THE DETERMINATION OF CORONA OXIDATION OF POLYETHYLENE FILM BY MULTIPLE INTERNAL REFLECTION SPECTROSCOPY

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ABSTRACT

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The acceptance of polyethylene film as a packaging material is in part due to the development of methods to oxidize its inert surface to accept printing inks. Two of the methods currently used for oxidation of film surfaces are flame treatment and high frequency (corona) discharge. While ink adhesion is increased by oxidation, heat seal properties are decreased. Various methods have been devised to determine the degree of surface treatment which are based on the force required to pull two treated films apart.

The development of multiple internal reflection (MIR) spectrophotometric techniques presents a means for observing the surface oxidation products formed. The purpose of this work was to determine if the change in oxidation products on a polyethylene surface caused by a change

in the power of a corona discharge can be determined by M. I. R. techniques.

The work was done by using a Lepel high frequency power source to provide a corona discharge to the surface of polyethylene film. A two electrode discharge was applied to the film on a revolving drum. Spectra of samples of the treated films were obtained with a Beckman IR-4 spectrophotometer fitted with a Wilks Model 9, Single Beam MIR attachment and a Wilks MIR-11 Reference Beam Attenuator. The carbonyl absorption band at 5.8 microns and the olefinic unsaturation absorption band at 6.1 microns were referred to the methyl deformation band at 7.6 microns to provide analytical ratios. The baseline technique of band measurement was used. The data were plotted against watt-hours of treatment per thousand square feet. An expansion series was presented as an approximation to the curve form.

The results of the work show that the change in surface oxidation with change in corona treatment power can be determined by M. I. R. techniques. The increase of carbonyl and olefinic unsaturation approach limiting values at approximately the same rate and over the same power range. The curves derived from the data indicate that analytical working curves could be made for correlating treatment with resulting effects on ink adhesion and heat seal of the film.

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INTRODUCTION

Background

The relatively inert olefin polymers, polyethylene and polypropylene, have found wide use in the packaging industry. This acceptance is due in part to the development of methods to change the character of their surfaces so they can accept printing inks.

The two types of treatment used to obtain this surface characteristic are (1) chemical and (2) physical. The former are either solvents or oxidizing solutions while the latter are usually flame or electronic in nature. The physical methods are becoming the most popular because of their lower cost and ease of handling(3). These will be discussed briefly.

With the flame treatment of the film, the flame strikes the film as it passes over a water-cooled, chrome plated drum(31). The flame height and character must be uniform to give the uniform treatment. The flame angle must be such that the hot gases pass over the film. Because of the variation due to resin polymerization, formulation and fabrication of different producers, the films require different gaps between flame and film to give equal treatment.

The electronic treatment consists of passing the film over a grounded metal roll while subjecting it to the electrical discharge from one or more high frequency electrodes(13). Either the roll or electrodes are covered with a dielectric material. The dielectric serves to provide a uniform treatment. The separation of electrode from the film varies with the character of the film as with the flame treatment. Film surface temperature is raised about 30°C and, in air, ozone and nitrogen oxides are formed during the discharge.

Tests for determining the degree of treatment of films are numerous. Some of the more familiar ones are: 1) the Chapman Test, 2) the tilting platform test, 3) the Monsanto Scotch Tape Test, 4) the Tennessee Eastman Test, and 5) the St. Regis Heat Seal Test(3).

The Chapman Test uses ink to adhere two treated pieces of film together. The force required to pull the two pieces apart is a measure of the degree of treatment. The tilting platform test is based on the wetability of the film surface. The larger the angle required to start a drop of liquid down a film surface, the greater the treatment. The Monsanto test is based on the adhesion of a pressure-sensitive tape to a film surface. The force required to remove the tape is the measure of treatment.

The Tennessee Eastman test is also based on the force required to separate a treated film from another surface. Force is proportional to treatment. Treated film is heat sealed to aluminum foil. Force is recorded with a tensile tester. The St. Regis test is based on an untreated sample as standard. Minimum sealing conditions are established and are then related to other samples of the series both with minimum sealing conditions and a tensile test. The relationship of ink adhesion and the temperature required for good heat seal is approximately inverse(27). Thus, a single test capable of correlating treatment with ink adhesion and sealability would be useful.

The elucidation of the surface reaction occurring during flame treatment was the beginning of efforts to develop more quantitative methods for measuring levels of treatment. Kreidl and Hartman, who were the first to develop a commercial flame treatment for polyethylene, had the change of surface identified by infrared analysis as being oxidation(12). A treatment depth of less than 0.00001 inch was reported.

At about the same time, the effects of electronic treatment of polyethylene were investigated by infrared analysis(20). The treatment was shown to be of such a low concentration that twelve treated surfaces (six samples) in series were required to obtain a transmission spectrum. The presence of carbonyl and carbon-carbon double bonds were found at 5.85 and 6.10 microns respectively. It was indicated that the unsaturation arose during the corona treatment and oxidation was facilitated by it. The difficulty of quantitative measurement has been the lack of an instrumental technique to determine the low concentrations.

