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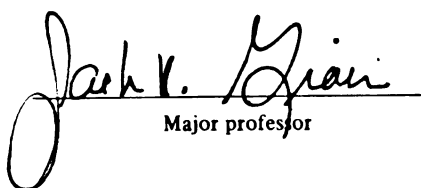
THE EFFECT OF SURFACE MODIFICATION
ON THE PRINTABILITY OF POLYOLEFIN FILM

presented by

CHANIN KULSETTHANCHALEE

has been accepted towards fulfillment
of the requirements for

MASTER degree in PACKAGING


Major professor

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**THE EFFECT OF SURFACE MODIFICATION
ON THE PRINTABILITY OF POLYOLEFIN FILM**

By

Chanin Kulsetthanchalee

A THESIS

**submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

THE EFFECT OF SURFACE MODIFICATION ON THE PRINTABILITY OF POLYOLEFIN FILM

By

Chanin Kulsetthanchalee

Presently, there are several types of surface modification techniques used in industry. Corona treatment, was employed in the present study because of its availability and ease of treatment, as compared to other techniques such as chemical treatment. The effect of surface modification on the printability of polyolefin films was evaluated after contact angle measurements were performed and surface free energy values had been determined, respectively. A modified application of the SPEC*SCAN 2000 computer software was employed for estimation of the area percent of printed surface peeled from the printed film. Electron Spectroscopy for Chemical Analysis (ESCA) was performed to characterize the surface composition of film samples. The results obtained were not conclusive. However, the results of surface free energy estimations proved satisfactory, as anticipated. The higher the corona treatment level, the higher the surface free energy value, as well as the better adhesion of the ink to the film.

..For my Parents and All Beloved Ones...

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Sincerely,

Chanin Kulsetthanchalee

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Chapter 1

INTRODUCTION

Polyolefin films are of widespread use, especially in packaging applications. Several important applications such as adhesive bonding, lamination, printing and painting require good adhesion to polymer surfaces. Printing, as a major method of producing printed media, is one of the major types of today's communication and has become the focus of attention in the packaging industry. As a result of this concern, materials used to produce good quality and effective printing are also the focus of concern.

Since polyolefin film is a non-absorbing substrate, it is difficult to employ it as a printing substrate, unless surface modification is achieved. As a result, it is usually necessary to carry out a pre-treatment to achieve the required adhesion level. The requirement for printability is that the printing ink must wet the surface and adhere to the polymeric substrate. Polyolefins, which refer to polyethylene and polypropylene, are generally known to be difficult to print materials, due to their low surface free energy and poor wetting ability.

Oriented polypropylene (OPP) was first introduced in 1960 (Marra, 1988). Since then, it has replaced several other commercially used packaging materials in a variety of packaging applications, and has become one of the leading commodity flexible packaging films. This dramatic growth is attributed to

oriented polypropylenes outstanding physical properties and relatively low cost.

OPP also offers a number of additional important properties such as:

(i) moisture protection; (ii) longer product shelf-life; (iii) better optical clarity; (iv) excellent mechanical properties; and (v) chemical inertness

(Adamson,1976) The inertness of the polymer surface, however, results in poor ink adhesion. Therefore, surface treatment is required to activate the substrate. This is usually done by a high voltage discharge treatment (corona treatment) , and to a lesser extent, by flame treatment (Brewis,1985).

Mangipudi et al.(1995) suggested and showed that to obtain true surface free energy values, measurements should be made with a Surface Forces Apparatus (SFA), which was originally developed by Israelachvili et al.(1972), rather than through contact angle measurements. The authors evaluated corona treated polyethylene film and confirmed that an increase in surface modification led to an increase of surface energy. Mangipudi et al. also proposed that contact angle measurements gave only an estimation of surface free energy values, since it was not sensitive to small changes in surface composition.

Hollander et al.(1994) found that a combination of contact angle measurements (goniometry) and chemical derivatization reactions could supply semi-quantitative information about functional groups on the upper most surface layers of polymer film. Further, the authors found that when there is little, or a lack of information relative to the chemical structure of the polymer surface, this combination, rather than simple contact angle measurements, was regarded as valuable complimentary methods for the surface analysis of a polymer.

Strobel et al.(1990) studied the aging in air of corona treated polypropylene film and found that the effects of aging on such film were minimal. They also found that aging did not affect ink adhesion for the particular polypropylene film and ink studied.

In these studies, the tests for ink adhesion were performed manually, although based on the following ASTM standards :

ASTM D 3359-93 Standard test method for measuring adhesion by tape test

ASTM D 897-78 Standard test method for Tensile properties of adhesive bonds

ASTM D 1876-93 Standard test method for Peel resistance of adhesives

(T-Peel test)

ASTM D 903-93 Standard test method for Peel or stripping strength of adhesive bonds

ASTM D2979-88 Standard test method for Pressure-sensitive tack of adhesives using an Inverted probe machine.

Thus, according to the studies described above, Strobel et al. (1990) assumed that the choice of probe liquids used for contact angle measurements was appropriate for estimating surface free energy values. Further, the method used in calculation and interpretation was well defined by Park (1994).

In the present study, high density polyethylene film will be subjected to various levels of corona discharge treatment, in order to determine the effect of the corona treatment on the surface free energy of the polyolefin film, and its effect on ink adhesion to the film surface. Therefore, the primary objectives of this study include:

Objectives

1. To determine the effect of corona discharge treatment of high density polyethylene (HDPE) films on surface free energies, as well as the corresponding dispersive and polar free energy components of the total surface free energy, by measuring the contact angles of various liquids on the respective film samples.
2. To determine printability and related characteristics of the corona treated and non-treated polyolefin films, such as wettability and ink adhesion properties through a modification of typical test methods and ASTM standards. The ASTM standard method of test for ink adhesion on the film samples will be modified, so as to minimize the effect of tape application pressure, storage time, peel rate and the peel angle on the ink adhesion peel test.
3. To evaluate the use of the Spec*Scan 2000 system, to estimate and compare ink adhesion to the polyolefin surface, as a function of different corona treatment levels.
4. To evaluate and analyze the obtained data to determine a correlation between corona treatment level and ink adhesion.

Chapter 2

SURFACE PHENOMENA BACKGROUND

Kraus (Kraus,1954) has summarized the results of many direct measurements of the work of adhesion. These measurements were made using precision calorimeters, with the solid in a finely powdered form having a known surface area. The value of work of adhesion for a large class of solid-liquid systems is in the range of 200 to 300 ergs/cm², the adhesion in these systems being due, presumably, to dispersion forces. If the liquid has a dipole moment, the work of adhesion is usually increased by 100 to 200 ergs/cm² because of the electrostatic attractions resulting from the dipole. Those liquids capable of hydrogen bonding show the largest values of work of adhesion, 700 to 1000 ergs/cm² being observed with metal oxides and water.

Two dissimilar substances, brought into intimate contact, exert attractive forces on each other across their common interface. Often these forces are of sufficient magnitude so that the substances tenaciously resist separation. This phenomenon is called adhesion. It is essentially a surface phenomenon, being strongly dependent upon the nature of the surfaces and upon the intimacy of contact of the surfaces.

An interface is an essential feature of an adhesive bond. A related phenomenon, cohesion, refers to attractive forces acting among like molecules and is a bulk rather than a surface phenomenon. Cohesive forces are

responsible for the close packing of molecules in solids and liquids, as contrasted with gases.

Adhesion is an important aspect of bonding operations such as extrusion coating and thermoplastic laminating. In other bonding operations such as heat sealing, an adhesive bond is formed initially, but because of chain diffusion, the interface gradually disappears and the bond becomes cohesive in nature (Marra 1988).

In order to make printing ink adhere to various polymer films, it is necessary to activate the surface of the film. Activation is a surface phenomenon, in which a change in the chemical or physical nature of the surface is induced by passing the film through a gas flame or a corona discharge.

The effect of surface treatment is typically characterized by changes in the surface free energy components, namely the dispersive (nonpolar or London, γ_s^d) and non-dispersive (polar or acid-base, γ_s^p) (Carley et al., 1978). These surface free energy components can be calculated by analyzing contact angle measurements of a liquid phase on the polymer film surface. (Kaelble, 1971)

Based on the work of Zisman (1964) for critical surface tension of wetting (γ_c) and Fowkes (1990) for surface energy based on dispersive components, Dann (1970) carried out contact angle measurements using a series of liquids on polymer surfaces and found that polar force components and dispersive force components should be additive, to evaluate surface

tension and surface energy of low energy surfaces. Carley and Kitze (1978) have well developed the relationship of the respective surface free energy contributions, to characterize adhesion properties and estimate the effect of corona treatment of polyethylene (PE) films. These investigators also measured the films adhesion strength directly, using an adhesive-tape peel test and surface tension tests. Based on the results of their studies, Carley and Kitze (1978) proposed that the polar component of surface free energy was a key to understanding the changes in adhesion properties of the PE film, following corona-discharge treatment.

2.1 Wetting and Adhesion Theory

Wetting is defined as the extent to which a liquid makes contact with a solid surface. The wettability of liquids with a respective surface can be characterized by measuring the peripheral contact angles between the surface of a small sessile drop of the liquid and the horizontal surface of the solid. Adhesion is the intimate bonding together of surfaces on which interfacial forces are acting. The work required to pull the interface apart from two faces can also be estimated. (Kinloch, et al. 1991)

Contact angle measurements provide a simple, inexpensive method to obtain direct information on wetting by the contact angle of a liquid, and can estimate the surface free energy in terms of a solid, as described in Figure 1. At equilibrium, and in the absence of interfacial reactions, the extent of wetting on the surface by the liquid is determined by the force balance between the

three phase contacts, as illustrated in Figure 1. This balance of interfacial forces was initially described by Young in 1805 (Adamson 1976), and it is now known as Young's equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad [1]$$

where the terms γ_{lv} and γ_{sv} are the surface tension of the liquid and the solid in equilibrium with the vapor, respectively, and γ_{sl} represents the interfacial tension between liquid and solid with the contact angle (θ).

The equivalent equation was expressed in algebraic form by Dupre' in 1869, along with the definition of work of adhesion (Adamson 1976).

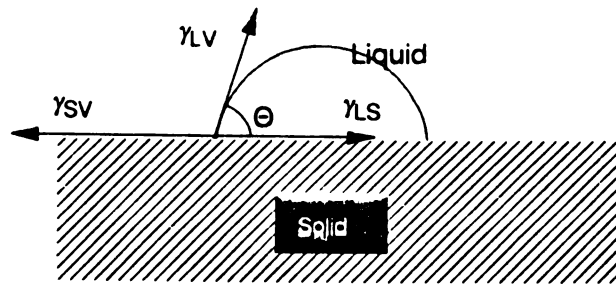


Figure 1 : The surface tension balance at a point of three-phase contact at equilibrium for ideal surface

An ideal surface is a smooth surface, without interfacial reactions with a liquid drop. The surface free energy (SFE) (γ_s) of a polymer can also be expressed by the equilibrium spreading pressure (π) of a test vapor due to the adsorption of vapor molecules, as described in equation [2].

$$\gamma_s = \gamma_{sl} + \pi \quad [2]$$

where (π) is defined as the reduction of (γ_s) due to the adsorption of vapor by the surface, when the vapor obeys the ideal gas laws as in equation [3]

$$\pi = RT \int^{p_0} \Gamma d(\ln p) \quad [3]$$

where (p) is the vapor pressure, (p_0) is the saturation vapor pressure; R and T are the gas constant and temperature, respectively, and Γ is the surface concentration of absorbed vapor. For a polymer with low surface energy, (π) can usually be neglected so that equation [1] is approximated by:

$$\gamma_s = \gamma_{sl} + \gamma_{lv} \cos \theta \quad [4]$$

Equation [4] provides a means to describe the spreadability (or wettability) of liquids on a solid surface. The criteria of the spreading of a liquid on a solid can be expressed by defining the parameter S_e , the equilibrium spreading coefficient.

$$S_e = \gamma_s - (\gamma_{sl} + \gamma_{lv}) = \gamma_{lv} (\cos \theta - 1) \quad [5]$$

When (θ) is zero, i.e. $\cos \theta = 1$, $S_e = 0$, the liquid spontaneously spreads over the surface because of the negative free energy associated with the process. When (θ) is not zero, i.e. $\cos \theta < 1$ and $S_e < 0$, then the liquid is non-spreading over the surface.

The work of adhesion involves the separation of two phases, which are originally in intimate contact with each other. The work of adhesion, W_A , can be combined with equation [4] to give a direct relationship between W_A and wetting, yielding;

$$W_A = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} = \gamma_{lv} (1 + \cos \theta) \quad [6]$$

Equation [6] indicates that W_A can be maximized when the liquid exhibits a zero or near zero contact angle. In addition to the concept of the wetting equilibria being described by thermodynamic relationships with contact angles, the rate at which the contact angle equilibrium is approached depends on such factors as the driving force for wetting, the viscosity of the liquid, and the roughness of the solid surface.

2.2 Surface Free Energy Estimation

Surface energies of solids such as a polymer film are usually estimated from the contact angle measurements using probe liquids of known surface characteristics. Most of the contact angle methods developed to estimate the surface free energy of a solid are based on Young's equation as shown in Equation [1], by using a liquid drop on the smooth and undeformed surface of the solid. Since the surface free energy of a solid cannot be directly measured, various methods of estimating the surface free energy of a solid have been developed and the one used for this work was described in the Appendix .A.

2.2.1 Solid Surface Energy Determination using SFE components

This method is based as Fowkes' proposal that surface free energy components exist, which are due to particular types of intermolecular forces, including dispersion forces, dipole-dipole forces, or hydrogen-bonding interaction. (Fowkes, 1964). It has been recognized that the surface free energy is the result of two major components; namely dispersion forces (or London forces) and polar forces, which are considered as acid/base interactions, and is expressed as follows:

$$\gamma = \gamma^d + \gamma^p \quad [7]$$

where the superscripts *d* and *p*, respectively, are dispersion and polar force components of the surface energy of a solid, such as a polymer film.

Fowkes (1964) then applied the geometric mean to the dispersive force components for estimating the surface energies involving only dispersion forces:

$$\gamma_{ab} = \gamma_a + \gamma_b - 2 [(\gamma_a^d \gamma_b^d)]^{1/2} \quad [8]$$

where γ_a and γ_b are the surface energies of the two phases, and superscript d is the dispersive component of the interfacial energy.

