Mixing water with electrical energy: successful printing with water-based inks

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Under pressure to reduce solvent emissions, many converters are turning to water-based inks and using an in-line corona treater to boost adhesion to polymer substrates.

When polymer substrates were first introduced, the converting industry was faced with wettability and adhesion problems between the new substrates and the solvent-based inks, adhesives, and coatings then in use. Substrate producers found themselves facing an additional quality parameter. Besides manufacturing products of consistent gauge, opacity/clarity, barrier characteristics, and machinability, they had to ensure that the substrate surface was compatible with the available coating materials. This problem was eventually solved through the cooperative efforts of film suppliers, ink suppliers, and manufacturers of surface-treatment equipment, who together developed an interrelated system of compatible substrates, coating materials, and treatment processes.

The test for wetting tension (ASTM D2578) became the accepted definition of a substrate's surface characteristics. Wetting tension, measured in units of dynes per centimeter, was determined using mixtures of formamide and cellosolve. The dyne level thus became the controlling parameter for predicting compatibility between a substrate surface and a coating material. Production experience and laboratory work led to the evolution of an accepted rule of thumb: For proper wettability and adhesion, the substrate wetting tension should be approximately 10 dynes higher than that of the coating material.

Surface-treatment processes were developed—flame treatment, spark-gap treaters, metal-electrode treaters, and bare-roll treaters. These processes enabled manufacturers to supply converters with polymer substrates with well-defined surface characteristics. Simultaneously, suppliers of coating materials were called upon to develop inks, adhesives, and coatings that were compatible with the available substrates. Solvent-based materials were formulated to achieve the required wettability and adhesion along with the necessary gloss, opacity/clarity, and machinability.

The converting industry solved the problem of poor adhesion by restoring equilibrium to the system of polymer substrates, solvent-based coating materials, and treatment processes. The process is illustrated symbolically in **Fig. 1**. This equilibrium is being shifted again in response to environmental considerations that are legislating the gradual abatement or elimination of solvent-based coating materials. Manufacturers of coating materials have responded by expanding and improving a series of partially water-based and 100% solid materials. As illustrated in **Fig. 2**, the switch to water-based coatings has once again disrupted the balance among substrates, coatings, and treatment processes. This article examines the use of a second, in-line corona treatment at the time of conversion to provide effective adhesion between water-based coatings and polymer substrates.

Of course, some converters may choose to continue using solvent-based coatings by purchasing systems that permit solvent recovery for purification/reuse or disposal/incineration. However, current solvent-recovery technology requires extensive machine retrofitting and relatively high-cost additional equipment. As a result, only very-high-volume converters or those with specialty end products are finding recuperative systems economically viable for answering environmental restrictions. The vast majority of converters and commercial printers will find water-based coatings to be the most acceptable resolution to restrictions governing environmental emissions.

Water-based coatings: key issues

Analysis of substrate surface characteristics

The industry is striving to develop test methods that will provide the relevant parameters needed to reestablish the equilibrium between substrates and coating materials. In the process, many of the generally accepted theories, assumptions, and rules of operation are being reexamined and questioned. Despite the large body of laboratory work that has been performed, three basic questions remain:

1. What is the mechanism by which corona treatment improves bonding between substrate and coating material?
2. What is the specific relationship between wettability and adhesion?

