1. Introduction

Coating is a complex subject if formulators want to formulate defects free and yet obtain the best stable performance coating. The most complex part of coating is the wetting and dispersing of stabilizing solid particles in the system. Thus, dispersion of solid in liquid involved extensive colloid chemistry in order for us to understand how these particles can be wetted dispersed and eventually stabilized. Stabilization of pigments is the most important factor in coating to ensure a well dispersed pigmented coating.

Below are the definitions for wetting, dispersing as well as stabilization in relation to coating.

1.1. Wetting

In general term, wetting is referred to a compound added to a liquid in small quantities in order to enhance the spreading of the liquid on a surface or the penetration of the liquid into the solid particles in the liquid or/and the solid substrate that gets in contact with the liquid. Thus an effective wetting agent for coating should be a surfactant that has affinity groups to solid particles and able to replace air and moisture that traps in the solid particles in order to spread and penetrate to the surface of the solid particles.

1.2 Dispersing

Dispersing is an act to move and separate an agglomerate particle to smaller particles. The ideal stage is to disperse the agglomerate particles to it primary particles size. However, for some pigments, it is impossible to do so. Most of the time, in coating systems, this action will mostly depends on the mechanical forces, which are applied to it such as stirring, grinding etc. A dispersing agent will only help to accelerate this process so that the time needed is shorter.

1.3 Stabilization

This is the most complex process and a good wetting and dispersing agent should have these properties. Poor stabilization will lead to many defects that we will discuss later. Stabilization of solid particles in coating is defined as the ability to keep all solid particles separated in a certain distance and stop agglomerates, aggregates and flocculates after long period of storage. Solid particles in liquid will move around and collide with each other according to Brownian motion. If these particles are not well stabilized, due to the attraction forces (will be discussed in detail later) between the particles, these forces will re-agglomerate and flocculation them together and this is not desire by all formulators.

2. Agglomeration, aggregates and flocculation

In coating, in almost all cases, the solid particles that present in the formulation will be the pigments that use for coloring, extender that use as filler and/or other solid material for special purposes like fire retardant, anti-fouling, waxes, matting agent and etc. The pigments will be the most import solid materials as it give color, which is the most direct appearance and is the one of the main purposes, decoration, other than for protective purpose.

Let us look into the reasons why flocculation of pigments occurs even after they have been well dispersed in the resin/solvents matrix.

As mentioned earlier, solid particles move around in the system by Brownian motion. Thus, they do collide with each other every second or even in shorter time. If there are forces enough to separate them after they collide, then this system is stable. However, due to the fact, that the size of pigments are very small, the attraction forces between these small particles are very strong and most of the time needs external forces to separate them, where re-grinding or applying substantial shear force is needed. Thus, the best way to prevent flocculation of pigment is to prevent them come very close or near to each other.
The charts below show the surface characteristic of solid particles such as pigment, extender etc against flocculation tendency.

Diagram 1: The smaller the particles, the stronger their flocculation tendency. Also, if a particle charges are too high, the stronger their flocculation tendency.

There are few types of flocculation. Agglomeration is referred to as where the pigments are strongly attracted to each other and if we do fineness check of the system, it will show more course fineness. This is serious flocculation and needs re-grinding in order to separate the pigments again.

Another flocculation will not show physical increase in fineness. They are bond together with weak hydrogen bonding and London Van Der Waals forces and when subjected to small amount of shear force like spraying, brushing or even shaking, most of these weak bonds will be destroyed. However, they re-form again very quickly once the shear force is withdrawn. This is the type of flocculation, which we want to overcome in order to formulate a stable coating formulation.

2.1 Flocculation Forces

Inter molecular forces of particles are the main attraction forces that cause flocculation. These inter molecular forces are extensively discuss in slip and leveling chapter, they are dispersion forces that involved London Dispersion forces and polar forces that involved dipole forces, hydrogen bonding and ionic forces.

As shown in diagram 1, the diameter of the solid particles plays a major role in flocculation tendency. Another factor will be the distance of two separate particles, as shown in diagram 2.
Where,

\[ \begin{align*}
V_A & \sim \frac{D}{S} \\
V_R & \sim E \cdot \delta \cdot \frac{D}{S}
\end{align*} \]

Further proof, that *keeping two particles apart or preventing them to come close to each other* is the best way to prevent flocculation. This is due to the fact the diameter of the solid particles in coating are constant in size or in other words, formulators want to achieve the fineness of the pigment close to primary particle size where they are in the range of 0.01 - 2µm.

However, not only attraction forces exist, there are also repulsion forces that try to separate two particles. Static charges can exist on the surface of the pigments due to the charges on the surface, mainly for inorganic pigment, as well as static charges accumulated on the surface, mainly for organic pigment. The repulsion forces are related to the thickness of the classic electrical Double layer.

Thus, in order to have a stable dispersion, we need to dominate the repulsion forces. The incorporation of a dispersant, whether they are conventional or high molecular weight, is to increase this repulsion forces.

In conventional wetting and dispersing agent, we try to charge the surface of the pigment to have the same charges and this will increase the repulsion forces. However for high molecular weight dispersing agent we try to use steric hindrance to avoid them come too close to each other where at that distance the repulsion forces is dominant or both forces are close to zero.