Owens et al. (1969) presented an equation to describe the interfacial energy between two surfaces by combining all interactions, including dispersion forces, into a single γ^p term. They assumed that the geometric mean expression could be extended to polar interactions and subsequently to Equation [9] in the solid/liquid system, as follows;

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2 [(\gamma_s^d \gamma_l^d)]^{1/2} - 2 [(\gamma_s^p \gamma_l^p)]^{1/2} \quad [9]$$

where d and p denote the dispersion and polar components of the interfacial free energy, respectively.

Finally an equation to allow estimating the surface free energy of a solid can be described by combining equation [9] with equations [4] and [7], which eliminates the interfacial energy of the solid and liquid phrases:

$$\gamma_l (1 + \cos \theta) = 2 [(\gamma_s^d \gamma_l^d)]^{1/2} + 2 [(\gamma_s^p \gamma_l^p)]^{1/2} \quad [10]$$

where γ_l is the surface tension of the liquid, which is the sum of both the dispersion and polar force components.

$$\gamma_l = \gamma_l^d + \gamma_l^p \quad [11]$$

By making contact angle measurements with two probe liquids of known characteristics; two equations can be set up for one common solid surface and the equation solved for the unknowns, γ_s^d and γ_s^p . The surface energy of the solid, γ_s is then the sum of these two components.

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad [12]$$

Dann (1970) evaluated the surface energy of many liquids used for contact-angle measurements from the previously reviewed equations. Basically, Dann determined only the dispersion-force components of the liquid surface tension, γ_l^d , by measuring contact angles against a solid that was intended to have only a dispersion-type surface energy. The author measured contact angles of various liquids on paraffin, assuming γ_s^p as zero, and evaluated the dispersion component of the liquid using equation [13]

$$\gamma_l^d = 4\gamma_p^d (\cos \theta) / \gamma_l \quad [13]$$

where γ_l^d is the dispersion force component of the liquid surface free energy; γ_l is the total surface free energy of the liquid, which can be directly measured by using the Du Nouy ring method (1919) or the Wilhemy plate technique (1863); and γ_p^d is the paraffin surface free energy of the dispersion-force component, which was known to be 25.5 [dynes/cm]. Then γ_l^p , the polar (or non-dispersion) component of the liquids surface tension, was calculated by using equation [7]

Some typical liquids used in the contact angle method to characterize the solid surface free energy and their associated solvents are summarized in Table1.

2.2.2 Solution for the work of adhesion

This method is based on the surface tension that can be divided into two components, the dispersion force and polar force components, and is represented by $\gamma = \gamma^d + \gamma^p$ (Equation [7]). The equation $w_A = 2(\gamma_s \gamma_l)^{1/2}$ can be extended with the concept of Owens, et al.(1969) by the following equation ;

$$w_A = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad [14]$$

Combining this equation with the Young-Dupre Equation [6] yields:

$$\gamma_l (1 + \cos \theta) = 2(\gamma_s^d \gamma_l^d)^{1/2} + 2(\gamma_s^p \gamma_l^p)^{1/2} \quad [15]$$

Table 1 : Surface Tension of various solvents at 20°C ^(a)

Solvent	dynes/cm	Solvent	dynes/cm
n-Heptane	19.5	Butyl cellosolve	27.3
Isopropyl acetate	21.2	n-Butyl acetate	27.6
Isopropyl alcohol	21.4	Cyclohexanone	27.7
Ethyl alcohol	22.3	Toluene	27.7
Acetone	22.3	Cellosolve	29.4
Methyl alcohol	22.6	2-Nitropropane	30.0
Isobutyl alcohol	22.8	Methyl Cellosolve	33.0
sec-Butyl alcohol	23.0	Cellosolve acetate	33.6
Diethylene glycol	23.0	Dimethylformamide	35.0
Methyl isobutyl ketone	23.6	Methyl Cellosolve acetate	35.1
Ethyl acetate	23.9	1,1,2,2-Tetrachloroethane	36.0
Methyl ethyl ketone	24.6	Dimethyl sulfoxide	43.0
Cyclohexane	25.5	Ethylene glycol	48.4
Tetrahydrofuran	26.4	Formamide	58.2
Carbon tetrachloride	27.0	Glycerol	63.4
Chloroform	27.1	Water	70.8

(a) Satas, D., *Plastics Finishing and Decoration*. VanNostrand Reinhold, 1986

2.3 Calculations of both contributions to SFE of polymer

Contact angle measurements have been widely used to calculate the values of the dispersion force, γ_s^d and polar force, γ_s^p , components to the total surface free energy, γ_s , by solution of equation [10] or [14]. Kaelble and

Cirlin (1971) used two fluids to calculate the surface energy from geometric mean approximations. Carey et al.(1978) used four liquids rather than two liquids to characterize the surface free energy of a series of test surfaces and Kinloch et al. (1991) have developed a series of equations to reduce errors during calculation of surface energies on the solids by using four liquids.

The following details the derivation of equations and methods.

2.3.1 Determinant method

Kaelble, et al.(1971) analyzed the experimental values of work of adhesion acquired by using the equation $w_A = \gamma_l (1 + \cos \theta)$. In their analysis a pair of simultaneous equations is derived for two liquids, m and n , on a common solid surface:

$$(w_A)_m = 2(\gamma_s^d)^{1/2}(\gamma_l^d)_m^{1/2} + 2(\gamma_s^p)^{1/2}(\gamma_l^p)_m^{1/2} \quad [16]$$

$$(w_A)_n = 2(\gamma_s^d)^{1/2}(\gamma_l^d)_n^{1/2} + 2(\gamma_s^p)^{1/2}(\gamma_l^p)_n^{1/2} \quad [17]$$

where θ is the contact angle of the liquid on the solid surface. Thus, if the values of θ , γ_l^d , γ_l^p for the two liquids are known, these equations may be solved to yield the dispersion and polar force components to the surface free energy of the solid surface. The total surface energy is then simply the sum of these components. However, this method has some limitations when using contact angle data for only two liquids, and suffers errors when calculation of the surface energies is performed with other liquids.

Equations [16] and [17] have a linear relationship in the schematic representation of $(\gamma_s^d)^{1/2}$ versus $(\gamma_s^p)^{1/2}$ as shown in Figure 2, where four linear relationships obtained from four individual liquid contact angle analyses are illustrated. Previously reported studies have solved for the two unknowns by solving for each individual pair of lines and then averaging the results. This direct approach was found, however, to lead to considerable errors in the values of γ_s^d and γ_s^p , which had been calculated.

Kaelble et al.(1971) suggested that the pairs of lines having values exceeding the boundary conditions should be excluded to minimize errors, where D_{boundary} is given by:

$$D_{\text{boundary}} = [(\gamma_l^d)_m (\gamma_l^d)_n]^{1/2} - [(\gamma_l^p)_m (\gamma_l^p)_n]^{1/2} \geq \pm 10 \quad [18]$$

Though this condition was shown to contribute somewhat to reducing the scattering, the conditions of D_{boundary} remain an unverified condition. According to this method, point A and B in Figure 2 are disregarded in the calculation of the surface energy of solids, which may lead to some errors.

2.3.2 The least square method

Kinloch (1987) proposed this method to make it possible not only to calculate the surface energy values by including all the contact angle data, but also to reduce errors in calculations, based on the slopes of the straight lines

shown graphically in Figure 2. It is possible to use Equation [15] and [17] with the method of least squares to obtain the best values of the dispersion force, γ_s^d , and polar force, γ_s^p , components for each treated surface. This is based on the data obtained from a number of liquids instead of just two (Park 1994). The derivation of this procedure and a computer program for solving equations are detailed below.

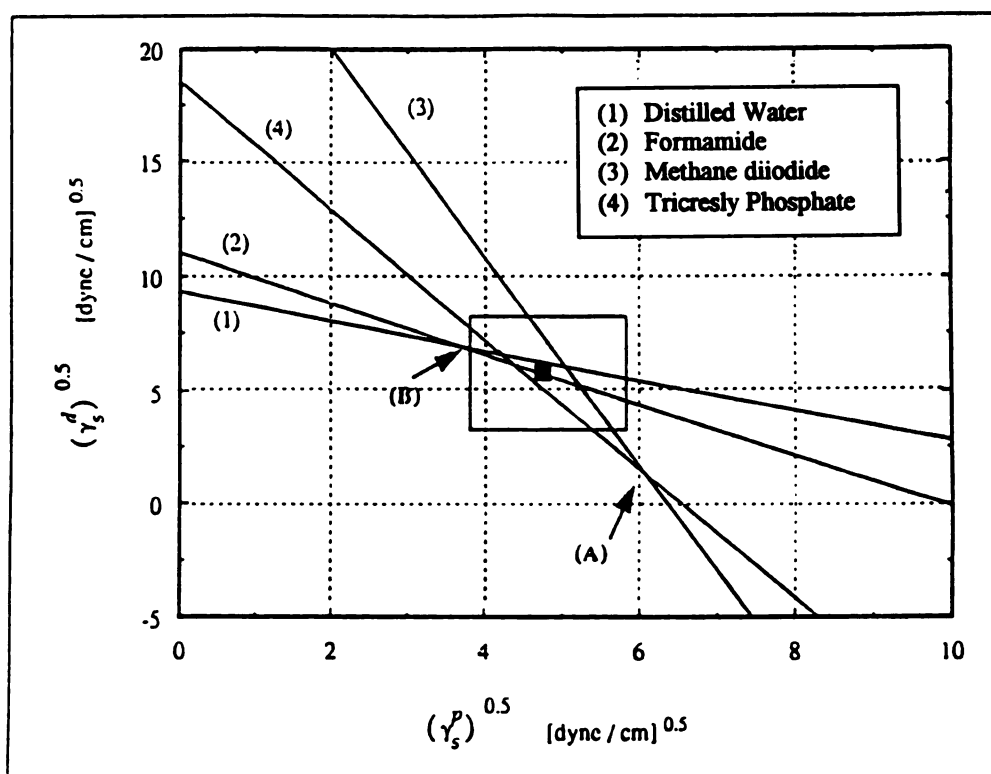


Figure 2 Typical individual relationship of $(\gamma_s^d)^{1/2}$ versus $(\gamma_s^p)^{1/2}$ deduced from one of the equation [16] or [17]

2.3.3 Derivation of least squares method

Equation [15] can be rewritten for each liquid used for the contact angle measurement on the common film surface as follows:

$$2(\gamma_l^d)^{1/2} / \gamma_l \cdot (\gamma_s^d)^{1/2} + 2(\gamma_l^p)^{1/2} / \gamma_l \cdot (\gamma_s^p)^{1/2} = 1 + \cos \theta \quad [19]$$

When k number of liquids are used for the contact angle measurement, Equation [20] can be simplified as in the matrix form with two unknown components of the surface free energy:

$$[A]_{k \times 2} [X]_{2 \times 1} = [B]_{k \times 1} + [e]_{k \times 1} \quad [20]$$

where matrix $[A]$ represents the constant coefficients of the two unknowns, $(\gamma_s^d)^{1/2}$ and $(\gamma_s^p)^{1/2}$, in Matrix $[X]$. Matrix $[B]$ represents the constant values from the right-hand side of Equation [19] (i.e. $1 + \cos \theta$), and matrix $[e]$ is the error involved in balancing the individual equation.

When m number of contact angle measurements for each liquid on a film are recorded, then equation [20] can be extended as:

$$[A]_{k \times 2} [X]_{2 \times m} = [B]_{k \times m} + [e]_{k \times m} \quad [21]$$

Matrix $[B]$ is taken to the left-hand side of the equation [21], and multiplied by both sides of the equality with the transpose of the left-hand side:

$$\begin{aligned} & \{ [A]_{k \times 2} [X]_{2 \times m} - [B]_{k \times m} \}^T \{ [A]_{k \times 2} [X]_{2 \times m} - [B]_{k \times m} \} \\ & = \{ [A]_{k \times 2} [X]_{2 \times m} - [B]_{k \times m} \}^T \{ [e] \} \end{aligned} \quad [22]$$

where superscript T presents the transpose of the matrix concerned. The equation can be expanded to:

$$\begin{aligned} & \{ [X]^T [A]^T [A] [X] \}_{m \times m} - \{ [X]^T [A]^T [B] \}_{m \times m} \\ & - \{ [B]^T [A] [X] \}_{m \times m} + \{ [B]^T [B] \}_{m \times m} = [E]_{m \times m} \end{aligned} \quad [23]$$

When the partial derivative of matrix [E] is employed for the two unknowns (X_1 and X_2) and made to zero to minimize the error then:

$$\partial [E] / \partial X_1 = [A]^T [A] [X] + [X]^T [A]^T [A] - [A]^T [B] - [B]^T [A] = 0 \quad [24]$$

$$\partial [E] / \partial X_2 = [A]^T [A] [X] + [X]^T [A]^T [A] - [A]^T [B] - [B]^T [A] = 0$$

Since the above two equations are the same, rearranging one of the equations gives:

$$\{ [A]^T [A] [X] - [A]^T [B] \}_{2 \times m} + \{ [X]^T [A]^T [A] - [B]^T [A] \}_{m \times 2} = 0 \quad [25]$$

Equation 25 is in the form of $[z] + [z]^T = 0$. In order to satisfy the equality to zero, then both matrixes should be individually equal to zero. Therefore:

$$\{ [A]^T [A] [X] \}_{2 \times m} = \{ [A]^T [B] \}_{2 \times m} \quad [26]$$

and

$$\{[X]^T[A]^T[A]\}_{m \times 2} = \{[B]^T[A]\}_{m \times 2} \quad [27]$$

Equation [26] is the transpose of equation [27] Therefore one of these two equations is required for analysis for contact angle measurements. Matrix [X] in the above equations can be solved by one of equations below:

$$[X]_{2 \times m} = \text{inverse}\{[A]^T[A]\} \{[A]^T[B]\}_{2 \times m} \quad [28]$$

and

$$[X]_{m \times 2} = \text{inverse}\{[A]^T[A]\} \{[B]^T[A]\}_{m \times 2} \quad [29]$$

There are several advantages to using this method, namely: this method yields the least errors, it accepts all the data, and it is very simple to employ into a computer program. A computer program to solve this equation can be written by using fortran, basic, or any software which can calculate the matrix. In the present study. "Microsoft Excel"™® (Microsoft corp.) software has been used to solve the matrix [X] in Equation [28].

