

1. Introduction

It is difficult to go through a whole day without coming in contact with foaming materials. The soap and toothpaste that we used in the morning before going to bed, the polyurethane foam seat cushion of the sofa or car seat, or the foamed polystyrene take away boxes that fill our food in the restaurants.

In the above cases, foam is desired to achieve the finishing or result that we needed. However, for paint manufacturers and applicators, in order to ensure a smooth and even final paint film, foam will be one of the main tasks to overcome especially for those paints that are applied by brush and roller.

Thus, additives like defoamer are needed to prevent the formation of bubbles when liquid paints are subjected to external mechanical disturbance during application and production.

1.1 Foam

In general term, foam can be defined as dispersing of gas (normally air) in liquid. It can be generated during production of a coating like in grinding phase, mixing and filling or during application. It also can be produced when liquid paint wetted porous surface like wood substrate. For a paint formulator, foam that is generated during application and porous surface wetting process are the problem that he or she wanted to solve.

Not all foam is the same. Some are transit type like the bubbles in Champagne and some are stubborn type like the foam in shaving cream depending on the viscosity of the medium and the surfactants involved.

2. Foaming or Defoaming

Foam is generated if a disturbance force is applied to a liquid. The question is; what is the lifetime of the generated foam. There are many physical and chemical factors involved in determining the stability of the foam or bubbles.

2.1 Theoretically Approach

The stabilization of a bubble is depending on the elasticity of their thin liquid membrane. Thus, higher elasticity will result in a more stable bubble and vice versa. In order for us to understand more on the importance of this factor, let us look at Gibbs elasticity parameter that is shown below.

$$E = 2A \frac{d\gamma}{dA}$$

E = Elasticity Parameter
A = Bubble Surface Area
 γ = Liquid Surface Tension

Diagram 1: Gibbs Equation On Elasticity.

According to Gibbs Equation, in order for a bubble to obtain some elasticity, the surface tension of the liquid has to change accordingly with the surface area of the bubble so that the values of $d\gamma/dA$ will always more than zero. Any single foam that fails to change its surface tension during the contraction and expansion of the bubble will lead to bursting of the bubble due to high rigidity.

