Extrusion coating

Part 1: corona after-treatment of LDPE coating

Antti Savolainen and Jurkka Kuusipalo
Professor and researcher, Tampere University of Technology, Institute of Plastics Technology, Tampere, Finland

Hannu Karhuketo
Research and development manager, United Paper Mills, Valkeakoski, Finland

ABSTRACT *The purpose was to analyze the operation of a corona treating device and to find out the effects of corona treatment in gluing, printing and heat sealing. Extrusion coating experiments were carried out with a Jylhä 120-mm extruder and an Ahlbrandt System GmbH corona treater. Surface energy decreases sharply in two to three days and reaches an almost constant value in two weeks. The lower surface energy level of thinner coatings arises from a faster decrease as a function of increased storing temperatures. This can be explained by a decreased electret over the surface of the coating. Gluing tests show that at 36 mN/m, peel strength increases rapidly. At 38 mN/m, the surface energy reaches an adequate surface wetting. Corona treatment causes depolymerization on the TiO_2 filled LDPE surfaces, leading both to blocking of the web and to a sudden decrease in the heat sealing temperatures.*

KEYWORDS:
Adhesion
Corona treatment
Extrusion coating
Gluing
Printing
Surface tension
Wettability

A plastic surface shows poor adhesion in gluing and printing, partly because its surface energy is low. ("Surface energy" is also known as "surface tension" or "wetting tension.") We know that corona treatment can increase the surface energy. However, there is still much we do not know about measuring the efficiency of the corona treatment and estimating the decrease in surface energy with time.

The surface needs to be thoroughly wetted in gluing and printing. One boundary condition is the spreading of the covering agent on the surface of a plastic with the contact angle of 0°. The value of the contact angle is determined in the equilibrium state by Young's equation:

$$\cos\phi = \nu_{surf.} - (\nu_{surf.,\ liq.}/\nu_{liq.})$$

where

$\nu_{surf.}$ = surface energy of a solid material

$\nu_{liq.}$ = surface energy of a liquid

$\nu_{surf.,\ liq.}$ = surface energy between a solid and a liquid.

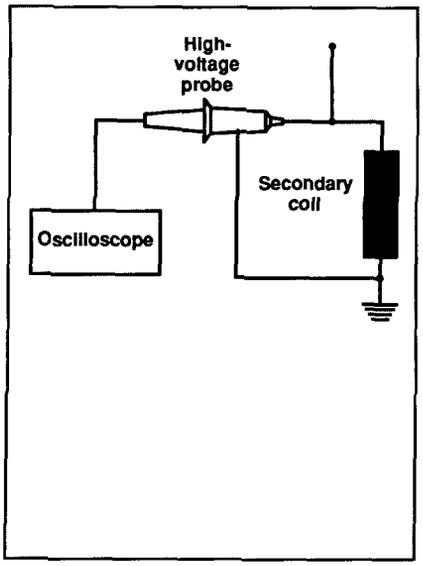
The adhesion is influenced not only by chemical effects but also by the surface profile of the plastic—i.e., the roughness of the surface.

Printers have an unwritten requirement for the surface energy of the plastic: the surface energy has to be at least 10 mN/m higher than that of the printing colors. In practice, there is a demand for printable plastic products with a surface energy of 36–42 mN/m (*1*).

There are two different mechanisms at work in corona treatment—oxidation and corona charging. In oxidation, the electrons break C-C and C-H bonds on the surface of LDPE (low-density polyethylene), producing free radicals. Ozone molecules, which are free radicals of oxygen and oxygen molecules in the air gap, will react to free radicals on the surface and produce oxidation products (*2*). Electron spectroscopy for chemical analysis (ESCA) of the surface shows acids, aldehydes, and other unsatisfied chemical products on a corona-treated surface of LDPE (*3*). By increasing the film thickness, the effect of the oxidation increases (*4*).