Chapter 3

SURFACE ACTIVATION OF POLYMERS

The author has reviewed in detail the topic of surface activation corona discharge and since the detailed review of this topic is considered beyond the scope of this dissertation, an abbreviated summary of the topic area as described by McKelvey (1962) is presented below.

“Even though nonpolar polymers, such as PE, PP, do not adhere well to other materials, there are still many applications in which they are bonded to paper, metals, inks, and other plastics. It is necessary to activate the surface of the nonpolar material before it comes in contact with the other adherend in order to achieve satisfactory adhesion in these bonding operations.”

“A wide variety of techniques have been used for surface activation. These include sundry chemical treatments involving chlorine gas, ozone, and other oxidizing agents, exposure to hot gases and flames, and exposure to various types of electrical discharges.”

“According to Allan (1959), complete wetting is a necessary condition for good adhesion. Activation increases the wettability (decreases the contact angle) of a surface toward a polar liquid. Because materials such as polyethylene are wet by printing inks only after being activated, surface activation is a necessary prerequisite to the printing of polyethylene.”

"In addition to making polyethylene compatible with printing inks, activation appears to increase its adhesion to metals and metal oxide surfaces. It has been reported that the adhesion of polyethylene to stainless steel increases with the degree of oxidation of the polyethylene."

"Most investigators agree that activation is the result of the formation of polar groups in the surface. Rossman (1956) activated polyethylene film samples with a flame, a glow discharge, and a brush discharge from a Tesla coil. Spectrophotometric examination indicated that oxidation occurred in all three cases. Hines (1957) conducted similar studies on polyethylene film that had been flame activated. He concluded that hydroxyl and ether groups, probably in the form of formals and hemiformals, were formed on the surface. Various chemical treatments for the activation of polymer film surfaces have been reported and are reviewed by Bloyer(1955) .The simultaneous action of chlorine gas and ultra-violet radiation proved moderately successful. Wolinski (1955) reported that films could be activated with a combination of ozone and a hydrogen halide or ozone with nitrous oxide. Horton (1954) patented a process for surface activation via oxidation with chromic acid and other strong oxidizing agents. Kreidl et.al.(1955) reported that activation is obtained by exposing the surface of polyethylene to a high temperature, while the bulk of the material is kept at a low temperature. He proposes using hot combustion gases, hot air, exposure to open flame without actual contact, and exposure to electric heating elements."

“There are two activation processes of commercial importance. One process, patented by Kritchever (1953), involves the direct exposure of the film surface to an open flame. The other process, patented by Traver (1957), involves passing the film through an electric field in which rapid electron bombardment of the surface occurs.”

Brewis (1994) stated that adhesion to polymer surfaces needed for good printing required surface pretreatment, such as the use of corona discharge or flame treatment, in order to attain the required adhesion level. In practice, there are various types of surface pretreatments which are essential for providing good adhesion to polymer surfaces. These include flame treatment, chemical etching treatment, plasma treatment, and corona discharge treatment.

According to Lane and Hourston (1993), various commercial applications of polyolefins, such as adhesive bonding, printing, and extrusion coating, which require good adhesion, may give rise to some problems.

The effects of corona discharge treatment on ink adhesion to high density polyethylene are described in detail below. The effects of the other pretreatment techniques on polyolefins are also briefly discussed.

Pretreatment techniques other than corona discharge are described initially, followed by a detailed review of the corona discharge procedure.

3.1 Flame treatment

Flame treatment: It is used to improve ink adhesion to molded polyolefin, acetal copolymer and polyethylene terephthalate containers. That is, an object is passed over one or more burners, which consist of a large number of closely-spaced jets which are fed with an air-gas mixture.

(Brewis 1985)

Flame treatment is believed to help oxidize and make the surface easily wettable, because flames generally consist of excited species of O, NO, OH, and NH, that will remove hydrogen from the plastic surface, which is contacted for a period of less than 1 second with the oxidizing portion of the flame. Ayres and Shofner (1972) found that the optimum treatment time for an unspecified polyolefin was 0.02 seconds.

The treatment level may be affected by variables such as the air-to-gas ratio, distance of surface to be treated from the visible blue tips of the flame, and speed of the part passing through the flame.(Satas, 1986)

The treatment is suited to various shapes of objects. Round containers, for example, can be treated on all sides by rotating them, or by dropping them through a ring burner. The treatment can also be used in, in-line processing. When applied prior to corona discharge, flame treatment helps improve the printing quality, since the flame will break down the crystallites, and render the surface more susceptible to corona discharge treatment. Moreover, the treatment allows additives, which are usually restricted to antioxidants and anti-static agents, to survive during the process (Brewis,1985)

For sheeted objects, the process is preferred for use with sheeting with a thickness greater, rather than less than 0.6 mm (23.6 mil)

3.2 Chemical treatment

Chemical treatment: The polymer surface is exposed to certain types of chemical oxidizing agents such as chromic acid, permanganate compounds, and or sulfonate compounds, which results in chemical reactions and microroughness on the surface of the object (Satas,1986). Brewis (1985) accumulated several interesting formulations of compounds for this treatment.

Chemical treatment is not an easy or convenient process, because it requires immersion and exposure to chemical reagents within a specific period of time. Further, it requires that the object be precleaned and replaced by a new one at a certain time interval, in order to avoid contamination. Thus, this treatment can be employed with irregular shaped objects, or only after other simpler and lower cost methods have proven to be unsuccessful. Polyethylene, polypropylene, acrylonitrile-butadiene-styrene terpolymer (ABS), poly(phenylene oxide), polyether, and polystyrene can either be treated by this method or by one of the other treatments described. The surface energy of these polymers are summarized, as shown in Table 2. (Lekan 1988)

ABS and PP parts, for instance, may be chemically etched for metallic plating. Conversely, fluorocarbon polymers are more likely to be treated by this chemical treatment procedure. The major disadvantages of chemical treatment are its corrosive nature and the effluent problem. However, chromic acid etching

improves bondability by removing amorphous or rubbery areas and forming cavities, since surface oxidation might occur and leads to surface wettability.

Table 2 : Surface free energy of typical polymers ^(a)

Polymer type	dyne/cm	Polymer type	dyne/cm
Polypropylene -PP,OPP	29-31	Polyethylene - PE	30-31
Polytetrafluoroethylene (Teflon) - PTFE	19-20	Polyvinyl fluoride (Tedlar)	28
Polystyrene - PS	38	PET	41-44
ABS	35-42	Polycarbonate - PC	46
Polyamide	< 36	Polyimide	40
PMMA	< 36	Polyaryl ether ketone	< 36
Epoxy	< 36	Polyacetal	< 36
Fluorinated ethylene propylene - FEP	18-22	Polyphenylene oxide - PPO	47
Rigid PVC	39	PBT	32
Plasticized PVC	33-38	Polysulfone	41
Polyester	41-44	Polyethersulfone	50
Polyvinylidene fluoride	25	Polyarylsulfone	41
Nylon	33-46	Polyphenylene sulfide	38

(a) Lekan S.F., "Corona treatment as an adhesion promoter for UV/EB curable coatings" *Journal of Radiation Technology*, 1988.

To achieve maximum adhesion strength, the degree of surface porosity must be compatible with the level of etching.

3.3 Plasma treatment

Plasma treatment: The interaction of the surface of a monolayer material with a chemical plasma (ions, electrons, atoms and radicals), which is formed

when power is applied to a typical gas like oxygen, nitrogen, hydrogen, argon and the like at low pressure, leads to rapid chemical modification of the surface, which improves wettability and adhesion characteristics.

Compared to ozone and corona discharge treatments, plasma treatment is a more rapid process and leaves less damage to the polymer surface. Schonhorn and Hansen (1966), as cited in Satas (1986), showed that a polyethylene surface can be effectively treated by an inert gas plasma produced by a radio frequency field, which improved the polymer films bondability. Commercially, this method is used for difficult-to-treat polymer surfaces. Garbassi et al. (1994) stated that plasma treatment is required to be carried out in a vacuum chamber and gas feed, to maintain appropriate pressure and composition of gaseous mixtures.

Parameters which affect plasma treatment are sample and chamber geometry, pressure, gas flow rate, and the electromagnetic force.

There are two types of plasma treatment: cold and hot plasma treatment. The former treatment is carried at a low temperature and at a low pressure, while the latter treatment is carried out at very high temperatures (5,000 - 10,000° K) and at atmospheric pressure. Cold plasma treatment is used in micro-electronic fabrication, which deals with plasma etching of inorganic substrates such as silicon. Hot plasma treatment deals with hard or wear resistant coatings, which involve melting an inorganic powder such as a ceramic and spraying the molten substance on metal surfaces.

3.4 Corona discharge treatment (CDT)

Corona discharge treatment (CDT): It occurs in the electromagnetic field between two electrodes, one of which is at a high potential and the other is grounded. The treatment is carried out at atmospheric pressure, and at relatively low temperature. The gases in the field are ionized yielding oxygen-containing excited species which react with the polymer surface.

Several theories for the observed increased adhesion after CDT have been proposed. The most important ones involve degradation, cross-linking, oxidation, hydrogen bonding, ozonation, and electret formation.

The electret formation theory is contradictory to radical-based degradation, oxidation, and hydrogen bonding concepts. Electret as an electrical counterpart of a permanent magnet, by which the electrical potential is caused, consists of different phenomena such as homocharges and heterocharges. (Kim et al. 1971)

Homocharges are developed from external polarization, which is affected by the injection and subsequent trapping of charge carriers (electron from the ionized air molecules), while heterocharges are developed from internal polarization. The term 'homocharges' refers to the surface charge, which has the same polarity as the electrodes.

Internal polarization consists of atomic-, dipole-, barrier- and space-charge polarization, which results in net charges at the surface, with an opposite polarity to that of the electrodes.(Stradal et al. 1975)

Electrons, protons, excited atoms and ions in the plasma of corona discharge could cause carbon-to carbon and carbon to hydrogen bond breakage on the polymer surface. (Satas,1986), resulting in the formation of free radicals. The radicals formed are long-lived and can react with oxygen and/or nitrogen, resulting in the introduction of polar groups on the polymer surface, thus making it more easily wettable. Other changes also occur during the corona discharge treatment. Low molecular weight material, which might be on the surface may cross-link, and consequently modify the surface properties. For example, the heat sealing temperature of the treated film is lower than the one without treatment.(Blythe et al.1978) It has been proposed by Baszkin et al. (1976) that the wettability of a treated polyethylene surface is decreased, if its temperature was raised to 85°C. This can be explained by the redistribution of external groups, due to incremental chain mobility at the temperature of testing. Some of the lower molecular weight scission products, such as various processing additives, may migrate into the bulk polymer, therefore depriving the surface of lower molecular weight polar materials.

The corona discharge treatment can be erased from the film by contacting with a metallic surface. Therefore, contact of a corona treated surface with metal should be avoided. The wetting tension of corona treatment film may also change during storage. This change can be attributed to the migration of low molecular weight compounds to the surface. This is illustrated in Figure 3, where the wetting tension of a corona treated polyethylene surface is plotted as a function of time following Corona treatment.

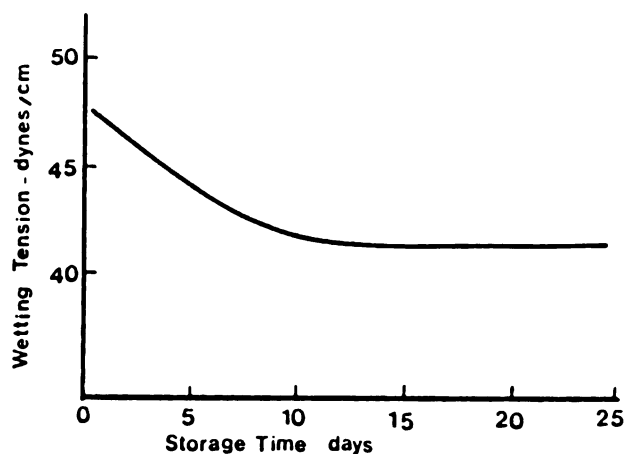


Figure 3 : Effect of storage after corona discharge treatment on the wetting tension of a polyethylene surface.

Surface activation by corona discharge requires relatively simple equipment, is easy to control, and yields uniform and reproducible results. The process, which has considerable commercial importance, is shown schematically in Figure 4. The equipment consists of a power supply that provides a high voltage alternating potential to a sharp-edged electrode. A rotating metal drum, maintained at ground potential, is located so that there is a narrow gap between its surface and the edge of the electrode. The films are carried by the drum through the gap, thus exposing its free surface to the electrical discharge.

An equivalent electrical circuit for the process is also shown in Figure 4.

It assumes that the plastic film is nonconducting, and thus introduces only capacitance into the circuit. In its unionized state, the air in the gap is essentially nonconducting, but when ions are present, an electric current can be carried

across the gap. The air, therefore, is represented as a capacitor and a resistance in parallel, with one or the other predominating, depending upon the condition of the air. Hence, before breakdown of the air (ionization), the equivalent electrical circuit consists of two capacitors in series and, after breakdown, of a capacitor and resistance in series.