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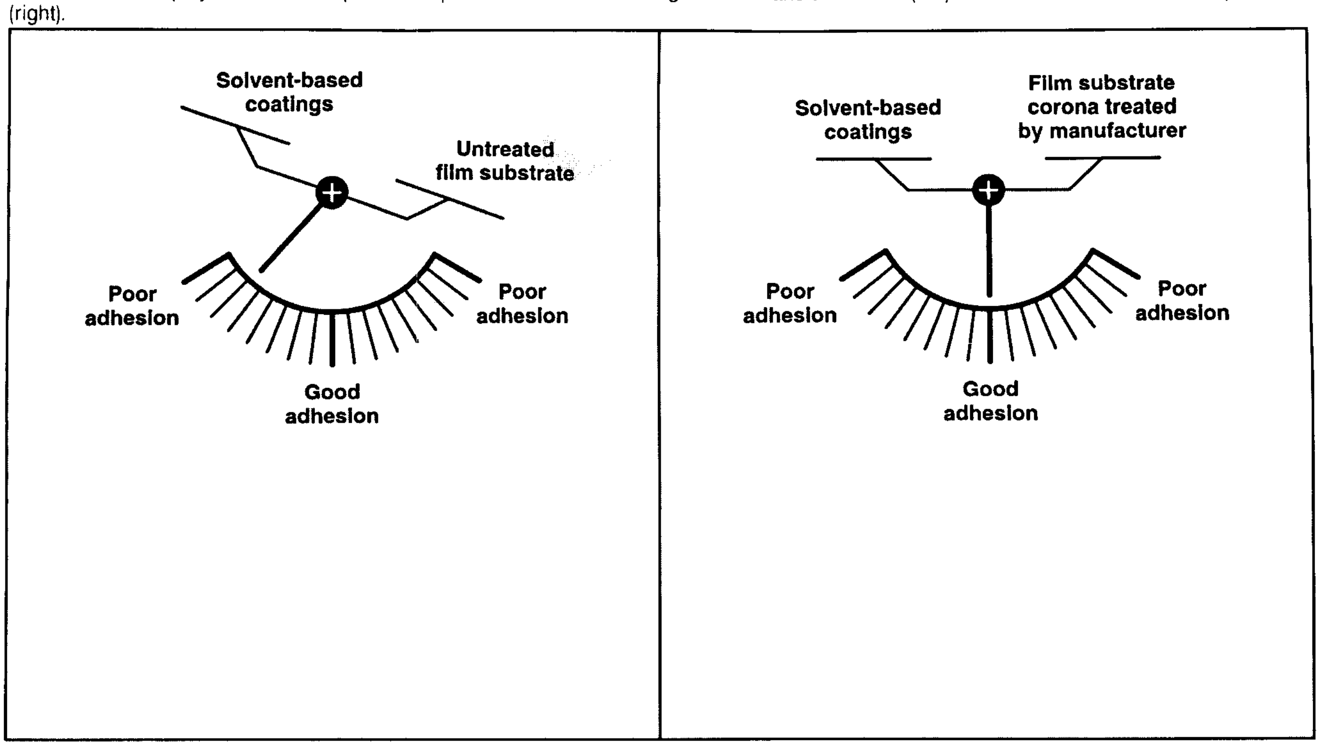
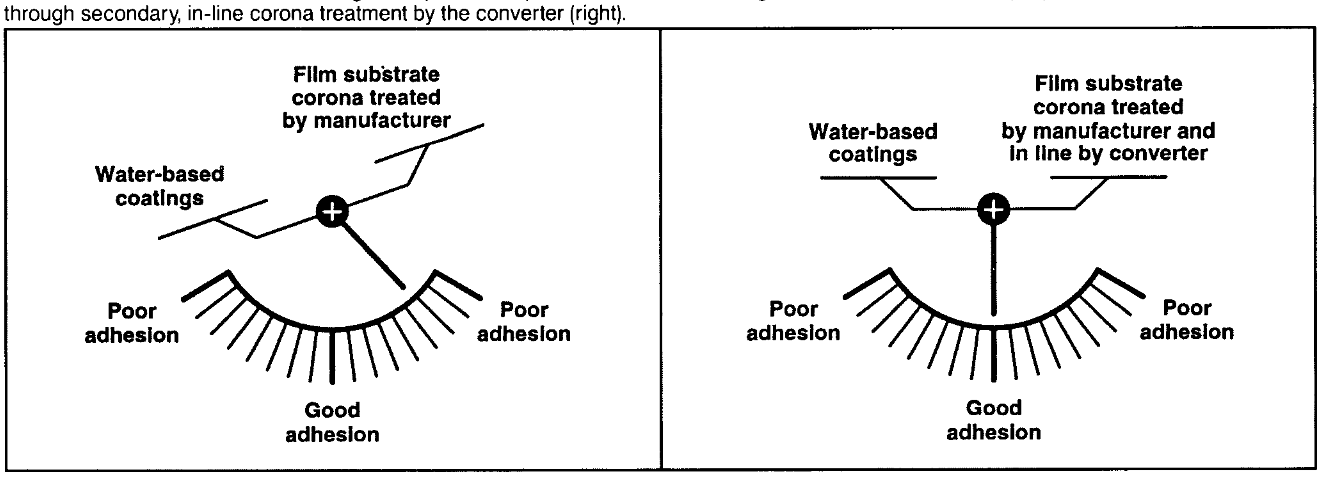
1. Introduction of polymer films disrupted the equilibrium between coating materials and substrates (left). Corona treatment restored equilibrium (right).