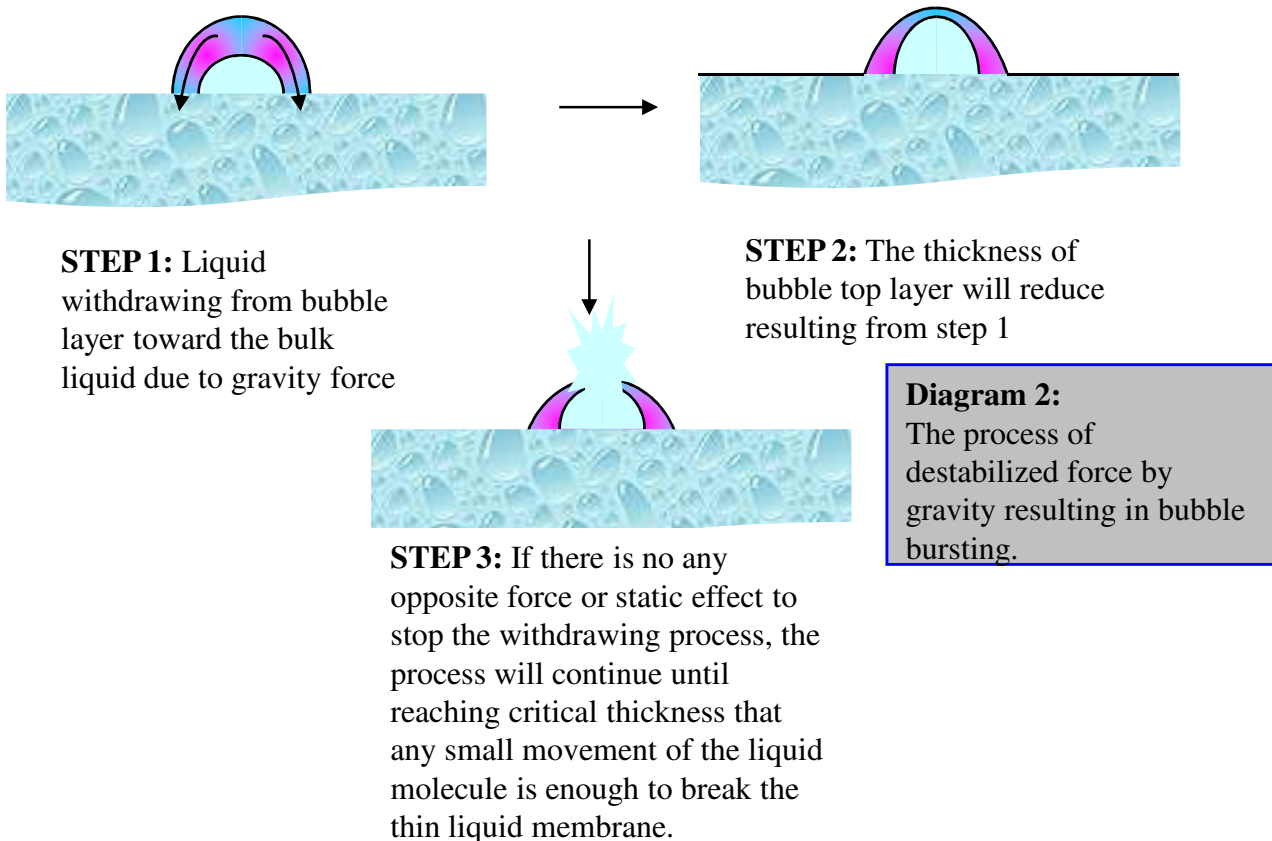
Pure liquid has almost the same surface tension all around the surface and it will almost stay as it is in any situation as long as no external material been added or changed its physical status from liquid phase to gas or solid phase. Thus, Gibbs Elasticity equation illustrated to us that pure liquid is not able to stabilize any foam.

Unfortunately in most of our coating formulations, there is no single formulation that involved only pure single liquid with same molecular structure and same molecular weight. Thus, we still need to deal with this problem constantly.

3. Destabilize Foam Factor

3.1 Gravity Force

When foam is formed, due to gravity forces, the liquid on the bubble will withdraw from bubble towards the bulk liquid. When the thickness reached it critical thickness, which is nearly 100\AA , a simple movement of molecule on that thin layer will result in bursting of that bubble. This process take place very fast within a few second. Further illustration show in diagram 2.



The above illustration supports the Gibbs equation as given on the previous page. Thus, no liquids are able to stabilize any foam in their original/pure form.

4. Foam Stabilizing Factors

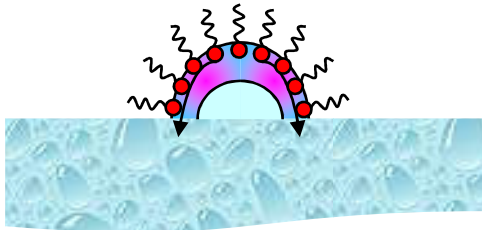
4.1 Marangoni Effect

As we understand from previous explanation on how foam can be destroyed. Thus, in order for a bubble to be stabilized, a second material need to be added to ensure a more elastic bubble film. Most of the time a surfactant that can reduce the surface tension as well as very compatible with the system can serve the purpose.

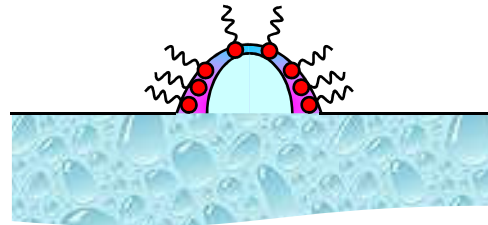
Marangoni effect will explain the effect of surfactant in stabilizing the bubble by using surface tension difference generated during the withdrawal of liquid from the bubble to the bulk liquid.