Corona discharges, which are characterized by high voltages and low currents, occur at atmospheric pressure when one of the electrodes has sharp edges or points. The discharge begins when the electrode potential increases to the point where partial ionization of the gas takes place. The gap becomes filled with a pale violet glow, a hissing noise is heard, and the odor of ozone

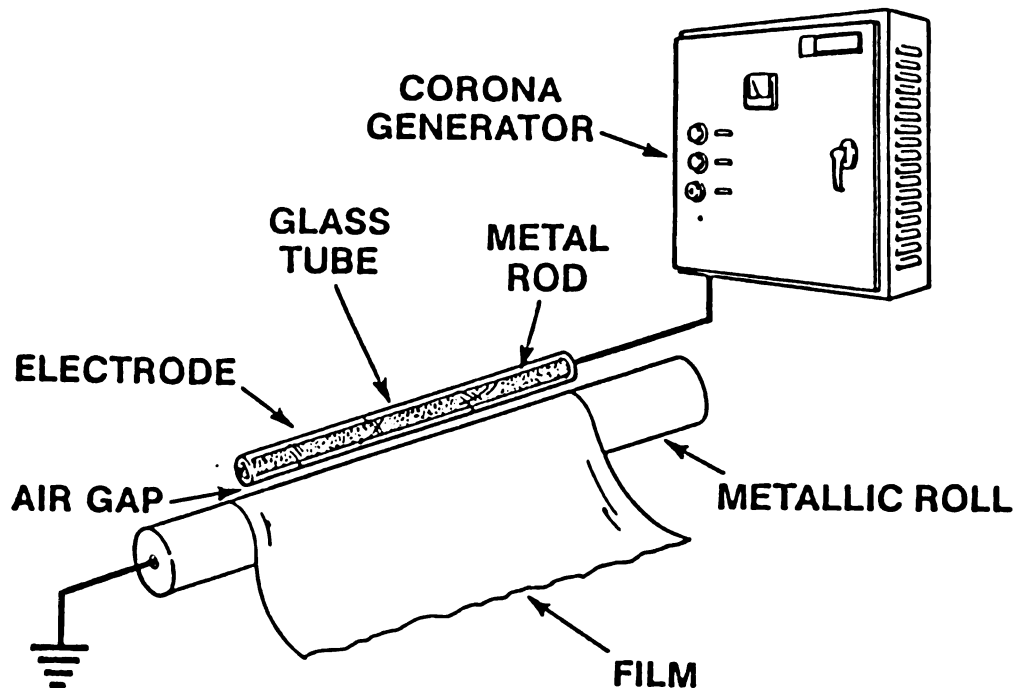


Figure 4 : Apparatus for surface activation of plastic film by corona discharge with equivalent electrical circuit.

can be detected. Bright blue streamers emerge from sharp points on the electrode and terminate in the gap. If the plastic film were not present, or if it should rupture so that the streamers could reach the other electrode, sparking and then arcing would result, and the current would increase drastically.

The current in the corona discharge is carried by electrons and ions. During the first half cycle, charged particles of the same polarity as the electrode collect on the film surface. This reduces the effective field strength and thus quenches the corona before the end of the half cycle. When the polarity of the electrode changes, the oppositely charged particles now on the film surface cause an increase in the gradient in the gap, and the corona starts at a lower applied potential than in the initial half cycle. Therefore the plastic film has the effect of enabling the discharge to be sustained at a lower applied potential. The primary operating variables in the activation process are the voltage and frequency applied to the electrode, the distance between the electrode and the film surface, and the linear speed of the film. The following kinetic analysis of surface activation via corona discharge attempts to relate these variables to the degree of activation of the film. The key assumptions in the analysis are as follows :

1. Activation is due to the production of polar groups on the surface of the film.
2. Polar groups can be produced only at certain reactive sites on the surface of the film.
3. The key step in the formation of a polar group is the collision of a charged particle with a reactive site.

Leach and Pierce (1993) stated that good quality ink should remain on the surface of the printed packages for as long as the paint's lifespan. They add that the adhesive properties of the ink depends upon its compatibility with the vehicle system, the type of pigments and their percentage, as well as the degree of dispersion in the final ink. Of the three, the vehicle system seems to be the most influential factor in determining the ink's adhesive properties; namely, the degree of vehicle penetration into an absorbent substrate and the film-forming ability of the ink resin, with a molecular affinity for the substrate on non-absorbent substrates. Thus, it is very crucial which type of ink resin should be employed. There are two means by which the vehicle system has an influence over the adhesion of an ink. That is, it produces wetting and flow-out of ink, which provides a continuous film essential for good adhesion. Moreover, the vehicle system is good for penetrating the substrate. The surface of Poly(vinyl chloride) PVC, for example, can be softened, which causes chemical and physical bonding.(Satas,1986)

Chapter 4

EXPERIMENTAL PROCEDURES

4.1 Methods of Contact Angle Measurement

The surface energy of non-treated and treated films was calculated from the analysis of contact angle of the following liquids on polymer surfaces: distilled water, formamide, di-iodomethane, and tricresyl phosphate. The values of surface energy of the four liquids are shown in the Table 3.

Table 3 : Surface energy of liquids used in the experiment ^(a)

Liquids	Surface energy of the corresponding component (dynes/cm)		
	Dispersive	Polar	Total
Formamide	32.3	26.0	58.3
Distilled water	22.0	50.2	72.2
Di-iodomethane	48.5	2.3	50.8
Tricresyl phosphate	36.2	4.5	40.7

(a) Feast W.J. et.al. 1992. Polymer Surfaces and Interfaces II. John Wiley&Sons

4.1.1. Apparatus and materials used for contact angle measurements

A contact angle Goniometer (Model 100-00 115, Rame-Hart corporation, Mountain Lake, New Jersey) was used to measure the contact angle of liquids on polymer surfaces in this study. Apart from the Goniometer, contact angle measurements required the following : glass slides, double-side adhesive tape,

the four contact angle liquids mentioned above, a pipette 'Pipetman' (0-200 μ l), and polymer test films.

Materials

• Film sample

Corona discharge treated high density polyethylene films (1.5 mil thickness) obtained from Tredegar Film Products (Richmond, Virginia) were used in the present study. Treatment levels were 0, 1.8, 2.2, 2.6 and 3.0 Kw, respectively.

• Liquids used in Contact angle measurement

Distilled water (Deionized grade)

Formamide CAS 75-12-7

(super pure grade $\geq 95\%$)

Methylene Iodide, CAS 75-11-6

(purified grade)

Tricresyl Phosphate, CAS 1330-78-5

(technical grade : 80% para, 20% meta)

All above were supplied by Fisher Scientific (Fairlawn, N.J.07410)

4.1.2. Sample preparation for contact angle measurements

Pre-cleaned and air-dried films approximately 2 x 1 inch² were mounted very smoothly on a glass slide by using double adhesive tape. The sessile drop method of measuring contact angles was used in this study, at ambient atmosphere at room temperature. Droplets of 5~7 μ l size were formed on the

polymer film surfaces delivered from a Pipetman ® pipet (0~200 µl) in such a way as to make the angles advance. A minimum of 12 contact angle measurements were made to calculate the surface energy of the test polymer film by the computer software program, as detailed in the appendices section. Angles were read to the closest degree by using a 10 x microscope with a protractor eyepiece. The procedure employed to measure the contact angle for the respective film samples was as follows :

1. The polymer test film was mounted on top of the adhesive tape after a piece of double-side adhesive tape had been placed on a glass slide of 2.5 x 1.25 inches. It is crucial that air bubbles be avoided from the space between the laminates. Within 48 hours, the film sample will reach the equilibrium state where the air will gradually disappear.

2. The microscope was focused on the nearest edge of the film surface and the film surface and 'base-line' adjusted to achieve coincidence. This setting was not changed during the reading of the contact angle. (See Figure 5)

3. A pipette was set to produce droplets of 5-7 µl on polymer film samples, depending on the test liquids, to form the droplets deposited onto the film as a sessile drop of about 2.5 mm diameter with the Pipetman ® pipet (0~200 µl). At least 12 contact angle values for each liquid were measured within an error of 3 degrees. The contact angle values were then converted into surface energy

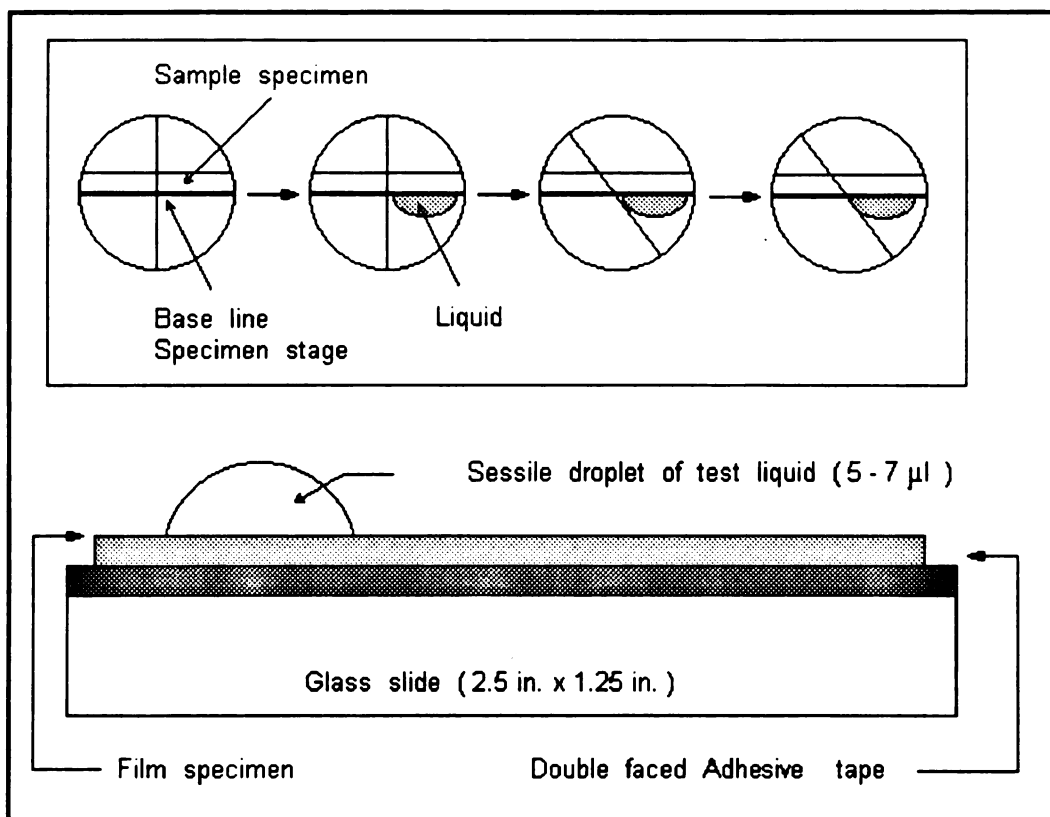


Figure 5 : The view from eyepiece len of Goniometer and sessile drop on sample

values of the polymer film, by the computerized software, as described in the appendices.

4. After the glass slide with polymer sample was placed face-up on the specimen stage of the Goniometer, the microscope was adjusted to aim at the horizontal reference line in order to measure contact angle values.

5. The specimen stage was adjusted to be able to view the nearest edge of the left angle of the sessile drop. The microscope, again, was reset by shifting the cross hair line which it, at the beginning, would be perpendicular to the base line when looked in the eyepiece lens, as shown in Figure 5.

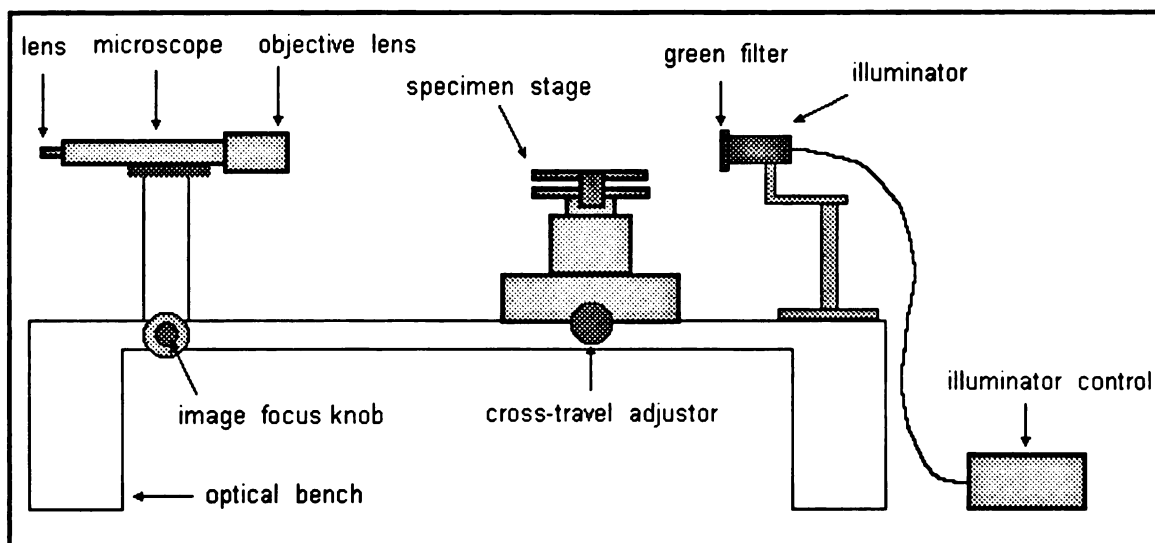


Figure 6 : Goniometer schematic (model 100-00 115, Rame-Hart, Inc.)

6. The measuring cross line was adjusted to tangency above the base of the drop to create a wedge of light bounded by the two cross lines and the drop profile.

7. The cross line was slowly rotated in order to measure it, while adjusting the cross travel of the specimen stage so that the wedge of light would be gradually extinguished and the cross-line would attain tangency with the drop profile at the base of the drop.

8. At least 12 measurements of contact angle values were measured for each liquid on the same samples which the process was repeated as above.

For water and formamide which have high surface tension, as they form relatively large contact angles on the film, the contact angle readings were able to be taken after 30 seconds. Meanwhile, the other two liquids (i.e., di-iodomethane and tricresyl phosphate), which have low surface tension, spread rapidly on the film. Therefore, the contact angle must be read as soon as the droplets formed, within a 30 second period.

4.1.3. Calculation of surface energy of solid

The measured contact angle values on the film surfaces from the four liquids were used to calculate surface free energies, and the corresponding dispersion and polar components, according to the method of solving the equations described by Park (1994).

The following equation, which describes the interaction of liquids with a solid surface, was based on the geometric means of the force interactions and the sum of the dispersive and polar terms.

$$\gamma_l (1 + \cos \theta) = 2 (\gamma_s^d \gamma_l^d)^{1/2} + 2 (\gamma_s^p \gamma_l^p)^{1/2} \quad [30]$$

where γ_s^d and γ_s^p can be calculated by solving two equations which were set up by contact angle measurements with four liquids of known surface tension values. The least square method was used to obtain the best values of the surface energy of the test solid.

