CHARPER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Types of Surfactants

Surfactant or surface active agent is a chemical substance which is used to reduce the surface tension at the 2 interfaces such as liquid-gas interface, liquid-liquid interface, liquid-solid interface, and gas-solid interface. It consists of 2 parts; hydrophobic part (tail group) and hydrophilic part (head group). Surfactant can be classified into 4 categories depended on characteristic of head group (Gale Cutler *et al.*, 1987).

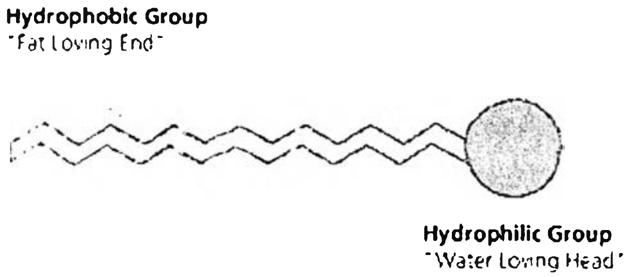
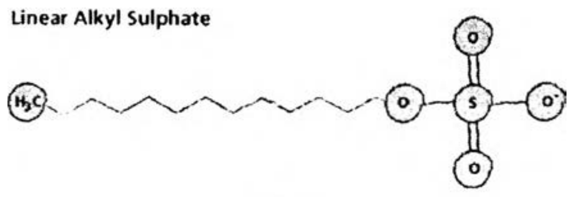


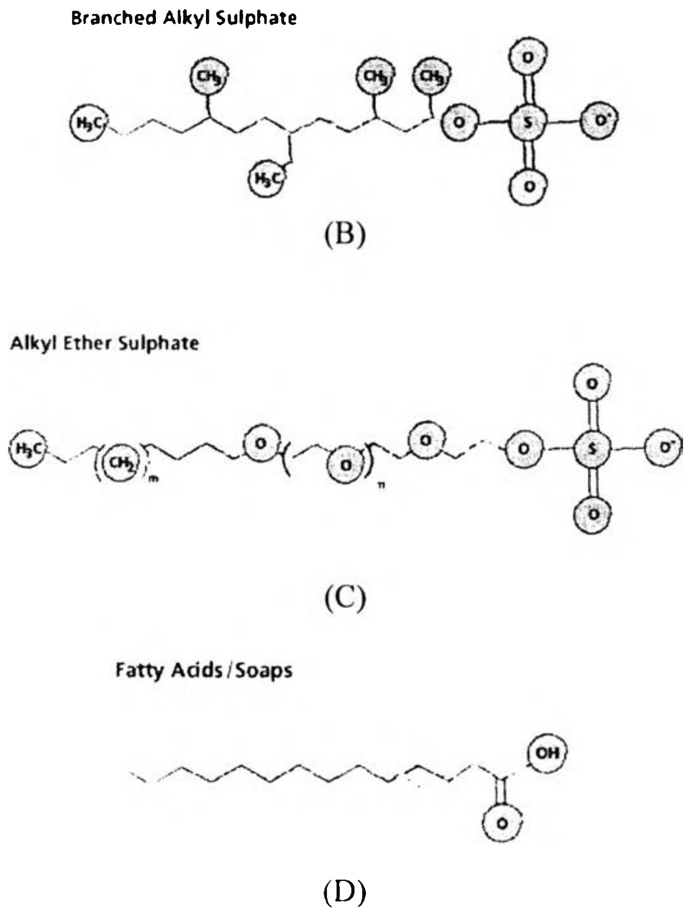
Figure 2.1 Structure of surfactant.

2.1.1 Anionic Surfactants

Head group contains negative charge. It is effectively for particulate soil removal. The examples of this type are



(A)



Branched Alkyl Sulphate

(B)

Alkyl Ether Sulphate

(C)

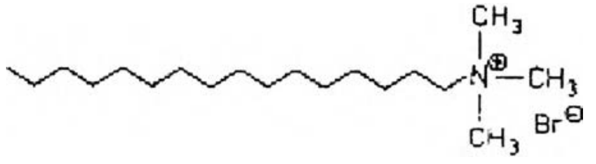
Fatty Acids/Soaps

(D)

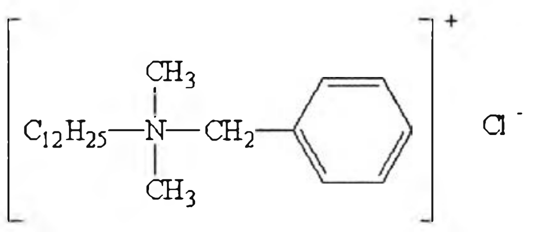
Figure 2.2 Anionic surfactants: A) Linear Alkyl Sulphate, B) Branched Alkyl Sulphate, C) Alkyl Ether Sulphate, and D) Fatty Acids/Soaps.

