

CHAPTER II

LITERATURE SURVEY

2.1 High Density (Linear) Polyethylene

Linear polyethylene can be produced in several ways, including coordination polymerization of ethylene, and polymerization of ethylene with supported metal-oxide catalysts. Commercial production of polyethylene, using the second and third routes named, began 1957 and reached a volume 5 billion lb/yr in 1979 (Billmeyer, 1984).

2.2 Ink

Ink can be defined as a dispersion of pigments or dyes in a fluid carrier (vehicle). There are two types of inks available for the printing of commercial plastic packaging materials: ultraviolet curing printing inks and conventional inks. UV curable inks are usually used for printing on plastic closures (caps, lids, etc.) while conventional inks are used for both the screen and pad printing processes to print rigid plastic containers such as blow molded bottles.

Conventional printing inks are composed of pigments, binders, carriers, and additives. Organic and inorganic pigments give color and opacity to the ink and influence its fluidity. Binders, which are mostly low molecular weight polymeric resins disperse the pigments and retain them on the plastic surface after printing. The carrier is a liquid that provides fluidity for the ink and transfers the ink from the printing system to the plastic substrate. After application of the ink onto a surface, the carrier should evaporate quickly and

completely. Additives in the ink include waxes, surfactants, drying agents, and antioxidizing agents.

Conventional printing inks are classified as either solvent-based or water-based depending on the type of carrier. The carriers for solvent-based inks are solvents, solvent mixtures or water miscible solvents whereas water-based inks use water as the carrier, which could contain up to 20% alcohol (Gecol, 1998a).

It is essential that the ink wets the surface of the plastic to produce a uniform covering and to bond strongly to the surface during printing. There are a number of treatment processes used for plastic surfaces in order to increase the surface energy of the plastic and thereby enhance the wettability of the ink. These processes are chemical treatment, flame treatment, corona discharge, plasma treatment and ultraviolet treatment. Flame treatment is the most common process used to improve ink adhesion to molded polymer articles such as rigid plastic containers.

It is believed that flame treatment oxidizes the surface of the plastic and makes it more easily wettable. Flames contain excited species of O, NO, OH, and NH, which can remove hydrogen from the substrate surface; the oxidation that follows is thought to propagate by a free radical mechanism. The plastic surface is contacted for a period of less than 1 second with the oxidizing portion of the flame. The gas is burned using 10-15% excess air over the stoichiometric ratio in order to obtain an oxidizing flame with a temperature of 1090-2760 °C (Satas, 1986).

2.3 The Nature of Surfactants

A surfactant, surface active agent, is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of a system and altering to a marked degree the surface or

interfacial free energies of those surfaces or interfaces (Rosen, 1989). It is a polar compound consisting of an amphiphilic molecule, i.e. a molecule with a hydrophilic head attached to a long hydrophobic tail (Kouloheris, 1989). At a particular concentration (known as the critical micelle concentration, CMC) surfactant molecules become more favorable to form aggregates called micelles as shown in Figure 2.1. A surfactant can be placed in one of four classes depending on what charge is present in the chain-carrying portion of the molecule after dissociation in aqueous solution: anionic, cationic, nonionic, and amphoteric surfactants (Jakobi and Lohr, 1987).

