# CHAPTER II

# THEORETICAL BACKGROUND

## 2.1 Thickeners

A thickener is a substance capable of giving the required degree of viscosity to a print paste as for example starches and gums and which, in general, must be chemically inert to the other ingredients of the print paste. A thickener is made with one or more thickening agent [3].

The primary functions of a thickener are:

(1) To prevent spreading of the printed pattern on the fabric by counteracting the capillary forces of the fibres

(2) To act as a medium of transfer for the dye from the print paste into fibre.

Four significantly different approaches may be used to produce thickeners, using [4]:

- a low concentration of a polymer of relatively high molecular mass (r.m.m.),
- a high concentration of a material of lower r.m.m. or of highly branched chain structure,
- an emulsion of two immiscible liquids, similar to the emulsions used as cosmetic creams, or a foam of air in a liquid,
- a dispersion of a finely divided solid , such as betonite.

### 2.1.1 The Selection of Thickening Agents

In the selection of thickening agents, it is necessary to take into account requirements other than viscosity, which can usefully be classified in five categories [5]:

1. Print paste stability

The thickener must be stable and compatible with the dyes and auxiliaries to be used. The pH of the print paste must be considered, as some polymers, for example, sodium alginate, are only usable within a limited pH range and form gels when acids or strong alkalies are added. Hydrolysis of the polymer chain links may also be significantly accelerated by acid or alkaline conditions. In addition, most natural polymers are also biodegradable. The micro-organisms responsible for the degradation are present in the air, and thickeners provide nutrients and ideal conditions for their growth and reproduction. Enzymes are produced that break down the polymer, with a consequent and often rapid fall in viscosity. To avoid this hazard through cleaning of thickener containers and the addition of preservatives, such as formaldehyde or phenols (e.g. o-phenylphenol), are recommended.

2. Properties of the dried thickener film

Linear polymers are adsorbed more strongly than highly-branched polymers, and therefore show good adhesion. However, the linear polymers that are useful thickening agents have large numbers of hydroxyl or carboxyl groups along the chain. Natural polymers of this type form brittle films because of the substantial intermolecular hydrogen bonding that occurs.

3. Effect on color yield

Penetration is viscosity-dependent for any thickener, but some thickeners appear to restrain penetration more than expected on the basis of viscosity. This is so far starch-based thickeners, and has been attributed to their gel-like structure. In the case of printed pigments, the color yield may also be significantly affected by the transparency of the thickener-binder film and by any tendency of the thickener to promote or prevent aggregation of the pigment.

4. Ease of preparation

The times required to prepare thickeners, and the precautions to ensure that the pastes have satisfactory and consistent properties, are very different for different thickening agents.

Natural starches are cheap, but to burst the grains and obtain a proper dispersion required time or special equipment. It is also difficult to redisperse. The physical and chemical modification of starch, and of other natural polymers, has therefore become common practice in order to provide products that are disperse and, have more consistent properties (as a result of blending to a standard level)

5. Cost

It was common to look at the cost of the thickening agent itself and the cheapest materials were widely used, however; it is essential to look at many other aspects to decide which material will give the required quality at the lowest overall cost. The concentration to be used, cost of preparation, stability, print penetration, color yield can in total be more important than basic price of the polymer.

### 2.1.2 Classification of Thickening Agent [5, 6]

Thickening agent can be broadly divided into three main categories, namely:

1. Natural products

Nature has provided large quantities of many polymer that are soluble or dispersible in water to give viscous pastes. Each plant species synthesizes one or more polysaccharides from the constituent sugars, and some plants produce them in purity and in quantities that make extraction very simple.

The sources of useful polysaccharides may be classifies as

- plant seeds which contain starch or similar products as a good reserve and may be cultivated for industrial use (guar, for example)
- seaweed, the only source of alginate
- plant gum-exudates, of which the best known are gum arabic and gum tragacanth
- the cultivation of selected micro-organisms, carried out under controlled conditions, converting waste carbohydrate into useful polymers, such as xanthan
- cellulose pulps, from which cellulose ethers are produced.

The polysaccharides may be homopolymers, composed entirely of one sugar unit, or heteropolysaccharides with or more hexose or pentose units assembled in a relatively ordered sequence. The polar side-groups may all be hydroxyls, as in starch, cellulose and guar gum, or they may include carboxyl groups as well, as in alginate and gum arabic. Less frequently, other water-soluble groups are found.

An equally important structural feature is the degree of chain branching, which affects the solubility, film and viscosity properties. Long, linear polymers give high viscosity at low solids contents, but the viscosity falls with increasing shear. Highly-branched polymers, such as amylopectin, are more soluble and are required in higher concentrations for a given viscosity, but show less change under shear.

The interaction of polysaccharide and water is complex, but important. In liquid water, swelling occurs as accessible segments of the polymer become fully hydrated and move away from adjacent chains. The kinetic energy of these segments then causes the rupture of some intermolecular hydrogen bonds and more chain segments can be solvated. Where polymer chains are well-ordered and bonded, however; especially in crytalline region, the structure will be maintained and such insoluble units may be linked together, forming gel.

If enough of the intermolecular forces can be broken, the polysaccharide goes into colloidal solution. A principal feature of colloidal solutions is their instability. For example, starch paste obtained by heating tend to form gels on cooling, as new intermolecular bonds are formed. The intermolecular bonds are of two types: hydrogen bonds and hydrophobic bonds. A proper understanding of the latter depends upon the recognition of the structure of water and the effect of solutes on that structure.

2. Chemically modified natural products

These thickening agents can be classified as:

(a) Carboxymethyl starch, Hydroxyethyl starch

(b) Water-soluble cellulose derivatives, cellulose ethers, for example, these cellulose ethers are the most widely used water-soluble polymers in the surface coating industry, the most common types are:

- sodium carboxymethyl cellulose (SCMC)
- sodium carboxymethyl-2-hydroxyethyl cellulose

- 2-hydroxyethyl cellulose (HEC)
- methyl cellulose (MC)
- 2-hydroxypropyl methyl cellulose (HPMC)
- 2-hydroxyethyl methyl cellulose (HEMC)
- 2-hydroxybuthyl methyl cellulose
- 2-hydroxyethyl ethyl cellulose (EHEC)
- 2-hydroxypropyl cellulose (HPC)

(c) Gum derivatives, such as Meyprogum, Indalca Nafka crystal gum

3. Synthetic-polymer thickeners

This group of thickeners is derived from petrochemical sources and most of the available commercial products are manufactured by using the addition polymerization technology of acrylic monomers.

Synthetic-polymer, namely, polyvinyl pyrolidone, polyvinyl acetate and polyethylene oxide, are thermoplastic polymers which give preudoplastic solution and confer varying degree of thixotropy to formulation. As they are fully synthetic, a wide range of molecular weights is possible, which controls the viscosity of each system.