The surface energy of corona-treated LDPE diminishes with time,

1. Measurements from the secondary coil of the HV transformer

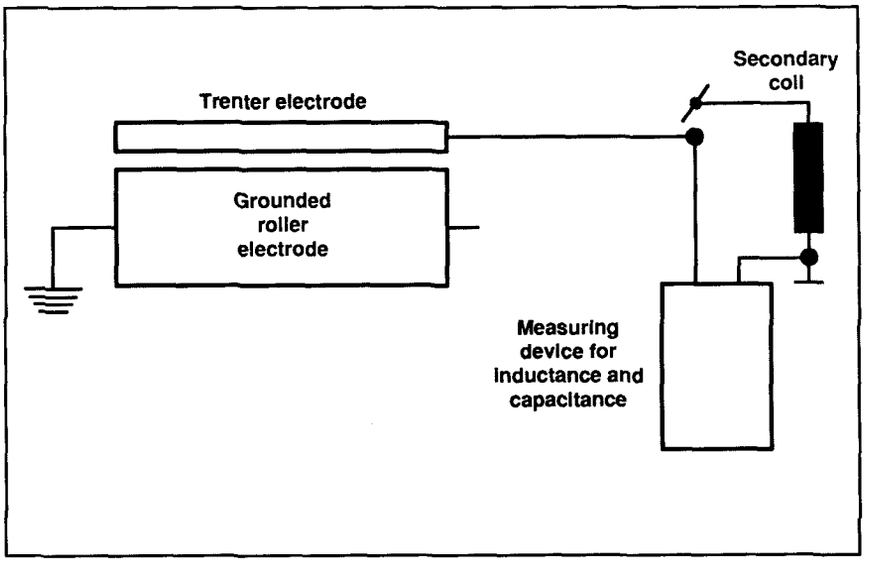


I. Materials and experimental conditions

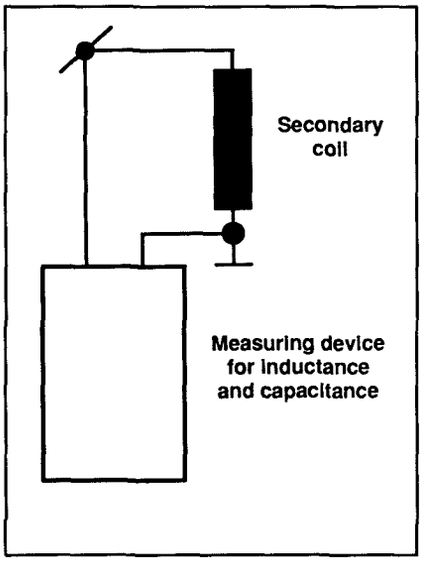
	Test run			
	1	2	3	4
LDPE polymer*	4524	4524-90	4524	7518
Color	Bright	White	Bright	Bright
Density, g/cm³	0.924	0.924	0.924	0.918
Melt index, g/10 min	4.5	4.5	4.5	7.5
Coating, g/m²	20	20	20	20
Chill roll	Hazy	Glossy	Hazy	Hazy
Temperature, °C	310	310	310	310
Air gap, mm	270	270	270	270
Air temp., °C	22.6	24.2	21.0	21.0
Rel. humidity, %	40	46	46	30

*Neste Corp.

2. The scheme for measuring capacitance



3. The scheme for measuring inductance



partly because some oxygen is lost through the film. Another effect that decreases the surface energy is depolymerization in electron bonding. Too much treatment produces an excess of polar groups, which impairs success in printing and gluing.

The corona treatment also causes a permanent charge on the plastic surface—that is, an electret. The influence of the charges will remain sometimes for years, depending on the plastic material (*5*). The existence of charges can be studied by an electrically charged powder such as jeweler's rouge. The powder produces ordered shapes (Lichtenberg's shapes) on a charged surface area (*6*).

With these different mechanisms at work, corona treatment is a complex phenomenon. Our purpose was to analyze the operation of a corona treater and to study the influence of corona treatment in gluing, printing, and heat sealing.

Experimental procedures

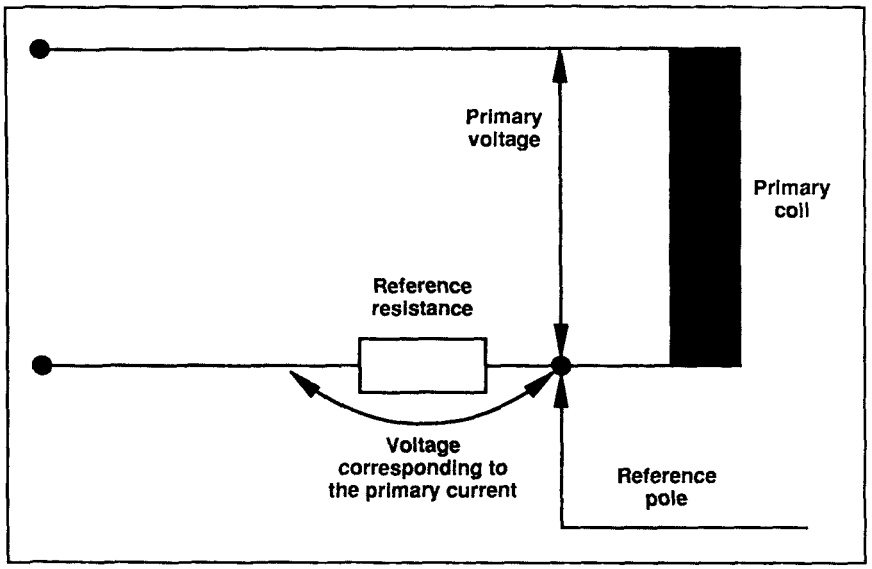
Coating experiments were carried out using a Jylhä 120-mm extruder and an Ahlbrandt System GmbH corona treater. In Test Runs 1-4, a 50-g/m² paper was coated with Neste Corp.'s LDPE, which has the qualities shown in **Table I.** Bobbins (or rolls) and separate sheets of extrusion-coated paper were stored in an air-conditioned room with a relative humidity of 50% and a temperature of 23°C.