2.1.2 Cationic Surfactants

Head group contains positive charge. It is effectively for oily soil removal. The examples of this type are



(A)

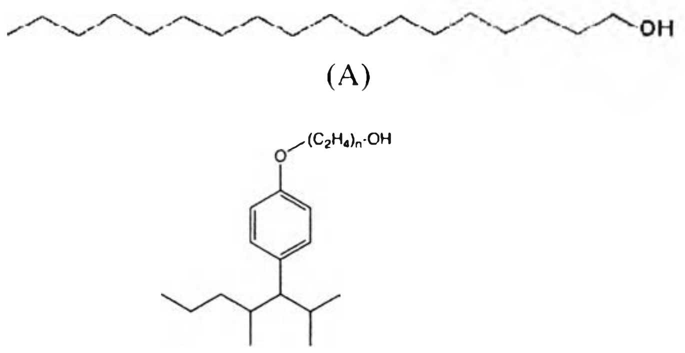


(B)

Figure 2.3 Cationic surfactants: A) Cetyltrimethylammoniumbromide (CTAB), and B) Benzalkonium Chloride.

2.1.3 Nonionic Surfactants

Head group does not contain electrical charge. It is effectively for grease removal. The examples of this type are



(A)

(B)

Figure 2.4 Nonionic surfactants: A) Octadecyl alcohol (Stearyl alcohol), and B) Nonoxynol.

2.1.4 Zwitterionic Surfactants

Head group can be negatively charged, positively charged, or no charge) depending on the acidity or pH of the water. It is effectively for high concentrations of electrolytes, acids and alkalis.

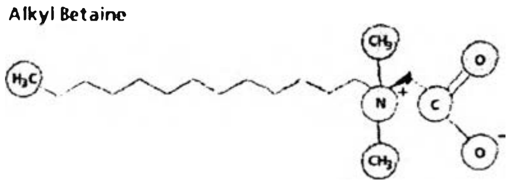


Figure 2.5 Zwitterionic surfactant.

2.2 Classification of Soils

There are many types of soil in detergency study.

2.2.1 Oily Soils or Water-insoluble Liquid Soils

Such as hydrocarbons, saturated or unsaturated fatty acids, and ester of fatty acids and alcohols. They are very hydrophobic liquid. So they do not dissolve or mix with water.

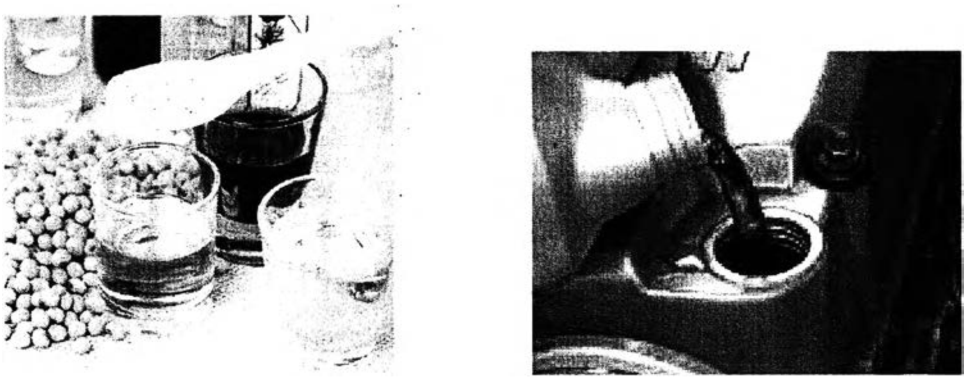


Figure 2.6 Oily soils.

2.2.2 Particulate Soils or Solid Soils

Such as clay, alumina, silica, iron, dust, metal oxide and carbon black. They have several properties which affect the detergency such as size, shape, and surface geometry of soil.

Figure 2.7 Particulate soils.

2.2.3 Stains

Such as coffee, tea, blood, ink, and fruit juices stains. They can form chemical or physical bond with substrate and become difficult to remove. So the substrate can be destroyed by this type of soil.

Figure 2.8 Stains.

2.3 Adhesion of Soil to Fabrics

2.3.1 Mechanical Bonding

Dirt in inter-yarn capillary system.

2.3.2 Hydrogen Bonding

Clays and other polar soils to hydroxyl groups in cellulose fabric.

2.3.3 Electrical Forces

Both fabric and particulate soil are similarly charged. But polyvalent cations can cause the attachment between particulate soil and fabric.

2.3.4 Oil Bonding

CH_2 group interaction between particulate soil and fabric.

2.4 Cloud Point and Krafft Point

Cloud point and krafft point are the unique property of nonionic and anionic surfactant, respectively. They indicate the temperature at which the solubility equals the critical micelle concentration (CMC). It means that at this temperature surfactant solution begins to separate into two phases (becoming cloudy) as shown in figure 2.9. These properties are important to determine the storage stability of the surfactant solution.

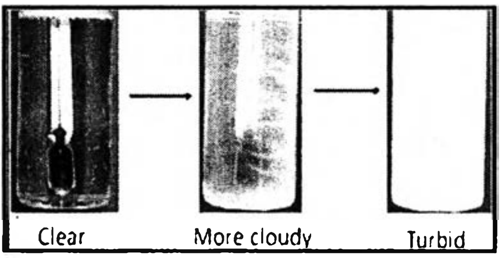


Figure 2.9 Cloud Point characteristic.