Copolymer of acrylic acid has been used more widely. Relatively low cost copolymer of, for example, methacrylic acid and ethyl acrylate, gives low viscosity dispersion in water, in which the molecules are randomly coiled.

### 2.1.3 The Interrelationship between Low and High Solid Thickening Properties

**Table 2.1** The Interrelationship between Low and High Solid Thickening Properties [7]

| **Characteristic Property** | **Type of Thickening** | |
|---|---|---|
| | **Low Solids** | **High Solids** |
| Flow | Short | Long |
| Effect of increasing shear on viscosity | Viscosity falls off rapidly | Little or no falling off of viscosity |
| Yield of dye | Generally high | Usually of a lower order than low solids thickenings |
| Levelness of print | More difficult to achieve than with high solids thickening | Generally good |
| Viscosity | High | Medium to low |
| Handling of dried or baked print | Flexible film giving moderate good handle | Film tend to be hard, brittle and way crack off fabric |
| Nature of polysaccharide chains | Very long and straight with little or no side branching | Short than low solids type, heavily branched coiled in solution |
| Price of made up thickening | Relatively low | More expensive than low solids type |

## 2.2 Starch

The reserve carbohydrate stored usually in the seeds, roots or stems of plants. It is second in abundance [8]. Although starch is widespread in plants, only a few sources are sufficiently abundant to make the extraction of the starch commercially feasible. These sources are corn, tapioca, potato, sago, waxy maize, wheat, sorghum, rice and arrowroot.

Starch is in a white powder form, and the unaided eye can detect little difference between the various starches extracted from different plants. All the starches are insoluble in alcohol, most solvents and cold water. A dilute solution of iodine stains starch a blue to bluish-red.

The molecular formula of starch must be $C_6H_{10}O_5$. This formula was verified by combustion analysis [9]. Partial hydrolysis products precipitated from aqueous solution by alcohol were dextrorotatory and, hence, were named dextrins.

### 2.2.1 Molecular Structure

Starch is a homopolymer of glucose (D-glucopyronosyl) units, with most of the units joined by $\alpha$-D (1→4) linkages [10]. Most starches contain 20-30% of linear chain polymer, known as amylose, together with an irregularly branched material, amylopectin. Amylopectin has an $\alpha$-D (1→6) linked branch for each 15-30 glucose unit. Figures 2.1 and figure 2.2 show amylose and amylopectin structure, respectively.

In linear starch segments the $\alpha$-D (1→4) linkages and $^4C_1$ (D) chain conformations introduce a natural twist. Under a certain condition, a tightly coiled helix is stabilized by hydrogen bonds between the C-2 and C-3 hydroxyl groups on adjacent chains.

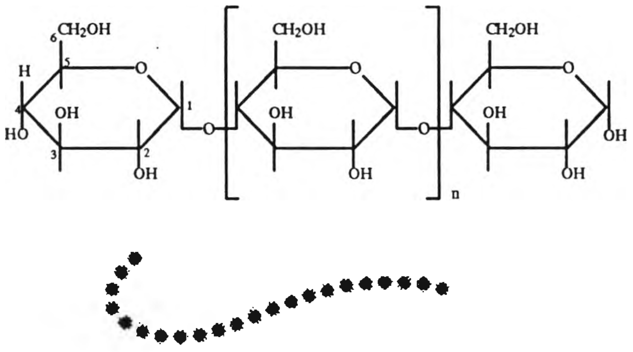

**Figure 2.1** Chemical structure of amylose chain [10]

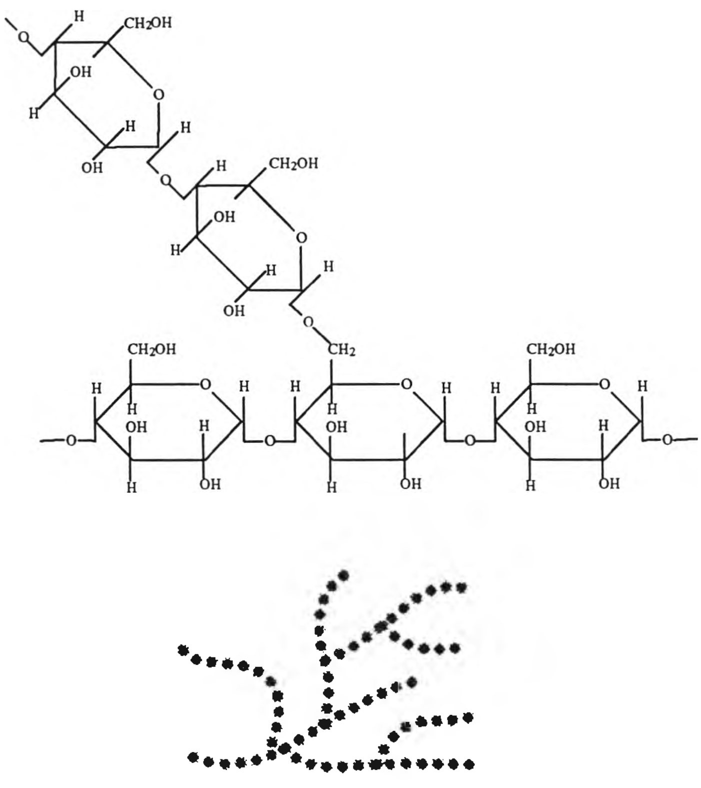

**Figure 2.2** Branched amylopectin starch molecule [8,10]

In the natural state, starch is always found in a strongly aggregated state, organized in granules around crystallization nuclei [8, 10]. It is necessary to break drown the granules, by boiling or by grinding and dispersion in hot water. On continuous heating in water, starch granules absorb water, increase many times in size. When the temperature of the suspension of starch in water is increased to a critical point, called the gelatinization temperature, water penetrates the granules to hydrate and swell then to produce a viscous paste, semi-opaque and finally transparent. Gelatinization temperatures vary 60-75°C from starch to starch.

If the viscous paste is dried rapidly, cold-water-dispersible starches are obtained, but slow drying allows substantial reaggregation and crystallization to occur and the product is no longer dispersible in cold water. The use of hydrogen-bond breakers, such as urea and strong alkalis, will assist dispersion in water.

Starch pastes containing amylose are not stable and may form gels and precipitates of amylose aggregates. The precipitates are not easily redissolved. Stability can be improved by additions of formaldehyde, probably by formation of hemiacetals.

Amylopectin, in contrast, form clear, stable solution, not subject to retrogradation. Chain branching evidently prevents the molecular orientation and regularity of intermolecular bonding necessary to cause gelling and precipitation. When in solution, the amylopectin molecules can be pictured as approximately spherical, with a relatively dense core and flexible, deformable, outer regions of solvated chain branches.

Different native starches have different proportions of amylose and amylopectin, and probably also different degrees of chain branching and r.m.m. values range from 2 to 6 x $10^5$ for amylose and 4.5 x$10^4$ to 4 x$10^8$ for amylopectin.