When a bubble is generated by an external sheer force, the usual withdrawal process by gravity forces will take place immediately. This withdrawal process will result in more surfactants being drain away together with the liquid from the top part of the bubble making it thinner. Therefore it created a situation were by the top part of the bubble would have higher surface tension than other parts.

Surface tension is a state of energy where it flows from low surface tension to high surface tension. The liquid on the bubble will flow from low surface tension area, the lower area of the bubble, towards the high surface tension area, the top area of the bubble, and this will create another opposite force that caused a re-flow process of the liquid back to the top part of the bubble. When these two forces achieve equilibrium before the critical thickness of the foam, we will have a stabilized foam or bubble. The whole process is illustrated more in diagram 3.

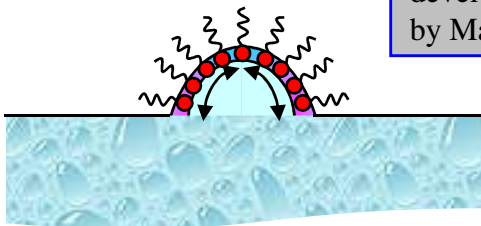


STEP 1: Liquid withdrawing from bubble toward the bulk liquid due to gravity force

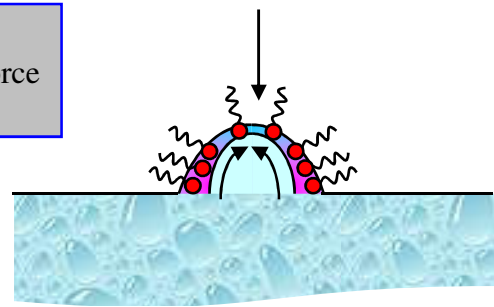


STEP 2: The effect of the withdrawal process, the top part have less thickness than other parts making less surfactant can be occupied on top.

Diagram 3: Process of developing stabilized force by Marangoni Effect



STEP 4: The withdrawal and re-flow forces will come to an equilibrium status and if it is achieved before the critical thickness, than we will have a stable bubble.

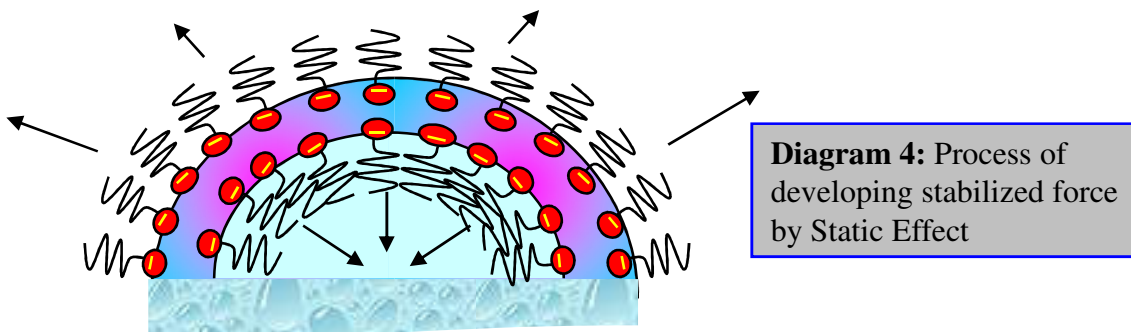


STEP 3: Surface tension gradient appear as top part have high surface tension that the other parts. When opposite force is created, the liquid will flow from low surface tension area will flow to high surface tension area. The liquid will begin to re-flow back to the top.

4.2 Static Effect

Surfactants always carry a polar or electrical charged head with a hydrocarbon tail. In the liquid layer of the bubble, the surfactants will orient themselves as in diagram 4. Thus, when the liquid withdrawal process started, it will bring the polar/charged head of the surfactants close to each other.

Therefore, the same charge of those polar/charged heads will start to repel each other. The direction of this repulsion forces are heading to the centre of the bubble for those surfactants in the inner layer and creating an opposite force on the opposite direction of the bubble centre. An equilibrium state will be achieved, thus resulting in a static phase that stops further drainage of liquid to the bulk liquid. If the equilibrium state of the layer of bubble is thicker than the critical thickness, stable foam is created.