A computer based program was developed by Park (1994) in order to calculate the surface free energy of polymers with polar and dispersive components and for providing a graphic representation of $(\gamma_s^d)^{1/2}$ versus $(\gamma_s^p)^{1/2}$, where the four linear relationships are plotted using one of the simultaneous equations given in the above equation. The procedure of Kaelble (1971), using the determinant method, and of Kinloch et al.(1991), using the least square method, were fully detailed in the theoretical sections.

4.2 Application of Printing Ink

Materials and apparatus

- **Film sample**

Corona discharge treated high density polyethylene films (1.5 mil thickness) obtained from Tredegar Film Products (Richmond, Virginia) were used in the present study. Treatment levels were 0, 1.8, 2.2, 2.6 and 3.0 Kw, respectively.

- **Printing inks**

A B&D™ opaque white, flexographic printing ink, manufactured by Sun Chemical Corporation, (Carlstadt New Jersey) and provided by Cellofoil film Inc., (Battle creek, Michigan) was used in the present study.

The composition of the printed ink is as follows :

Ingredients [% by weight of total formula]

Solids components	50.3
Ethyl alcohol	22.8
n-propyl acetate	12.9
n-propyl alcohol	8.5
Isopropyl alcohol	5.4
M&P naphtha	0.3
Total	100.0

- **Anilox roller with a 2.5 inches bandwidth**

1. Samples from the five film rolls were removed and were cut into pieces of 12 x 5 inches each.

2. The external side of the film, which was treated by corona discharge at 4 different levels, were marked in order to differentiate it from the non-treated side.

3. The cut pieces of film were placed on white paper, with the non-treated facing the paper and they were attached together by an adhesive tape.

4. Multi B&D opaque white ink, contained in a disposable glass pipet, was dropped on an Anilox roller with a 2.5 inches bandwidth. The ink was then rolled onto the treated side of the cut film to provide a printed surface.

5. The film was then left to dry at room temperature for approximately 30 minutes.

6. After drying, the printed film samples were again cut into stripes of (1.5 - 2) x 11 inches, which consisted of no stains or any other visible printing flaws.

7. Each piece of the selected printed film was labeled to identify its level of corona discharge treatment.

The entire process was repeated until acceptable results were obtained for each film sample.

4.3 Sample preparation for the Peel Adhesion Test

1. The Scotch brand tape (No. 610) was placed on the printed surface of a film sample of 1.5 to 2 x 11 inches.
2. A rubber roller of 5.2 lbs. was used to apply the tape at a constant pressure, so as to provide uniformity from sample to sample.
3. The printed sample film was then cut into a piece of 1 inch in width and 11 inches in length.
4. The sample film was wrapped in aluminum foil and stored at ambient temperature to be used within 48 hours.

4.4 Peel Adhesion Test

Traditionally, the peel adhesion test is conducted manually, with no standardized methods. In the present study, the test procedures were designed to be more scientifically oriented and standardized. Namely, the terms and procedures employed in the present study were based upon the ASTM standards. The ASTM standard methods modified for application in this study are as follows:

ASTM D 3359-93 Standard test method for measuring adhesion by tape test

ASTM D 897-78 Standard test method for Tensile properties of adhesive bonds

ASTM D 1876-93 Standard test method for Peel resistance of adhesives

(T-Peel test)

ASTM D 903-93 Standard test method for Peel or stripping strength of adhesive bonds

ASTM D2979-88 Standard test method for Pressure-sensitive tack of adhesives using an Inverted probe machine.

One of the objectives of the study was to assess the relationship between changes in surface energies of the film and ink adhesion, in order to evaluate the effects of surface modification of polyolefin films on the films printability. The test methods employed were designed to determine the adhering ability of an ink coatings, to a film substrate, by using pressure-sensitive adhesive tape, under a specific set of test conditions. The test for untreated film is employed as a control.

Apparatus & Test specimen

•**Tensile Testing Machine** -Instron Universal Tensile tester model SFM-20, (United Calibration Corporation, Huntington Beach, California).

A power-driven machine, with a constant rate-of-jaw separation which shall have the following features :

- The applied tension, as measured and recorded, should be accurate within one percentage.
- Specimens shall be held in the testing machine by grips which clamp firmly and prevent slipping during the test.
- The rate of travel of the power-actuated grip shall be uniform throughout the tests. In this study, a crosshead speed of 20 inch per minute was used for each samples tested.
- The machine shall be autographic giving a chart having the distance of separation as one axis and the applied load as the other axis of coordinates.

A 500 gram load cell was employed to utilize the sensitivity of the machine during test and to make possible the measurement of the force with minimal fluctuations during the test. The test system was operated by using a computer controlled system (United Calibration Corporation) at the Composite Material and Structure Center (CMSC), MSU.

- **Polyethylene film samples** were coated with printing ink and cut into strips of the size of 1.5 x 11.0 inch

- **Tape test** - Scotch tape No.610 ® (™ of 3 M Products, St.Paul, Minnesota)

Conditioning

Test condition at room atmosphere (23 ± 2 °C and 50 ± 5 % R.H.). Prior to testings an alignment check was made by placing the provided metal plate between the upper and lower jaws to insure that the tension is uniform and symmetrical.

4.5 Method for Measuring Printing ink Adhesion by Peel Test

The tensile machine used in the test was initially standardized with a 500 gram load cell and programmed by a computer to run at a rate of 20 inches per minute.

A length of 1 inch from one end of the adhesive tape was attached to the upper clamp jaw and a 1 inch length from the same end of the sample film was attached to the lower clamp jaw. The substrates were then thoroughly separated by the clamp jaws. A schematic diagram of the test apparatus is presented in Figure 7. The sample -tape composite for testing ink adhesion is shown as well.

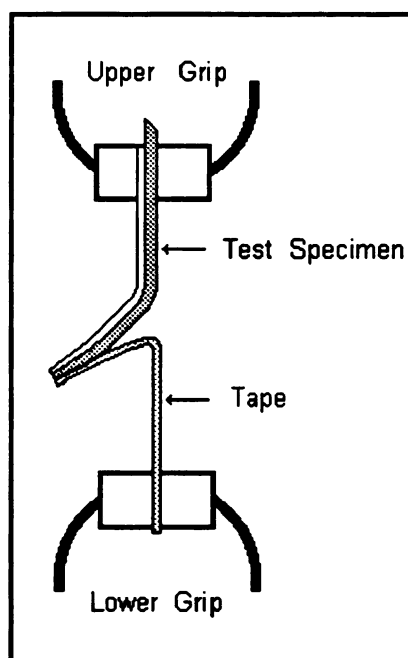


Figure 7 : Peel Testing Apparatus scheme

When the tape was peeled from the sample film, the differences between the extension(%) and the load (gms) as a function of different corona treatment levels were recorded. The peeled area was observed to determine the degree of ink adhesion. The ink on the film which was treated at a higher corona treatment levels was expected to show a lesser degree of peeling from the film surface, than from film exposed to lower treatment levels.

The load, which measures the force of peeling the tape from the film, was recorded. An autographic plot of the load (lbs) and extension of peeled distance was obtained.

The appearance of the ink coated film surface was observed and the condition of the surface recorded. For further analysis, the ink-stained tapes

and the ink-peeled film samples were stored in resealable bags, for further analysis with the application of the SPEC * SCAN 2000 system.

4.6 Quantitative measurement of the peeled areas of the sample film

In this study, the SPEC*SCAN 2000 system, (Apogee Systems), which is a pulp & paper gray scale visual impact dirt counting system, was adapted for use with polymer film. It should be noted that the SPEC*SCAN 2000 system is normally used for dirt and fiber content analysis of the pulp and paper, based upon the TAPPI T 437 om-90 standard developed by Apogee Systems, Inc. These measurements were conducted at the Department of Pulp and Paper Science, Western Michigan University, Kalamazoo, Michigan.

The SPEC*SCAN 2000 system is computerized with a high resolution flat bed image scanner. It operates on the SPEC*SCAN 2000 software supplied by Apogee Systems, Incorporated.

For analysis, the peeled film was placed on the scanner, covered with black paper simulating dirt, and the area of grayness (the peeled area) was then scanned and quantified by the apparatus. The peeled area was determined in square millimeter (sq. mm) and then converted in proportion to the total printed area of 1x10 sq. in (6451.6 sq. mm). The calculated data was reported in tabular form. The results of the measurement of the peeled areas of the respective test films were compared with one another, in terms of the different levels of corona treatment film.

Definition of terms used

Pressure-sensitive adhesive - a viscoelastic material which in solvent-free form remains permanently tacky. Such material will adhere instantaneously to most solid surfaces with the application of very slight pressure. (Refer to Scotch brand TM number 610)

Flexible - indicates a material of the proper flexural strength and thickness to permit a turn back at an appropriate 180° angle in the expected loading range of the test without failure.

4.7 ESCA Analysis

The surface composition of the films was determined by Electron Spectroscopy for Chemical Analysis (ESCA), using a Perkin-Elmer PMI model 5400 system with a standard Magnesium source ($K\alpha$ 1, 2) operated with 1253 eV at 300 w 15 Kv, 20 mA at the Composite Materials and Structure Center (CMSC) MSU. The instrument employed a 180°hemispherical energy analyzer operated in the fixed analyzer transmission mode at a pass energy of 89.75eV and a position sensitive detector for signal collection. Spectra were collected using an analysis area of 3x 10mm. Spectra were collected using a 45 ° take off angle between the sample and the analyzer lens. Survey spectra were collected for each of the samples to identify elements present and surface atomic concentration was calculated.

In the ESCA experiment, identification of elements and their compounds is based on peak position, expressed as binding energy, and peak shape. When only one type of bonding is present, the peak shape will be symmetrical. For multiple types of bonds it is possible to see asymmetric peak shapes due to differing binding energies leading to overlapping peaks.

Error in quantitative results from the ESCA experiment has been generally accepted to be within ten percent for survey analyses and within five percent for high resolution work.

Quantitation in the ESCA experiment is described as surface atomic concentration. For example, if a sample is composed of 57% sulfur, 6% oxygen and 37% carbon this is interpreted as: for a surface consisting of 100 atoms, 57

are sulfur, 6 are oxygen and 37 are carbon atoms. The limits of detection for the ESCA experiment are generally accepted to be more than 0.2%.

Surface atomic concentrations are calculated using sensitivity factors. These factors include instrumental factors and the photoelectron cross section for each element. X-ray photoelectron spectroscopy is very sensitive to fluorine, which has a large photoelectron cross section. In the Perkin-Elmer PHI XPS spectrometers, the sensitivity factor of fluorine is set equal to one and all other factors are scaled accordingly. Surface atomic concentrations are calculated by the following equation:

C_x = surface atomic concentration of a given element, where there are i elements

I_x = area of the given element's peak in the ESCA spectrum

S_x = sensitivity factor of a given element

$$C_x = \frac{I_x / S_x}{\sum I_i / S_i} \quad [31]$$

Chapter 5

RESULTS AND DISCUSSION

5.1 Contact angle measurements

A Rame-Hart Goniometer model 100-00-115 was employed to measure the contact angles of liquids with weak polar properties, such as di-iodomethane and tricresylphosphate and those with strong polar properties, such as formamide and distilled water, on solid surfaces. The results of the measurement of the contact angles of the test liquids on high density polyethylene films which were treated at different levels of corona discharge are summarized in Table 4. The results of the non-treated HDPE film are also summarized for comparison. For better illustration, the results are presented graphically in Figure 7, where histograms of the contact angles measured for the respective HDPE film samples are given.

As shown, significant changes in the contact angle values of the probe liquids were observed for the HDPE film following corona treatment. For the test liquids with strong polar properties, the contact angle values showed a continual decrease with increased corona treatment time, while for the test liquids with weak polar properties, the contact angle values appeared to be fairly constant following the 1.8 kw treatment condition. This implies that the polar component of the surface free energy increases incrementally with the treatment level, while the dispersive surface free energy component showed no significant change with corona treatment level.

Table 4 : Contact angle values obtained for Corona discharge treated HDPE film samples

Samples	Contact Angle Measurement, average mean (degrees) ^(a)			
	Distilled water	Formamide	Di-Iodomethane	Tricresyl Phosphate
Non-treated	89.00±2.0	67.00±1.0	46.00±1.0	34.50±1.5
P-1.8 k	66.00±1.0	50.00±1.0	27.00±1.0	23.00±1.0
P-2.2 k	60.00±1.0	44.00±1.0	29.50±2.0	15.00±1.0
P-2.6 k	55.50±1.5	43.50±0.5	29.50±1.5	15.50±1.5
P-3.0 k	54.00±1.0	39.00±1.0	27.50±2.5	20.00±2.0

(a) Averaged values of at least 10 different measurements, performed on different positions of the sample surface.

