

THE EFFECT OF TIME AND CONTACT ON CORONA TREATED SURFACES.

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ABSTRACT

The effect of time and surface contact on corona treated material can be measured and evaluated. Both components cause degradation of dyne level readings of wettability. However, the most significant cause, though it can be isolated, cannot be completely eliminated. A solution to the problem is possible but requires cooperation between material producers and converters.

The use of solvent base inks for printing on polyethylene surfaces is rapidly giving way to more environmentally acceptable inks. This has been accelerated by more stringent environmental regulations being enacted at the local, state and federal levels. It is possible to use solvent recovery systems that satisfy these environmental regulations, but they are expensive to install and present some operational problems. The majority of converters are electing to change to water-base inks. It is expected that this trend to water-base inks will continue.

Adequate ink adhesion with water-base ink cannot be achieved unless the polyethylene surface is modified in such a way that its surface tension is greater than the surface tension of the ink. The surface tension of the polyethylene surface is measured by what is commonly referred to as the Dyne test which is covered by ASTM Standard D2578. A practical article on this test method appeared in the February 1985 issue of T APP1.2

A common method used to increase the surface tension of the polyethylene surface is corona treatment which consists of passing the surface through a corona field generated by a high frequency electrical discharge.³ Considerable research has been conducted over the years in the attempt to determine what happens to the polyethylene surface when subjected to this corona field and the answer is still somewhat in question. A common theory is that a modification of the top molecules of the polyethylene film occurs and various molecular radicals consisting of key tones, acids, aldehydes, etc., are produced.⁴⁻⁵ These radicals tend to be polar in nature and as such, have less tendency to repel water.

This paper will not attempt to explain what happens during the treatment but will deal with what happens after treatment. It will also point out why much of the research work that has been done in the past may have led to erroneous conclusions.

It has long been known that some of the beneficial results obtained by the corona treatment degrades after treatment. It has been felt that the primary cause for this loss is that any subsequent rubbing of the treated surface over idler rolls, reel drum, etc., tends to wipe off the treatment. This effect can supposedly be demonstrated by wiping selected areas of a sample before running the Dyne test. It has also been demonstrated that natural aging of the product, in roll form, will reduce the treatment and it has been theorized that this is a result of diffusion of the radicals formed during treatment.⁶⁻⁷ This paper will point out that both of these causes are minor when compared to the primary cause for the loss of treatment.

RECENT STUDIES HAVE REVEALED THAT ALMOST ALL OF THE

LOSS OF TREATMENT OCCURS IMMEDIATELY AFTER TREATMENT WHEN THE TREATED SIDE OF THE SHEET CONTACTS THE OPPOSITE SIDE. THIS WILL HAPPEN AT THE END OF THE MACHINE WHETHER THE PRODUCT WINDS UP IN ROLL FORM OR IS SHEETED IN LINE.

This loss of treatment, between the time of manufacture and the time of use, has become a major problem for the supplier. In the attempt to assure their customers a satisfactory product, they have resorted to higher and higher levels of initial treatment. This has not adequately solved the problem since the higher the initial treatment level the greater the loss. The final result, at the point of use, is only a slight improvement when compared to a more moderate initial treatment. These attempts to treat to higher levels has created problems for the supplier and often results in an "off-quality" product for the end user. A partial list of these problems and their causes are as follows:

1. Pinholes

If the base sheet contains a spot of high moisture or some other extra conductive material, the strong corona shorts through the spot and burns a small hole through the substrate.

2. Blocking

The molecular radicals formed by the corona have an attraction for the molecular layer on the other side of the web and when the two sides come in contact, as in roll form, a self-adhering condition exists.⁵ It is not unknown for this attraction to be greater than the internal bond of the substrate and actual substrate delamination to occur when the product is unrolled. The longer the roll is in storage and the tighter the wind, the more severe the problem. Blocking occurs more often near the core of the roll.

The cause for this condition will be discussed in more detail later.

3. Scratches

Considerable heat is generated by the corona electrodes which results in thermal expansion of the equipment. The air gap between the electrodes and the polyethylene surface is quite small and can only be adjusted for cross web uniformity while the system is shut down. During operation the thermal expansion can warp the conventional metal electrode assembly enough to cause areas to actually touch the web - which results in a scratch. Increasing the overall gap to correct the problem may then result in areas of low treatment.

Over the years, corona treater suppliers have done an excellent job of minimizing this thermal warping, but it remains a fact of life that the higher the treatment level attempted, the greater the heat generated and the greater the chance for thermal expansion on conventional metal electrodes. Also, the wider the unit the greater the problem, therefore, on narrow width units, as would be used on printing presses, the problem is not as significant. Bare-roll treaters have eliminated the scratching problem.