Testing of coated paper samples

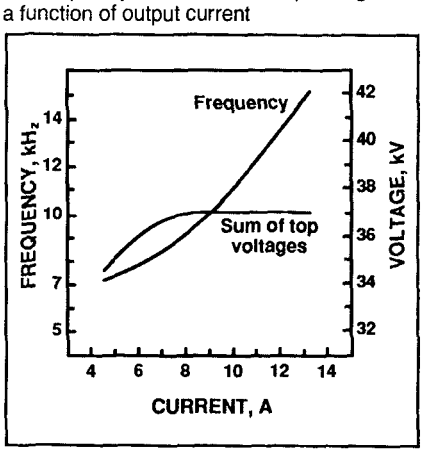
Surface tension tests. In measuring the surface tension of LDPE, we used the ASTM D 2578 method (for mixtures of ethylcellosolve and formamide) and a contact angle method (the Lorentzen-Wettre 2-2 device with distilled water and 1,1,2,2-tetrabromoethane).

Gluing experiments. We used both corona-treated and untreated surfaces in gluing experiments. Twenty-nine grams of polyvinylacetate (PVAC) was applied to one square meter of surface.

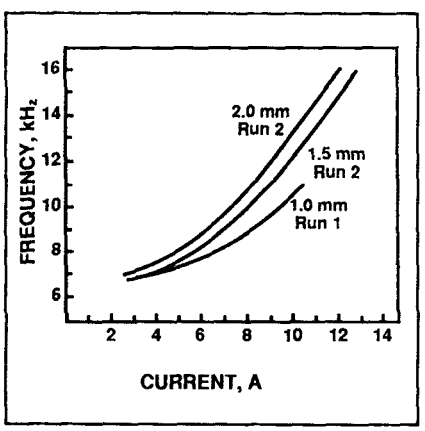
4. Measurements from the primary coil of the HP transformer



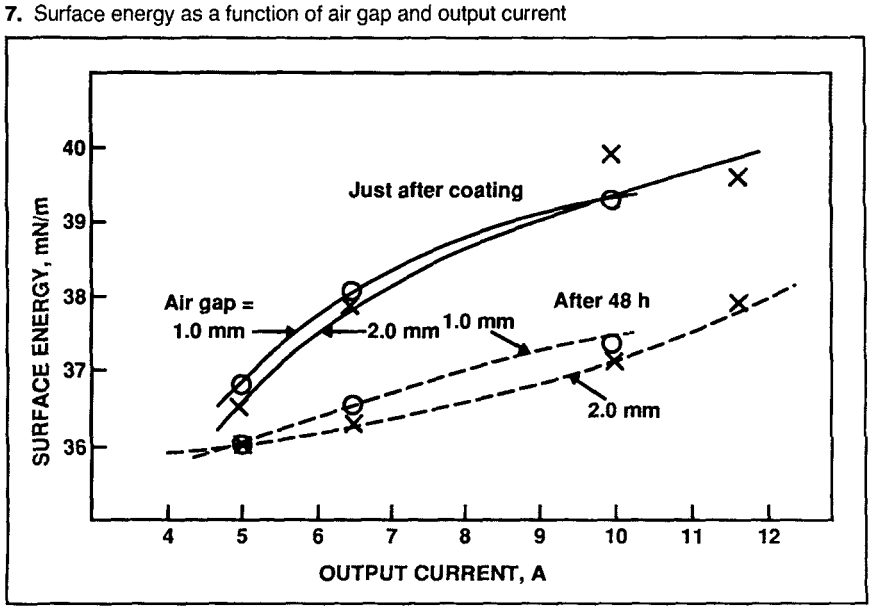
5. Frequency and the sum of top voltages as a function of output current



6. Influence of the air gap on the frequency.



7. Surface energy as a function of air gap and output current



Corona-treated and untreated sheets were glued and then covered with a pergamine paper. The covered sheets were allowed to dry for three days before the draw experiments were performed.