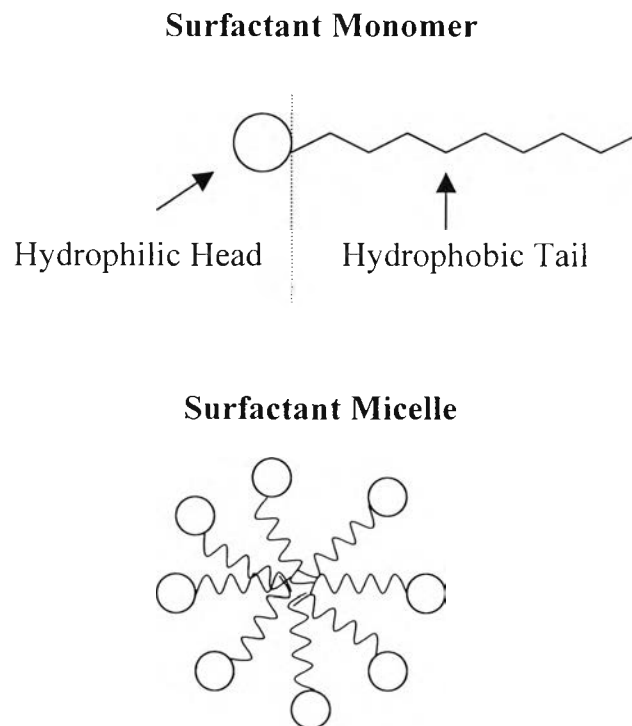


Figure 2.1 Surfactant molecule/ion and a representation of a surfactant micelle in a surfactant solution somewhat about the critical micelle concentration (adapted from Wilson and Clarke, 1994)

2.4 Mechanism of the Deinking Process

Deinking process, as suggested by Borchardt (1994), is fundamentally a laundering, detergency, or cleaning process. The term detergency, when applied to a surface-active agent, means the special property it has of enhancing the cleaning power of a liquid (Rosen, 1989). In general, cleaning consists essentially of two processes: (1) removal of the soil (ink) from the substrate (plastic surface), and (2) suspension of the soil in the bath (aqueous solution) and prevention of its redeposition.

2.4.1 Removal of Soil from Substrate

The mechanism of the removal of solid soil by aqueous baths depends on the nature of the solid soil (Rosen, 1989).

2.4.1.1 *Liquefiable Soil*

The first stage in the removal of solid soil is believed to be liquefaction of the soil. Penetration of the soil by surfactant (and associated water molecules) from the cleaning bath with resulting liquefaction may be a key process in the removal of this type of soil. In cases where penetration of the solid soil by surfactants or other additives does not occur, an increase in the temperature of the cleaning process may result in its liquefaction. The liquefied soil is then removed by the “roll-back” or “roll-up” mechanism in which the contact angle that the liquefied soil makes with the substrate is increased by adsorption of surfactant from the cleaning bath.

Figure 2.2 illustrates the situation of a liquefied soil particle adhering to a substrate in the cleaning bath. The work of adhesion of the soil for the substrate is given by the expression (Rosen, 1989)

$$W_a = \gamma_{SB} + \gamma_{LB} - \gamma_{SL} \quad (2.1)$$

$$= \gamma_{LB} (\cos \theta + 1) \quad (2.2)$$

and the contact angle by the expression

$$\cos \theta = \frac{\gamma_{SB} - \gamma_{SL}}{\gamma_{LB}} \quad (2.3)$$

where:

W_a = work of adhesion

γ_{SB} = surface tension of the substrate-bath interface

γ_{LB} = surface tension of the liquefied soil-bath interface

γ_{SL} = surface tension of the substrate- liquefied soil interface

θ = contact angle of the liquefied soil on the substrate

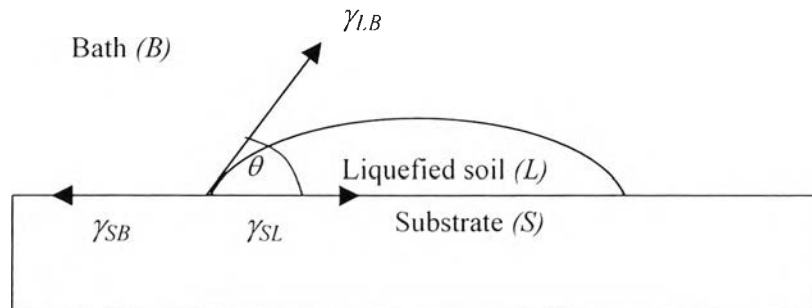


Figure 2.2 Contact angle at the bath-liquefied soil-substrate junction

When surfactants of appropriate structure are present in the bath, they will be adsorbed at the substrate-bath (SB) and liquefied soil-bath (LB) interfaces in such a fashion (i.e. with hydrophilic groups oriented toward the aqueous bath) as to reduce γ_{SB} and γ_{LB} , with consequent reduction in the work to remove the soil from the substrate. Reduction in γ_{SB} will also cause a decrease in $\cos \theta$ and an increase in θ , resulting in the observed roll-back of liquefied soil.