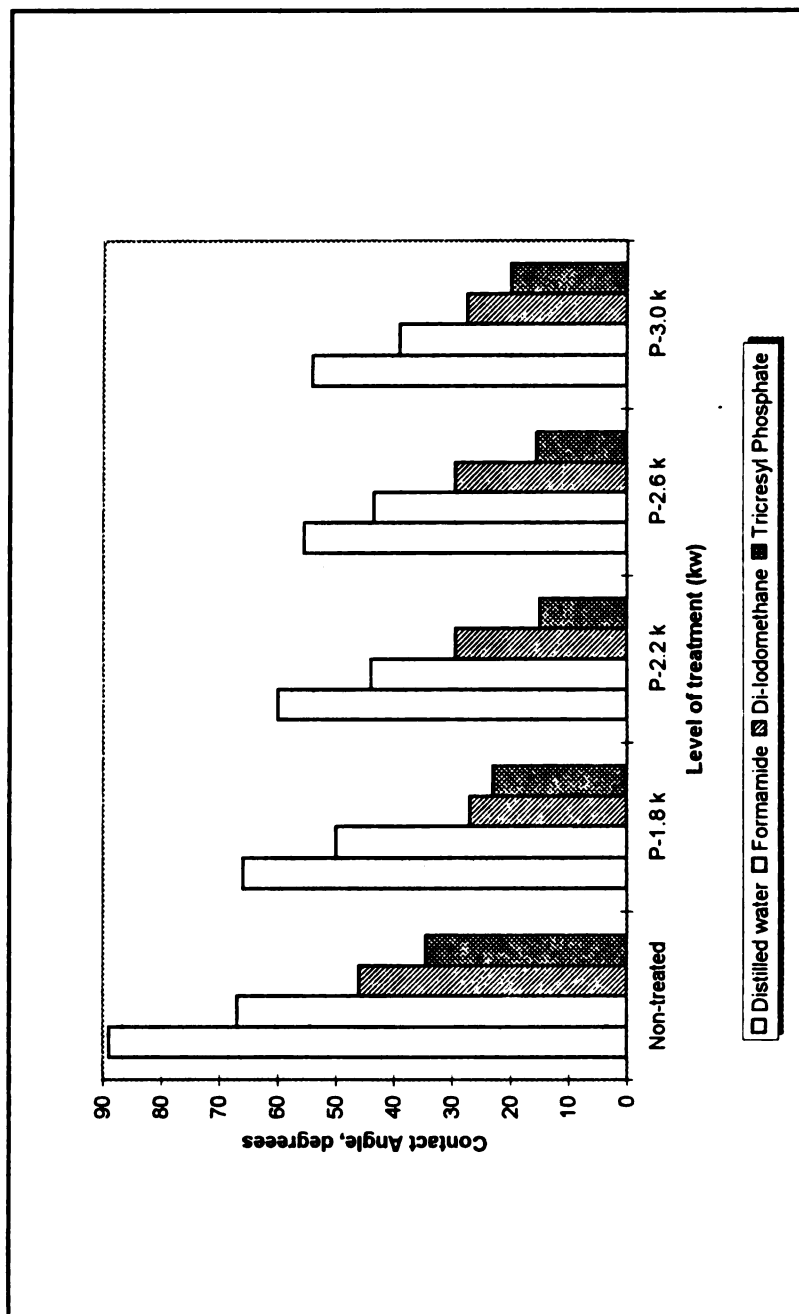


Figure 8 : Contact angle measurement of the corona treated film using different liquids

5.2 Surface free energy of film samples

Surface free energies and their corresponding polar and dispersive components were calculated using a Microsoft Excel software program together with "The least square method" adapted by Park (1994).

The polarity, defined as the ratio of the polar component to the total surface free energy (γ_s^P / γ_s^T) was also determined (Wu, 1982). The results of surface free energy determinations are summarized in Table 5, which provides a comparison of the surface free energy values of the untreated and corona treated film samples.

Table 5 : Surface Free Energy of Corona Discharge Treated HDPE film

Samples	SURFACE FREE ENERGY OF FILMS (dyne / cm)			Polarity (% percent)
	Dispersive component	Polar component	Total	
Non-treated	33.1879	2.0860	35.2739	5.9137
P-1.8 k	33.3725	9.7337	43.1063	22.580
P-2.2 k	32.0673	13.7144	45.7817	29.956
P-2.6 k	30.7980	16.0161	46.8141	34.212
P-3.0 k	30.0632	17.8541	47.9172	37.260

For better illustration the results are presented graphically in Figure 9, where histograms of the surface free energy and the associated polar and dispersive components, determined for the respective HDPE film samples, are

given. The effect of corona treatment level on the polar, dispersive and total surface free energy values is also presented graphically in Figure 10, where the respective surface free energy values are plotted as a function of corona discharge level.

As shown, the observed increase in the values of the total surface free energies for the corona treated HDPE films can be attributed to the increased contribution of the polar component.

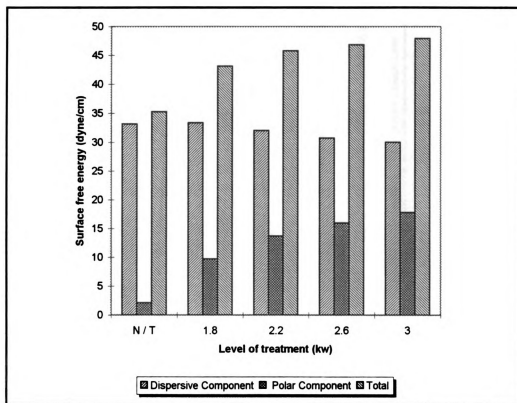


Figure 9 : Effect of corona treatment level on the polar, dispersive and total surface free energy values

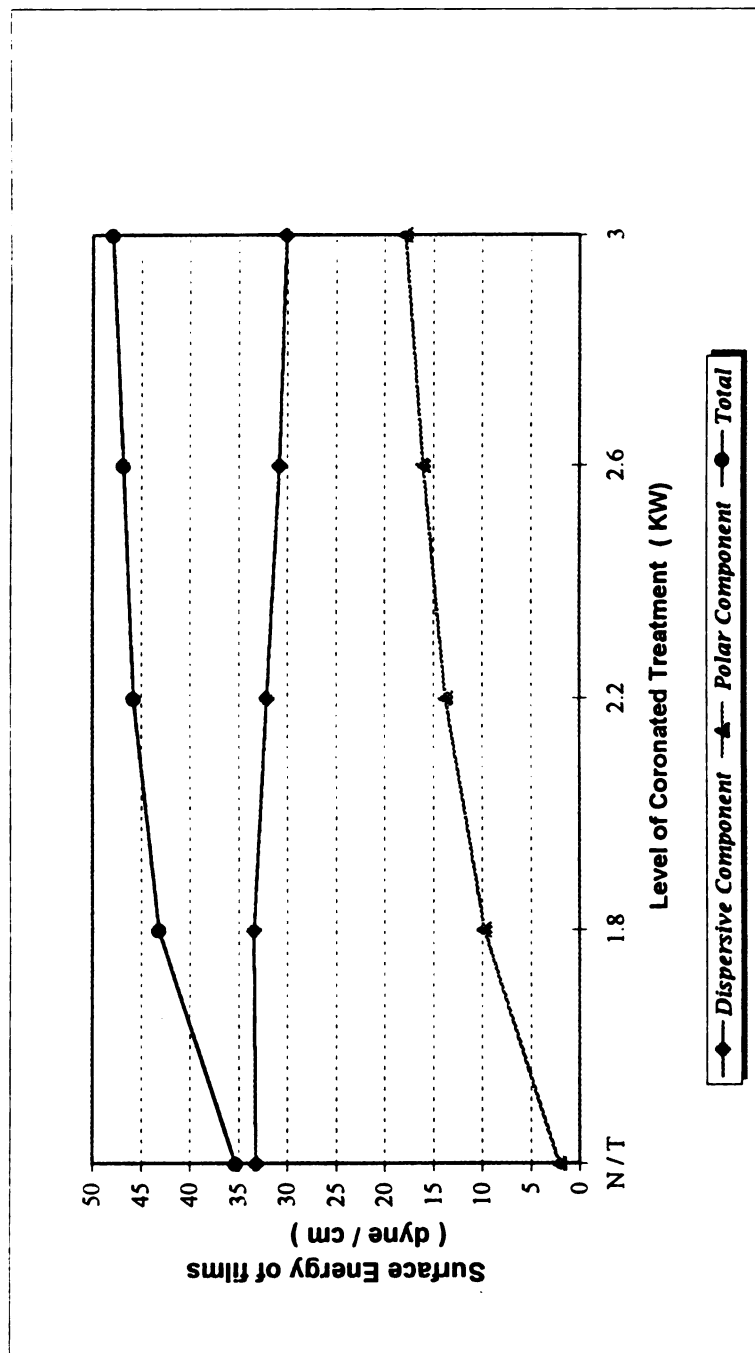


Figure 10 : Relationship between the corresponded components and the total surface energy

5.3 Ink Adhesion

The results obtained from the SPEC*SCAN 2000 system used in this study showed that the ink on the tested areas of the non-treated polymers was totally or nearly completely peeled from the film, while the ink applied to the corona treated polymers showed significantly less transfer to the adhesive tape surface, at all levels of treatment. The area percent peeled, ranged from approximately 98 % for the untreated film to less than 2 % for the high corona treatment (3 KW), as illustrated in Table 6.

Table 6 : The area percent of ink peeled as a function of corona treatment level.

SAMPLE #	UNTREATED	P-1.8 KW	P-2.2 KW	P-2.6 KW	P-3.0 KW
1	97.09	27.62	9.09	6.89	1.12
2	97.78	24.43	14.74	7.04	2.89
3	96.35	21.15	12.71	4.94	0.25
4	95.61	26.34	12.48	5.06	2.14
5	98.82	23.74	15.04	5.87	2.56
6	99.11	23.13	12.59	4.33	1.87
7	98.44	24.07	15.27	6.28	0.83
8	96.79	20.61	14.11	4.65	2.03
9	98.53	26.82	13.12	6.52	0.47
Average	97.61	24.21	13.24	5.73	1.57
S.D.	1.2149	2.4175	1.9002	1.0129	0.9388

Thus, showing that corona treatment of polyolefin polymers is a significant aid for enhancement of ink adhesion.

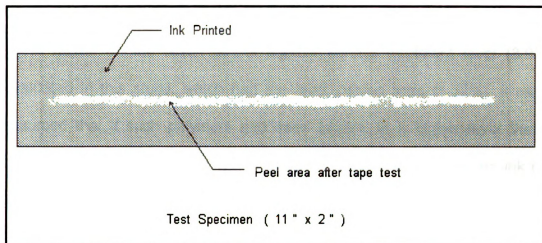


Figure 11 : The illustration of printed specimen after peel test

As shown in Figure 11, where the image of the printed film sample is displayed, a portion of the ink coating was removed by the peel test. By using this modified ink adhesion technique, as previously described, the area percent of the ink surface which was peeled away can be described as being a portion of the total area of the printed ink surface. However, it is necessary to point out here that, according to the data in Table 6, the values of the peeled areas, measured on a percentage basis, were based on an approximation scale. Here the peeled area percent is calculated using some type of grid or a small rectangular area and the numerical area percent values are averaged. Thus, the peeled area adjacent to both sides of these regions would be

difficult to interpret. As a result, an error from this procedure still exists, due to the reading limitation of the software. In terms of practical use in industry, the ink peel test is typically evaluated by a single, visual inspection. This might somehow affect the ability to differentiation between the treatments even at different treatment levels.

Based on the result of the highest corona treatment level (3.0 kw) evaluated in this study, which had the least peeled area (1.57%), it can be assumed that if such polymers had been treated at a higher level that the peeled area may have been further diminished or even showed no ink peel. Therefore, the plot of the percentage of the peel area versus the level of treatment can be seen, as shown in Figure 12. Typical results indicated that the film without treatment showed little or no ink adhesion and thus gave the highest percentage value of the ink peeled. Further, test films with the higher levels of corona treatment showed the least amount of the ink, which was peeled away. At the highest level of the treatment, there is such a minimal amount of ink peeled that only one percent of ink coating was peeled from the substrate when tested.

By using a tensile testing procedure, the data for the peel test were recorded graphically in a manner typical of tensile testing curves. The peeled area on the sample was generated during this process. In practice, the upper grip of the tensile tester held the sample and the lower grip held the tape specimen affixed to the printed surface. However, the results did not represent a satisfactory level of agreement and many fluctuations occurred during the

testing. The force of adhesion, therefore, could not be calculated accurately due to the significant level of error. Thus, this study employed the peeling procedure only to create the peeled area, which provided samples for quantitative measurement, using the modification technique for the SPEC*SCAN 2000.

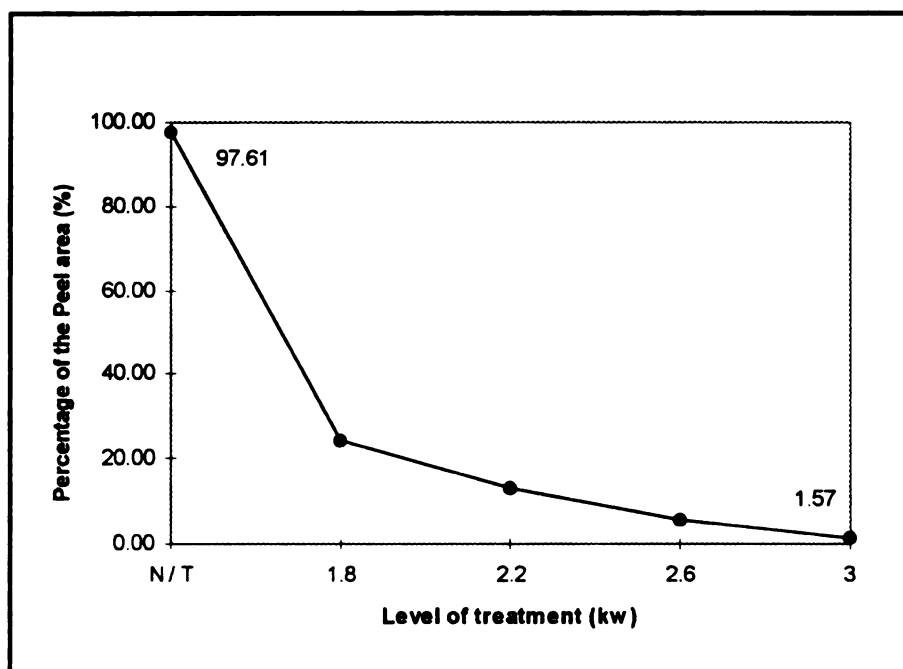


Figure 12 : The relationship between the level of treatment and the percentage of the area which was peeled off

5.4 The results of ESCA survey method analysis

Operating the photoelectron spectrophotometer with a wide scan and low resolution allows for the identification of elements at the polymer surface. Quantitative analysis of the amount present for each element is $\pm 5\text{-}10\%$. No chemical state information is available, due to low resolution of the scan.

A high resolution scan with a narrow window and better resolution allows employment of peak position, along with the shape of the peak to determine chemical state information from the sample surfaces. Curve fitting can be done where peaks are fitted under the spectral envelopes to interpret data as different functional groups presented.

When comparing the ESCA analysis of corona treated polyethylene treated at 3.0 versus 1.8 kw, there were no significant differences in either surfaces within experimental errors for C $89 \pm 1\%$ and O $11 \pm 1\%$, as shown in Table 7.

Only a high resolution scan can indicate whether there are differences in the chemical state of the treated polyethylene at 3.0 versus 1.8 kw corona discharge treatment. The O 1s and C 1s peak shapes and position are similar. Therefore, there appears to be no significance difference between the two sample treatments with respect to surface atomic composition.