2.5 Surfactant Adsorption

This process can be used to describe how the amounts of surfactant adsorbed onto a solid-liquid interface depend on these factors: 1) the nature of the structural groups on the solid surface 2) the molecular structure of the surfactant being adsorbed 3) the environment of the aqueous phase such as pH, electrolyte content (Rosen, 1989). The general adsorption isotherm of surfactants can be divided into 4 regions. Four-regime isotherm was typically observed for adsorption of ionic surfactant on oppositely charged solid surface and adsorption of non-ionic surfactant on silica surface (Paria, 2004). In the below figure shows the amount of surfactant adsorbed on the surface and the equilibrium surfactant concentration in log scale.

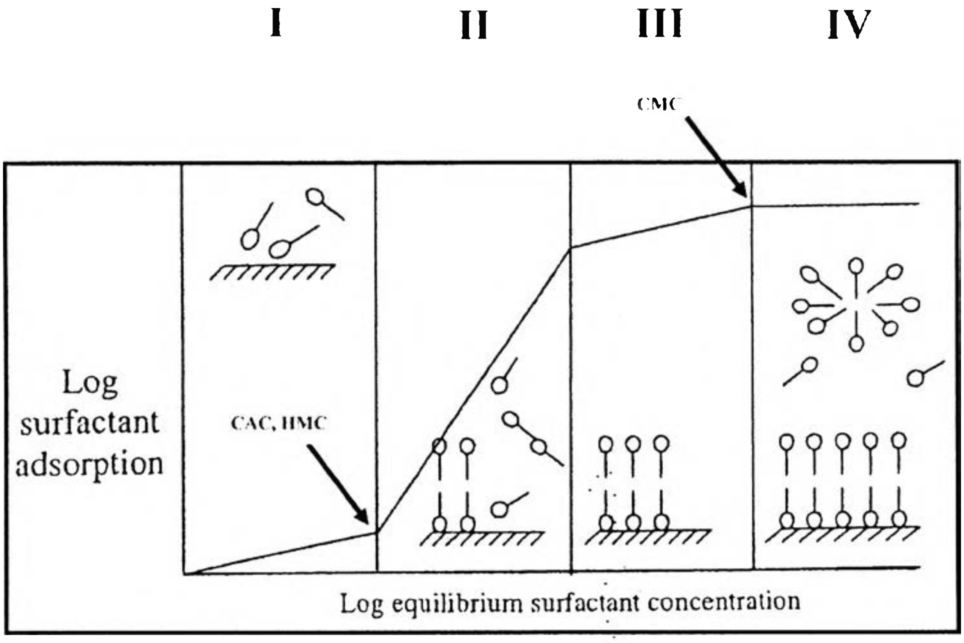


Figure 2.10 Four- regime adsorption isotherm of surfactant.

Region I: As in this region, the concentration of adsorbed surfactant monomer is quite low. Therefore, the interaction between each surfactant ions does not occur. The mechanism of adsorption is occurred from the electrostatic interaction (attraction) between head groups of ionic surfactants and charged surface or hydrogen bonding between surface and proton acceptors in head groups of nonionic surfactants. This region can also be called Henry's law region, it shows the linear relationship between the surfactant equilibrium concentration and adsorption density (Ogino *et al.*, 1992).

Region II: The formation of monolayer (hemimicelles) or bilayer (admicelles) on the surface is occurred due to hydrophobic bonding between hydrocarbon tails of surfactant and the surface (Tabatabal *et al.*, 1993). The isotherm slope is sharply increased when compared with region I. The transition point from region I to region II is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC). There are some residual spaces for further adsorption of surfactant.

Region III: In this region, the slope of adsorption isotherm decrease relatively to the slope in region II, this effect occurs from the increasing of adsorbed surfactants on the surface and then the surface become similar charge to the surfactant and the surface being to repel the surfactant ions.

Region IV: In this region, the surface becomes saturated with adsorbed surfactant and then the micelle formation will be occurred which results in a plateau region (Tabatabal *et al.*, 1993). This region, surfactant adsorption becomes nearly constant with increasing surfactant concentration. The transition point from region III to region IV is called the critical micelle concentration (CMC). At sufficiently high concentration of surfactant molecule in aqueous solution, Micelle will be formed (Micellization) as shown in figure 2.11

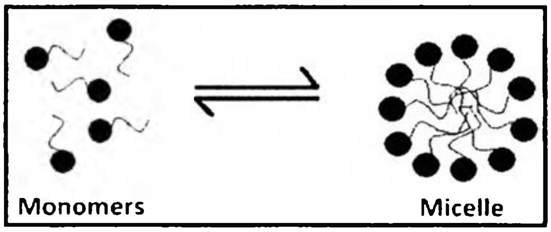


Figure 2.11 Micellization.

CMC is important characteristic of each surfactant in order to affect some physical properties of the solution such as surface tension and solubilization. These properties can also be used to indicate the cleaning performance. At lower CMC, it means less surfactant is needed to saturate interfaces and form micelles. As can be seen in figure 2.12, at very low concentration (1st section) of surfactant only slight change in surface tension is detected. For the 2nd section, after surfactant concentration is increased, the surface tension will be decreased. The last section shows that surface becomes fully loaded, no further change in surface tension.