4. Corona Marks

A very high treatment intensity creates a surface condition that may result in marks from idler rolls or the reel drum. These marks are not a disturbed area, as a scratch would be, but are a visual dulling of the sheet gloss. To the unaided eye, they may look the same as a scratch, but examination under magnification, with low angle cross illumination, reveals the difference. Newer conventional and bare-roll treaters have eliminated this problem.

5. Uneven Treatment Across The Web

Generally, the wider the sheet being treated the greater the problem and higher treatment levels only serve to magnify the problem. The most common manifestation of this problem is lower dyne levels on the edge of the sheet. This effect has been known to extend inward from as little as two inches to as much as a foot. When a multi-roll set-up is being produced; i.e., the parent roll is slit to narrow rolls for the customer - this results in rolls from the same production run having widely varied dyne results.

6. Heat Sealing Problems

The true effect of high initial treatment on heat sealing is not documented, but preliminary indications are that it may interfere with the sealing properties of the products

7. Down Time

The high power settings required to achieve the high treatment levels are not conducive to long life of the equipment. Various components of the electrical package such as transformers, diodes, rectifiers, etc., burn out prematurely. The mechanical portion also suffers shorter life with electrode or conventional roll burn-out being a common problem. Again, newer conventional and bare-roll treaters have eliminated this problem.

8. Efficiency Loss

The problems created as a result of using high power levels thus cause down-time, lost production and "off-quality." These, in turn, increase the cost of manufacture which must be absorbed by either the supplier or the end user.

It is known, and a dodge sometimes used, that a less glossy finish will result in higher dyne tests. The finish of the polyethylene surface is controlled by the finish of the chill roll. A lower gloss finish is created by utilizing a chill roll with microscopic pits in the finish which create microscopic bumps on the polyethylene surface. This type offinish will, in fact, give higher dyne results. Unfortunately, it does little to improve ink adhesion. The reason lies in a fallacy in the test procedure. After the dyne solution draw down is made, the dyne reading is measured by the time required for solution crawl or beading to be exhibited. A surface with a multitude of microscopic bumps will mechanically impede the crawl of the test solution. This will naturally be interpreted as a higher dyne reading, but this mechanical impedance will not have an equal effect on ink adhesion.

Tests conducted on samples obtained immediately after the treater station, as well as in the roll, have revealed losses as high as 17 dyne points. The work also shows that the amount of loss is dependent on two factors - namely: THE AMOUNT OF INITIAL TREATMENT AND THE COMPOSITION OF THE SURFACE CONTACTED BY THE TREATED SURFACE. See Table 1

TABLE 1

	Test	Loss
Initial sample just before contact	56	
After contacting untreated polyethylene surface on opposite side	39	17
After contacting corona treated polyethylene surface on opposite side	39	17
After contacting bare bleached base sheet on opposite side	43	13
After contacting flame primed bare base sheet on opposite side	39	17
After contacting slip sheeted bleached bond paper	44	12
After contacting slip sheeted bare aluminum foil	45	11
After contacting slip sheeted unbleached paper	49	7
Non-treated polyethylene surface	35	

The samples obtained before contact with the opposite side were taken on-the-fly during actual manufacture of the product. Additional on-the-fly samples down the length of the machine showed no loss of treatment after contacting and passing over following rolls. Dyne test

results remained at the same level as immediately after the treater until the point of contact with the opposite side.

Research work was conducted on the experimental extruder of Enron Company in an attempt to add to the above information and to obtain samples that had not contacted the reverse side of the sheet for ESCA scan testing.

The maximum loss on contact that was obtained during this trial run was ten points of dyne - from 56 to 46. However, there are two major differences between this extruder and the one where the original tests had been conducted. The most significant is that the experimental extruder has a single head therefore it was not possible to tandem extrude and treat in one pass. It was necessary to do the reverse side coating one day and the top coating with treating the following day. This resulted in the treated side contacting "old-cold" poly that had already contacted a base sheet surface where as in tandem extruding, the treated side contacts fresh hot poly that has not been in contact with any organic surface. A second major difference is the reduced contact pressure between the two surfaces on the experimental extruder versus the production machine. These two conditions could well reduce the amount of loss and cannot be used as a true measure of what will happen during a production run on a tandem extruder.