5. Criteria's To Be A Defoamer

All AFCONA defoamers are based on two main criteria in order to ensure that they will perform as what have been designed. Both requirements are necessary to work together side by side to ensure excellent performance.

The two basic requirements are as below.

- 1) A defoamer must have limited compatibility with the system and must able to do so even after long term storage.
 - *A limited compatibility will ensure the defoamer will be de-wetted by bubble layer liquid in order to destabilize the Marangoni and Static Effect. The de-wetting process that takes place will push away the liquid on the layer of bubble and this will accelerate the drainage process that leads to bubble breaking. A more detailed explanation will be shown in Diagram 5.*
- 2) A defoamer must be able to reduce the surface tension of the system.
 - *In order for a defoamer to enter particular foam, they must be able to penetrate and spread evenly on the foam of the liquid layer resulting in a lower surface tension. This it can be explained by the equation below.*

A positive value of Penetration Parameter, E, will ensure that a defoamer goes in the liquid layer of the bubble.

$$E = \gamma_l - \gamma_d - \gamma_{dl} > 0$$

*where, γ_d = defoamer surface tension
 γ_l = liquid surface tension
 γ_{dl} = defoamer and liquid surface tension*

A positive value of spreading parameter, S, that will ensure that a defoamer will be evenly spread through the whole bubble.

$$S = \gamma_l - \gamma_d - \gamma_{dl} > 0$$

The whole process can be illustrated below in diagram 5.