2. Introduction of water-based coatings disrupted the equilibrium between coating materials and substrates (left). Equilibrium can be restored through secondary, in-line corona treatment by the converter (right).



3. Do wetting-tension solutions provide an accurate and suitable measurement of the surface characteristics that affect printability and adhesion?

By reviewing past work, we can establish a practical system of operation that assures reliable, repeatable results for most converting operations on most substrates. By implication, if not by specific data and proven theory, we can begin to answer these three questions. Certainly, we can provide a framework for future study so that these questions can be answered more definitively.

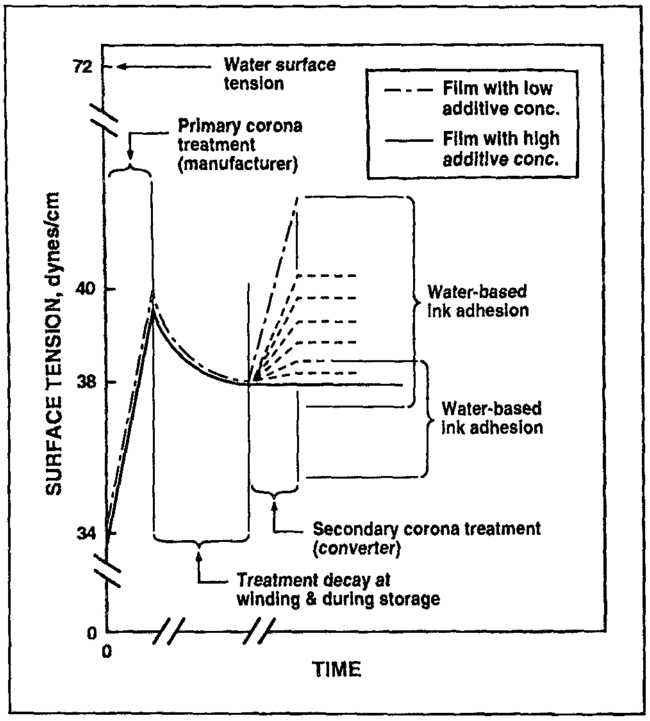
The new water-based and 100% solid coating materials have higher surface-tension characteristics than the previously used solvent-based materials. All water-based inks contain some solvent (usually alcohol), and most are formulated for wetting tensions between 32 dynes and 40 dynes. This places emphasis on the surface-tension characteristics of the various substrates used in converting processes, with attention focused on two important considerations.

1. What factors affect the surface characteristics of the substrate?
2. How can the surface tension of the substrate be increased at the time of converting?

Factors affecting substrate surface characteristics

There is general agreement that corona treatment improves wettability and adhesion for most polymer films. Although the reason for this improvement is subject to

3. Effects of primary and secondary corona treatment on surface tension



debate, there is underlying agreement on several issues.

Surface structure. At one time, corona treatment was thought to increase surface roughness. However, scanning electron microscopy of surfaces before and after corona treatment has shown this to be untrue (*1-3*).

Surface molecular analysis. Electron spectroscopy for chemical analysis (ESCA) has shown a linear relationship between surface oxidation, i.e., oxygen available at the surface, and wettability and adhesion (*1-4*) This analysis has been correlated with theories of surface energy level and the availability of polar sites at the surface (*3*, *5*). However, unpublished experiments with corona treatment in nitrogen atmosphere and in vacuum demonstrate increased wettability and adhesion ostensibly without increasing oxygen at the substrate surface. Whether nitrogen can perform a similar function as oxygen in increasing surface energy is yet to be shown. The energy-increasing mechanism of vacuum treatment also has not yet been defined.

Additives. Experimental studies have demonstrated that the impact of additives on the surface characteristics of polymer films varies with both the type of additive and the substrate (*2*). Significantly, certain combinations exhibit a negative impact on wettability without affecting adhesion of either solvent-based or water-based inks (*6*). This finding is supported by experience in the production environment.

Unpublished results of ongoing experiments dealing specifically with slip additives support the following tentative conclusions:

1. Additive concentration vs. bloom time (time in which additive migrates to the surface) is variable up to a threshold of 1000 ppm of additive.
2. Blooming occurs within 24 h.
3. Corona treatment encourages blooming of the slip additive to the treated side of the substrate.
4. Slip additives have a negative impact on both wettability and adhesion.
5. Secondary treatment counters the negative impact of slip additives on wettability and adhesion. In most instances, this allows the use of water-based coating materials.

