0.225
24	1.820	0.270	2.290	0.210
30	1.860	0.260	2.310	0.210
36	1.900	0.255	1.330	0.205
48	1.970	0.245	2.360	0.205
60	2.020	0.240	2.400	0.200
66	2.070	0.235	2.410	0.200
72	2.120	0.230	2.440	0.195

Effect of viscosity: The data in Figure 2.3 is the viscosity level of resin before milling and any pigment adding. The efficiency of dispersion process falls off very rapidly as shown in Figure 2.6.

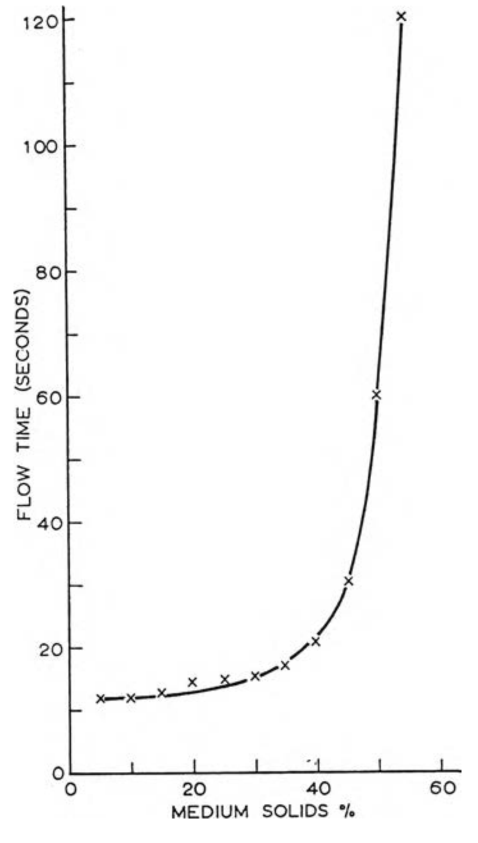

Figure 2.6 Effect of viscosity in relation of flow time and medium solid content [9]

W. Carr [10] has studied results of sand grinding versus ball milling in relation to pigment particle size of three organic pigments in decorative paint stainer formulations. The three pigment are Irgalite Blue GLS, Irgalite Green DBN Conc. and Irgazin Violet RLT. The binder used is long oil soya penta alkyd resin.

Experimental investigation has used the Jouce-Locbl-ICI disc centrifuge to measure particle size distribution accurately.

Result of the experiments have shown that sand grinding gives very much higher efficiency than that of ball milling, both in terms of time and ultimate fineness. The results are shown in Table 2.3, Figure 2.7 and Figure 2.8.

Table 2.3 Time comparison of sand grinding and ball milling [10]

Time of sand grinding	Equivalent time of ball milling		
	Green BBN	Blue GLS	Violet 6RLT
1/4 hour	8 hours	20 hours	11-12 hours
1/2 hour	10 hours	24 hours	13 hours
1 hour	12 hours	36 hours	17 hours
2 hour	80 hours	60 hours	24-26 hours
4 hour			72 hours

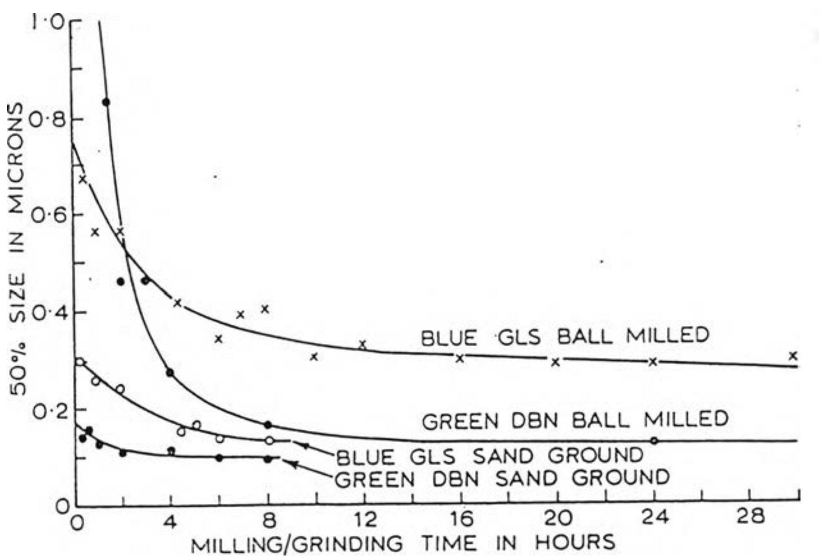

Figure 2.7 Milling and grinding times to give 50% diameter for Irgalite Blue GLS and Irgalite Green DBN [10]