The balance between both forces can be draw in different figure depending on the characteristic of the particles involves, however for a simplified explanation, a diagram is show as below:
As shown in diagram 4, the best separation distance between two particles is at best at the critical distance or even better at where combination of both forces is at zero. In most cases, the Dcd distance is best at 200 Å or 2x10^{-8} m. However, for some difficult and small particles size organic pigments and carbon black this distance is greater than 200 Å. Therefore, for these difficult to disperse pigments, a higher molecular weight dispersant is needed in order to obtain the best pigment stabilization.

3. Ways to do stabilization

As discussed earlier, the reason for the flocculation to occur and the way to prevent it is to have a good stabilization on the pigment particles. Stabilizing can be achieved through many ways

3.1 Pigments pre-treatment

This is an easy method in which a good pigment pre-treatment is incorporated to the surface of the pigment in order for them to be easily wetted and stabilized by resins that are used in a particular system. This method may be effective if the treatment that is applied on the pigment is compatible with the resins used in the system. Most of the times, as the pigments are going to be used in many coating systems and this includes water and solvent based system, it is impossible to find a universal pigment treatment material that have good compatibility with all system yet effective. Further more, most of the time, these pre-treatment can only improve the wetting properties and not the stabilization properties.

3.2 Dispersing Resins

Another possibility is using a good dispersing resin to wet and stabilize the pigments. However most of the times these resins are low in molecular weight, so it can provide good wetting but poor steric hindrance for stabilization. If these resins are high in molecular weight, it will give other problems like solubility, compatibility, lowering the solid content of the final paint and high solvency power solvents are needed for this type of resins (as this will limit to only certain system only) etc.

If charges are incorporated by electrostatic effect in order to stabilize the pigments, these charges will also limit the compatibility as it increases the polarity of the dispersing resin. High charges also mean they are more hydrophilic, it will influence the final properties of the paint such as chemicals resistance, water resistance, corrosive resistance etc.

3.3 Resins in the system

Nowadays the demand for good appearance as well as a more protective and functional coating is undeniable. This results in the creation of more and more sophisticated resins, such as acrylic, polyester etc. These resins have very bad wetting properties to the pigment surface. Thus by changing these resins to have better wetting and incorporating pigment affinity groups into the resin, it will decrease the protective function of these resins. The same argument happens as discuss in dispersing resin by increase the molecular weight as well as incorporate a charge site on the resin.

4
3.4 Dispersant as additives
This method will be the most commonly used and most effective method to solve the stabilization problem. The dosage used for these dispersants is low but the effectiveness is high. Thus, it will not influence the designed properties of the final coating.

4. Basic criteria’s to be a dispersant
There are few criteria’s that dispersants need to fulfill in order to be considered as a possibility of a dispersant that can give wetting, helping in dispersing and the stabilizing the pigments.

4.1 Compatibility
A good dispersants need to have good compatibility with the system in order to allow them to strengthen themselves into the resin matrix to provide stabilization.

4.2 Low surface tension
Better wetting achieved with low surface tension; it allows them to wet the pigment and will be a great help in the dispersion stage to accelerate wetting.

4.3 Pigment affinity group, anchoring group
Another important criterion for a dispersant is where it must have pigment affinity groups to allow itself a firmly anchor on the pigment surface. There are many chemical groups that can be used and will be discussed extensively later in the next chapter.

5. Dispersant additives and their history
Based on all the criteria that were mentioned above, generally it can be classified into 3 types of additives available in the market, they are wetting agent, dispersing agent and polymeric dispersant. Most of the time a wetting agent also functions as a dispersing agent (true for solvent based) thus, in actual case there is only two types of dispersants available in the market.

Wetting and dispersing agent is a low molecular weight surfactant type of molecule, which helps in wetting the pigment particles by a liquid carrier in the dispersion process. Most of these wetting and dispersing agents are based on ionic structure that based on neutralization of acid and alkaline group or non ionic structure that based on polyether, hydroxyl and amine group.

Going back in time to 60 years ago or even longer, we know that at that time there is no organic pigment or carbon black. All pigments were metal oxides. The oxygen and metal compounds are bonded together by ionic bonds. Therefore this resulted in the crystallization of such ionic bonding compound with charges on the surface with '+' for the metal atom and '-' for the oxygen atom. By using ionic structure molecules, they can find absorbing site easily on the highly charges metal oxide pigment surface. Those ionic sites on the wetting and dispersing agent normally called the pigment affinity groups, where they have the preferred orientation in which it is absorbed onto the pigment surface due to their ionic behavior. Thus, sometime these kinds of wetting and dispersing agents also called Conventional Wetting And Dispersing Agents.

The color shades that are provided by metal oxide pigments are normally opaque and their appearance are 'not clean' or sometime referred as ‘dirty’. The requirements for better and more attractive colors as well as the introduction of metallic finishing, increases the
demand for organic pigments and carbon blacks as they are highly needed in order to fulfill the demand from the market.

There are some obstacles faced by coating formulator in order to produce a stable coating or to retrieve the best out of such pigments. The main problem that they are facing is flocculation and this problem will result in color change upon storage, reduction in transparency and giving a ‘clean shade’ appearance.

We all know that organic pigment and carbon black do not have charges on their crystal surface because they are bonded with covalent bonding. Therefore, ionic wetting and dispersing agents will have the difficulty to find any charged surface to anchor and because of this, they loose the affinity to anchor to the pigment surface and due to this fact, they are not efficient enough to stabilize the organic and carbon black pigments. Moreover the size of such pigments are very small, at least five times smaller than metal oxide pigment, smaller particles size also increases the attraction forces between two pigments and promote more flocculation. New and more effective dispersants are needed to solve such problem, Polymeric Dispersants were introduced.