Loss of corona treatment. Experience has shown that the effects of corona treatment (as measured in units of dynes per centimeter) diminishes over time. Experiments have demonstrated that treatment is lost in two stages: (a) by contact of the treated surface with both the machine roll and the untreated surface on the opposite side of the web when wound and (b) through aging (*4*). In one experiment, ESCA measurements demonstrated a 5-24% decrease in oxygen levels over a seven-week period, with a corresponding reduction in wettability. However, adhesion properties were not changed by the decrease in oxygen levels (*3*).

Test methods for evaluating surface treatment

Wetting-tension solutions. Measurement of surface tension with wetting-tension solutions (per ASTM D2578) has long been recognized as the most practical method for use in a production environment. Recently, this test method has been questioned from several standpoints.

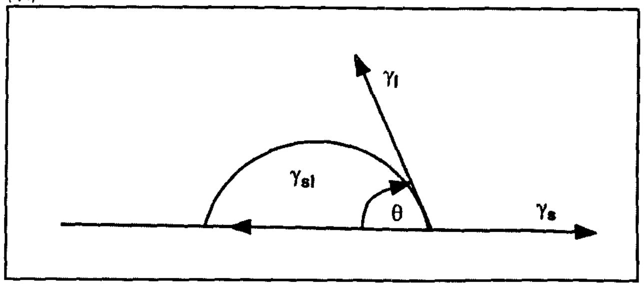
First, the materials used in this test method—formamide and cellosolve—are known to be toxic. Although these solutions are not highly toxic, anyone using them should exercise the appropriate precautions. Special care must be taken by pregnant workers or women in their child-bearing years. In fact, it is a reasonable precaution to remove these workers from all contact with the solutions.

Second, there are serious questions about the accuracy of test results obtained with wetting solutions (*5*, *7*). These concerns are centered on two recently observed developments:

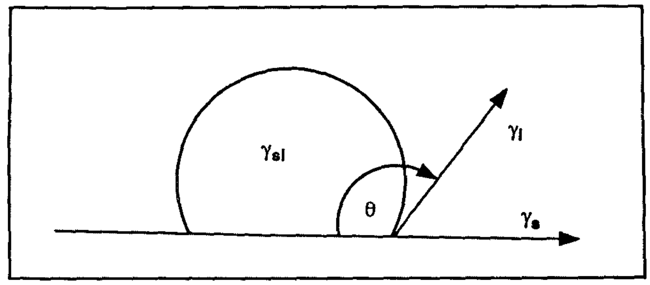
1. Production experience has demonstrated that, in some cases, wetting-solution dyne readings do not accurately predict printability and adhesion with water-based materials. **Figure 3** shows that in some instances, secondary treatment has little or no effect on substrate surface tension as measured by wetting solutions. Yet, in every case, secondary treatment dramatically improved printability and adhesion of the substrate.
2. There is a tendency for substrates to contain greater amounts and a wider variety of additives than previously used. These additives are thought to mask true surface characteristics and to contaminate wetting solutions, leading to inaccurate readings.

The reasons for inaccurate or inconclusive readings with wetting solutions have not been fully documented. The solutions are finely balanced mixtures of the two components, which have very specific wetting tensions. Contamination by even small amounts of moisture or additives would alter readings, and such contamination could easily occur in a production environment. Also, ambient temperature and the temperatures of the solutions and the substrate at the time of readings must be closely controlled for true readings. In any event, there

4. Substrate surface tension (γ_s) greater than liquid surface tension (γ_l)



5. Substrate surface tension (γ_s) less than liquid surface tension (γ_l)



is a growing opinion that wetting solutions may not accurately measure all of the surface characteristics that determine wettability and adhesion.