## 2.3 Rheology [11]

Rheology is the study of the flow and deformation of matter. The aim of this science is to define and evaluate such words as consistency, tack length of flow, stiffness and body in terms of the physical properties of the material.

### 2.3.1 Flow in Ideal System

Isaac Newton was the first to find the basic law of viscometry describing the flow behaviour of an ideal liquid.

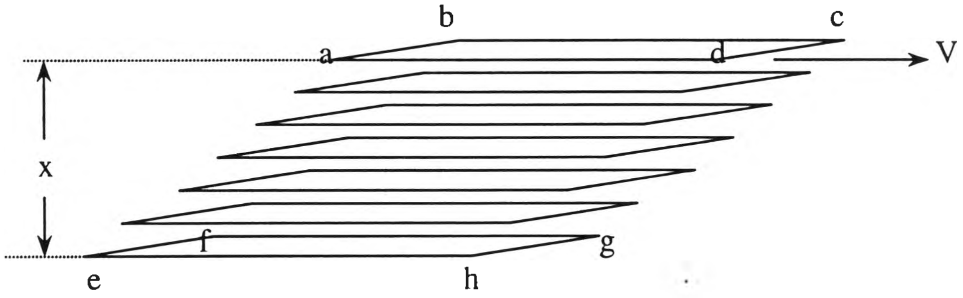

**Figure 2.3** Newtonian flow [11]

Consider two parallel planes, abcd and efgh of area A (Figure 2.3) in a fluid, holding efgh stationary and subjecting abcd to a force F resulting in a movement of velocity V, the intervening fluid may be looked upon as having many planes sliding over one another. The nearer the planes are to plane abcd, the greater is their velocity. Consequently, there is a velocity gradient between the planes abcd and efgh:

$$velocity\ gradient = \frac{dV}{dX} = D\ (rate\ of\ shear)(s^{-1}) \qquad (2.1)$$

the shearing stress is given by the force per unit area

$$\tau = \frac{F}{A} \tag{2.2}$$

For a newtonian liquid $\tau$ is proportional to $D$, i.e.

$$\tau = \eta D \tag{2.3}$$

where $\eta$ is a constant for the liquid under examination and is known as the coefficiency of viscosity. The unit of viscosity is the pascal second and is derived as follows:

$$\text{Shearing stress} = \text{force per unit area} = \text{newton } m^{-2} = \text{pascal} \tag{2.4}$$

$$\text{Shear rate, } D = \text{velocity gradient} = \frac{dV}{dX} = \frac{m\,s^{-1}}{m} = s^{-1} \tag{2.5}$$

$$\text{Coeffiiency of viscosity} = \frac{\tau}{D} = \frac{\text{newton } s}{m^{2}} = \text{pascal } s \tag{2.6}$$

### 2.3.2 Newtonian [12]

These fluids have the same viscosity at different shear rates. The flow curve for an ideal liquid is a straight line, the ratio of all pairs of $\tau$ and D values belonging to this line is a constant. This means that $\eta$ is not affected by changes of shear. All liquids for which this statement is true are called “Newtonian”.

The flow and viscosity curves of a Newtonian fluid are shown in Figures 2.4 and 2.5, respectively.

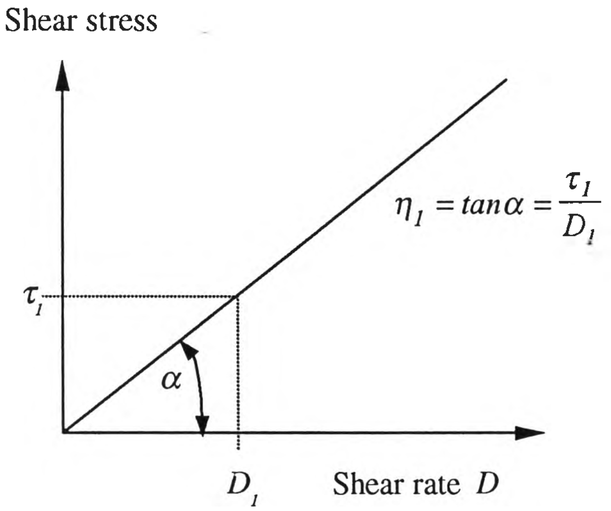

**Figure 2.4** Flow curve of a newtonian liquid [12]

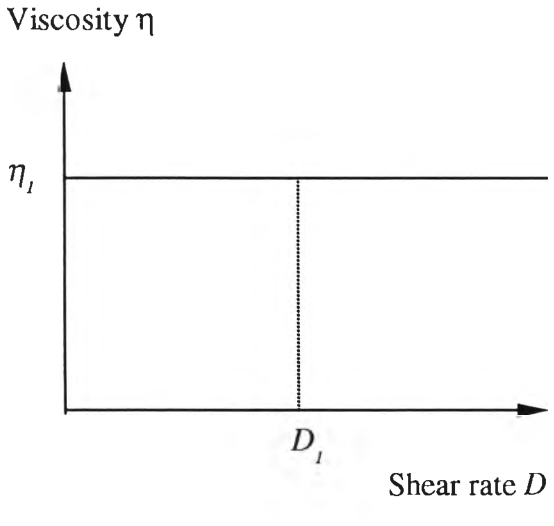

**Figure 2.5** Viscosity curve of a newtonian liquid [12]

### 2.3.3 Non-Newtonian Liquid [13, 14]

All other liquids not showing this simple "ideal" flow behavior are called "Non- Newtonian". From the flow curves thus obtained, it is found that the behavior of viscous liquids can be classified into five categories, shown diagrammatically in Figure 2.6 [13].