Polymeric dispersant additives consist of a functional copolymer, which supports pigment dispersion process by providing control on rheology and effective stabilization of pigment particles against re-agglomeration and flocculation. They based on different concepts as compared to conventional wetting and dispersing agent by anchoring to both organic or inorganic pigment surface and using steric hindrance concept to provide stabilization and anti-flocculation. An extensive discussion will be presented in a later stage.

Diagram 6: Difference between wetting and dispersing agent to as compared polymeric dispersant.

<table>
<thead>
<tr>
<th>General Main Effect</th>
<th>Conventional Wetting and dispersing agents</th>
<th>Polymeric Dispersants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduce surface tension to facilitate wetting during grinding process.</td>
<td>- Reduce surface tension to facilitate wetting during grinding process</td>
<td>- Reduce surface tension to facilitate wetting during grinding process</td>
</tr>
<tr>
<td>Using difference in charges to perform the anchoring process</td>
<td>- NOT using difference in charges to perform the anchoring process</td>
<td>- Use steric hindrance for stabilization</td>
</tr>
<tr>
<td>Using repulsion of same charges and attraction of different charges for stabilization</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Chemistry

Conventional Wetting and dispersing agents: Low molecular weight surfactant, most of the time contain ionic group as pigment affinity

Polymeric Dispersants: Functional copolymer with special pigment affinity group

Molecular weight

Conventional Wetting and dispersing agents: 500 – 2000

Polymeric Dispersants: 4000 - 25000

Dosage, solid on pigments weight

Conventional Wetting and dispersing agents: 0.4% - 5.0%

Polymeric Dispersants: 2% – 40%

5.1 Conventional wetting and dispersing agent

As mentioned earlier, this is a low molecular weight material that has ionic structure, mostly used in solvent-based, and some none ionic structures are more use in water-based systems. Many types of chemicals can be use in this category. Most of the time, they are acid and amine and or amide salt or just pure acid group or amine and/or amide group. However, for water based, aliphatic polyether is widely used. Below are some of the examples of some chemicals group use as conventional wetting and dispersing agents.

Cationic: Oleylamine

Anionic: Sodium oleate
As we can see, these wetting and dispersing agents use a charged polar head as the pigment affinity group and these groups are responsible to absorb on the pigment surface. The rest of the molecules are stretched into the resin matrix to provide stability of the system. However, the above examples are only based on single charge head per molecule. Nowadays most of the dispersant have multiple charge head in order to ensure an effective anchoring efficiency.

The diagram shows how a conventional wetting and dispersing agent oriented themselves on the pigment surface.

Diagram 7: Chemical compounds commonly used as conventional wetting and dispersing agents

Diagram 8: Different types of conventional wetting and dispersing agents oriented themselves on pigment surface.

An example of a tertiary amine conventional wetting and dispersing agent

An example of a multiple charge head conventional wetting and dispersing agent
5.1.1 Control flocculation

Conventional wetting and dispersing agent sometimes also known as control flocculation agent. Looking back to diagram 8, due to the high polarity and ionic structure of the dispersants itself, it will promote formation of hydrogen bonding. The dispersants on pigment surface are bonded together by hydrogen bonding with a nearby dispersants on another pigment surface. The more polar head per molecule, the more hydrogen bonding bridges that they will form. If we observe it in a bigger picture, all pigments are actually bonding to each other which in a flocculated system. This effect is known as control flocculation.

This effect also gives the conventional wetting and dispersing agent anti-settling property as the additional function. Furthermore, by making use of this effect, conventional wetting and dispersing agents also can be used as an post addition additive to solve flooding and floating problem as it will flocculate those none flocculated pigments to the same degree of flocculation of the flocculated pigments. In this way they will have the same particle size, so flooding and floating will not be observed. However, the process of flocculation will reduce gloss and create haziness to the final coating.

Another additional usage for this effect is to use in combination with a suitable high molecular weight dispersant to act as a good co-grinding aid to prevent flooding and floating.

5.1.2 Limitations of conventional wetting and dispersing agents

As previous mentioned, conventional wetting and dispersing agents are not really effective in organic pigments and carbon black due to the fact that these pigments are low polar and do not carry charges on the surface. The anchoring group of the conventional wetting and dispersing agents are unable to find a suitable site for them to anchor on the surface of these pigments. Let us look into some of the pigment structure for a clearer picture.

Diagram 9: A simple model of charge distribution on the surface of a Titanium Dioxide pigment

These charges allow easy anchoring of conventional wetting and dispersing agent to ‘hook’ on.
In addition to the none polar property of the organic pigment and carbon black it makes them difficult to be wetted and anchored. The particles size of these pigments are also much smaller as compared to inorganic pigments. They are at least five times smaller than inorganic pigments. The static repulsion forces as explain earlier on none charge particles are also relatively smaller. All these attributes make them relatively higher in attraction forces and more difficult to stabilize. Thus, better and more efficient dispersants are needed to fulfill the needs of modern coating technology.

5.2 High molecular weight dispersants

High molecular weight dispersants are introduced in early 1980. This technology has been improved and diversified very rapidly since then. Today there are many range of high molecular weight dispersants available in the market to suite the different demands and requirements of coating formulators.