Contact angle. An accurate test method for surface tension is needed if the industry is to establish a new equilibrium between substrate surface characteristics, coating-material characteristics, and production processes. Some years ago, Zisman worked with equations developed by Young to develop the mathematical and practical underpinnings for evaluating surface tension through accurate measurement of contact angle (*8*). Zisman's work cannot be fully discussed here, but **Figs. 4 and 5** and Eq. 1 provide a simple demonstration of the theory.

$$\gamma_l \cos\theta + \gamma_{sl} = \gamma_s - \pi_e \qquad (1)$$

where

γ_l = free energy of liquid against saturated vapor

γ_s = free energy of solid against saturated vapor

γ_{sl} = free energy of the interface between liquid and solid

θ = equilibrium contact angle

π_e = equilibrium pressure of the absorbed vapor of the liquid on the solid

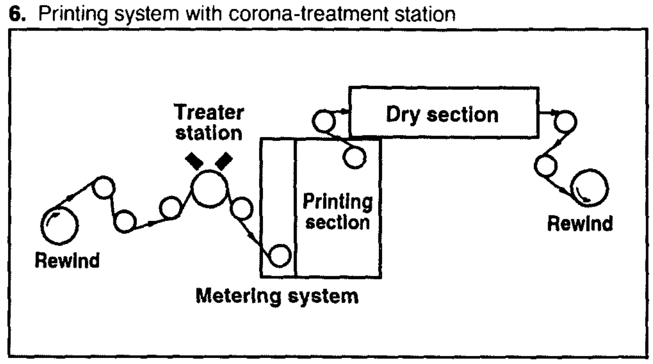
Much of the experimental work done over the past few years has ignored wetting-tension solutions as a method of measuring surface tension in favor of measuring contact angle (*1-3, 5, 6*). Several companies are marketing devices that can accurately measure contact angle.

Practical results of in-line secondary treatment

There is an obvious need to scientifically validate the current relationships among substrates, coating materials, and methods. Unfortunately, the converting industry cannot stand still while awaiting conclusive results. Further, all three elements are continually changing to meet practical production requirements.

The practical demands of this dynamic environment have led to the evolution of a cooperative system. The substrate producer, the manufacturer of coating materials, the converter, and the supplier of treating equipment all work together, with each group assuming a portion of the responsibility for making the system work. The system works like this:

6. Printing system with corona-treatment station



1. Substrate producers are providing surface-treated materials with higher surface tensions than previously supplied. Because of problems with blocking, back-side treatment, additive content, blooming, etc., the substrate producer cannot provide polymer substrates with sufficient surface tension to allow successful implementation in all converting processes (*4, 5*).
2. Manufacturers of water-based inks are providing formulations with reasonably low surface tension, despite the high surface tension of water (72 dynes).
3. Converters and commercial printers are typically increasing printability and adhesion by providing a secondary, in-line corona treatment (*4*). The effect of secondary treatment on wettability (as measured by wetting-tension solutions) varies, as seen in Fig. 3. However, as a practical fact, converting operations at typical line speeds can be completed successfully with secondary treatment. Without secondary treatment, most converting processes cannot be successfully completed at typical line speeds.

In addition, converters and commercial printers who use a variety of coating materials will find that in-line secondary treatment improves coverage and adhesion for both solvent-based and water-based coatings. In some cases, this will allow higher line speeds with no decline in product quality.

Sizing corona treatment systems for water-based coatings

Installation of a corona treatment system on a converting line will not in itself enable the line to handle water-based inks, coatings, or adhesives. For example, as seen in **Fig. 6**, a typical printing press contains a metering system, a

I. Surface tension for typical polymer substrates

	Surface tension, dynes/cm
Hydrocarbons	
Polypropylene	29-31
Polyethylene	30-31
Polystyrene	38
Polystyrene (low ionomer)	33
Acrylonitrile butadiene styrene	35-42
Polyamide	< 36
Polymethyl methacrylate	< 36
Polyvinyl acetate/polyethylene copolymer	33-44
Epoxy	< 36
Polyester	41-44
Rigid polyvinyl chloride	39
Plasticized polyvinyl chloride	33-38
Phenolics	N.D.
Fluorocarbons	
Chlorotrifluoroethylene (Aclar®)	20-24
Polytetrafluoroethylene/ polyethylene copolymer	20-24
Fluorinated ethylene propylene	18-22
Polytetrafluoroethylene (Teflon®)	19-20
Polyvinylidene fluoride	25
Polyvinyl fluoride (Tedlar®)	28
Engineering thermoplastics	
Polyethylene terephthalate	41-44
Polycarbonate	46
Polyimide	40
Polyaramid	N.D.
Polyaryl ether ketone	< 36
Polyacetal	< 36
Polyphenylene oxide	47
PBT	32
Polysulfone	41
Polyethersulfone	50
Polyarylsulfone	41
Polyphenylene sulfide	38
Nylon	33-46
Elastomers	
Silicone	24
Natural rubber	
Latex	N.D.
Polyurethane	N.D.
Styrene butadiene rubber	48
Fluoroelastomer	
Fluorocarbon copolymer elastomer	< 36

N.D. = not determined.

printing section, and a dryer section, all of which must be capable of operating effectively with water-based coating materials. These major elements must be reviewed along with any other machine component that comes in contact with the water-based material.