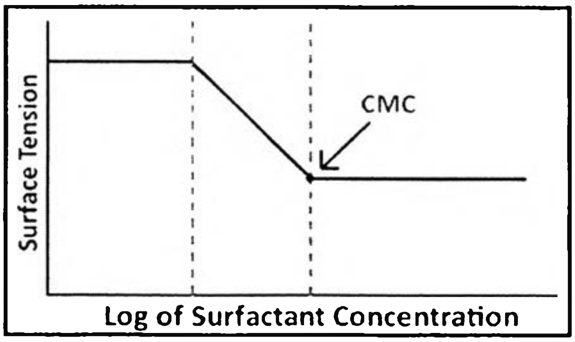


Figure 2.12 Surface tension vs. Surfactant concentration.

2.5.1 Electrical Double Layer

The surface of particle acts as the electrode via the charges on its and the solution is consisted of only electrolyte. The particles dispersed in the solution are counterbalanced by opposite charges of electrolyte in surrounding solution. So the attraction between charged surface of a particle and ions in the surrounding solution will be occurred. The electrical double layer is formed as in Figure 2.13

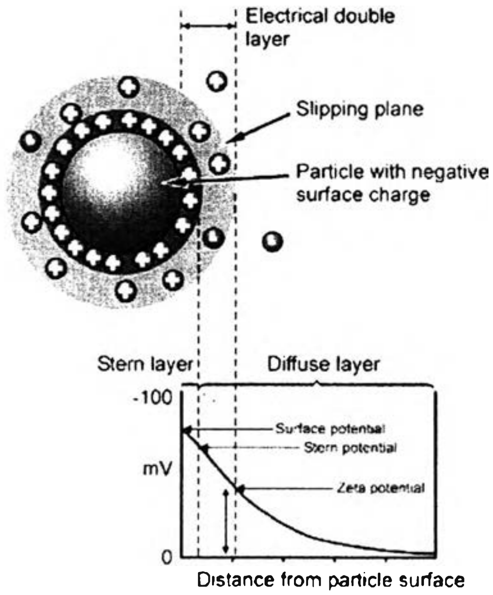
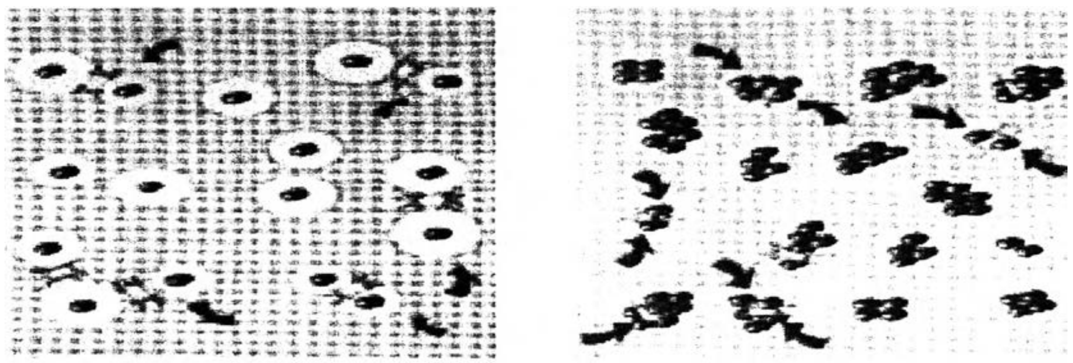


Figure 2.13 The electrical double layer around a particle with negative charges and electrical potentials surrounding the particle.

2.5.2 Zeta Potential

Zeta Potential (ζ) is the value of electrical potential difference between the surrounding solution and the layer of solution which attached to the dispersed particle. It can be used to indicate the charge stability of colloidal dispersions by applying an electric field across the liquid suspension and measuring their average velocity via the mobility of particles. For high value (positive or negative) of zeta potential, it means that the colloidal dispersion system is quite stable or disperses well while low value (positive or negative) of zeta potential or approach zero means that the colloidal dispersion system tends to aggregate as in figure 2.14.



(A) (B)

Figure 2.14 A) Particle disperses well and B) Particle aggregation.

The factors affect the zeta are the changing in the pH of solution, the conductivity of the medium, and the concentration of a particular additive in contact with the molecules. At low pH, the solution consists of positive charge from H^+. Therefore, the zeta potential tends to be positive value. At the isoelectric point which has balancing in positive and negative charge, so the zeta potential tends to be zero. In case of high pH, the zeta potential tends to be negative value as show in figure 2.15.

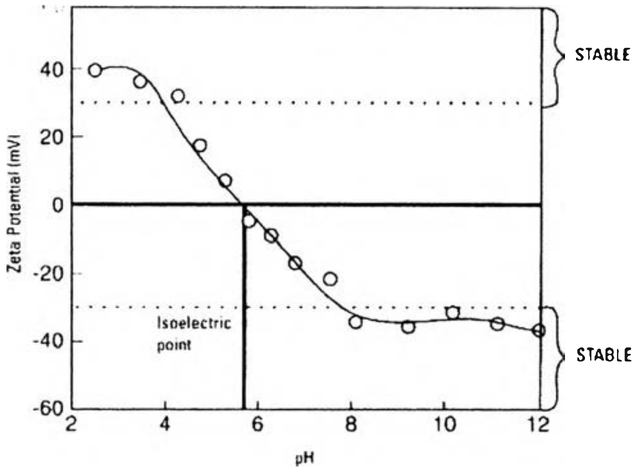


Figure 2.15 A plot of the zeta potential measured as a function of pH.