The C 1s peak shape indicates the surface of PE film has been oxidized. Non-oxidized C 1s peaks are very symmetric. There are no shoulders to the higher binding energy side indicating oxidation had occurred and also the absence of any other atoms such as nitrogen and sulfur. Curve

fitting could provide a better idea on group functionality, however an initial survey of the data indicates oxidation, probably C-O (could be C-O-C or C-O-H) When oxides are present, for example, the C-O bond , the binding energy will shift + 1.5 eV from 285.0 eV to C-O at 286.5 eV as compared to 288.0 eV for the C=O group.

Table 7 : ESCA determination for the surface compositions of the film sample at variable exposure levels of the corona treatment.

Sample	Percentage Atomic Concentration ^(a) , ^(c)		
	Corona treated (Kw)	C (%)	O (%)
Non-treated	0.0	100.0	0.0
P-1.8	1.8	90.04	9.96
P-2.2	2.2	89.55	10.45
P-2.6	2.6	88.0	12.0
P-3.0	3.0	87.0	12.0 ^(b)

(a) Averaged values of at least 3 measurements, performed on different positions of the sample.

(b) ESCA survey found other possible elements e.g. Si on sample surface

(c) This interpretation of the ESCA data was edited from the comments and opinion of

Dr.Cara L.Weitzsacker at CMSC, Michigan State University

Summary & Conclusion

Polyethylene is a saturated hydrocarbon structure, of the class of polymer called polyolefins. Like other saturated hydrocarbon substances, it has very low polarity and very low reactivity. Its surface wetting tension is low, approximately 30 dynes / cm. This inertness implied that wetting and adhesion of inks will not occur unless the surface is activated.

It has been demonstrated that the level of corona treatment depends on the power applied in the air gap and perhaps the machine speed, as well as wattage, unit area and unit time. At the highest treatment level for the test films, this study has shown that the total surface free energy was comprised primarily of the polar component of the total surface free energy. This result was confirmed by the ink peel area test. The printed ink area remained sustainable on the corona treated films after the peel tape test. Whereas the non-treated sample showed nearly total removal of the printed ink from the polymer surface. The amount of ink which was removed by the peel test was quantitatively evaluated by using a modification of the SPEC*SCAN 2000 technique and the test procedure developed. As a result, the percentage of ink peeled from the film surface could be estimated more accurately than by the more traditional method typically employed. It was found that the film exposed to the highest level of corona treatment showed the least amount of the ink peeled from its surface i.e. 1.57 % As the corona treatment level was reduced,

the results showed that increasingly higher percentages of the printed surface were peeled from the polyethylene film.

Analysis of the film surfaces using the ESCA technique was ineffective in determining chemical changes of the substrate with respect to surface functionality. It did show, however that the surface was oxidized as a result of corona treatment.

APPENDIX A

**Samples of calculation program used to
determine the
Surface free energy of the film samples**

(Step 1: List all measurements of contact angles taken from film samples)

Water	F	D	P
90.0000	68.0000	45.0000	34.0000
89.0000	67.0000	46.0000	34.0000
90.0000	67.0000	45.0000	34.0000
88.0000	66.0000	47.0000	35.0000
87.0000	68.0000	47.0000	36.0000
90.0000	68.0000	46.0000	35.0000
89.0000	68.0000	47.0000	34.0000
88.0000	67.0000	47.0000	36.0000
87.0000	66.0000	45.0000	34.0000
90.0000	67.0000	46.0000	36.0000

(Step 2: Convert step 1 data to be a product of cosine as below)

0.0000	0.3746	0.7071	0.8290
0.0175	0.3907	0.6947	0.8290
0.0000	0.3907	0.7071	0.8290
0.0349	0.4067	0.6820	0.8192
0.0523	0.3746	0.6820	0.8090
0.0000	0.3746	0.6947	0.8192
0.0175	0.3746	0.6820	0.8290
0.0349	0.3907	0.6820	0.8090
0.0523	0.4067	0.7071	0.8290
0.0000	0.3907	0.6947	0.8090

(Step 3 : Product of addition of 1+ cosine from step 2)

1.0000	1.3746	1.7071	1.8290
1.0175	1.3907	1.6947	1.8290
1.0000	1.3907	1.7071	1.8290
1.0349	1.4067	1.6820	1.8192
1.0523	1.3746	1.6820	1.8090
1.0000	1.3746	1.6947	1.8192
1.0175	1.3746	1.6820	1.8290
1.0349	1.3907	1.6820	1.8090
1.0523	1.4067	1.7071	1.8290
1.0000	1.3907	1.6947	1.8090

(Step 4 : Product of transpose matrix from step 3)

1.0000	1.0175	1.0000	1.0349	1.0523
1.3746	1.3907	1.3907	1.4067	1.3746
1.7071	1.6947	1.7071	1.6820	1.6820
1.8290	1.8290	1.8290	1.8192	1.8090

(Step 5 : Product of Mutiplication of Matrix of step 3.1 & step 4)

1.4051	1.4071	1.4083	1.4061	1.3990
0.7292	0.7347	0.7321	0.7392	0.7359

(Step 4 : Product of transpose matrix from step 3) <continued>

1.0175	1.0349	1.0523	1.0000
1.3746	1.3907	1.4067	1.3907
1.6820	1.6820	1.7071	1.6947
1.8290	1.8090	1.8290	1.8090

(Step 5 : Product of Mutiplication of Matrix of step 3.1 & step 4) <continued>

1.4005	1.3999	1.4181	1.3989
0.7312	0.7353	0.7451	0.7292

(Step 6 : The result of surface energy as shown)

5.7589	5.6872	5.7568	5.7703
1.4135	1.5547	1.5834	1.3759
5.7842	5.8406	5.7020	5.6666
1.4241	1.3201	1.5821	1.5881

(Step 1.1 : List the SFE of liquids used for calculation)

Dispersion	Polar	Total	
21.8000	51.0000	72.8000	W
32.3000	26.0000	58.3000	F
48.5000	2.3000	50.8000	D
36.2000	4.5000	40.7000	P

(Step 2.1: Product of 2 X sq.root of each component by total SFE "A")

Dispersion	Polar
0.1283	0.1962
0.1950	0.1749
0.2742	0.0597
0.2957	0.1042

(Step 3.1 : Transpose number of step 2.1 "A' ")

0.1283	0.1950	0.2742	0.2957
0.1962	0.1749	0.0597	0.1042

(Step 3.2 : Product of A*A)

0.2171	0.1065	1.0000	0.0000
0.1065	0.0835	0.0000	1.0000

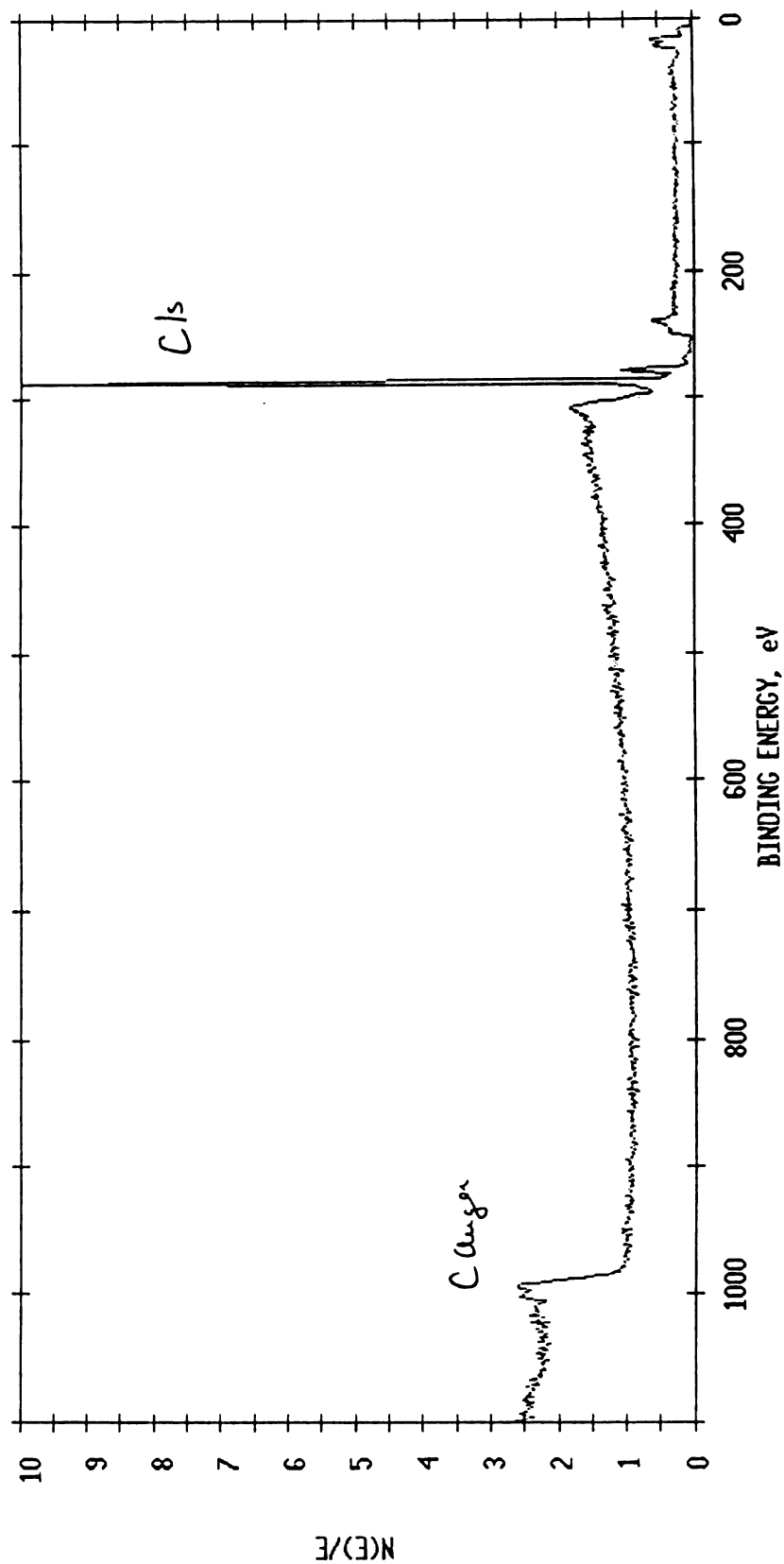
[Step 3.3 Product of inversion of (A*A)]

12.2920	-15.6681	0.2171	0.1065
-15.6681	31.9444	0.1065	0.0835

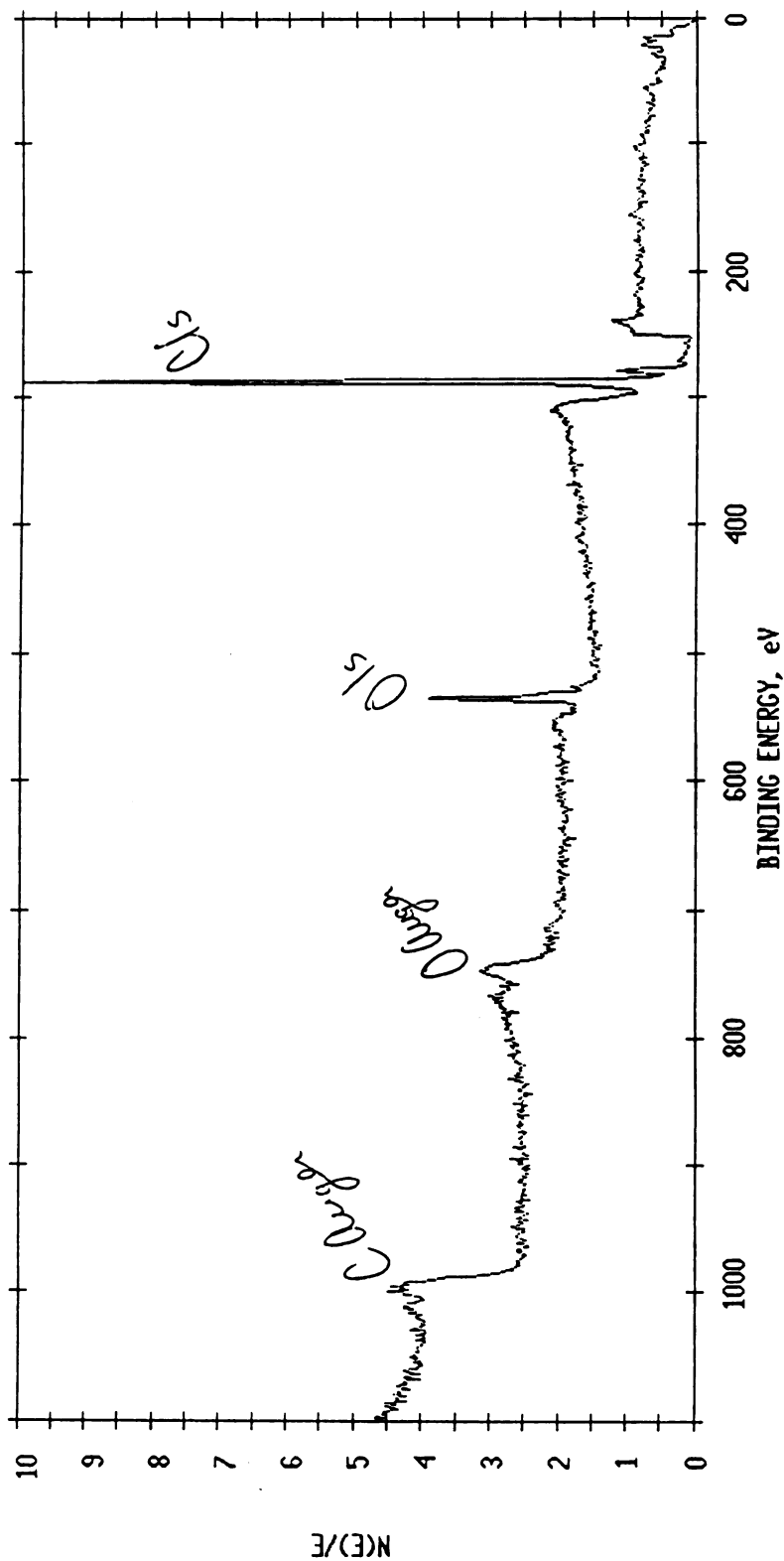
APPENDIX B

Samples of the analysis data from the Electron Spectroscopy for Chemical Analysis (ESCA)