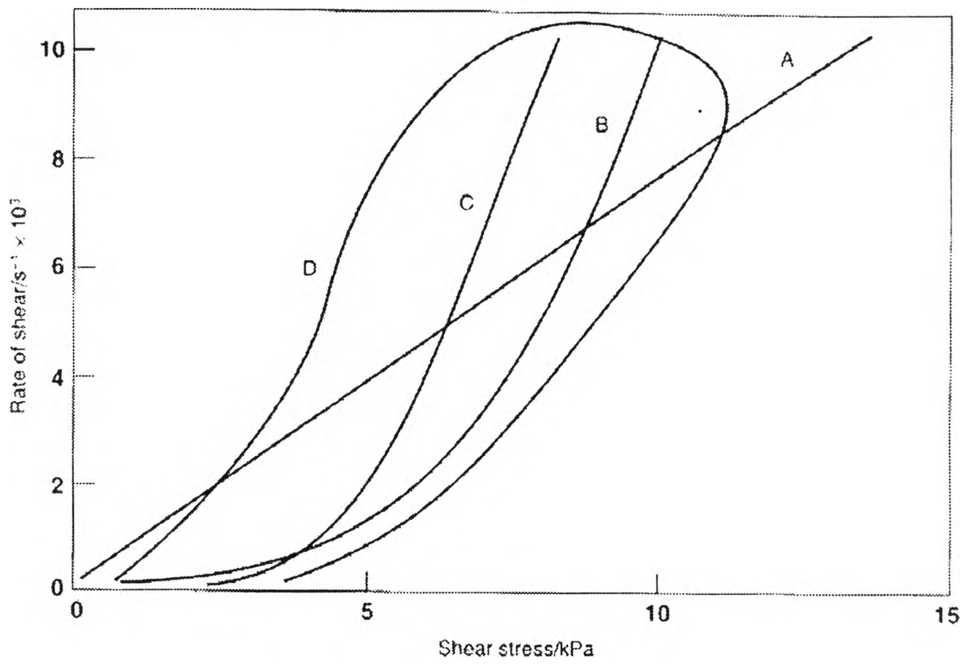

**Figure 2.6** Typical flow curves demonstrating behaviour of viscous liquid [13]

A few materials, such as gum arabic paste, poly(vinyl alcohol) solutions and silicone oils, are esstially Newtonian (curve A in Figure 2.6), with viscosity independent of shear. Most print pastes show that is also known as pseudoplastic behavior or shear thinning properties, (curve B in Figure 2.6), with a significant reduction in apparent viscosity as the shearing stress is increased. The change is reversible, the viscosity increases immediately, shearing is then reduced. A significant number of pastes do not flow at all units the shear stress exceeds a minimum value, known as the yield value (curve C in Figure 2.6). Beyond this value, they may show either linear or nonlinear flow properties. The former has been called Bingham systems, after E. C. Bingham, who defined the term "plastic viscosity" as the ratio (shear stress-yield value): rate of shear. The concept of plastic viscosity has been extended to shear-thinning print pastes, with flow curves that approach linearity at high shear, by extrapolating the linear section of the curve back to the stress axis to define a yield value.

A great number of substances such as emulsions, suspensions, or dispersions of high technical and commercial importance are included in pseudoplasticity. It will be worthwhile to indicate some reasons for the shear thinning effect of pseudoplastic material.

Many liquid products that seem homogeneous throughout are in fact composed of several ingredients: particles of irregular shape of droplets of one liquid are dispersed in another liquid [14]. On the other hand there are polymer solutions with long entangled and looping molecular chains. At rest all of these materials will maintain an irregular internal resistance againt flow, i.e. a high viscosity.

With increasing shear rates mathstick-like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chain-type molecules in a melt or in a solution can disentangle, stretch, and orient parallel to the driving force. Particle or molecular alignments allow particles and molecules to slip pass each other more easily and this shows up as reduced viscosity.

For most liquid materials, the shear thinning effect is reversible, often with some time lag, that is the liquids regain their original high viscosity when the shearing is slowed down or is even terminated: the chain-type molecules return to their natural state of non orientation, deformed droplets return to ball-shape and the aggregates reform due to Brownian motion.

A fourth type of behavior, found in pastes with high pigment concentrations, has been called dilatant, but is better described as "shear thickening" to avoid the assumption that volume expansion necessarily occurs. This is the phenomenon seen on wet sand when pressure causes particles to touch and the friction between particles prevents their movement into expanded spaces. Free liquid is drawn into these spaces, making the system look dry.

Finally, there is the phenomenon known as thixotropy, shown by gelatine solutions and betonite suspension, for examples (curve D in Figure 2.6). In this case the measured values of viscosity depend on the duration of shear as well as the rate of shear, and increased resistance to shear is observed after a long rest time than after shorter times. The probable explanation is that intermolecular bonds are broken by shear and slowly reformed after shearing ceases.

## 2.4 Screen Printing Inks

### 2.4.1 The Principle of Screen Printing

The characteristics of screen inks become clear when consider the basic characteristics of the process.

Screen printing (formerly called silk-screen printing) is a stencil process whereby ink is transferred to the substrate through a stencil supported by a fine fabric mesh of silk, synthetic fibres or metal threads stretched tightly on a frame. The pores of the mesh are "blocked-up" in the non-image areas and left open in the image area. This image carrier is called the screen [15].

During printing the frame is supplied with ink which is flooded over the screen. A squeegee is then drawn across it, thereby forcing the ink through the open pores of the screen. At the same time the substrate is held in contact with the screen and ink is thereby transferred to it. The principle of screen printing is shown in Figure 2.7

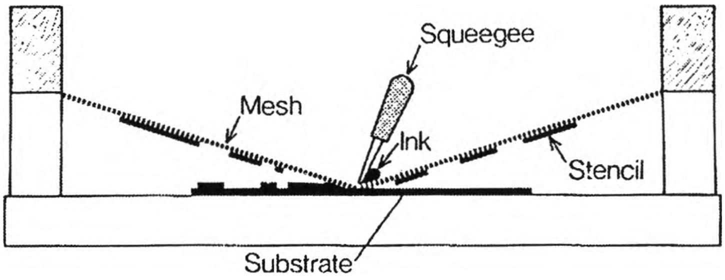

**Figure 2.7** The principle of screen printing [15]

Because of their simplicity, screen can be produced cheaply and this makes it an attractive process for short-run work. Furthermore, since the image is produced through a screen rather than from a surface, which impression pressure is very low. This makes it ideal for printing on fragile boxes or awkward shapes.

To a certain extent, the thickness of the ink film printed can be controlled by the pressure, sharpness and angle of the squeegee blade. The more upright the blade the thinner the deposit of ink. Thus, in general, fine work required a more upright blade. However, the type of ink, stock and machine govern the blade setting also.

### 2.4.2 The Nature of Screen Inks [16]

Screen inks are often referred to as" paints" because of their similarity to some sign paints and because they often applied at thickness for greater than most printing inks. However, their formulations indicate that they are correctly called "Inks"

Screen inks differ from other printing inks in another important way. To transfer well from roll to roll, most printing inks must be "long" i.e., they show some tendency to form a string when pulled away from a wet surface. Screen inks do not have to transfer form one roll to another. Therefore, they are short and "buttery". Short inks pass through the openings of the screen without leaving fuzzy edges. If the inks were long, they would form strings when the screen was lifted from the wet print; there strings would ruin the print.

### 2.4.3 General Properties [17]

Screen printing inks are carefully formulated to conform to the certain printing and finish specification.

1. Printability

An ink must be liquid enough to pass through the screen without blocking or clogging up the small openings.

2. Rheology

The ink must have specific flow and defoamation properties which allow it to pass through the screen freely and then form a solid film on the surface of the substrate. If an ink is too stiff it may not flow out enough after printing, leaving clearly visible mesh marks on the surface of the dried film. Early examples of screen printing exhibit this fault. On the other hand, if the ink flows too freely it may lack the necessary cohesion to form a firmly structured film on the substrate. Ink, which lacks body will tend to "bleed" at the edges of the film, that means the effect increases with the absorbency of the stock.