2.6 Mechanism of Oily Soil Removal

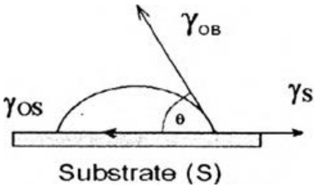
There are several mechanisms in oily soil removal. However, the three primary mechanisms; roll-up, emulsification, and solubilization were well accepted (Verma *et al.*, 1998; Rosen, 2004)

2.6.1 Roll-up Mechanism

Roll-up or roll-back mechanism is complete detachment of oily soil from substrate. This mechanism can remove oil droplet with two processes. First, an increase in the contact angle between the oil droplet and the substrate due to reduce in interfacial tension (IFT) between oil and water. Second, the occurrence of the repulsion force between head group of surfactant.

2.6.1.1 The Increased Contact Angle Process

This process can be explained by Young's equation which is as follow:



$$\cos\theta = \frac{\gamma_{SB} - \gamma_{SO}}{\gamma_{OB}}$$

Figure 2.16 The contact angle between an oil droplet and substrate in bath (surfactant solution).

When surfactants are present in the bath (B) or surfactant solution, they will adsorb at two interfaces. First interface is interface between substrate and bath (SB). Another is interface between oily soil and bath (OB). As the result, the interfacial tension (IFT) between the substrate and the bath (γ_{SB}) and that between oily soil and bath (γ_{OB}) are reduced causing the decrease in cos θ and the increase in θ, resulting oily soil detachment from substrate. However, this mechanism will be accomplished when the contact angle is more than 90 °. The higher contact angle, the soil is more easily removed (Broze, 1994). If the contact angle is 180 ° (cos θ =1), which means that the soil will be spontaneously completely removed. If the contact angle is between 90 ° and 180 °, the soil must be removed by hydraulic currents in the bath (Figure 2.17 In contrast, if the contact angle is less than 90°, the soil will not be completely removed which there is some part of the soil remaining in the substrate. To remove the residual soil, mechanical work or some mechanical (e.g. solubilization) will be used.

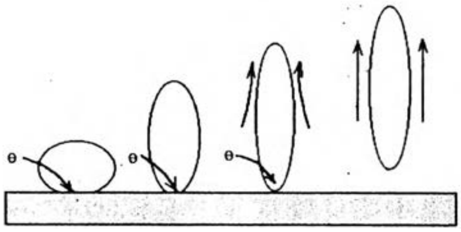


Figure 2.17 Roll-up mechanism shows the complete removal of oil droplets from the substrate by hydraulic currents when $\theta > 90$ °.

2.6.1.2 Surfactant Head Group Repulsion Process

After the surfactants adsorb at substrate-bath interface (SB) and oily soil-bath interface (OB), the head group of surfactants which adsorb at substrate-bath interface repulsing with the head group of surfactants which adsorb at oily soil-bath interface. From this repulsion, the oil droplet can be raised from the substrate. (Figure 2.18)

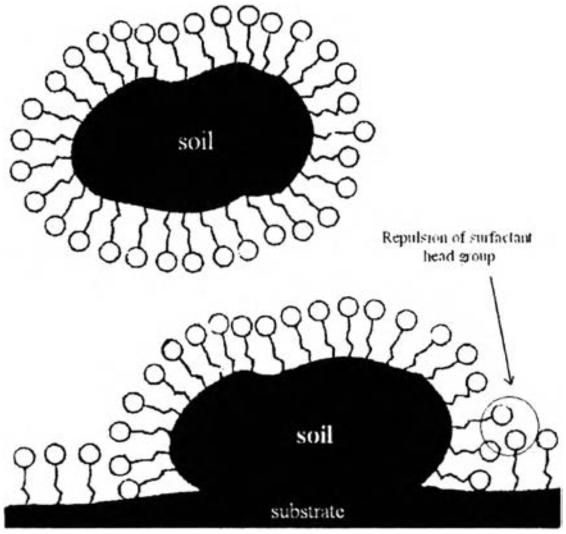


Figure 2.18 Repulsion force of surfactant head group.

2.6.2 Emulsification Mechanism

Emulsification, or snap-off, or necking mechanism, will take place when the contact angle between the oily soil droplet and the substrate is less than 90°. The principle of this mechanism is same a roll-up mechanism but the difference is the contact angle between the oil soil droplet and the substrate. Nevertheless, the disadvantage of this mechanism is some residual soil remaining on the substrate since the soil/bath interfacial tension is decreased, but the substrate/bath interfacial tension is not change substantially (Figure 2.19).