If the contact angle is 180° , the bath will spontaneously completely displace the liquefied soil from the substrate; if the contact angle is less than 180° , but more than 90° , the soil will not be displaced spontaneously but can be removed by hydraulic currents in the bath (Figure 2.3). When the

contact angle is less than 90° , at least part of the soil will remain attached to the substrate, even when it is subjected to hydraulic currents in the bath (Figure 2.4).

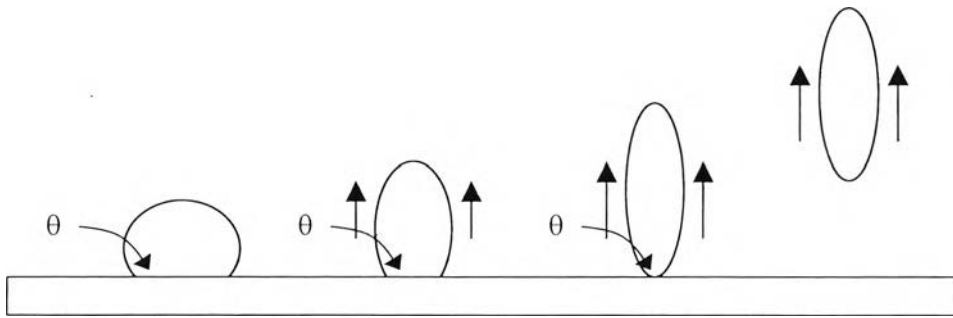


Figure 2.3 Complete removal of soil from substrate by hydraulic currents (arrows) when θ remains constant at $> 90^\circ$

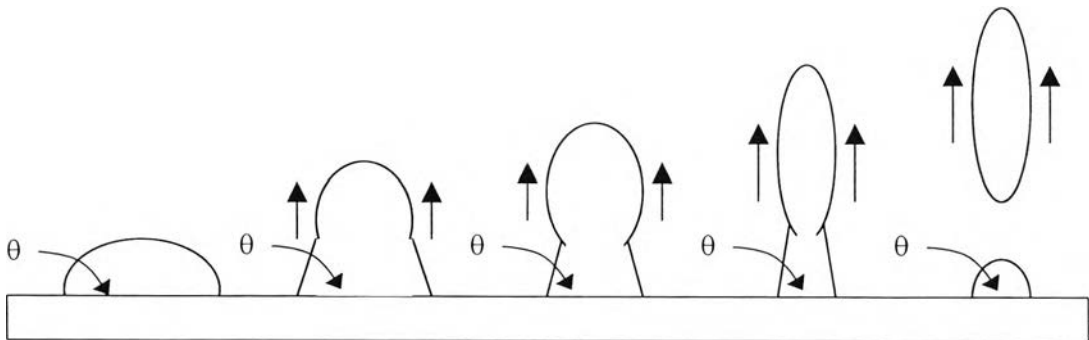


Figure 2.4 Rupture and incomplete removal of large soil from substrate by hydraulic currents (arrows) when θ remains constant at $< 90^\circ$. A small soil particle remains attached to the substrate

2.4.1.2 Particulate Soil

The adsorption of surfactant and other bath components at the substrate-bath and particle-bath interfaces causes a decrease in the work required to remove the particle from the substrate since the free energy change per unit area involved in this process is the work of adhesion W_a , given in this case by the expression

$$W_a = \gamma_{SB} + \gamma_{PB} - \gamma_{SP} \quad (2.4)$$

where:

W_a = work of adhesion

γ_{SB} = surface tension of the substrate-bath interface

γ_{PB} = surface tension of the particulate soil-bath interface

γ_{SP} = surface tension of the substrate- particulate soil interface

Adsorption of surfactants at these interfaces can result in a decrease in γ_{SB} and γ_{PB} , with a consequent decrease in the work required to cause removal of the particle from the substrate.

2.4.2 Suspension of the Soil in the Bath and Prevention of Redeposition

Suspension of the soil in the bath and prevention of redeposition are accomplished by different mechanisms, depending on the nature of the soil.

2.4.2.1 Liquefiable Soil

“Solubilization” has long been known to be a major factor in the removal of liquefied soil and its retention by the bath (Rosen, 1989). Solubilization is accomplished by Figure 2.5 (Baler, 1998). Firstly, surfactant molecules adsorb on the soil and substrate surfaces. Then the soils mix with surfactant molecules. The forming micelles desorb from the surfaces

with soil being held in the interior of the micelles. Finally, the micelles diffuse into the bulk of the solution (Borchardt, 1994).