3. Adhesion

The ink must be capable of adhering firmly and permanently to the substrate. One of the reasons why there are so many different kinds of ink is that many surfaces, especially those made from plastic, will not readily accept conventional paper and board inks. These difficult substrates usually required an ink which is formulated to bond physically and chemically to the surface.

There are two main types of inks for printing on plastics[18]. One type is the "aggressive" ink, which contain a solvent that softens the plastic surface, allowing the ink to adhere. Aggressive ink must be used with a particular type of plastic, for example, polystyrene, vinyl plastics. The other type is the "nonaggressive" ink, which do not attack the surface but adhere to the surface because of mechanical and chemical bonding. In order to obtain ink adhesion on polyethylene and polypropylene, the surface must first be treated with a corona discharge.(ref chemical)

4. Drying

The ink must form a dry film after it reaches the substrate. Most ink required to dry rapidly on the substrate whilst remaining stable on the screen.

5. Finish

The ink must provide the required finish characteristic. Depending on the formulation it may have a matt, semi or high gloss finish. The dry film must be resistant to scratching and scuffing. It should also be capable of receiving subsequent printings and finishing processes without crazing, cracking or peeling.

6. Color

The pigment must provide richly saturated colors with good light and weather resistance. The colors should be intermixable.

7. Toxicity

The ink must conform to the current health and safety regulations. All inks must be clearly labelled, and hazardous substance contained in them must be clearly indicated on the label.

### 2.4.4 Water-Based Screen Inks

Restrictions on solvent emissions have increased the interest in water-based screen inks. Water-based inks for nonabsorbent substrate like polyethylene, polypropylene, and polyester films dry by evaporation since the substrates are not porous and cannot absorb the inks. Water evaporates very slowly, making the inks hard to dry. However, with good raw materials and careful formulation, useful inks are produced.

In common, most conventional solvent-based inks are composed of resins, solvents, pigment and additives. However, for water-based screen inks, many of the requirements are specific to them [19].

When screen printing on some plastics, it is possible to base formulations on resins that bear similarity to the substrate, e.g. acrylic resins for sheet acrylic, amino resins for melamine formaldehyde mouldings, vinyl resins for self-adhesive PVC sheet. Resin selection is the most important factor in achieving good adhesion. In addition, inadequate flexibility can result in poor ink adhesion. In this situation, modification with plasticizer or flexibiliing resins will improve matters.

The ability to reduce the surface tension of water is of great important in water-based ink because decreased surface tension translates to enhanced substrate wetting in actual formulations. Surface tension reduction in water-based ink is generally achieved through the addition of surfactants. Performance attributes resulting from the addition of surfactants include enhanced surface coverage, fewer deflects, and more uniform distortion [20].

In addition to using an adhesive-promoter in water-based ink composition, it can improve the adhesion or bonding properties to a substrate.

The common problem for water-based screen inks is foaming. Foaming is a condition, which might happen when a monomolecular film of a surfactant which is fairly insoluble in the bulk of the liquid is present on the surface of the liquid [21]. Elasticity of the liquid surface can cause foaming with a determental effect, if not controlled prior to printing. Ideally foaming should be inhibited by formulating to ensure that the surface tension is kept low. This is often difficult because of the surfactants used in the formulation of inks or in the gradients used to make them. If foaming does occur it increases rapidly with agitation. Prevention is better than curing but where foaming does occur it should be dealt with as soon as possible.

Defoaming agent acts in one of two ways:

(1) By being a good solvent for the surfactant. This causes the monomolecular film, so essential to foaming, to be dispersed into the bulk of the liquid. When this happens the tendency towards foaming is greatly reduced.

(2) By adding a small quantity of material which is immiscible with the system, and which drastically lowers the surface tension of the system. This

reduction in surface tension causes existing bubbles to burst and creates a physical condition such that stable bubbles and foams cannot form.

This latter type of defoamer is frequently added in a form which makes it readily dispersible over the surface, for example as a liquid or an emulsion.

There are many defoaming agents and they are usually classified as silicone or non-silicone, the former being the most popular type. Silicone fluids and emulsions are often used as defoaming agents. There are fluids for non-aqueous media and for emulsions ranging from 10 to 30% silicone in water-based system.

## 2.5 Printability of Plastic Film

Printing on non-absorbent substrates, e.g. plastic films, opens a number of problems different from those when printing on paper and board. Some of the most common problems related to printability and ink spread and adhesion between plastic film and dry ink [22].

The first step in obtaining good adhesion and print quality is to assure that the ink evenly wets out on the substrate. As a result, the more interfacial area between the liquid and substrate, the greater the possibility of achieving sufficient bonding.

To achieve the proper wetting, various surface forces must come into play; the primary ones are the surface tension of the ink and the surface energy of the film.

### 2.5.1 Surface Tension and Surface Free Energy

Consider a drop of a one component liquid in equilibrium with its vapour and in the absence of an external force. The drop spontaneously assumes the form of a sphere, the shape which corresponds to the minimum surface to volume ratio. It can therefore be inferred that work must be done on the drop to increase its surface area, and hence that the surface molecules are in a state of higher free energy than those in the bulk liquid. This is in part explained by the fact that surface molecules have fewer nearest neighbours and, as a consequence, fewer intermolecular interactions than bulk molecules. There is then, a free energy change associated with the isothermal, reversible formation of a liquid surface and this is termed the surface free energy or, more correctly, the excess surface free energy. The terms are often used to mean specific (i.e. per unit area) surface free energy, the units of which are mJ $m^{-2}$. It must be emphasized that this surface free energy is not the total free energy of the surface molecules but the excess free energy which the molecules posses by virture of their being in the surface [23].

Surface Tension of liquid is a phenomenon that directly results from intermolecular forces between molecules of liquids. In other words, molecules at the surface of a drop of liquid experience a net force that draws them to the interior, which creates a tension in the liquid surface [24].

The force of tension is tangential to the surface of liquid. The surface tension units of measurement are:

$$Force/length = \frac{mN}{m} = \frac{dyne}{cm} \tag{2.7}$$

The symbol used here will be $\gamma$.

The surface energy of a solid defines molecular forces of its interaction with other surface. It is measured as free energy per unit area:

$$Energy\,/\,area = force\,/\,length = \frac{mJ}{m^2} = \frac{mN}{m} = \frac{dyne}{cm} \qquad (2.8)$$

### 2.5.2 Surface Energetics and Contact Angle

There are no direct, reliable methods for determining surface energy or surface tension of solids. However, there are two main indirect methods of solid surface measurement, that is contact angle and inverse gas chromatography methods. In this thesis, contact angle measurement will be discussed, it is probably the most common method of solid surface tension measurement. Contact angle data, especially in the case of polymeric material, can be obtained with low price instruments and with simple techniques.