Adhesion, or peel strength, was measured with an Instron tensile testing instrument. The width of the samples was 5 mm, and the draw speed was 200 mm/min.

Printing experiments. To evaluate the printing behavior of the coated papers, we conducted tape tests and IGT printing experiments. The printing colors used in tape tests were Winter 2521 Akvaflex (viscosity = 25 s using DIN 4 cup[1]) and Winter 2533 MKW (viscosity = 20 s). IGT tests were carried out with magenta as the offset printing color.

Heat sealing experiments. We studied the heat sealing of coated papers with a Sentinel heat sealer device. The samples (about 50 mm wide) were heat sealed with the plastic sides facing each other. The heat sealing pressure was 275 kPa, and the sealing times were 0.5 and 1.0 s.

Studying the electret. We used Poropack Q powder (polarized plastic balls, size 100-120 mesh) to evaluate the charging of the LDPE surface in corona treatment. The surfaces were photographed.

The behavior of the corona device

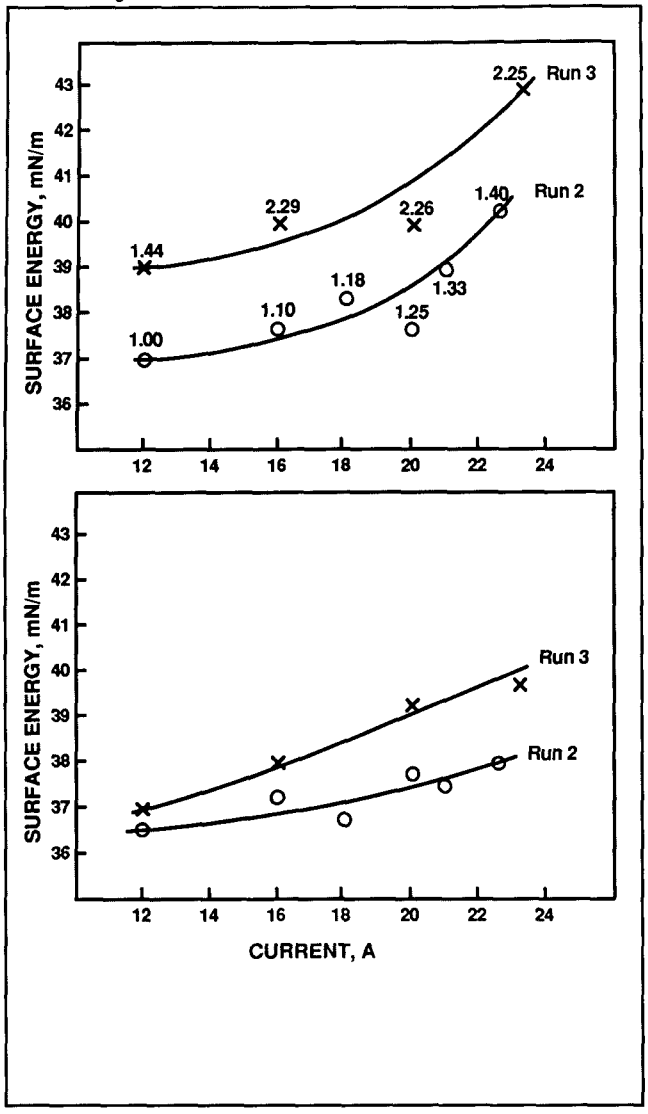
We measured the voltage from the secondary coil of the high-voltage (HV) transformer. These HV measurements were carried out without the web and with an air gap of 1.5 mm. The measuring arrangement is shown in **Fig. 1**.

The capacitance of the corona treatment system was measured without the web and with an air gap of 1.5 mm. The arrangement is shown in **Fig. 2**. We measured the inductance of the HV transformer under similar conditions, in accordance with the switching arrangement shown in **Fig. 3**.