Basically, the fundamental chemicals structure of high molecular weight dispersants that are widely accepted by most formulators are Polyurethane, Polyacrylate and Polyester. The reason for these three basic groups are chosen is due to their wide compatibility with most common resins available in the market.

The main differences between a high molecular weight dispersant and conventional wetting and dispersing agent are the molecular weight, stabilization, anchoring mechanism on the pigment surface and dosage.

5.2.1 Molecular weight

Below is a common structure of a high molecular weight dispersant. The high molecular weight structure is needed in order to ensure a good steric hindrance effect and the ability to separate two pigment particles to a distance where it can reach the critical distance or where the attraction forces between them is near to zero.
As we can see that the molecular weight has to be high in order to accompany all the important groups as shown in diagram 11. However, the main purpose is actually to create a barrier between two pigment particles so that they can be separated at least at the critical distance.

5.2.2 Stabilization

Stabilization is one of the most important features in high molecular weight dispersants and is achieved through steric hindrance. What exactly is steric hindrance?

In general term, steric hindrance is defined as repulsion between the electron clouds on bulky groups of a molecule or between molecules. Let us see some examples how steric hindrance works in practice.

Consider a reaction in diagram 12. This reaction is very much depending on the R's groups. If the R's groups are hydrogen, then the reaction is possible to happen, however if these R's are methyl groups, then the reaction is not possible to happen. Steric hindrance created by the tertiary structure is not favorable to allow the nucleophile to enter close enough to have the reaction be initiated.

Another simple example of steric hindrance on molecules approaching each other is also illustrated as in diagram 13.
Diagram 14 shows how these dispersants oriented themselves on the pigment surface and how they interact with each other. It also shows how steric hindrance play a part in keeping pigment particles stay none flocculated.

Diagram 13: Illustration of 2 different isomers of pentane on steric hindrance

2 linear molecule of n-pentane can be very close to each other, minimum steric

2 bulky neo-pentane can not be too close to each other, maximum steric hindrance

Diagram 14: When 2 pigment particles approach each other, steric hindrance will keep them separate before the attraction forces dominate.

The steric hindrance takes place, further approach is not possible and these 2 particles will be separated.
5.2.3 Anchoring mechanism on the pigment surface

High molecular weight dispersants are not based on charges to anchor on to the pigment surface. The pigment affinity groups that present in the dispersant are basically three groups, Amine (mainly tertiary amine), Carboxylic Acid as well as cyclic ring. The reason why these three groups are chosen, is to make use of the intermolecular attraction forces that we discussed earlier in the slip and leveling section to form a bond on the surface of the pigments.

We are not going to go in detail on the intermolecular attraction forces as this has been extensively discuss in the slip and leveling section. Thus, basically, forces that we need to create between the dispersants and the surface of the pigments are London Van Der Waals (London Dispersive), Hydrogen bonding as well as dipole-dipole interaction.

Before we can fully understand the anchoring mechanism as well as why these groups are chosen, let us look into the pigment structure. These pigment structure has been discuss before in diagram 9 and 10, we shall look into it again.

As shown in diagram 15, the high charges surface of the inorganic pigments allows easy anchoring of the affinity group from the dispersants and they can form a very strong bond. Higher charges and ionic behavior of these surfaces also means that they are higher in surface tension, making it easier to be wetted by an organic molecule. The ionic structure allows almost all types of intermolecular bonding to happen on the surface of the pigments.

Diagram 16: Molecular structures of some organic pigments

As they are all bonded by covalent bonds, making the surface low polar and low surface tension
For organic pigments, if we observe carefully, it contains nitrogen derivative as well as aromatic ring. These structures are needed to give organic pigments certain desired deep and clean colors, also known as chromogen for pigments that responsible to provide color. Thus using anchoring groups in the dispersant that also base on cyclic ring and amine (mainly tertiary amine), it will create a dipole-dipole interaction, hydrogen bonding as well as London Van Der Waals attraction forces.

However, for carbon black, the main attraction forces will be the London Van Der Waals where the sharing of orbital between aromatic rings and only aromatic cyclic ring structure will be effective to do anchoring onto the surface. Thus most of the time carbon black will be the most difficult pigment to stabilized and further more high jet-ness carbon black have very small particles size that even make the situation even worse.

Below are some simple illustrations on how these interactions will be created on the surface of the pigment.
Please take into consideration that all of the above examples are just hypothetical concept in the understanding of the anchoring mechanism. There may be more forces of attraction being involved. In practice, by incorporating these pigment affinity groups in a high molecular weight dispersant, the stabilization of pigments improved tremendously which further proved this concept.

5.2.4 Dosage

In all cases, high molecular weight dispersants need higher amount of dosage as compared to conventional wetting and dispersing agents. Many formulators have the assumption that high molecular weight dispersant should have lower dosage and is more effective. In practical, this is not true.

An efficient and stabilized dispersion of pigments can only be reached if almost all surface of the pigment are wetted and covered by the dispersant. Therefore, the dosage of dispersant is strongly depending on the surface area of the pigments.

Conventional wetting and dispersing agent is much lower in molecular weight than the high molecular weight dispersant. Comparing the same dosage level in weight of these two dispersant, conventional wetting and dispersing agent will have more molecules and therefore it means that they can cover bigger surface area than high molecular weight dispersants. This without saying that in order to cover the same surface area, high molecular weight dispersant need to add in higher dosage comparing to a low mole weight conventional wetting and dispersing agent to cover the same surface area.