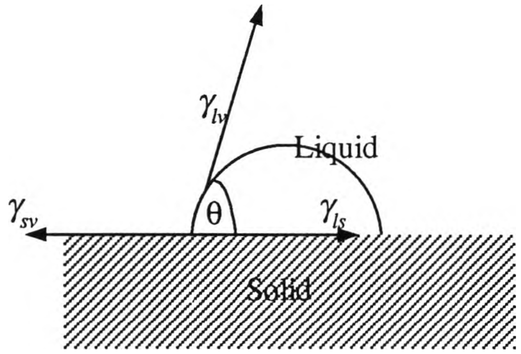

**Figure 2.8** Equilibrium contact angle [25]

At the basis of the measurement of solid surface tension by contact angle there is the equilibrium at the three-phase boundary, shown in Figure 2.8 [25]. The drop of liquid that is part on a solid surface will modify its shape under the pressure of the different surface interfacial tensions, until reaching equilibrium. In 1805, Thomas Young described the three-phase equilibrium in term of the vectorial some shown in Figure 2.8 resulting in the following equation of interfacial equilibrium.

$$\gamma_v - \gamma_{sl} = \gamma_{lv} \cos\theta \tag{2.9}$$

where $\gamma_{ij}$ is the interfacial tension between phases $i$ and $j$, subscripts $s$, $l$ and $v$ refer to solid, liquid and vapour, respectively; and $\theta$ is the equilibrium contact angle. The solid-vapour interfacial tension is linked to the intrinsic solid surface tension, or the surface tension of the solid in equilibrium with its own vapour or in vacuum, by the following relationship:

$$\pi_e = \gamma_s - \gamma_{sv} \tag{2.10}$$

and $\pi_e$ is called the spreading pressure, which represents the decrease of solid surface tension due to vapour adsorption. Equation 2.10 shows that, if $\pi_e$ is negligible, the role of the spreading pressure will increase, for a given liquid, with increasing solid surface tension. It is generally accepted that if the contact angle is larger than about $10^{\circ}$, the spreading pressure can be safely neglected.

Equilibrium contact angle is obtained only on an ideal solid surface. An ideal solid surface is a perfectly smooth, chemically homogeneous, rigid, insoluble, and nonreactive surface.

### 2.5.3 The Actual and Apparent Contact Angles [26]

When real surfaces are considered, one should distinguish between two additional definitions of contact angles: the actual and the apparent. The actual contact angle (Figure 2.9) is the angle between the direction of the tangent to the solid-liquid interface at that point. The usual optical methods for measuring contact angles yield the apparent contact angle (Figure 2.9). This is the angle between the direction of the tangent to the seemingly smooth solid surface, as seen by using relatively low magnification, and the direction of the tangent to the lf interface. On perfectly smooth solid surfaces, the apparent contact angle is identical with the actual one. On rough surfaces, they may be very different.

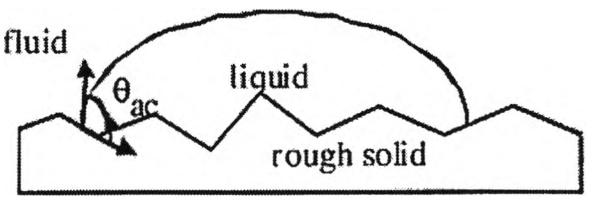

**Figure 2.9** The actual contact angle [26]

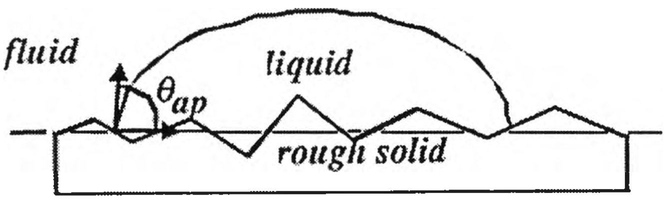

**Figure 2.10** The apparent contact angle [26]

### 2.5.4 Contact Angle Hysteresis

#### 2.5.4.1 Effect of Roughness [27]

In 1936, Wenzel reasoned that within a measured unit area of a rough surface there is more surface than in the same measured unit area on a smooth surface. While specific surface quantities are, the same on the two surfaces, the relative magnitude of the vectors composing the Young equation are modified, as shown in Figure 2.11. Wenzel proposed the following equations:

$$r(\tau_s - \gamma_{sl}) = \gamma_{lv} \cos\theta_w \tag{2.11}$$

where $r$ is the so-called roughness factor:

$$r = \textit{actual surface/geometric surface} \tag{2.12}$$

as illustrated in Figure 2.11. The subscript "*w*" indicated that the angle appearing in Equation 2.11, usually called the Wenzel angle, is different from that of the Young equation (Young angle, or $\theta_y$). Their relationship is the following:

$$\cos\theta_w = r \cos\theta_y \tag{2.13}$$

Since the roughness factor is always greater than unity, Equation 2.13 shows that the effect of roughness is to magnify the wetting properties of the solid, that is the Wenzel angle will increase with roughness if the Young angle is greater than 90° and will decrease if it is less than 90°.

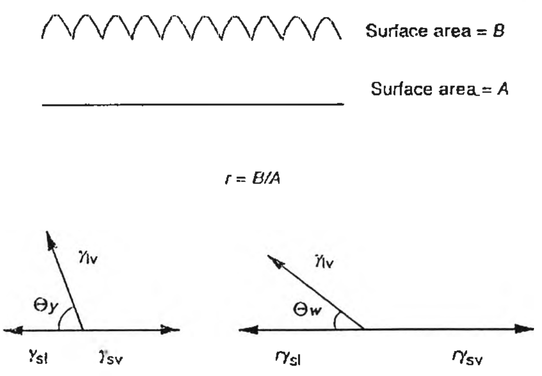

**Figure 2.11** The Wenzel relationship [28]

Contact angle measurements are dependent upon the direction in which the measurement is made. When a drop is laid down upon a surface and advances over the surface as it spreads, the contact angle in this situation is known as the advancing contact angle or recently advanced angle. If liquid is withdrawn from a drop that has already come into equilibrium with the surface, the contact angle is known as the receding contact angle or recently retreated angle. In general, the advancing angle is larger than the receding angle. The phenomenon of having a different contact angle under advancing and receding conditions is known as contact angle hysteresis, as Equation 2.14.

$$H \equiv \theta_a - \theta_r \tag{2.14}$$

where $H$ is hysteresis, $\theta_a$ is advancing contact angle and $\theta_r$ is receding contact angle.

A number of reasons for contact angle measurements are hysteretic, specifically: nonhomogeneous surface chemistry, surface roughness, and molecular rearrangement in the solid induced by liquid and vice versa.