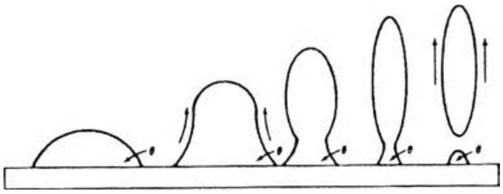


Figure 2.19 Emulsification mechanism shows partial removal of oil droplets from substrate θ < 90 ° (Rosen, 2004).

2.6.3 Solubilization Mechanism

Solubilization, or oil uptake capacity, is oil adsorption inside the core of the surfactant micelles. The roles of this mechanism are; (1) removal small amount of residual oil which cannot be removed by roll-up or emulsification and (2) prevention the oily soil from redeposition on the substrate. The solubilization depends on several factors, such as nature of oil and surfactant, surfactant concentration, electrolyte concentration, and temperature. The solubilization will substantially occur when the concentration of surfactant solution are above the critical micelle concentration (CMC) where surfactant will form micelles. The capacity of solubilized oil in the micelle core depends on the chemical structure of the surfactant, surfactant concentration, shape of the micelles and temperature. When the surfactant concentration is low, the small amount of oily soil can be solubilized. On the other hand, at high surfactant concentrations (10-100 time the CMC), large amount of oily soil can adsorb in the micelle core which is similar to microemulsion formation (Schwartz, 1972). The difference between solubilization and emulsification is the thermodynamic stability of keeping all the oily soil from redepositing on the substrate which the emulsification cannot prevent all the redeposition of the oily soil on the substrate. An important of solubilization is not only in detergency aspect but also in polymerization, waste water treatment, separation of materials, etc.

Figure 2.20 Solubilized oil in surfactant.

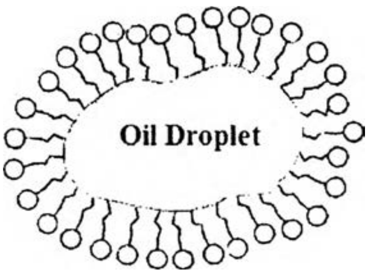


Figure 2.21 Emulsification of oil droplet.

2.7 Mechanism of Particulate Soil Removal

The particulate soils always present with the other types of soil such as oily and greasy soil. The particulate soils contribute to the toughness of the soil deposit, and the grease acts as cement, binding the particle together. The presence of to oily and particulate soil also affects the detergency process, especially soil removal. These complications depend on location of oil on particulate soil and fabric, conditions of soiling and washing, nature of particulate soil and fiber, and characteristics of fabric (Utermohlen *et al.*, 1949). For the first step, just after wetting is to attack the oily-greasy component. The particulate soils are then made available. Adding of anionic surfactant onto the liquid-solid interface will be the effective method in order to clean the particulate soils by decreasing of either interfacial tension or adhesion force between particles. For the mechanism of particulate soil removal, after anionic surfactants are added and then the surface is fully of negative charge. The electrostatic repulsion between adjacent particles is occurred. So the particles will be removed from the surface of fabric and suspend in the solution.

2.8 Detergency

Detergency is ability of a detergent to remove dirt (soil) from a surface via several mechanisms of surfactants which adsorb on the surface. The surfactant provides the special cleaning action by lowering interfacial tensions, emulsification, solubilization and charge modification in cleaning process in order to remove soil from substrate and prevent removed soil to redeposit (Tongcumpou *et al.*, 2003).

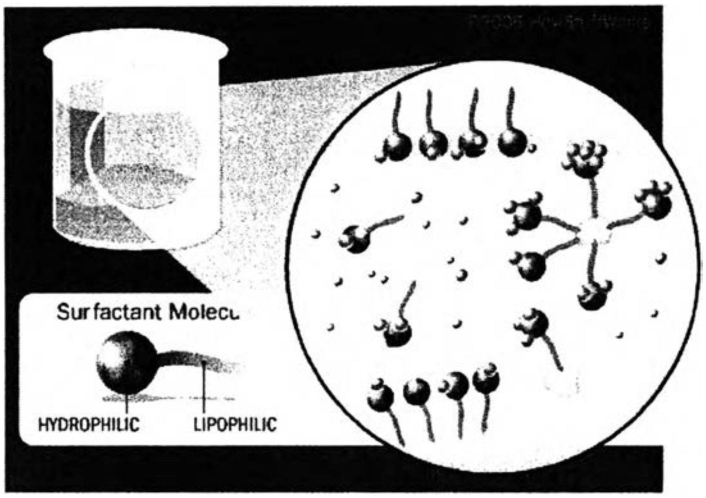


Figure 2.22 Removal of soil by surfactants from the substrate.

2.9 Factors Affecting Oily Soil Detergency

In the study of detergency formulation and performance, Linfield *et al.*, (1962) found that agitation speed, washing time and detergent concentration affected the detergency performance. Webb *et al.*, (1998) suggested soil removal from fibrous substrate was depended on the nature of the soil, the order of application, temperature and type of detergent formulation.

Recently, Germain (2002) conducted detergency experiment using a tergotometer and concluded that several factors such as agitation speed, temperature, and amount of detergent should be taken into consideration.