In general, the recommended dosages of high molecular weight dispersants are as follow:

<table>
<thead>
<tr>
<th>Pigment types</th>
<th>Based on solid to solid calculation</th>
<th>Based on surface area value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium Dioxide</td>
<td>2 - 3%</td>
<td>10% on oil absorption</td>
</tr>
<tr>
<td>Iron Oxide pigments</td>
<td>3 - 4%</td>
<td>10% on oil absorption</td>
</tr>
<tr>
<td>Chrome oxide pigments</td>
<td>2 - 4%</td>
<td>10% on oil absorption</td>
</tr>
<tr>
<td>Filler (Clay, CC powder, Kaolin, Barium Sulfate)</td>
<td>1 – 2%</td>
<td>10% on oil absorption</td>
</tr>
<tr>
<td>Matting agents</td>
<td>2 - 3%</td>
<td>10% on oil absorption</td>
</tr>
<tr>
<td>Phthalocyanine Pigments</td>
<td>15 – 25%</td>
<td>15 – 25% on BET Value</td>
</tr>
<tr>
<td>Organic Red</td>
<td>15 – 25%</td>
<td>15 – 25% on BET Value</td>
</tr>
<tr>
<td>Organic Yellow</td>
<td>15 – 25%</td>
<td>15 – 30% on BET Value</td>
</tr>
<tr>
<td>Organic Violet</td>
<td>15 – 30%</td>
<td>15 – 30% on BET Value</td>
</tr>
<tr>
<td>Regular Carbon Black</td>
<td>20%</td>
<td>20% on DBP Value</td>
</tr>
<tr>
<td>High Channel Black</td>
<td>30 – 40%</td>
<td>30 – 40% on DBP Value</td>
</tr>
</tbody>
</table>

Diagram 18: Dispersant and pigment surface anchoring through intermolecular attraction forces

Diagram 19: Recommended dosage of high molecular weight dispersant on several common pigments, filler and matting agents
6. Test methods for optimal stability by dispersing agent

There are several methods to check the dispersing agent performance in terms of stabilization. The most common and fastest checking method is by doing a draw down and observing the color strength and transparency. For inorganic pigments, it should be opaque and for organic pigments and carbon black, it should have high transparency. Later these dispersions will be store under an accelerated environment, 50 - 60°C to observe its long term stability.

With this method, we are only able to check and compare the performance with a control and several dispersants but it will not tell us anything in terms long-term stability of the dispersion immediately. Long-term stability is the most important factor, as this will reflect the performance ability of the dispersants. If all pigment dispersions have to wait for few weeks in order to know the result, it will be too late and time consuming to formulate a good paint. Thus, we recommend two quick methods to choose those pigment dispersions that will be waste of time to perform storage test and those worth doing it.

6.1 Rub Out Test

After dispersion is done, let down to final paint formulation (can skip this step depending on milling formulation), mix in colors pigment paint with the white based, draw down and start rubbing in circle on a spot until the paint is semi dry. If the paint need very long time to dry, than repeat the rub out after several minutes interval time. Compare the rub out area and the untouched area. If the color becomes darker, then your color is not well stabilized, if the color becomes lighter, then your white based is not well stabilized.

The theoretical background of this rub out is that if flocculation happens to certain pigments, they will have bigger particles size. As we know that bigger particles size will reduce the tinting strength of the pigment. However these flocculated particles are weakly bonded and connected to each other, upon small shear force i.e. rubbing by finger, it will break the flocculation and bring it back to its original dispersed size and by this color strength will be strengthen resulting in color different observed. This phenomenon will be discussed further in detail when we talk about pigment dispersing and stabilizing problem on flooding and floating.

Diagram 20: An illustration of how color different can be observe on a not well stabilized system upon rub out
Rub out test is a fast and quick test to determine a rough estimation on the pigment dispersion stability. Based on diagram 20 and 21, we observe that from the rub out test, we are still not 100% sure that the system is sufficient stabilized. If both white pigment and color pigment are flocculated on the same degree, there will be no rub out or a very little rub out can be notice. Thus in order to be 100% sure, we recommended another method, pour out test.
6.2 Pour out test

The method for pour out test is also quite simple to perform. After dispersion is completed where fineness is achieved, let down the system to final paint formulation (can be done without this step depending on milling formulation), dilute them to a viscosity of 13 – 15 seconds on F#4 cup or NK#2 cup. Add in very small dosage of Polysiloxane leveling agent, 0.1 – 0.2%, such as AFCONA – 3030, to avoid Bernard Cells formation, Silking. The details of silking can be found in the slip and leveling section. Please note that AFCONA – 3030 is not necessary needed in the final formulation as may be other slip and leveling agent gives better overall performance, thus the additional of AFCONA – 3030 is just for this test purpose to eliminate Bernard Cells or Silking to avoid a wrong observation result on the pouring result.

Pour down the paint slowly, at vertical position, onto a clean glass panel or high density polyester sheet. Allow the panel to stand vertically until they are semi dry. Force dry by baking the panel in an oven for system curing at room temperature or bake to the paint system curing temperature for baking paint.

Observe the poured paint. A well stabilized system should have a uniform paint film and it should be very transparent and high gloss for organic pigments and carbon black, and for inorganic pigment, it should be also uniform film, high gloss but opaque. For some inorganic pigment like iron oxide a small rub out should be carry out immediately after pouring, a well stabilized iron oxide pigment should not have any rub out at all.