### 2.5.5 The Fokes Hypothesis [28]

Fowkes proposed a separation of the surface energy of a material into the potential energy of interaction. The Fowkes hypothesis is a first order approximation which, simply stated, is that the surface energy of a material can be divided into component parts. Thus :

$$\gamma = \gamma^d + \gamma^p + \gamma^i + \ldots \tag{2.15}$$

where $\gamma^p$ is the polar contribution to the surface energy, $\gamma^i$ is the dipole induced dipole contribution to the surface energy and $\gamma^d$ is the dispersion force contribution to the surface energy. Fowkes also made a fundamental hypothesis important to the study of interface and adhesion, namely that materials exhibiting only dispersion force interactions interact with other surface by only those interactions. It was also Fowkes' contention that polar force and dipole-induce dipole force were insignificant when one of the two materials at an interface was non-polar. Mathematically this can be stated:

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d + \gamma_2^d)^{1/2} \qquad (2.16)$$

where $\gamma_1$ and $\gamma_2$ are surface energies as we have previously defined them and $\gamma_1^d$ and $\gamma_2^d$ are the dispersion force components of the surface energy of material *1*, and *2* respectively. Applying Equation 2.16 to a solid-liquid interface gives :

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d + \gamma_l^d)^{1/2} \qquad (2.17)$$

If $\pi_e$ is assumed that to be small and $\gamma_{lv} \approx \gamma_l$, $\gamma_s$ can be eliminated by combining Equation 2.17 and Young 's equation, we can write.

$$\gamma_{lv}(1 + \cos\theta) = 2(\gamma_s^d + \gamma_l^d)^{1/2} \qquad (2.18)$$

Equation 2.18 sometimes called the Young–Good–Girifalco–Fowkes equation. Fowkes's suggestion brought interfacial tension closure to the microscopic world. From the point of view of contact angle measurement, it gave rise to a number of different equations, beside the dispersion component, the other component of the interfacial tension. Hydrogen bonding and interaction between permanent dipoles were, in general, lumped together in a so-call polar component. Several different treatments extended the geometrical mean approach of Equation 2.18 also to the polar term, as follows :

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d + \gamma_l^d)^{1/2} - 2(\gamma_s^p + \gamma_l^p)^{1/2} \tag{2.19}$$

where the subscript p indicates the polar component [28].

### 2.5.6 Polarity [29]

The separation of the total surface tension or energy into two types of forces across an interface can be described as follows. Since an interface is a phase boundary, attractive force exist between the two phases. They may be classified as two general types: dispersion and specific. The dispersion forces are ubiquitous in nature, arising from electron orbitals, which are present in all materials. The specific or non-dispersion forces are present only in some substances. They can arise from a variety of causes, the primary ones being di-pole or polar attractions, although, there can be other causes. It is conventional to lump these specific forces together and call them "polar" forces.

With the dependent measurements, the surface energy can be resolved into these two components, thus yielding important information regarding the nature of the surface forces of both liquids and solids. To characterize the polarity of a solid, two liquids of known polarity and surface tension are required. Water and methylene iodide are commonly used for this purpose, but other fluids can be used. To determine the polarity of a liquid two known solids are required. Pure polyethylene pellets and pure teflon pellets are usually used, characterized materials. Knowing contact angles for two known materials enables solving the equation for determining not only surface polar component.

The surface tension or energy of liquid and solid is regarded as being composed of two contributions, dispersion and polar, such that [30]

$$\gamma_l = \gamma_l^d + \gamma_l^p \tag{2.20}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2.21}$$

where $\gamma_l$ is the surface tension of fluid.

$\gamma_s$ is the surface energy of solids.

$\gamma_l^d$ , $\gamma_l^p$ are dispersion and polar surface tension of liquid, respectively.

$\gamma_s^d$ , $\gamma_s^p$ are dispersion and polar surface energy of solid, respectively.

To determine the polarity of solid and liquid by solving the Equation 2.22

$$\gamma(1+\cos\theta)/2=(\gamma_s^d\,\gamma_l^d)^{1/2}+(\gamma_s^p\,\gamma_l^p)^{1/2} \tag{2.22}$$

and then :

$$\%Polarity=\frac{100\times Polar\ component}{Total\ surface\ energy} \tag{2.23}$$

### 2.5.7 Wetting Tension

The wetting tension of a given solid is an estimate of its surface energy. Even though the wetting tension value is usually smaller than the surface energy, it is often equated with it an is a satisfactory measure for the purpose of evaluating corona treated film [31].

The wetting tension concept can be explained by a simple test. In the test, droplets of liquids, whose surface tension values decrease from one liquid to the next ($\gamma_{l_1} > \gamma_{l_2} > ... > \gamma_{l_n}$) are placed on the sample surface, and their contact angles are measured. The contact angles decrease from liquid to liquid until one liquid has a zero contact angle. Therefore, the wetting tension of solid is considered equal to the surface tension of the liquid that just exhibits a zero contact angle. The liquid surface tension was given a special name, the critical wetting tension of the solid surface or $\gamma_c$. This method is known as the Zisman plot. The mathematical formulation of the Zisman relation is as follows [32]:

$$\cos\theta=1+b(\gamma_c-\gamma_{lv}) \tag{2.24}$$

where $\theta$ is the contact angle, $\gamma_{lv}$ is the interfacial tension between the probe liquid and air saturated with the vapor of liquid, $\gamma_c$ is a critical wetting tension and b is the slope of the line.

### 2.5.8 Adhesion [33]

As a definition, adhesion is the joining together of two dissimilar materials, while cohesion is the joining together of different portions of the same materials.

When printing, beside the wettability of the surface required for the image, sufficient adhesion of the printing ink film to the substrate is necessary.

The forces between the molecules of the solid and of the liquid must be stronger than the attraction forces among liquid molecules themselves. Thermodynamically expressed this means:

$$\textit{Adhesion Work, } W_A > \textit{Cohesion Work, } W_C\ (\overset{\wedge}{=} 2\gamma_s) \tag{2.25}$$

The adhesive forces are based on the fact that forces originating from any surface of a condensed phase will bind other substances to this surface. Binding may also occur because the forces of the surface are only partly satisfied.

Dupre' described reversible adhesion work $W_A$ between liquid and solid per unit of surface as follows:

$$W_A = \gamma_s + \gamma_l - \gamma_{sl} \tag{2.26}$$

when the Young-Dupre' equation $(\gamma_s = \gamma_{sl} + \gamma_l \cos\theta)$ is applied, Equation 2.26 for the adhesion work of a liquid at a solid (at normal temperatures, which do not cause strong vapour condensation) results, when $\theta > 0$ and $\gamma_l >> \gamma_c$