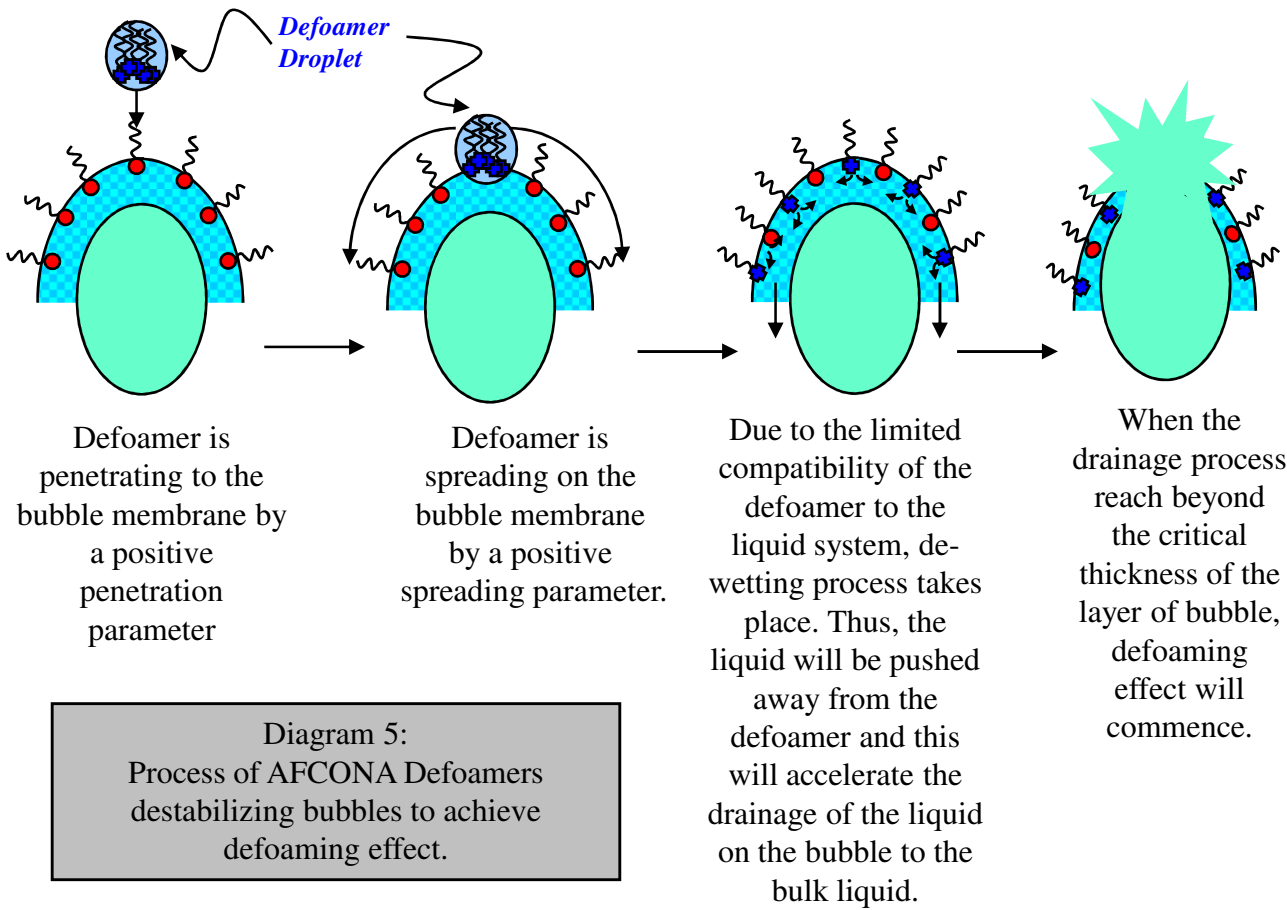
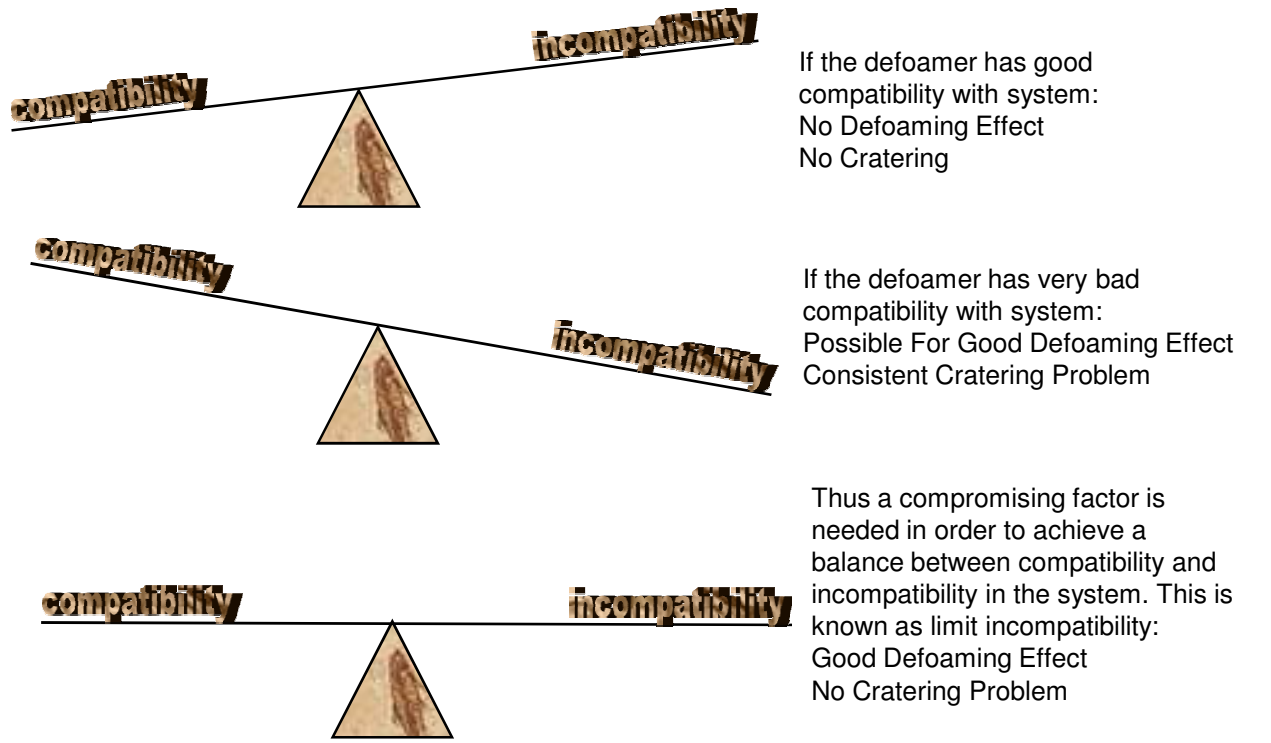


Diagram 5:
Process of AFCONA Defoamers destabilizing bubbles to achieve defoaming effect.