The theoretical part of this pour out test is not to apply any shear force or very minimum shear force in order not to destroy any flocculation that formed in the dispersion. Thus by diluting the paint to a very low viscosity, it will increase the Brownian Motions that increase the rate of pigment particles colliding to each other. This will increase and accelerate flocculation rate if the system is not stabilized. Using pouring method where a very low shear force is applied to it, or where only gravity force is applicable, this will not destroy those flocculated pigments if there are any of them. If the system is flocculated, the observation as mentioned earlier will appear and this will all relate to flocculation problems.

Pour out is a more accurate and precise method to determine flocculation. Most of the time, pigment dispersion that passed through pour our test will be very stable upon storage to give good color consistency, higher gloss and no rub out. Therefore, this will be a more preferred method to use to determine the stability of pigment dispersion.

Below are few panels to show the pour out result of a well stabilized system and none stabilized system.

Diagram 22: Illustration on a well stabilized and a not stabilized organic red on pour out result

A well stabilized system for organic red that has high transparency and high gloss

A flocculated system for organic red that is matt and low transparency

We can also observe flocculation when the paints are stored in the can. Most of us have seen this phenomena before and most of the time we just ignored it as upon stirring the paint will return to it homogenous form.

In order for us further to illustrate this, the difference between a stabilized system and a flocculated system can be observed in a glass bottle. If these two paints go through the pouring test, the same result and appearance will also be observed on the panels. The differences that have been mentioned are shown below.
7. Problems related to poor stabilization

If a system is not sufficiently stabilized, many problems can be observed and these will lead to paint defects or reduction in its performance or their maximum color strength is not achieved due to the pigments used were not fully utilized.

7.1 Poor color strength / tinting strength

The tinting strength of a pigment is very much depends on its particles size. The bigger the particles size, the lower the color strength. Thus, if a system is flocculated, the flocculated pigments grouped together to form a bigger particle and act as 1 particle. Bigger particles size of pigment eventually will result in lower color strength.

![Diagram 23: In can observation of a stabilized and a flocculated system](image)

where the pigments separate and formed an un-homogenous film

where the pigments dispersion formed a homogenous film

![Diagram 24: Color Strength vs. Pigment Particles Size](image)

Color strength

Optimal Range, approximate at 0.01 - 5µm, depending on pigment color and pigment structure

Pigment particles size, µm

Diagram 24: Color Strength vs. Pigment Particles Size
This problem can be solved by selecting a suitable dispersants to achieve a stabilized pigment dispersion system.

7.2 Color stability
In none stabilized system, flocculation happens immediately after dispersion process, however the degree of flocculation at that moment is vary, depending on the dispersant used and the formulation. If a system is flocculated, pouring test can immediately detect this defect.

Flocculation also can grow over time. For none stable system it will be just a matter of time, which will eventually lead to very severe floculation problem; some take days and some take months. Thus as the flocculation grow, as explain in 7.1, the color strength will be reduced and this will resulted to color changing gradually with time. This could be very obviously observed when a difficult pigment is use as a trade tinting dosage for a particular color.

Differences in gray color shade will be the easiest for human eye to detect; even the ΔE is less than 0.5. However, pigment black is one of the difficult pigments to stabilize. Thus, sufficient stabilized carbon black dispersion is needed to ensure a stable grey color shade.

This problem, again, can be solved by selecting a suitable dispersants to achieve a stabilized pigment dispersion system.

7.3 Flooding and floating
Flooding and floating are almost the same defect where flooding is referred to color separation that happens horizontally and floating is color separation on the surface of the paint, sometime refer it as vertically color separation.

Diagram 25: Color strength difference in practice for a blue pigment on a good stabilized system and a very poor stabilized system

Diagram 26: Above - Simple model to illustrate flooding and floating. Below – Floating phenomena in practice
7.3.1 Stokes Law on Flooding and floating

The problem of flooding and floating can be explained by Stokes Law, where it relates the falling rate of a particle with certain diameter and density in liquid. Below is the formulation of Stokes Law.

\[
g \frac{V}{18\eta} = (d_p - d_l) r^2
\]

Where:
- \( V \) = Fall rate of particle
- \( g \) = Gravity
- \( d_p \) = Density of the pigment
- \( d_l \) = Density of the liquid
- \( r \) = Radius of the particles

According to above equation, particles that have the higher fall rate will be the particles that will lie at the bottom, where particles with lower fall rate will float on the top. As all factors are constant as it happens in a same liquid with a same viscosity and density, the only variable factor will be the density of the pigment as well as the radius of the particles.

Let us do some calculation to see the effect on flooding based on the radius of the particle and density of the pigment. Take an extreme example of a mix color of Titanium Dioxide and Carbon Black.

**Assumption**
1) Only \((d_p - d_l) r^2\) is calculated as the rest of the parameters are constant numbers.
2) The density of the paint = 1 g/cm³
3) All pigments are not flocculated and grind to primary particle size.

**TiO2**
- Density = 4.1 g/cm³
- Average Radius = 0.23µm
- Rate of fall = \((4.1 - 1)(0.23)^2 = 0.164\)

**Regular Carbon Black**
- Density = 1.8 g/cm³
- Average Radius = 0.05µm
- Rate of fall = \((1.8 - 1)(0.05)^2 = 0.002\)
As we can see that the falling rate of Carbon Black is approximately 82 times less than TiO2. Therefore Carbon Black should be the one that float on the surface. However in practice, a dispersion of carbon black is impossible to get back to their primary particles size. We also observed in practice that carbon black is one of the most difficult pigment to prevent flooding and floating.