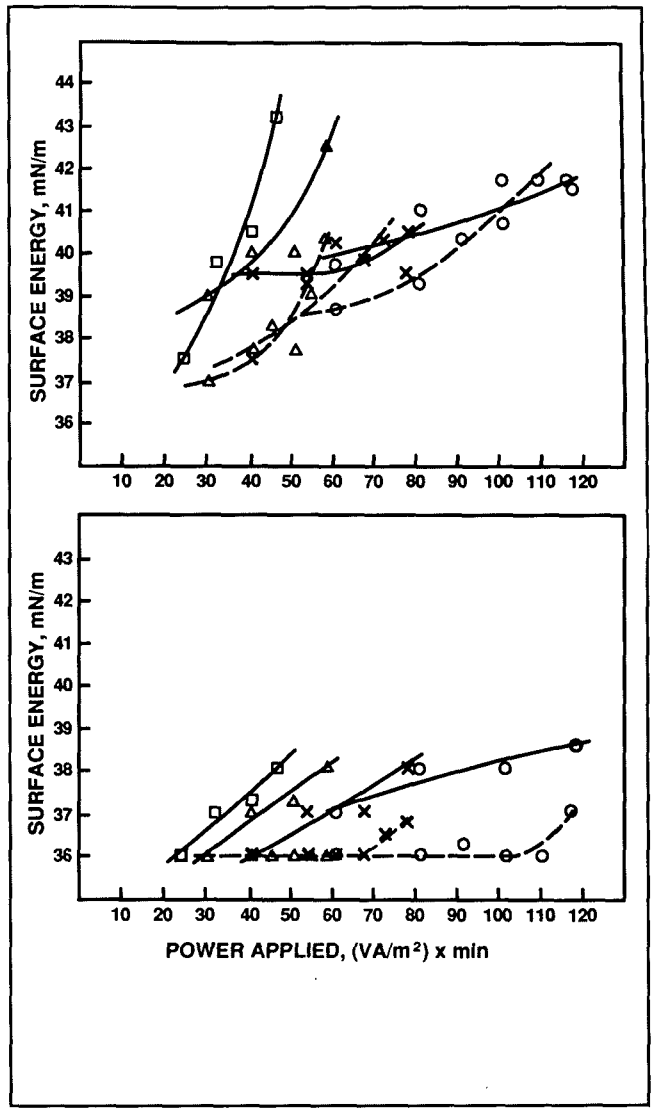
We measured the voltage and current from the primary coil of the HV transformer during Test Runs 1 and 2. The air gaps were 1, 1.5, and 2 mm. The measuring scheme is depicted in **Fig. 4**.

[1]The DIN 4 cup is filled with printing color, and the 4-mm hole in the bottom is opened. The time measured in seconds for the cup to empty is commonly taken as a measure of viscosity.

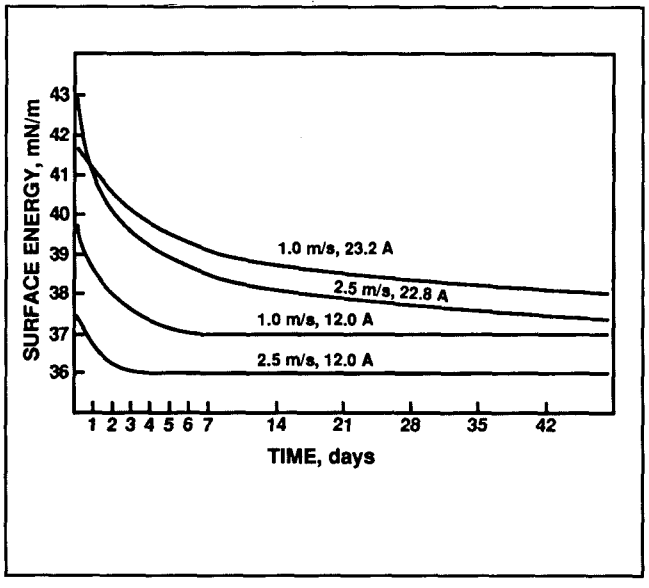
8. Surface energy as a function of output current. Top: a few minutes after coating. Bottom: after 48 h.



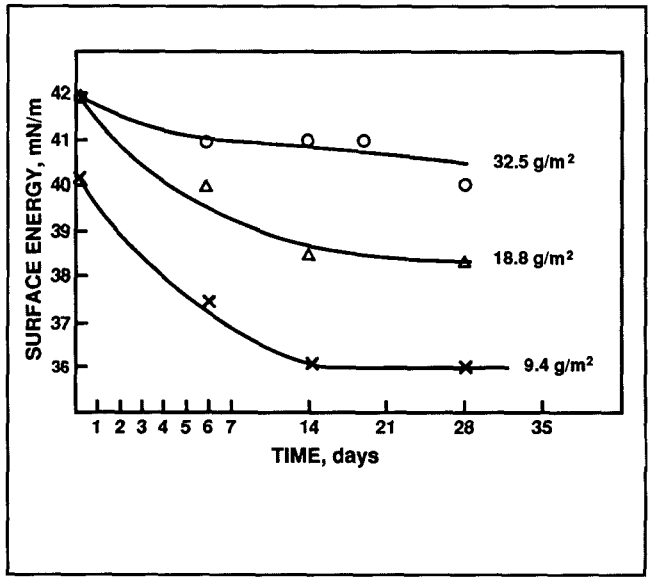
9. Surface energy as a function of power. Top: a few minutes after coating. Bottom: after 48 h.