$$W_A = \gamma_l (1 + \cos\theta) \qquad (2.27)$$

## 2.6 Literature Review

Arayamaythalert [2] prepared acrylic acid-cassava starch graft copolymer as a thickener for cotton fabrics printing. Native cassava starch was chemically modified in starch graft poly(acrylic acid), under a grafting copolymerization of acrylic acid onto the polysaccharide backbone via a hydrogen peroxide-ascorbic acid initiation method. Prior to the grafting reaction, starch was gelatinized at 80°C for 1 hour. Reaction variables of importance include concentration of acrylic acid, hydrogen peroxide, ascorbic acid, and starch; polymerization temperature; polymerization time and the addition rate of acrylic acid-hydrogen peroxide mixture. The poly(acrylic acid) grafted starch was subsequently saponified with 25% aqueous solution of NaOH at room temperature to convert carboxylic groups into carboxylate groups. The copolymers were characterized by infrared spectroscopy and nuclear magnetic resonance spectroscopy. GPC was used as a tool to determine the average molecular weight of the starch and grafted poly(acrylic acid), which has been hydrolyzed by glacial acetic acid and perchloric acid. Viscosity measurements of the grafted copolymers were carried out at various concentrations (6, 8, 10, 12% w/w) of the thickeners. The high molecular weight hydrolyzed (Na salt) cassava starch-acrylic-acid copolymers dissolve better in distilled water resulting from the salt and polarity of the molecules. The distribution of molecular weight is in the ranges of 9,600-77,500 and 101,000-652,000 for the grafted poly(acrylic acid) chains and 190, 300, 1,000 for the acid hydrolyzed starch, respectively. Water absorption of the new thickener was carried out in distilled water. The viscosity of thickener was also studied as a function of concentration (w/w). It is evident that the concentrations of the thickener after the viscosity and their rheological behavior known as shear thinning or pseudoplasticity.

Okieimen and Ebhoaye [34] synthesized graft copolymers of acrylonitrile and of acrylic acid monomers on cellulosic materials by use of ceric ion initiator in aqueous medium at a 50% (w/w) cellulose-monomer ratio. The variations of poly (acrylonitrile) grafts and of the efficiency of grafting with ceric ion concentration, and of poly(acrylic acid) graft with temperature are examined. It can be seen that, at a constant initiator concentration, both the graft level and efficiency of grafting increase with time, tending to level off at longer durations of polymerization. Although an increase in ceric ion concentration is accompanied by an increase in graft level, the efficiency of grafting decrease with increase in initiator concentration. Any unreacted or unadsorbed ceric ion in the polymerizing system could initiate homopolymerization by a transfer to monomer. The effect of temperature on the grafting of acrylic acid on the holocellulosic substrate is shown. The results show a decrease in the level of incorporation of poly(acrylic acid) grafts onto the backbone between 35°C and 40°C the graft level remaining virtually of grafting is more significant, decreasing from 54% at 35°C to 60°C

Ragheb et al. [35] prepared carboxymethyl starch (CMS) samples with different characteristics and investigated their suitability as thickening agents in textile printing. CMS samples of different characteristics could be obtained by changing the molecular size of starch via oxidation with sodium hypochlorite together with controlling the degree of substitution of the starch hydroxyls by changing the etherifying agent concentration. Pastes of these CMS samples exhibit pseudoplastic behaviors and their apparent viscosity decrease as the extent of oxidation increase. When used as thickness in printing polyester fabric with disperse dyes, these pastes being about prints the color strength (K/S) of which are comparable with these for conventional thickness, namely commercial CMS and sodium alginate. Mixing of sodium alginate with the prepared CMS samples increased the efficiency of the latter to act as the thickening agent. The highest K/S was obtained with CMS derived from starch oxidized using 1.25 g active chlorine/l. Mean while, the color fastness properties of the prints toward rubbing, washing and perspiration are nearly equal to those fabrics printed using the conventional thickeners such as sodium alginate or commercial CMS.

Eisenhart et al. [36] disclosed a method for improving thickeners for aqueous systems. The improvement was directed to the elimination of organic cosolvents which were conventionally added to aqueous solutions of certain hydrophobic thickeners. This method involved the reversible complexation of cyclodextrin compounds with hydrophobic moieties on the thickener molecule to suppress the viscosity of the aqueous solution containing the thickener so that such the solution containing the thickener so that such the solution can be easily handled. This was followed by decomplexing the cyclodextrin from was the thickener to permit the thickener to perform its intended function.

Schiefer and McClarnon [37] disclosed a method of flexographic or rotogravure printing onto a plastic substrate using a water-based ink. The improvement comprising adding to said ink from about 0.005 to about 5 weight percent of a low molecular weight silicone compound. The incorporation of the silicone compound provided good wetting of the substrate by the ink and results in improved printing characteristics.

Lassila et al. [38] revealed the use of alkylated alkylenedinines to reduce equilibrium and dynamic surface tension in water-based compositions, particularly coating, ink, and agricultural compositions.

Chen [1] studied surface properties of corona treated polyethylene film containing n-(2-hydroxyethys) erucamide as slip agent for enhanced adhesion of aqueous ink. It was fond that n-(2-hydroxyethyl) erucamide can import enhanced ink adhesion and goo slip characteristics for polyolefins. Contact angle and coefficient of friction measurements correlated the surface changes induced by slip agents and corona treatment in polyethylene films for aqueous ink adhesion and printability. N-(2-hydroxy ethyl) erucamide migrate to polyethylene surfaces at a moderate rate to give better corona treatment and enhance aqueous ink adhesion while maintaining gold slip properties. Enhanced results are also possible using this amide with finely divided inorganic filler.

Ealer et al. [39] showed characterization of surface-treated polyethylene spectroscopy for chemical analysis (ESCA) to determine the surface chemical changes induced by corona treatment in pure polyethylene-extruded films and in formulated resin systems. These data were correlated with surface tension and ink adhesion measurements to show the effects of treatment and additives on the final printability of the films, with particular emphasis on water-based inks. In addition, the effects of storing treated film prior to printing and treating it a second time were examined. The results showed that, formulated LLDPE films-treat and print at least as easily as high performance LDPE counterparts.

Hebeish et al. [40] prepared polyacrylamide-starch composite by polymerization or maize of rice starch with acrylamide (Aam) using potassium permanganate/citric acid initiation system. Major factors affecting the polymerization reaction were studied with a view to discover appropriate conditions for preparation of the composite. Results obtained imply that the total conversion (monomer converted to homopolymer and graft) increases by increasing concentrations to potassium permanganated from 0.5-0.20%, citric acid from 0.2-0.15 and acrylamide from 10-30% ows. Polymerization can easily be carried out at 40°C for 6 min at pH 4 using a material to liquor ratio 1:2.5 under a stirring rate of 350 rpm. The results further imply (a) that the apparent viscosity of the composite increases by increasing Aam concentration irrespective of the rate of shear, (b) that for 30% Aam concentration the composite consists of 77.7% starch and 22.3% polyacrylamine of which 10.4% are grafted, (c) that the size ability of polyacrylamide-starch composites is much better than that of native starches, and (d) that the kind of starch not only determines the total conversion by also the composition of the composite.

Sun et al. [41] presented a review of studies on corona effects of polyolefin films. It focused on the mechanism of corona treatment of polyolefin films by discussing the chemical and physical changes of this process and the self-adhesion mechanism. Corona discharge of polymeric film introduces polar groups into the surface resulting in increases in the surface energy. This improved substrate wetting and adhesion characteristics. The main chemical mechanism of corona treatment is oxidation. Corona treatment can also crosslink surface regions and increase film cohesive strength.