Theoretically, in order to have the same falling rate as TiO2, it needs approximately 9 carbon blacks. As mentioned earlier, it’s not possible to grind carbon black to its primary particles size, thus they are present in the system as several primary particles grouped together (normally are in the range of 3-6 for an efficient milling process) and act as one particle. Using a high molecular weight dispersant that absorb on the surface of the pigment will further increase the total radius tremendously where it can help to reduce flooding and floating. This means most of the time a very high molecular weight dispersant will give a better performance in carbon black than a low molecular type.

So, based on the same calculation, if these carbon blacks are not well stabilized and flocculates, the falling rate will increase tremendously in a factor of exponent 2. Below is a simple calculation to show a flocculated carbon black and it’s relation to the falling rate, an example of 20 primary carbon blacks flocculated together.

20 carbon black flocculated
Density = 1.8 g/cm³
Average Radius = 1µm
Rate of fall = (1.8 – 1)(1)² = 0.80, 5 times higher than falling rate of TiO2

As shown in the calculation above, the degree of flocculation determines the degree of flooding of carbon black. As TiO2 is very easy to stabilized making their falling rate quite stable and if a flocculated carbon was to mix with them, flooding occurs and upon rub out, these flocculated carbon blacks will be shown out. Bear in mind that flocculation can grow over time and the degree of flooding also will grow proportional to the flocculation rate.

That is also true that for high channel black, floating is always a problem because the primary size radius of this carbon black is even smaller at 0.01µm. Thus channel black is always recommended to use as a sole pigment for high jet-ness black color.

In conclusion, density and particle size are the main factors to induce flooding. However, density for each type of pigment is a constant value, which we can control, but particles size varies in with different values that relates to stabilization of pigment in dispersion. Controlling the particles size of a pigment through good dispersing aids to prevent flocculation is an important step to prevent flooding.

7.3.2 Explanation on floating

According to Stokes Law, particles with lower falling rate will float on the top and particles with higher falling rate will flood at the bottom. In practice we notice that even a flocculated pigment that suppose to flood at the bottom will always show some spots of on the surface of the paint. Stokes Law assumes that the liquid do not contain any evaporating solvents as we have in coating. Stokes Law also do not consider the interaction forces that exist between particles, resins and solvents where polarity, charges and etc are involved. In general, Stokes Law is a simple and general explanation concept for flooding and floating, especially for flooding, but in order for us to understand more on floating, other factors have to be considered.

The evaporation of solvent creates circulation forces circling beneath the surface of the coating. If the surface tension gradient of the system is great enough, we will also see the formation of Bernard Cells. Each circulation is a localized motion where an edge current will also be created according to Holmholtz flow distribution theory. This edge current traps the pigments in the circulation and due to different particle sizes have different mobility, separation occurs and floating will be observed on the surface. The floating effect also depends on the size of the circulations in which, if the film thickness is low, the separation is
very small and will not be visible to the human eye. So, when a coating is applied at normal thickness no floating effect can be noticed, however if it is in can, this effect is obvious.

Floating sometimes can be solved by adjusting the surface tension gradient of the liquid if the floating effect is the formation of Bernard cells. However if the floating is due to the flocculation of pigments, adding a surfactant may reduce the floating effect but will not eliminate the problem.

In general, the only way to solve floating, again, is to use a suitable dispersant to stabilized the pigments in dispersion.

7.4 Syneresis

None stabilized system will have the tendency to give synaeresis problem upon storage. This defect is a separation of liquid phase and pigmented phase. This is a two layer separation where the upper part is the mixture of resin, solvent and other soluble additives and the lower layer will be the flocculated pigments disperse in some resins and solvents. The defect is best illustrated in diagram 26.

Diagram 28: Synaeresis illustration

In a flocculated system, upon storage, the degree of flocculation will increase where more and more pigments are bond together. Each time 2 particles flocculates, the distance between these particles is shorter. Just imagine that if almost all pigments in the system are bonded to their adjacent pigment particles, the distance of each particles is shrinking, resulting in a shrinking effect where the pigments will reduce their occupancy volume in the system because the distance between particles are shorter. This will result in a separation where the pigmented phase will stay at the bottom (if the density of pigment is greater than resin solvent mixture) and the resin and solvent phase will stay at the top.

Flocculation occurs where almost all pigment are attach together. Resulting in shorter distance between each particles and the occupancy volume reduce, this created a shrinking effect that separate the system into 2 phases.

Diagram 29: explanation on how Synaeresis occurs in a flocculated system
Many coating formulators refer to Synaeresis as one of the settling problem where it can be solve by adding suitable anti-settling agent. This is not entirely correct. Addition of anti-settling agents, sometimes help to prolong the time for it to happen but doesn’t prevent it from happening. Addition of anti-settling agent, will increase the thixotropic behavior of the system and with a higher static viscosity, it will delay synaeresis process. Higher viscosity will slow down the Brownian Motions and thus slow down the rate of flocculation.

The way to solve this problem, again, select a suitable dispersant that can give a good stabilization to the pigment in dispersion.

7.5 Poor gloss / loss of gloss
It is obvious that in practice, a poor stabilized system will have lower gloss than a well stabilized system. Gloss is measured by using the reflection of light at certain angle and detected by a sensor on the degree of light that not been diffuse.

A flocculated system will have the micro floatation on the surface as well as micro deformation on the surface and these will scatter the light to give lower gloss or hazy appearance.