2.9.1 Surfactant System

Obendorf *et al.* (1982) found that the type of surfactant affected the detergency performance. An anionic detergent was found to remove oil from a cotton fabric more effectively than a nonionic detergent. As expected, anionic surfactants are effective on more polar fiber. However, there was little or no difference between two detergents in total oil removal from the polyester/cotton fabric.

The effects of nonionic surfactant and temperature on detergency efficiency were studied by Solan *et al.* (1988) for nonpolar soils (hexadecane, squalene, mineral oil) on polyester/cotton fabric. It was found that the maximum detergency efficiency corresponded with the phase inversion temperature (PIT). Moreover, they reported that the optimum temperature was increased when the degree of ethoxylation of the surfactant increased.

The effect of ethoxylation numbers in nonionic surfactant to soil removal was also studied by Wormuth *et al.* (1991). They found that the oily soil removal was influenced by the ethoxylation numbers in nonionic surfactant because when the ethoxylation numbers of the $C_{12\text{-}14}$ alkylpolyglycol ether was increased, the solubilization power of surfactant decreased which resulting the decrease in oily soil removal.

The advantages of using surfactant mixtures were reported by Ogino *et al.* (1992). They found that mixed surfactant systems generally exert greater than single surfactant systems for enhancing of solubilization. However, this enhancement does not apply to all mixed system.

Generally, a surfactant mixture that can exhibit a low oil-water interfacial tension is considered to provide superior oily soil detergency. Verma *et al.* (1998) measured the oil-water interfacial tension for a mixed anionic/nonionic surfactant system (NaLAS/C12EO3 and NaLAS/C12EO7) as a function of temperature and time. The oil-water interfacial tension was found to decrease as a function of time for all blends containing nonionic surfactant. It was proposed that the diffusivity of this hydrophobic fraction into phase lead to a decrease in oil-water interfacial tension.

The investigation conducted by Goel also gave similar results. Goel (1998) was reported the optimal EO moles (for maximal detergency) showed a monotonically increasing trend with increasing ratio of nonionic to anionic concentrations for a fixed level of electrolyte. The optimal EO moles also increased with increasing level of electrolyte in the system. However, the effect of nonionic/anionic ratio was much stronger than the effect of electrolytes on the optimal EO moles.

In the same year, Goel investigated detergency performance at different ratios of nonionic to NaLAS concentrations. He found that the minimum value of interfacial tension was a function of EO moles in the nonionic surfactant. These minima were found to exhibit high solubilization of oily soil and related to corresponding the maximum in detergency.

In 2003, Tongcumpou *et al.*, found that the formulation of microemulsion by mixed surfactant system of sodium dioctyl sulfosuccinate (AOT, a surfactant of intermediate HLB), alkyldiphenyloxide disulfonate (ADPODS, very hydrophilic surfactant), and sorbitan monooleate (Span 80, very hydrophobic surfactant) with motor oil and hexadecane can be considered as temperature- insensitive supposed by the results of Salager *et al.* (1979) and Anton *et al.* (1992). And she found that interfacial tension (IFT) values under supersolubilization (SPS) conditions were not substantially worse than under optimal conditions in a Winsor type III system (middle phase). In other words, quite low IFT can be attained without formation of a middle phase supposed by the results of Wu *et al.* (2000). In addition, the supersolubilization region was found to give oil removal almost as high as that in the middle phase region. Besides, she found that her microemulsion formation required fairly high salinity (16 wt %) to achieve the supersolubilization condition or optimum conditions that it is not practical for real application.

In 2005, Tongcumpou *et al.*, found that, for her microemulsion formulation, the oil removal in the rinse step was almost as high as that in the wash step for both supersolubilization and Winsor type III region. Because during the wash step, the spreading effect can occur supposed by other results (Thompson, 1994; Healy *et al.*, 1976)

In addition, Korphol *et al.* (2004) found out a mixed surfactant system of 1.5 wt% ADPODS, 5 wt% AOT, and 5 wt% Span 80 that exhibited a Winsor type III microemulsion at a low salinity of 2.83 wt%. With this selected formulation, detergency performance increased with increasing active surfactant concentration.

2.9.2 Nature of Oil

Scott (1963) found that the presence of polar oil enhanced removal of nonpolar oil. Before aging, squalene was easier to remove when it was in a mixture rather than when it was present as a single soil. However, the effect of mixing on the removal of squalene is reversed after aging.

There were a number of research works about polar/nonpolar soils removal (Gordon, 1967; Powe, 1963; Morris *et al.*, 1982). They conducted that residual oily soil contains a greater percentage of nonpolar components than fresh oily soil. Polar soils tend to be more easily removed in an aqueous detergent system.

Kissa (1987) claimed oil viscosity affected oil removal, the oil with lower viscosity was usually removed more rapidly from the substrate than one with a higher viscosity. Interestingly, the viscosity of the emulsion of used motor oil and the aqueous detergent solution was found to be five times higher than that of the original used motor oil.

The effect of polar soil components on the phase inversion temperature and optimum detergency conditions was also studied by Raney and Benson (1990). They proposed that the snap-off of the oil drops was resulted from the interfacial tension reduction at the soil/water interface, thus influencing the removal of nonpolar/polar soil mixtures. It was also suggested that a minimum quantity of polar material in the soil might be necessary to attain a high soil removal.