The extent of solubilization of the liquefied soil depends on the chemical structure of the surfactant, its concentration in the bath, and the temperature. At low bath concentrations only a relatively small amount of liquefied soil can be solubilized. At high concentration of surfactant can accommodate a much larger amount of soil matter because micelles are formed under these conditions. With ionic surfactants, concentrations are generally not used much above the CMC (Rosen, 1989).

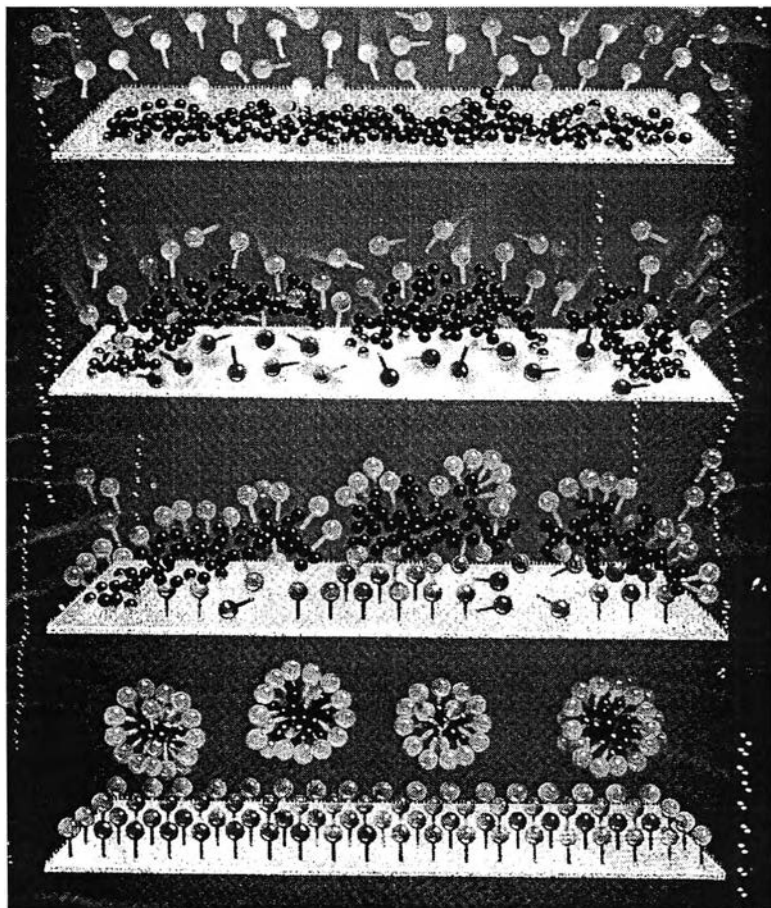


Figure 2.5 Detachment and dispersion of soil by the solubilization mechanism (adapted from Baler, 1998)

2.4.2.2 *Particulate Soil*

The formation of electrical and steric barriers is probably the most important mechanism for suspension of the particulate soil in the bath and prevention of redeposition. Adsorption of similarly charged surfactant molecules onto the detached soil particles prevents agglomeration of soil particles by reducing van der Waals attraction between them and by producing electrical and steric barriers to their close approach to each other.

2.5 **Related Research Work**

The pioneering work in deinking process was carried out by Scamehorn *et al.* (1997). The collaborative research group between the University of Oklahoma, the University of Tulsa, Kimberly-Clark Corporation, and other companies has developed an improved method of ink removal from plastic film to permit recycling of the material. The separating agents of choice were surfactants, which are biodegradable and nontoxic in comparison with organic solvents and bleaches.

The research program, approved by the National Science Foundation in the United States, developed a two-fold approach for solving the problem of deinking plastic films. Firstly, to determine the optimum conditions for utilizing aqueous surfactant solutions to remove inks, principally those of the widely used flexographic type, from polymer surface. Secondly, to develop modified inks that will maintain the required print quality and durability and are much easier to remove from plastic films than conventional inks.