6. Compromising In Using Defoamers

Diagram 6: Compatibility factor that influence the effectiveness and side effect of a defoamer.



As explained previously, one of the main criteria to be a defoamer is that it has to have some limit compatibility. Thus the compatibility or incompatibility of a defoamer with the system plays a main role in determining the effectiveness of a defoamer. However, we know that an incompatible material will also cause crater problems. Thus, as shown in diagram 6, certain extent of compromise is needed when using a defoamer.

Materials that have good compatibility with the system will in fact stabilize the foam and will not have any deforming effect at all, but none tendency to cause craters. However this will not serve our purpose to solve the foam problem.

Materials which are very incompatible with the system will have the possibility as a good defoamer but the drawback is that it will also give cratering site effect. That is why sometimes they need high shear force to improve the incorporation in order to ensure all defoamers added are well dispersed through out the system to avoid craters.

Therefore, in general term, normally a defoamer that is more compatible with the system will have less defoaming effect than the one that is less compatible.

As for all additives producers, constantly, searching for a defoamer that has the properties of good compatibility as well as come with good defoaming performance is highly desired and this can be achieve only by having a very special polymer that have some unique modification, thus the innovative and strength of an additives company will be truly review by having such a products in their product line.

7. Defoamers

Defoamers in today's market are mainly based on 2 chemical materials, i.e., High Molecular Weight Polysiloxane and Silicone Free specially modified polymers. The chemical nature for Polysiloxane can give better surface tension reduction than the non-silicone, thus it will give better incorporation due to better penetration and spreading factor as explained above. Due to it low surface tension, it also gives better de-aeration performance.

However, inter coat adhesion caused by silicone based material is also a cause of concern among paint chemists. Based on our experience, in most cases, this is not true for Polysiloxane based defoamers. In order for us to have a better understanding, let us look at the molecular weight in relation to the viscosity that is used for this purpose.

FLOW CONTROL
5-50 mPaS

SLIP/LEVELING
~ 100 mPaS

DEFOAMING
5000-50000mPaS

HAMMER FINISHES
>50000 mPaS

Diagram 7:Defferent molecular weight silicone used in different application

Due to its very high molecular weight compared to the slip and leveling additive, a silicone-based defoamer act as a heavy polymer that can't really migrate to the surface of the finishing coat in order to affect the inter coat adhesion. Silicone based defoamers will not give any slip property and this further proves that it will not surface to the top of the coating.

Non-silicone polymers normally can't beat the surface tension reduction ability compared to silicone polymers but they have advantages on having a better limit compatibility than the Polysiloxane. Thus it will have better defoaming and anti-foam effect but more difficult to incorporate. Therefore higher sheer force need to be applied in order to ensure no crater is obtained. However this factor still depends on the concentration of the solution.

Some terminologies that involve defoamers are defined below:

Defoaming - (destroy)

Defoaming performance of a defoamer is determined by how fast a defoamer can foam in a liquid system. Faster defoaming ability is desired by most paint formulators.

Deaeration -

De-aeration is the process of moving the foam from the inner layer of the paint to the surface of the liquid. Foam only can be destroyed on the surface of the liquid and a faster de-aeration property is desired by most formulator.

Anti-Foam -

Anti-foam is referring to a defoamer that has the ability to prevent foam formation or suppress the bubble formation after the system has been agitated. Less foam formation after the agitation is a good anti-foam defoamer and this is also the most desired performance that most paint formulator wanted.