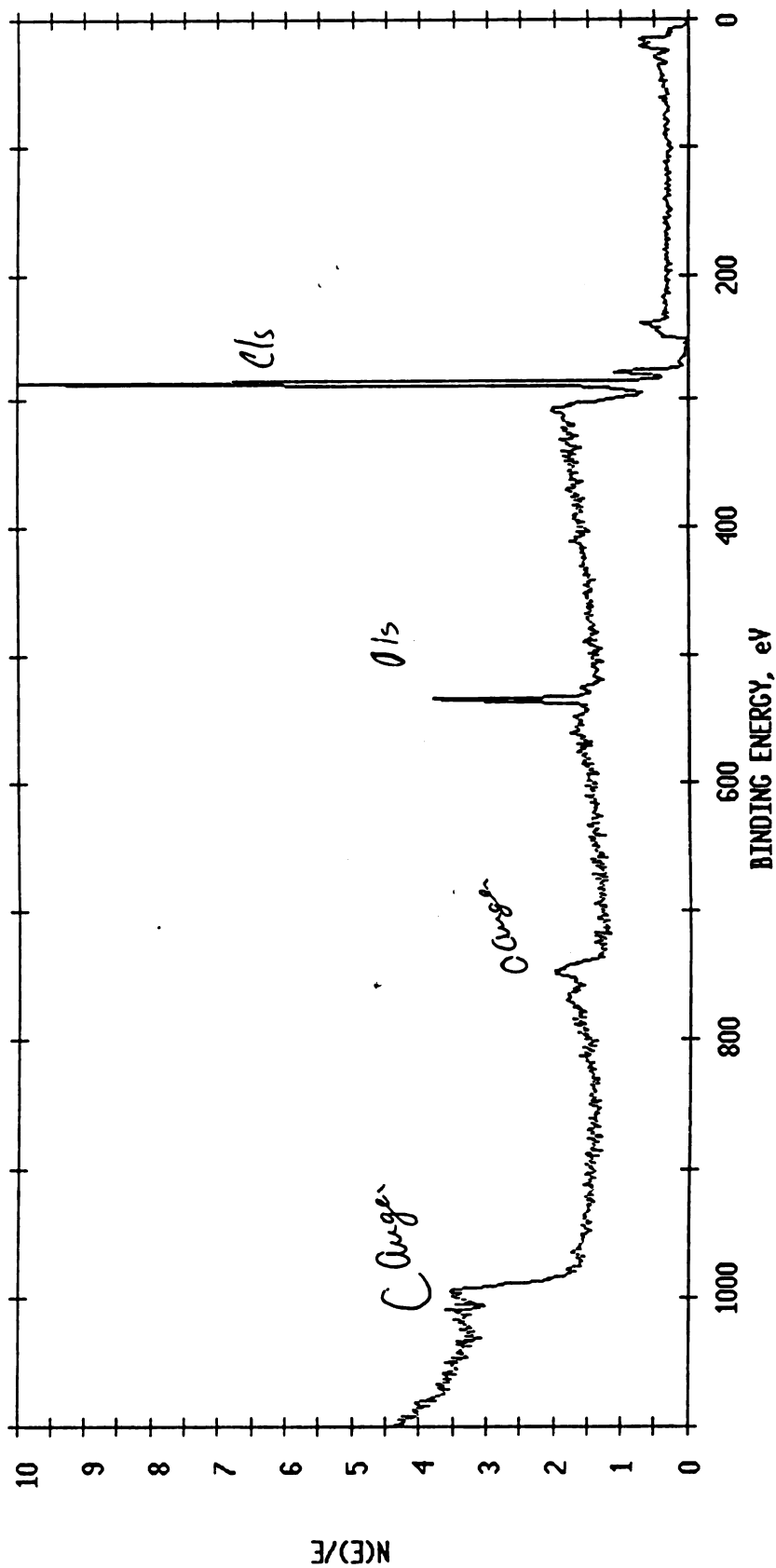
ESCA SURVEY 11/16/95 ANGLE= 45 deg ACO TIME=7.73 min
 FILE: ART100 UN polyethylene film (#1) Art/Dr. Giacin - Packaging
 SCAN 1: SCALE FACTOR= 2.997 k c/s, OFFSET= 0.176 k c/s PASS ENERGY= 89.450 eV
 SCAN 2: SCALE FACTOR= 0.749 k c/s, OFFSET= 0.044 k c/s Mg 300 H



ESCA SURVEY 11/17/95 ANGLE= 45 deg ACO TIME=10.82 min
 FILE: ART107 Corona Treated PE, 3.0 "inside (marked) surface) Art
 SCAN 1: SCALE FACTOR= 2.291 k c/s, OFFSET= 0.386 k c/s PASS ENERGY= 89.450 eV
 SCAN 2: SCALE FACTOR= 0.573 k c/s, OFFSET= 0.096 k c/s Mg 300 W



ESCA SURVEY 1/5/96 ANGLE= 45 deg ACO TIME=6.95 min
 FILE: 96D111 Corona Treated PE/Art/marked side, sample 1.8 (2nd)
 SCAN 1: SCALE FACTOR= 2.232 k c/s, OFFSET= 0.236 k c/s PASS ENERGY= 89.450 eV
 SCAN 2: SCALE FACTOR= 0.558 k c/s, OFFSET= 0.059 k c/s Mg 300 W



APPENDIX C

**Samples of original data
obtained from
the SPEC * SCAN 2000 system**

Western Michigan University

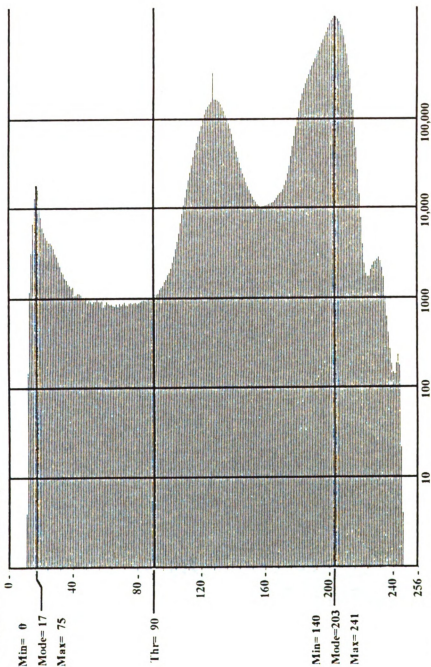
Spec-Scan 2000 - V.1.2.10

Scanner Settings: Apogee Systems, Inc
Grade Identification: Grade Id for Apogee
Load / Reel Number: Load Id for Apogee

1 sheets, each 8.5" x 11"

Total Area Scanned: 0.050825 sq.m.

Mon 18-Dec-1995 14:36
Resolution: 600 dots/inch
Threshold: 90 manual
White Level: 255
Black Level: 0
256-shade Grayscale mode



Overall Grayscale Brightness = 189.9 = 74.5%
Overall Grayscale Std Deviation = 28.2 = 11.1%

Western Michigan University

Spec*Scan 2000 - V.1.2.10

Scanner Settings: Apogee Systems, Inc
Grade Identification: Grade Id for Apogee
Load / Reel Number: Load Id for Apogee

1 sheets, each 8.5" x 11"
Total Area Scanned: 0.050825 sq.m.

Mon 18-Dec-1995 14:32

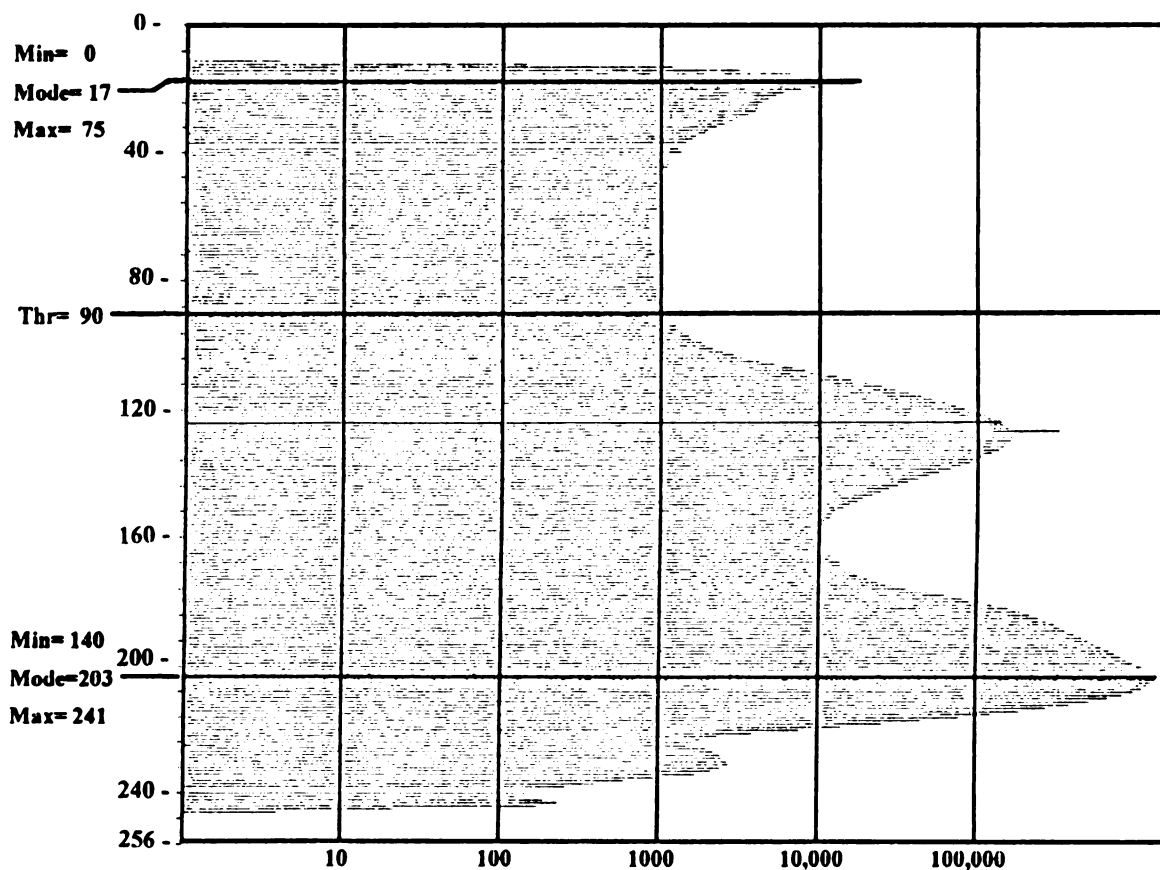
Resolution: 600 dots/inch
Threshold: 90 manual
White Level: 255
Black Level: 0
256-shade Grayscale mode

Sample Grayscale Brightness Analysis:

	<u>2σ Min</u>	<u>Mode</u>	<u>2σ Max</u>
Dirt Content:	0	17	75
Fiber Content:	140	203	241

Overall Grayscale Brightness = 189.9 = 74.5%

Overall Grayscale Std Deviation = 28.2 = 11.1%



Overall Grayscale Brightness = 189.9 = 74.5%

Overall Grayscale Std Deviation = 28.2 = 11.1%

Spec*Scan 2000 - V.1.2.10

Mon 18-Dec-1995 16:48

Scanner Settings: Art
Grade Identification: Printing Tape Measure
Load / Reel Number: Number 1

Resolution: 600 dots/inch
Threshold: 90 manual
White Level: 255
Black Level: 0
256-shade Grayscale mode

1 sheets, each 8.5" x 11"

Total Area Scanned: 0.050825 sq.m.

Categories:	Min Avg. Gray	Max Avg. Gray	Min Meas. Area	Max Meas. Area	Count	Area (sq.mm)	---- Calculated ---- Count (in 1 sq.meter)	PPM	Average Grayscale	Darkest Grayscale	Average Size (sq.mm)
Total >=0.04 sq.mm.	0	255	0.040	99999	124	138.640	2440	2727.8	49.89	13.00	1.118
Very Dark >= 0.04	0	60	0.040	99999	111	137.619	2184	2707.7	48.23	13.00	1.240
Medium Dark	60	90	0.040	99999	17	1.464	334	28.8	63.12	28.00	0.086
Light	90	255	0.040	99999							
Total 0.02--0.04	0	255	0.020	0.040	57	1.633	1121	32.1	61.28	28.00	0.029
Very Dark	0	60	0.020	0.040	27	0.853	531	16.8	55.89	28.00	0.032
Medium Dark	60	90	0.020	0.040	32	0.848	630	16.7	65.75	29.00	0.026
Light	90	255	0.020	0.040							
Total <0.04	0	255	0.000	0.040	267	3.333	5253	65.6	72.20	28.00	0.012

Spec*Scan 2000 - V.1.2.10

Mon 18-Dec-1995 17:18

Scanner Settings: Art
Grade Identification: Printing Tape Measure
Load / Reel Number: Number 1

Resolution: 600 dots/inch
Threshold: 90 manual
White Level: 255
Black Level: 0
256-shade Grayscale mode

1 sheets, each 8.5" x 11"

Total Area Scanned: 0.050825 sq.m.

Categories:	Min Avg. Gray	Max Avg. Gray	Min Meas. Area	Max Meas. Area	Count	Area (sq.mm)	----- Count (in 1 sq.meter)	Calculated PPM	Average Grayscale	Darkest Grayscale	Average Size (sq.mm)
Total >=0.04 sq.mm.	0	255	0.040	0.9999	68	1781.998	1338	35061.3	52.51	8.00	26.206
Very Dark >=0.04	0	60	0.040	0.9999	53	1781.003	1043	35041.8	48.92	8.00	33.604
Medium Dark	60	90	0.040	0.9999	16	1.116	315	22.0	64.88	32.00	0.070
Light	90	255	0.040	0.9999							
Total 0.02--0.04	0	255	0.020	0.040	17	0.495	334	9.7	67.29	27.00	0.029
Very Dark	0	60	0.020	0.040	3	0.100	59	2.0	56.00	27.00	0.033
Medium Dark	60	90	0.020	0.040	15	0.428	295	8.4	69.07	33.00	0.029
Light	90	255	0.020	0.040							
Total <0.04	0	255	0.000	0.040	240	1.599	4722	31.5	79.65	27.00	0.007

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