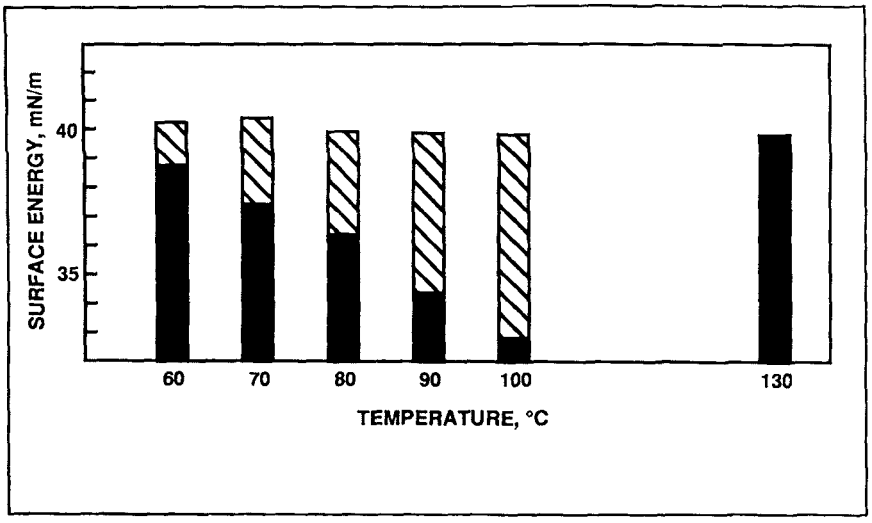
10. Surface energy as a function of storing time



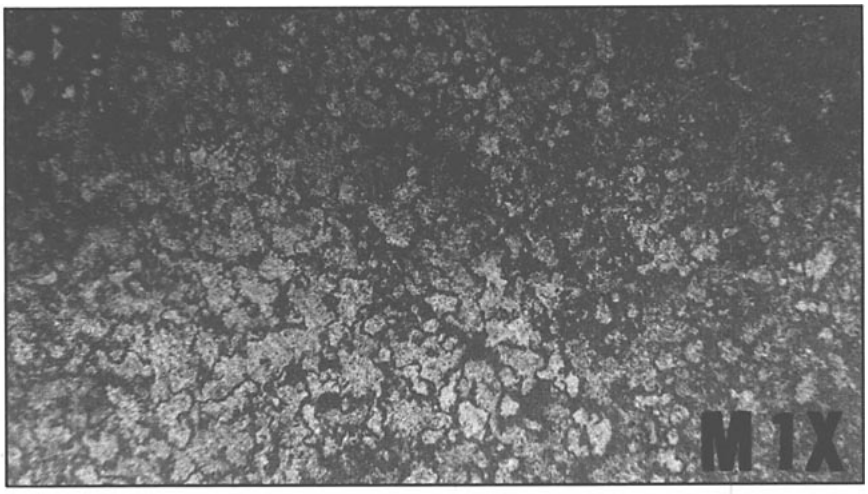
11. Surface energy as a function of coating thickness



12. Surface energy as a function of storage temperature (Test Run 4. Storing time = 10 min.)



13. Charged pulver on the surface of LDPE



Results and discussion

Analysis of the corona treater

Figure 5 shows the frequency and the sum of top voltages as a function of output current when measured from the secondary coil of the transformer. The frequency increased smoothly as a function of output current. The pattern of the top voltage is as expected: a constant value can be obtained as the output current increases above 7 A.

The inductance and capacitance were measured as L = 1.8 H (henry) and C = 6 nF (nanofarad). A resonant frequency of 1.5 kHz calculated from these values differs from the 15-16 kHz observed with the maximum output current of the corona treater. The maximum voltage, current, and power, however, can only be reached at the resonant frequency. Therefore, the calculated frequency—due partly to the measuring procedure—does not represent the true resonant frequency. Because of the incoherent capacitance of the transformer, the measuring of the resonance curve of the whole L C circuit instead of that of the separate L and C should give higher values.

Neither of the frequency values obtained with high output currents can represent explicitly the true resonant frequency. The maximum voltage has been reached with lower output currents than those needed to reach higher frequencies—i.e., 15-16 kHz (Fig. 5).

Figure 6 shows the frequency vs. the output current from the primary coil of the transformer. The increase in frequency with the increase in the air gap is a result of the whole system—i.e., the treater station with generator and transformer plus the backing roll.