8. Defoamer Testing Method

Defoamers need to be carefully selected to suit certain resin system. Usually, the most direct method to choose a defoamer is by incorporating it into the system and apply it to see the desired effect. If the result obtained, served its purpose as a defoamer, then we will proceed with other properties tests. The other tests are cratering, gloss influent in final coating, on line test and so on in order to ensure that it can be used in the formulation.

Here, we recommend a method that we can make a good comparison between a few defoamers simultaneously. The purpose of this method is to ensure that we are getting the best defoamer as well as de-aeration effect for a particular system. This test is also quite easy to carry out.

Requirements : Red Devil / TOUCH TC-0188 Shaker
High Speed Mixer
Glass Jars (100ml)
Polyester Foil
Applicators

a) For Normal Solvent based system

Procedure

Fill the glass jars to a certain level (not more than half) with the coating system and defoamers. Make sure that the level is almost the same. Mark the top level with a marker. Put the glass jars into the shaker. It also can be carried out by using a High Speed Mixer but make sure that the time and the speed are the same for each separate sample. However, TOUCH TC-0188 shaker is more preferable as we need to compare those samples in accurate dispersing time and as well as same sheer force in order to judge more precisely the defoaming and de-aeration properties.

Result

Observation

i) Defoaming effect comparison

Immediately after shaking or mixing, mark the increased foam level. Leave the glass jars aside and record the foam level over 1 minute, depending on how fast the foam disappeared. The sample with the lowest foam level will indicate the best defoamer among the samples that you have been tested. However, for resins with low viscosity, the foam level is unclear after it is taken out from the shaker making it difficult to determine the level of foam. Thus, we need to look at the tested samples on how much foam is trapped on the surface and during this observation time, the one with the least foam will be the best defoamer for the system.

ii) De-aeration effect comparison

De-aeration is the process of moving the foam from the inside of the liquid to the surface of the liquid. So, in order for us to judge the de-aeration property, we observe at the entrapment of micro-foam that still maintained inside and on the surface of the liquid. The least entrapment over a period of time will have the best de-aeration. However, please take note that a good de-aerator does not mean that it will be a good defoamer.

iii) Anti-foam effect comparison

Anti-foam is referred to material that has the ability to prevent foam formation or suppress the bubble formation after the system has been agitated. Based on the test conducted above, we will also be able to see the anti-foam performance of a defoamer. Immediately after the shaking or mixing, observe the quantity of foam generated on the surface. The more foam generated means less anti-foam performance. Thus, a good anti-foam material will be able to prevent foam formation as much as possible after agitation.

iv) Side effect comparison

As mentioned earlier, defoamer will gives some side effects due to it incompatibility with the paint system in order to be an effective defoamer. Due to it lower surface tension, most of the time it will change the leveling performance of the system as well as creating crater problems. To check the side effect, apply the selected defoamer system on polyester sheet with an appropriate thickness of an applicator. Observe the leveling performance as well as crater formation.

Final Stage

A selected defoamer will need to go through the real application for final confirmation of its performance.

b) For water based emulsion paint systems

For water-based emulsion, the same way to pre-select a defoamer as described in normal solvent-based system above also can be used. The same procedure as mentioned in normal solvent-based can be applied and the same observation can be seen to determine the defoaming, deaeration and anti-foam performances.

Please see diagram 8 for illustration of the observation.