Chi *et al.* (1998) found that highly unsaturated oily soil was easily oxidize upon aging resulting in increasing removal whereas saturated oils is relatively stable. In addition, they reported that aging made oils to penetrate deeper into the fabric and fiber structures resulting in removal more difficult.

2.9.3 Salt

Oil removal performance in the presence of electrolytes was reported by Webb *et al.* (1983). They found that, for the mineral oil, the removal time of the mixed system with 0.5 ml NaCl was about half that of the nonionic. They also found that an addition of a surface active compound having less active lead to a significant increase in the interfacial tension of the mixture and so adversely influenced the oil removal.

Moreover, detergent efficiency as a function of salt was observed to be independent on the temperature (Solan *et al.*, 1992). An optimum of detergent efficiency was obtained at optimum salinity 10 wt% NaCl which are favorable conditions for microemulsion formation.

The effect of temperature and salt concentration on detergency efficiency were investigated by Azemar *et al.* (1993). They concluded that detergency efficiency both with and without electrolyte increased with temperature in the same trends and reached an optimum. However, the optimum temperature for the maximum detergency efficiency was shifted toward a lower temperature as the electrolyte concentration increased (effect of salinity out).

2.9.4 Substrate

The performance relating to soil removal is influenced markedly by the nature of the substrate (Christ *et al.,* 1994). Recently, Chi (2001) investigated the effect of the substrate on the removal of oily soil and found it was higher for nylon than cotton or polyester. Squalene, a nonpolar hydrocarbon, was difficult to remove from polyester, a nonpolar substrate. On the other hand, cotton, a very polar substrate from polyester, a nonpolar substrate, might be expected to release oily soil fairly well in an aqueous detergent system, but this was not the case. Low removal of squalene from cotton was thought to be due to morphological characteristics of cotton that made oil difficult to be removed.

Soil removal from cotton fabrics that had been chemically modified by mercerization and carboxymethylation were studied by Obendorf (2001). It was proposed that the carboxymethylation changed the chemistry of the fiber by increasing the carboxyl group content, this structure changed was believed to reduce the amount of soil deposited in the lumen of fiber. In the mercerization was indicated that chemical accessibility and hydrophilicity of the fiber structure influence both soil deposition and soil removal of lipid soil.

2.9.5 Water Hardness

Hard water affects detergency in several ways. Incomplete soil removal normally occurs when hard water is used in detergency (laundering) (Tanthakit, 2009).

The presence of polyvalent cations, notably Ca^{2+} and Mg^{2+}, in the bath water is invariably detrimental to the cleaning process for a number of reasons (Rosen, 2004):

2.9.5.1 Adsorption of polyvalent cations onto the negatively charged substrate and soil reduces their electrical potentials, thus impeding soil removal and facilitating its redeposition. The detrimental effect attributed to this has been noted also in the detergency studied involving only nonionic surfactants.

2.9.5.2 *Polyvalent cations can act as linkages negatively charge substrate and negatively charged soil*, thus promoting soil redeposition. They can also act as linkages between the negatively charged hydrophilic groups of anionic surfactants and the negatively charged soil or substrate, causing adsorption of the former with their hydrophilic groups oriented toward the latter and their hydrophobic groups toward the bath. Adsorption with this orientation results in increases in the interfacial tensions at the substrate-bath and soil-bath interfaces, increasing in work of adhesion and impeding wetting and oily soil roll back.

2.9.5.3 *Adsorption of polyvalent cations onto solid soil particles* dispersed in the bath can reduce their (negative) electrical potentials and cause them to flocculate and redeposit onto the substrate.

2.9.5.4 At high polyvalent cation concentrations, the corresponding metal salts of anionic surfactants and other anions (e.g., phosphates, silicates) in the bath may precipitate onto the substrate. (Rutkowski, 1971) or produce other deleterious effects (Vance, 1969).

Prevention of soil redeposition can be done by adding of anti-soil redeposition agent such as Sodium carboxymethyl cellulose into the detergent. This agent can prevent the removed soil to redeposit back onto cleaned fabric by formation of barrier between suspended soil and cleaned fabric electrostatic repulsion for ionic surfactant and stearic hindrance for nonionic surfactants (Fong *et al.*, 1953).

2.9.6 Other Factors

In the study of detergency formulation and performance, Linfield *et al.* (1962) found that an increase in agitation speed, washing time or detergent concentration, resulted in increasing detergency performance to the maximum levels. They reported that the maximum detergency was obtained at around 150-170 rpm and around 15-20 min washing cycle.

Obendorf *et al.* (1982) reported both mechanical action and detergent concentration affecting the soil removal. An increase in either mechanical action or detergent concentration resulted in increasing removal of triolein, but its concentration in cotton fibers remained high.

In 1987, Raney *et al.* studied the correlation of PIT with detergency performance. The maximum detergency in ternary systems was found to occur when the temperature was near the PIT of the system composed of water, the surfactant and the hydrocarbon soil itself.

Webb *et al.* (1988) reported that builder is another influencing factor for enhancing the cleaning efficiency.