The behavior of LDPE surfaces

The surface energy. Figure 7 is a plot of the surface energy vs. the output current. The surface energy increases with greater output current. A minor increase in the surface energy is also obtained when the air gap is decreased. With an output current of 9 A, a value that represents the minimum resonant frequency, a surface energy of 39 mN/m can be obtained. This energy value is about 7 mN/m, or 22%, higher than that presented for an untreated LDPE surface. The surface energy decreases with time, as expected. The average decrease recorded after two days was about 5%.

Higher output currents (and frequencies) cause the surface energy to increase. A surface energy of 43 mN/m is obtained with the output current at 23 A, as shown in the upper curve in the top graph of **Fig. 8**. The lower curve in the same graph shows the results of the TiO_2-filled LDPE. Its surface energy was about 5% lower than that of the unfilled LDPE.

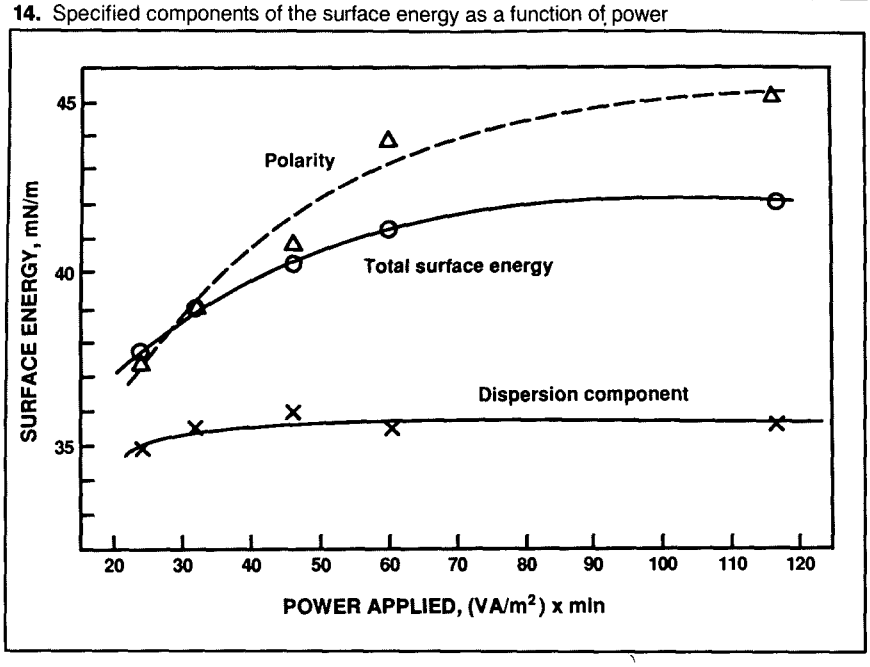
An interesting observation was the blocking of the TiO_2-filled LDPE on the reel at all web speeds. The corona treatment causes the plastic surface to depolymerize. The amount of short chain products increases, creating a possibility for the surface of the web to block. We deduce that TiO_2 promotes depolymerization from the fact that the higher surface energy of the unfilled LDPE did not favor any blocking.

The same trend is observed when comparing the surface energy as a function of power, as shown in **Fig. 9**.

The surface energy decreases sharply in two to three days, as shown in **Fig. 10**. The higher the output current in corona treatment, the higher the surface energy after this period of time. In practice, this means that better printability and a better gluing effect can be obtained for coated papers after long storage.

The profitability of an extrusion-coated paper depends partly on the cost of the plastic. The thinner the plastic surface, the more profitable is the product. The plastic layer should, however, cover the roughness of the surface and heat-seal it sufficiently. **Figure 11** shows the influence of the

14. Specified components of the surface energy as a function of power



II. IGT print test results

Sample	Test run	Surface energy, mN/m	Coated color, %
1	3	32	44.7
	3	32	44.8
17	3	36	46.4
	3	36	44.0
16	3	38	44.4
	3	38	42.3
2	3	41	46.0
	3	41	43.7

Printing speed = 1.0 m/s.
Compression = 300 N.

thickness of the LDPE layer on the surface energy in storing. When a thin coating is used, a sudden decrease is detected within two weeks, and no significant decrease is observed thereafter. The lower surface energy of the thinner coatings arises from a faster decrease in the temperature. The faster drop in temperature allows less time for the melt to oxidize in the air gap.