7.6 Transparency of organic pigment and carbon black
If we look into the spectrum of light, we will notice the spectrum of wavelength range from 200nm (0.2µm) for ultra violet light to 700nm (0.7µm) for red light. Diagram 30 shows the full spectrum of light.

To put it simply, if the pigment particles size falls in between the visible spectrum range or bigger, it will be an opaque appearance. If the particles size is below the visible spectrum, then the paint film will be a translucent appearance where they are close to become fully transparent. However if the particles are less than 0.2µm, it will give a full transparent appearance.
This explains why inorganic pigments are an opaque pigment as their particles size is in the range of 0.2 – 5.0µm after milling. For organic pigments and carbon black, their primary particles size is in the range of 0.01 – 0.10µm, which means, in most cases, they should have good transparency.

Coating formulators that want to obtain good transparency should select an organic pigment that has smaller in primary particles size in order to achieve this requirement. Please bear in mind that the milling process that is practiced by most paint factories is unable to grind the pigments less than their supplied primary particles size.

Diagram 31: Haziness and transparent effect on pigment size

7.7 Leveling and flow

We have discussed about flow and leveling extensively in the slip and leveling section. Flocculated system change the surface tension of the system and from this, it will also affect the surface tension gradient of the system. Flocculated particles have higher surface tension as they are not totally covered with dispersant and we know that solid particles always have higher surface tension. This will disrupt the surface tension gradient of the system and eventually caused poor leveling and flow. Further more flocculated system has higher viscosity and thixotropic behavior. This, in addition contributes to poor leveling.

8. Influence of other factors toward the efficiency of dispersants

Coating formulation is consists of many ingredients and dispersants is only a very small portion of it but one of the most important ingredient for a pigmented coating. Other ingredients in the formulation, if not selected carefully, will affect the efficiency of the dispersants performance.

8.1 Compatibility

As mentioned earlier, compatibility is the main key for a dispersant to work in a system. Without it, dispersants cannot stretch themselves into the resin matrix to gives stabilization.

8.2 Amount of milling resin

The amount of milling resin is also important. If the resin is added too much, it will act as lubricant in the milling base. This reduces the efficiency of the grinding process and eventually increase the grinding time.

This act will also reduce the performance of a dispersant, as absorption of dispersant on the surface of the pigment is an equilibrium state. Too much resin present will result more dispersant will stay in the resin phase rather than on the pigment surface. Moreover, it will reduce the possibility for the dispersant to anchor on to the pigment. Reducing the percentage
of resin will also allow pigment itself to work as grinding bead where they will crush and separate each other when they meet.

The best recommendation % grinding resins are as below.

<table>
<thead>
<tr>
<th>Pigment type</th>
<th>Grinding Resin % based on solid to solid to pigment</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>30 - 40% on pigment solid</td>
</tr>
<tr>
<td>Other inorganic pigment</td>
<td>50 - 60% on pigment solid</td>
</tr>
<tr>
<td>Organic Pigment</td>
<td>150 – 200% on pigment solid</td>
</tr>
<tr>
<td>Difficult organic pigment (PV 23, PR 177, PR 122 etc.)</td>
<td>250 – 350% on pigment solid</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>400 – 600% on pigment solid</td>
</tr>
</tbody>
</table>

8.3 Milling viscosity

Milling viscosity is also a very important factor to ensure a more efficient dispersing. A lower viscosity milling formulation will allow better grinding efficiency and indirectly increase the efficiency of the dispersants.

Bear in mind that, most inorganic pigment will reduce in milling viscosity after the fineness is going down where else, for organic pigment and carbon black, milling viscosity will increase proportional to the decrease of fineness. The best milling viscosity will be after fineness is achieved, the viscosity of the milling paste should be thixotropic but still liquid.

Additional of high mol weight dispersant will also reduce the milling viscosity.

8.4 Additional of synergic agent

Dispersing synergic agents are usually used together with a dispersant and they will be not so effective when use alone unless the resin have a very good wetting properties. Synergic agents help to improve the anchoring mechanism of dispersant on certain difficult pigments like carbon black, organic pigments and iron oxide pigments.

They have the affinity to the pigment surface and carry anchoring site for the dispersants. They will wet the pigment earlier than the dispersant and allow easy anchoring of dispersants on the pigment to provide stabilization. This action will also increase the particles size of the pigment in order to gives better anti-flooding and anti-floating as according to stokes Law.

Basically, these synergic agents availability are as below:

a) Blue to greenish Synergists for Phthalocyanine Pigment, Violet and Carbon Black, which are based on sulphonlic acid salts of Phthalocyanine pigments. This is a polar pigment derivative with partial dissolving ability in most solvents, partial dyestuff character. Thus, it will not influence the transparency of the principle pigment.

b) Yellow Synergists for organic yellow and red, which are based on sulphonic acid salts of yellow azo pigments. This is a polar pigment derivative with partially dissolving ability in most solvents, partial dyestuff character. Thus, it will not influence the transparency of the principle pigment.

c) Micronized Barium Sulfate for iron oxide pigment and organic violet (PV 23). A precipitated Ba$_2$SO$_4$ can also be used as filler. This material will affect the transparency of the principle pigment.
Diagram 32: How a synergic agent work to improve the dispersant performance

How synergic agent of a) and b) work to help improve the dispersant performance

How synergic agent of c) work to help improve the dispersant performance