Several types of analytical techniques to determine the effectiveness of deinking were developed by this program. These include an optical method for determining the extent of dye removal. This method used a Hunterlab Ultrascan Spectrophotometer for quantifying the amounts of residual inks remaining on clear film following deinking. Another analytical method used a

Coulter LS Series particle size analyzer for examining dispersed ink suspended in the aqueous wash solution

Lim and Teeters (1997) discussed the deinking of polyethylene packaging films printed with multicolor labels of commercial flexographic water-based ink using of aqueous solutions and alumina beads at pH 10. They also established a standard method for deinking and a method for quantifying ink removal. This experimental work shown that critical surface tension values for plastic films were obtained by measuring the contact angle of the plastic film using a variety of liquids and a Withelmy plate technique to determine the surface tensions of nine different inks. Attenuated total reflection (ATR) FTIR spectroscopy and an optical scanning method were used to quantify the amount of ink removal. It is well known that low surface tension liquids wet substrates that have higher critical surface tension values. They concluded that there is a relationship between the deinking of plastic film and the critical surface tension of the solid substrate. It was also found that higher pH solutions were required to deink plastic film having multiple layers of ink.

Gecol (1998a) observed the use of different surfactant solutions for the deinking of polyethylene plastic films printed with water-based ink by the flexographic process at various pH levels. Surfactants, in general, are environmentally innocuous compared to organic solvents. A back-scatter image of the surface containing both clear and printed parts of the plastic film was taken with a Scanning Electron Microscope (SEM) to view the surfaces layer by layer. Transmittance Electron Microscope (TEM) micrographs clearly indicated ink aggregates of approximately 2-5 μm in size in the re-extruded printed plastic film. The physical properties of plastic film after re-extrusion were also determined and compared with clear and printed plastic film. In her paper, she discussed the removal of water-based inks from plastic film using either water or selected surfactants with the use of porcelain beads (an abrasive material) under a variety of conditions and compared the degree of

deinking with that of clear, printed, and deinked plastic samples. The results of her research showed that deinking with only water were minimal at high pH values such as 11 or 12 since the binder in water-based ink is more soluble in water at higher pH. By adding abrasive material to the water, the deinking level at pH of 11 and 12 rose by a factor of approximately three. Furthermore, deinking with the use of surfactants at other pH levels indicated the relative effectiveness of surfactants in the deinking process. Finally, in her research she concluded that cationic surfactants are the only effective surfactants either below or above their CMC at various pH levels and anionic surfactants are the least effective surfactants, which is only slightly better than water for deinking.

Gecol (1998b) also conducted deinking tests on solvent-based printing inks from both commercial plastic packaging materials and plastic films made in her laboratory exhibiting individual colors (yellow, pink, rouge, green, gold, black, and violet) using surfactants under a variety of conditions. Several experiments were done to study the effectiveness of deinking on a mixture of polyethylene film printed with solvent-based inks. In addition, a scale-up deinking experiment was performed and the results showed that deinking of plastic film using surfactant solution is technically feasible. In her experiments it was also found that cationic surfactants are the most effective surfactants for the removal of solvent-based ink from plastic film and a solution pH of 11.5 or above is required for complete deinking. Finally, it was concluded that deinking of solvent-based inks requires more severe conditions, such as a very high pH and a more restricted choice of surfactant, than water-based inks.

Other work, which involved the removal of solvent-based ink, was done by Min (1999). Her work focused on the effectiveness of deinking high density polyethylene bottles printed with solvent-based ink. Three types of surfactants were used in her study, viz. Cationic, anionic, and nonionic

surfactants. ATR-FTIR spectroscopy and optical scanning method were used to determine the degree of deinking. Her results were in good agreement with the previous study of the deinking of polyethylene film (Gecol, 1998b). Cationic CTAB above CMC is the most effective surfactant for deinking at pH 12 with or without added abrasive. Pre-soaking time prior to mechanical agitation for 2 hours significantly increases the deinking level and decreases the shaking time needed for complete deinking. To increase the degree of deinking using nonionic surfactant (NP(EO)₁₀) above the CMC, pre-soaking in the surfactant solution for 48 hours prior to mechanical agitation is needed together with mechanical action in the presence of abrasive which help to detach the loosened ink from the plastic surface. But in Gecol's study (1998b) of the deinking of polyethylene film, only 2 hours shaking time was needed to obtain complete deinking with the use of nonionic surfactant. Anionic surfactant SDS was not effective for deinking even at high pH levels.