Additional work has shown that when the surfaces are pulled apart and then brought back into contact with each other, further loss occurs. It has long been known that Dyne readings are reduced by rewinder operations. It was thought that this was due to the machine rolls contacting the treated surface during rewinding. However, on-the-fly sampling at the rewinder reveals the same results as were obtained on the production machine. That is, there was no dyne loss due to rubbing on the machine rolls but loss occurred at contact of the web surfaces. Approximately 90% of the total loss occurred at first contact and the remaining loss at second contact. It was not possible to get a check on the loss suffered at the third, fourth, etc., contact but other data indicates that each subsequent contact reduces the treatment to a lesser and lesser degree until the test approaches the same level as an untreated sheet. HOWEVER, IT APPEARS THAT NO MATTER WHAT IS DONE IN NORMAL OPERATIONS, A VESTIGE OF THE ORIGINAL TREATMENT WILL ALWAYS REMAIN.

A study of the data indicates that the amount of loss that occurs is dependent on the degree of oxidation of the surface contacted by the treated surface. The greater the degree of oxidation, the greater the loss. When the reverse side was corona treated the loss was no greater than for a non-treated surface - this may contradict the previous sentence but perhaps the maximum destruction had been reached by the normal polyethylene surface. The fact that contact with aluminum reduced the dyne test is attributed to the presence of aluminum oxide on the foil surface. The difference in test results between contact with a bleached versus an unbleached surface is attributed to the presence of residual oxidation chemicals from the bleaching process.

An interesting additional point is that when both sides are treated, then both sides lose in dyne test, i.e., the treatment is not transferred, it is partially destroyed on both surfaces.

The higher the level of treatment and the greater the degree of oxidation of the opposite side, the greater the attraction of the two surfaces and the greater the opportunity for blocking. The two surfaces have a substantial attraction for each other and can be pulled apart only by rupturing the chemical bond that was created on contact. Often, during high speed unwind operation, a singing sound can be heard as the two surfaces are pulled apart. The same sound would be heard if the two surfaces had been lightly glued together - which, in fact, they were.

Further bonding, to a much lesser degree, occurs when the surfaces are recontacted and more damage is then done to the treatment. It is believed that this is due to recontact at a slightly different point and more radicals on the treated surface and oxygen on the opposite

surface are available for mutual bonding.

THIS BONDING, WITH SUBSEQUENT RIPPING APART, ALTERS THE REACTIVE END OF THE MOLECULE ON THE TREATED SURFACE AND THIS ALTERED END DOES NOT CONTRIBUTE TO INCREASED SURFACE TENSION. UNFORTUNATELY, IT IS THIS ALTERED MOLECULE THAT HAS BEEN SO PAINSTAKINGLY EXAMINED IN PAST RESEARCH WORK.

It is felt that loss on contact with further loss each time the surfaces are pulled apart and recontacted may contribute to the lower dyne test on the edges of the web. Often, due to edge bead conditions, the reel will have a hard edge which tends to cause a slack condition just in from the edge. This gives the sheet a chance to work, i.e., not remain in firm one-position contact as well as the rest of the reel. The problem may instead be caused by increased oxidation on the edges of the polyethylene web on the opposite side.

Samples were obtained, during the trial run at Enron, that are uncontaminated, i.e. they were removed on the run before the treated side had a chance to contact the reverse side of the sheet. Electron Spectroscopy for Chemical Analysis (ESCA) testing was done on all samples. The data validated the loss of treatment and related that loss to oxygen levels on the near surface of the samples. Complete ESCA test data and analysis is included in addendum 1 of this paper.

If the polyethylene contains additional components, such as slip additives, the initial treatment is reduced over time as these additives bloom to the surface and partially mask the radicals formed during treatment. However, it is felt that when polyethylene contains slip additives, treatment at the point of use is more effective if the sheet had been treated at the time of manufacture.

It is now apparent that there is only so much that the material supplier and corona equipment manufacturer can do to furnish a suitable product for the final end user. When they attempt to treat to higher levels the majority of the treatment is lost immediately upon contact but all the negative conditions mentioned still exist. However, it is also apparent that a small portion of the initial treatment remains regardless of what normally happens to the sheet after manufacture. This small residual makes further moderate treatment more effective. It is analogous to a primer coat of paint.

CONCLUSION

In conclusion, one can rate the sequences for processing in order of effectiveness for both the supplier and the end user.

Most Effective

A moderate treatment by the supplier at the time of manufacture followed by moderate treatment on the press just before ink laydown. This final treatment can be varied to optimize ink adhesion with heat sealing characteristics.

Second Most Effective

Treatment on the press only. This can lead to difficulties if the polyethylene contains slip additives. In any case, it is much more effective than treating at the time of manufacture as the treated surface will not contact the other side before the printing station thus the full results of the treatment still exists at the point of ink laydown.