Basic considerations

The appropriate size for a secondary corona-treatment system is determined by several application parameters. The starting points for estimating the size of a treatment system are (a) the capacity of the power supply (kilowatts) and (b) the width of the treater station, which determines the maximum web width that can be handled. These alone, however, do not provide sufficient data for a specific application.

Watt density

The ultimate goal of any surface-treatment system is to increase the product's surface tension (measured in dynes per centimeter), thus increasing the wettability and adhesion characteristics of the surface. Corona treatment systems achieve this by applying a given level of power over a certain period of time to the surface. This power/time parameter is measured in terms of watt density, as defined in Eq. 2.

$$WD = PS/(WW\ LS\ NST) \qquad (2)$$

where

WD = watt density, W/ft^2/min

PS = power supply, W

WW = web width, ft

LS = line speed, ft/min

NST = number of sides treated

Although the watt density applied is directly proportional to the increase in dyne level (surface tension), the relationship is not linear and is different for each type of material treated. The subtleties of this relationship will be discussed later. For the present, it is enough to know that a greater application in watt density generally leads to a greater increase in surface tension.

Watt density as a control function appears to make system sizing relatively easy until one considers all of the parameters that affect watt density. These parameters can be broken down into two broad categories:

1. System parameters—governed by corona system and machine design.
2. Material/process parameters—governed by material and process requirements.

System parameters. The most obvious system parameters are the size of the power supply (kilowatts) and of the station (web width). Applied watt density is directly proportional to power supply size and inversely proportional to station size, as seen in Eq. 2. Thus if web width is doubled, the watt rating of the power supply must also be doubled to maintain a given watt density. This straightforward relationship is complicated by two factors: line speed and the electrode's capacity to handle a given level of applied power.

Each type of electrode—wire, metal bar, metal shoe, or ceramic covered—has an upper limit on the amount of power it can accept per unit length. If a given watt density requires a power supply that is beyond the electrode's maximum rating, additional electrodes must be added. Further, an increase in the number of electrodes may create a need for a larger-diameter treater roll. Both of these factors may increase the physical size and cost of the treater station required for a given application.

Line speed is the second system parameter that complicates the sizing calculation. On a given system, the higher the line speed, the lower is the maximum watt density that can be achieved. Because line speed is inversely proportional to watt density, speed has a significant impact on system sizing and cost.

Material/process parameters. The most obvious material/process parameters are the composition of the substrate material and the process being performed (e.g., coating, printing). As these factors are analyzed in detail, their impact on corona treatment sizing becomes increasingly complex.

For example, assume the simplest case: all materials to be processed are "barefoot," i.e., virgin material with no additives. **Table I** lists the surface tensions of typical substrates used by the extrusion and converting industries (*9*). A quick glance at Table I reveals that most materials are defined by a range of surface tensions, and this poses a problem. The range in surface-tension values for a given material can be explained by several contributing factors, such as method of manufacture (blown film vs. cast film), variations in die temperature at time of extrusion, and the type and amount of impurities that are present even in the highest-quality film.

The surface tension of a given material will increase when it is treated at a given watt density. However, both the ultimate surface tension achieved and the amount of increase depend on the material's initial surface tension. For example, applying a watt density of 1.2 to polyethylene terephthalate (PET) at 41 dynes may raise it to 46 dynes, but applying that same watt density of 1.2 to PET at 44 dynes may raise it to only 48 dynes. Although the final dyne level is higher in the second instance, the incremental increase is less because of the initially higher dyne level. Further, the variation of the response of barefoot material to corona treatment is compounded when the material contains additives. The impact of additive loading is discussed later in this article.

Different substrates also respond differently to corona treatment. Some polyesters, for example, accept treatment readily and show rapid increases in surface tension under relatively low watt-density levels of 0.9–1.2. Polyethylene, on the other hand, accepts treatment less readily but shows a significant increase in surface tension under moderate watt-density levels of 2.0–2.5. Polypropylene is an example of a difficult-to-treat material, showing only moderate increases in surface tension under relatively high watt-density levels of 2.5–3.0.