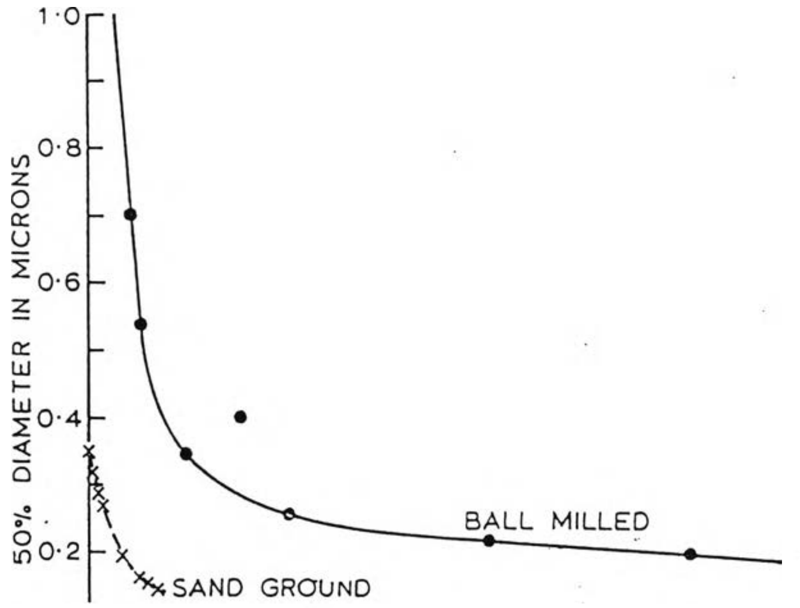

Figure 2.8 Relation between milling time and grinding time with 50% diameter of Irgazin Violet 6RLT [10]

The ball milling is an inefficient form of grinding for organic pigments in an absolute sense i.e. in its ability to break down the pigment aggregate into basic pigment particles. Although more efficient, sand grinding of organic pigment for 8 hours is still far from being 100 percent. The result is shown in Table 2.4.

Table 2.4 Degree of dispersion [10]

Grind	Degree of dispersion (%)		
	Blue GLS	Green DBN	Violet 6RLT
72 hours' ball milling	38	37	59
8 hours' sand grinding	62	46	83

W.E.C. Creyke and H.W. Webb [17] have studied the ratio of water to solids in cylinder grinding. The experimental cylinder is 16.25 in. diameter and 7.25 in. internal width, revolving at 55 revolutions per minute (83 percent of the critical speed). The internal capacity of the cylinder is 0.867 cu.ft. The material used for the test grinding is Caolad flint. The paint weights of the ground slips varies from 32-36 oz.. The "solid:water" ratios varies from 1.47:1 to 2.49:1.

The experimental procedure is charging raw materials and stirring to grind. The duration of grinding in each test is 7 hours. At the end of each hour, a sample is taken to determine the viscosity by a torsion viscometer and size distribution, by the Andreasen pipette.

The results show the remarkable fall in efficiency as the viscosity increases over a very narrow range. On the other words, it is possible to obtain greater grinding capacity, while the optimum viscosity is being maintained for maximum efficiency. The result is shown in Figure 2.9.

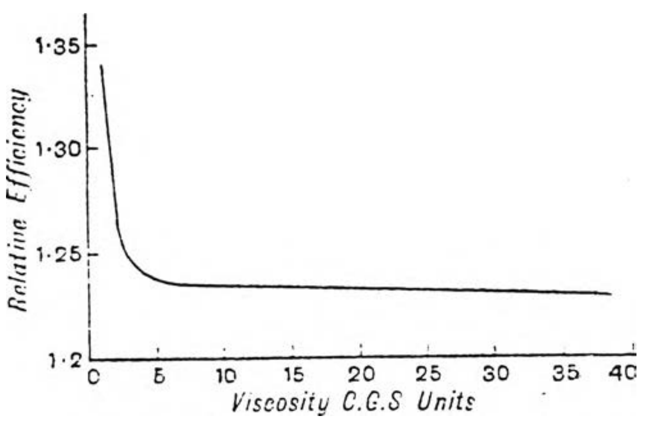

Figure 2.9 Effect of the absolute viscosity with relative grinding efficiency [17]