Least Effective

Treatment by supplier only. The problems and difficulties encountered have been covered but a quick summary may be in order:

- 1) Loss of a substantial portion of the treatment.
- 2) Production of pinholes, blocking, scratches, etc., caused by using extremely high power levels at the treater.

ADDENDUM 1: Electron Spectroscopy for Chemical Analysis

(ESCA) Data on Corona Treated Samples.

The following data is included as an addendum to this paper for two reasons:

- 1) to validate the general conclusions this paper has based on the ESCA data.
- 2) to preserve and present this data so that others might build upon the data base for future analysis.

All samples referred to in this paper were analyzed using Angle Dependent ESCA techniques. This method is very useful for characterizing the chemical and compositional differences within a very thin surface film «100Å).

The following data was collected at angles of 100 and 900. Based on an inelastic mean free path of 27 Å for the C1s, this translates into effective sampling depths of 5Å at 100 and 27 Å at 900. These calculations are based on the equation

$$d = A \sin e$$

where d is the effective sampling depth, A is the inelastic mean free path and e is the angle between the plane of the sample surface and the analyzer.

To simplify the discussion of the results, three samples were selected that represented different treatment levels and wetting characteristics. The noncontacted samples are designated 2, 3 and 4. The corresponding contacted samples, 2A, 3A and 4A, were also analyzed.

Table 2 lists the results obtained for the non contacted samples taken at an angle of 100 and 900. These results illustrate a definite correlation between surface oxygen (O) content and wetting characteristics. As expected wetting increases with increasing O content.

TABLE 2: ESCA results for noncontacted corona treated samples

Sample	Treatment Level	Wetting (Dynes)	e	Normalized Atomic Concentrations (Atom %)	
				Carbon	Oxygen
2	4.76	56	10	96.9	3.1
			90	96.8	3.2
3	2.38	52	10	95.3	4.7
			90	97.1	2.9
4	1.67	50	10	97.1	2.9
			90	97.8	2.2

Corresponding values for the contacted samples are given in Table 3. Again O concentration follows nicely the measured wetting values. Comparing the ESCA data for the contacted and noncontacted samples the O to wetting relationship remains constant while in most cases O levels in the contacted samples, and therefore the wetting, is lower.

TABLE 3: ESCA results for contacted corona treated samples

Sample	Wetting (Dynes)	e	Normalized Atomic Concentrations (Atom %)	
			Carbon	Oxygen
2A	50	10	96.7	3.3
		90	97.3	2.7
3A	52	10	96.2	3.8
		90	96.6	3.4
4A	46	10	97.7	2.3
		90	97.0	3.0

The drop in O concentrations in the contacted samples could be due to either the loss of surface O or the deposition of CHx contaminants. The contamination could be transferred by contact with the untreated side of the web. The second possible explanation is that contact itself caused a loss of O from the treated surface. Realistically, the changes observed are most likely due to a combination of these affects. Some transfer of contamination from contact with the untreated side is inevitable. At the same time, the friction and pressure associated with the rolling process could result in the loss or decomposition of certain CoO functional groups. This would be especially true for the peroxides and hydroperoxides formed.

In addition to the C and O atomic concentration values, computer curve fitting techniques were also employed to break down the C1s photoelectron line into its component peaks. A representative curve fit for the C1s line is shown in Figure 1.

The major component of the spectra is due to the CHx species. Other significant peaks are caused by:

- 1) C atom with single bond to O, full 1.2 eV higher binding energy.
- 2) C atom with two bonds to O at 2.6 eV.
- 3) C atom with three bonds to O at 4.2 eV.

Curve fits were performed on all samples. The results are tabulated in Tables 4 and 5.

TABLE 4 Curve fit data for noncontacted samples

Sample	Wetting (Dynes)	Watt Density	Relative Concentration (% of CTOTAV)			
			CHx	CoO	C=O	C-O
2	56	4.76	89.7	6.6	2.5	1.2
3	52	2.38	87.9	8.8	2.4	0.9
4	50	1.67	90.9	6.2	2.2	0.8

TABLE 5: Curve fit data contacted samples

Wetting (Dynes)	Watt Density	Relative Concentration (% of CTOTAV)			
		CHx	CoO	C=O	C-O
50	4.76	89.0	7.2	2.7	1.1
50-52	2.38	92.1	5.3	1.8	0.7
46	1.67	91.0	5.9	2.2	0.9

The curve fits did not exhibit any significant trends in relation to the measured wetting values. However, there is some evidence supporting a correlation between the treatment level (watt density) and the relative concentrations of the C = O and O

C = O species. These concentrations do exhibit some increase with a higher level of treatment. No direct correlation was observed for the CoO concentration with respect to either measured wetting values or treatment levels. Both contacted and non contacted samples exhibited the same trends. No significant differences were detected.