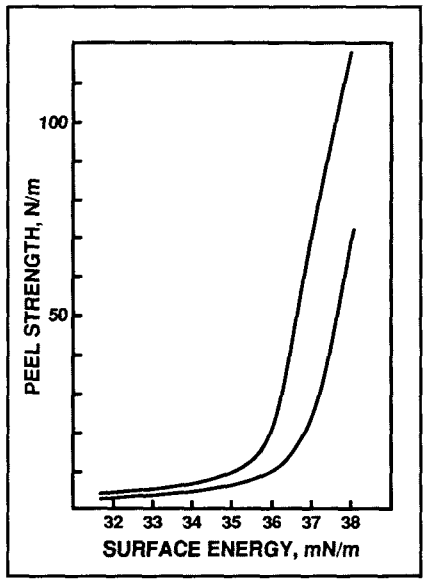
An interesting phenomenon is observed when storing coated papers at increased temperatures, as **Fig. 12** shows. The surface energy decreases evenly as a function of increased temperature. This can be explained by a decreased electret over the surface of the coating (*7*).

A careful analysis of the charged powder in **Fig. 13** indicates an electret similar to that introduced by Kim *et al.* (*6*). The decreased electret does not preclude, however, a simultaneous decrease in polarity. According to **Fig. 14**, the polar component of the surface energy increases strongly during corona treatment.

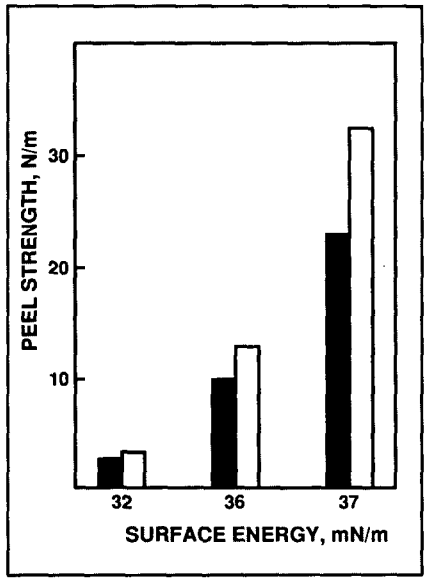
Polarity arises from orientation and induction effects. An increase in the heterogeneity of the polymer matrix at higher temperatures could reduce polarity by decreasing orientation effects. Increased heterogeneity could therefore decrease total surface energy.

The adhesion of the surface. The influence of the corona treatment on gluing is shown in **Fig. 15**. The peel

15. Peel strength as a function of surface energy



16. Peel strength as a function of surface energy in three days



III. Heat sealing results with and without corona treatment

Test run	Surface energy, mN/m		Heat seal temp., °C	
	Test run day	Sealing day	With treatment	Without treatment
1	38.0	36.0	128.2	18.6
2	40.3	37.7	96.2	127.4
3	40.6	37.5	129.4	129.4

Sealing after 1 week at 274 kPa for 0.5 s.

strength increases rapidly when the surface energy exceeds a limit of 36 mN/m. Adequate surface wetting is reached with the surface energy at 38 mN/m. The increase in peel strength after long periods of storage is due to the anchoring of bonds with time. Increased gloss on the plastic surface results in an increased peel strength, as shown in **Fig. 16**. This increase in gloss arises from an increased bond area on the glossy surface.

The results of IGT experiments do not indicate any change in adhesion of colors with increased surface energy, as shown in **Table II**. The forced wetting (the pressure of 300 N) where thermodynamic equilibrium in wetting is prevented from occurring successfully is the main reason for that.

The heat sealing of the coating. **Table III** shows the heat sealability of corona-treated and untreated surfaces. The heat sealing temperatures of untreated surfaces are quite unreliable, because only one untreated sample per test run was examined. (There were 15 corona-treated samples in the test.)

When TiO_2-filled samples are examined, we observe that a depolymerization takes place in corona treatment. This depolymerization leads to a sudden decrease in the heat sealing temperature.□

Literature cited

1. Weiss, H., Paper, Film & Foil Converter 60(7): 74(1986).
2. Bibee, D. V., 1981 Paper Synthetics Conference Proceedings, TAPPI PRESS, Atlanta, p. 1.
3. Carley, J. F. and Kitze, P. T., Polym. Eng. Sci. 20(5): 330(1980).
4. Kadash, M. M. and Seefried, Jr., Plast. Eng. 41(12): 45(1985).
5. Van Turnhout, J., Polym. J., 2(2): 173(1971).
6. Kim, C. Y., Evans, J., and Goring, D. A. I., J. Appl. Polym. Sci. 15: 1365(1971).
7. Schmidt, A., Coronaoberflachenbehandlung von mit Polyethylen Beschichteten Papierbahnen (Diplomarbeit), Fachhochschule Munster, Federal Republic of Germany, 1987.

Received for review Sept. 30, 1989.

Accepted Oct. 5, 1989