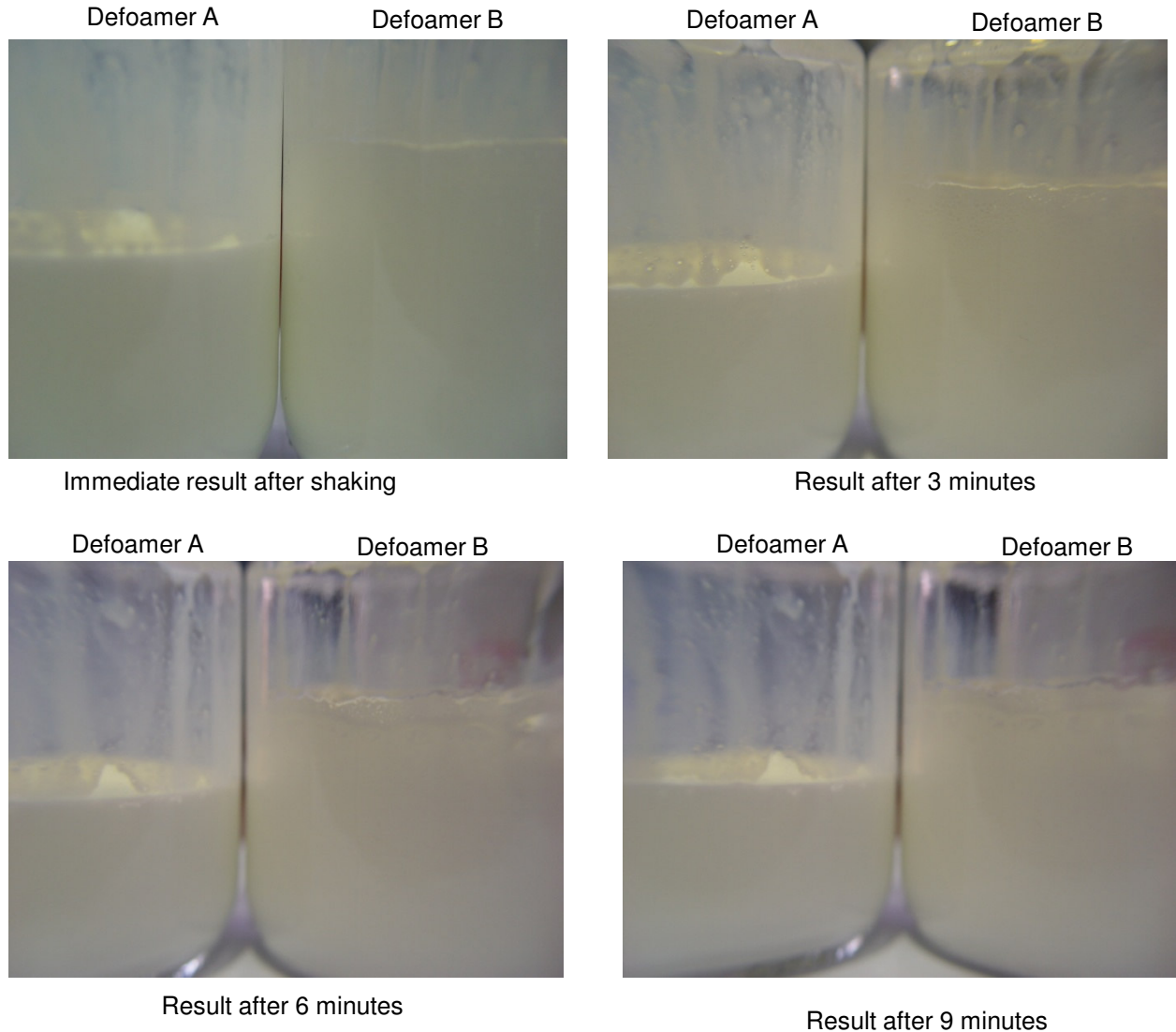


Diagram 8: Selection of defoamer on water based emulsion where defoamer A is much better than defoamer B on anti-foam and defoaming effect

However in water-based system, due to the system have high surface tension and this will result in easy foaming and foam is always a problem to be solved. The defoamers selected have to be effective in the pre-mix stage as well as in the final let down stage. Furthermore, in the formulation of emulsion, it involves thickener where the rheology of the paint is rather higher. Thus in such conditions, after the above pre-selection, full set real testing is needed, start from pre-mix, after mix and later real application by roller or brush on a big panel.

Water-based defoamers for emulsions are normally recommended to divide the addition of defoamer in to two steps. 40-50% of the total amount required defoamer is needed in the pre-mix stage and the rest should be added in the let down stage. Most defoamers for emulsion paints, are not stable under high shear force, they become more compatible to the system and they can not perform as a defoamer anymore. Thus, they need to be added again in the let down stage in order to boost back the defoaming performance in the system.