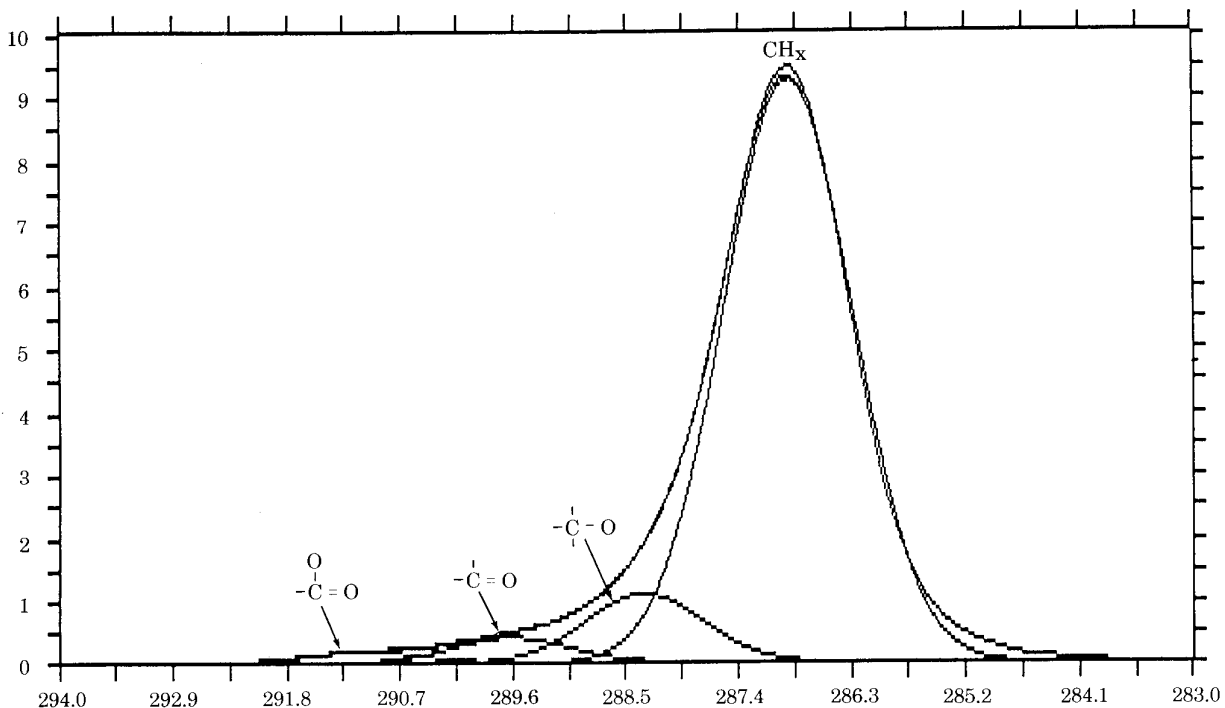


Figure 1 Typical curve fit for the C1s photoelectron line.

CONCLUSION

Based upon the results of this investigation, it is evident that the changes observed between contacted and noncontacted samples cannot be avoided. These results support the recommendation that corona treatment is beneficial at both the point of manufacture and just prior to printing. The oxygenated carbon species created during corona treatment are extremely fragile. These species are easily degraded over time and with pressure or friction. It is also evident that these CoO functional groups play a crucial role in ink adhesion. To circumvent the loss of these "active sites," it will be necessary to corona treat the web just prior to printing.

REFERENCES

P.B. Sherman	Alpes-Congress Grenoble 22-25	Mars 1976
David A. Markgraf	TAPPI Journal	February 1985
L.M. Salmen	Paper, Film, & Foil Converter	October 1978
Andreas Tietje	TAPPI Journal	1978
David A. Markgraf	Paper Synthetics Conference	June 1983
H.L. Spell and C.P. Christensen	TAPPI Vol. 62 No. 6	June 1979
D. K. Owens	Journal of Applied Polymer Science Vol. 19, pp 265-271	1975
H. L. Spell and C.P. Christensen	TAPPI Journal	1978
A. Honkanen, E. Laiho, & C. Berstrom	TAPPI Vol. 61 No.	Nov. 1978
I. Randell	Converter Vol. II N 8	Aug.-Sept. 1974
A.M. Adur, R.N. Shroff, & R.T.E. Sylvester	Paper Synthetics Conference	1981