On-line re-treatment is not unusual for additive-containing films that have been stored for an extended period of time after the extrusion process. Re-treatment is very common when water-based materials are used as opposed to solvent-based materials, which wet-out and adhere more readily. For example, a film with a surface tension of 31 dynes as extruded may be treated to a level of 40 dynes on the extruder. After shipment and storage, the effect of time and additive loading may reduce the film's surface tension to 36 dynes or less. At this level, solvent-based materials may well provide a high-quality product without further treatment. However, a water-based material may require that the film be re-treated to raise its surface tension to 40 dynes or more. Our

II. Typical watt density for application of water-based materials

Item treated[a]	*Application*	*Watt density*[b]
Substrate	Flexo printing	2.0–4.0
Substrate	Gravure printing	2.5–4.0
Substrate	Speciality printing	2+
Coating	Printing	2.0
Substrate	Coating	2.5
Substrate	Priming for laminating	2.0
Substrate	Adhesives	2.0
Substrate	Adhesives for laminating	Water wet (70 dynes)
Coating	Laminating	2+

[a]Substrates (polyethylene, polypropylene, polyester, etc.) containing moderate additive load and corona treated at time of extrusion.
[b]Watt density is a relative number, not an absolute level.

7. Data sheet for specifying size of corona-treatment system

TREATER DATA SHEET

TYPE OF LINE: ____________

PURPOSE OF TREATMENT: ____________

SUBSTRATE: LDPE ☐ LLDPE ☐ HDPE ☐ PET ☐ PAPER ☐ PP ☐ OTHER ____________ **METALIZED:** Transfer ☐ Vacuum ☐ **FOIL:** CLASS A CLASS B CLASS C

WHICH SUBSTRATES ARE PRETREATED: ____________

COATING/INK/ADHESIVE: Water based ☐ Solvent-based ☐ Extrudate ☐ 100% Solid ☐ Hot Melt ☐ UV ☐ EB ☐

WEB WIDTH	____ IN ____ MM		ADDITIVES	
TREAT WIDTH	____ IN ____ MM		SLIP	____ PPM
ROLL FACE	____ IN ____ MM		TOP	____ PPM
THICKNESS	____		ANTI-BLOCK	____ PPM
LINE SPEED	____ FPM ____ MPM		COLOR	____ PPM
WEB TENSION	____ PLI		ANTI-STAT	____ PPM
E-STOP WEB TENSION	____ PLI		EVA	____ PPM
WHICH SIDES TO TREAT	____		OTHER____	____ PPM
TREAT LEVEL (Dynes)	____			
OR				
WATT DENSITY(Watts/ft²/Min)	____			

MOUNTING LOCATION: ____________

SWITCHING OPTION: Low Voltage ☐ High Voltage ☐ None ☐

HAZARDOUS LOCATION: YES ☐ NO ☐ QUOTE AS OPTION ☐ OR WITH SYSTEM ☐

SPECIAL REQUESTS/COMMENTS:

____

SYSTEM SPECIFICATIONS:

____	FT2/MIN	____
____	WATT DENSITY	____
____	POWER SUPPLY	____
____	STATION	____
____	PLI (MAX)	____
____	W (MM)	____
____	WATTS/INCH	____

experience demonstrates that for a given surface-tension improvement, re-treating previously treated film requires a lower watt density than treating a film that has not been pretreated.

Table II provides rule-of-thumb treatment levels for application of water-based materials on substrates that have been at least minimally treated at the time of extrusion and contain a typical or moderate additive load.

To properly size a corona treatment system for a particular application, several specific parameters must be reviewed and considered. To ensure that this is done, treater suppliers have developed data sheets that systematically present all of the information that affects the sizing of a treater system. **Figure 7** is an example of a data sheet for general treater applications. Each item affects the physical or electrical design of the system and, ultimately, the system's ability to meet the performance and long-term reliability requirements of the application.

Conclusion

The complete story on corona treatment of substrates for use with water-based coating materials has yet to be written. Given that market conditions and technologies are continually evolving, the story will probably never end. Nevertheless, it is an unequivocal fact that in-line secondary corona treatment is a viable alternative for converters who are turning to water-based inks and coatings in this era of heightened environmental concern.□

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