The development of the principles of attenuated (frustrated) total reflectance (A.T.R.) by Fahrenfort(4) opened the way for identifying products of surface reactions, their reaction rates and concentrations. The extension of this principle to frustrated multiple internal reflection (F.M.I.R.) has allowed the identification of minute quantities of energy absorbing structures of organic and inorganic nature. The use of F.M.I.R. to establish a quantitative method for determining carbonyl concentration would be the first step in correlating treatment with ink adhesion and heat sealability.

This report briefly describes the principles of A.T.R.-F.M.I.R., some applications reported in the literature and the spectrum of polyethylene. The work done in this laboratory to determine the feasibility of using F.M.I.R. techniques to determine the change in carbonyl and carbon-carbon unsaturation on the surface of polyethylene with change in corona discharge power is described. A discussion of results, conclusions, and some recommendations for future work follow.

Attenuated Total Reflectance

The principle of total internal reflectance can be visualized by reference to a prism having highly polished optical surfaces. As radiant energy passes through the prism to a reflecting surface, it will be totally reflected internally if the energy strikes the surface at an angle exceeding the critical angle. (The critical angle is defined by $\sin \theta = n_2/n_2$ where n_1 is the index of refraction of the prism and n_2 is the index of the rarer medium.)

When a material that absorbs radiation is placed against the reflecting surface of the prism, the incident radiation is divided into two components--reflected and transmitted. The transmitted energy enters the sample to a depth dependent on the refractive index and angle at which it enters. The unabsorbed energy is reflected in relation to the amount absorbed. This is the attenuated (frustrated) total reflected radiation.

The depth to which the incident radiation penetrates the sample is dependent on the wavelength of energy, the refractive index of the prism and sample and the angle of incidence of radiation. This relationship has been expressed as(7)

$$x_{\frac{1}{2}} = \frac{0.693\lambda}{2(\sin^2\theta - n_{21}{}^2)^{\frac{1}{2}}}$$

where θ is the angle of incidence; n_{21} is the relative refractive index (n_2/n_1) and $x_{\frac{1}{2}}$ is the theoretical depth of penetration defined as the distance required for the incident energy to fall to one-half of its value at the point of entrance to the medium. The depth of penetration ranges from about 0.1λ for a grazing angle to an indefinitely large depth near the critical angle(8). Fahrenfort(4) and Harrick(7,9) have given mathematical treatments for the phenomena related to attenuated total reflectance.

It could be implied from the above that if the depth of penetration can be determined, film thickness can also be determined. This can be done providing the refractive indices of prism and film are known. The limit of thickness measurable can be extended (from about 0.1λ to λ) by changing the angle of incidence and by using a prism with a broad transmission range. Germanium, for example, with transmission between two and twenty-five microns allows measurement of films of 0.2 to 100 microns thick(8).

The refractive index of an absorber increases in the region of absorption. If the refractive index of the prism is less than that of the sample at this point, distortion of the absorption band occurs relative to that of the transmission spectrum. Thus, it is necessary to choose a prism having an index exceeding that of the sample at all absorption bands if A.T.R. spectra comparable to those of transmission are to be obtained.

The major disadvantage of the single attenuated reflectance technique is the weak spectra obtained. The multiple internal reflection technique (F.M.I.R.) takes advantage of several reflections occurring along the surfaces of an optical pipe(6) or flat prism. The advantage of this technique is the increase in sensitivity caused by the increase in reflection. In effect, an increased path length is obtained. After a few reflections along the plate, distinct reflections cease and the surfaces become sensitized. Surface contact with the sample becomes the sensitivity factor for detection purposes.

The flat prisms commercially available are cut with angled ends so that radiant energy can be trained normal to the end surface to give desired angles of incidence. The sample is placed along the flat sides of the prism for analysis. Table I lists five of the commercially available crystals used in F.M.I.R. spectroscopy.

The KRS-5 prisms cover a wide spectral range and have a relatively low loss of transmission. They were used in this work and will be discussed briefly. The material is forty-two mole percent thallium bromide and fifty-eight mole percent thallium iodide. The crystal has a cubic lattice but has a tendency to cold flow rather than to fracture. It is insoluble in most organic solvents and cold water but it is slightly soluble in warm water (0.05 g./ 100 cc @ 25°C). The optical advantage of this material is the high refractive index and the wide transmission range.

TABLE I

PROPERTIES OF MULTIPLE INTERNAL REFLECTION CRYSTALS(28)

Crystal	Ref. Index (n_D)	Critical Angle (degree)	Reflection Loss (2 surfaces @ 10μ) (%)	Wave-length (μ)
Germanium	4.0	15	52.9	2-11.5
Silicon	3.5	17	46.1	2-6.5
KRS-5 (TlBr/TlI)	2.4	24	28.4	1-25
KRS-6 (TlBr/TlCl)	2.2	27	24.2	0.4-20
Silver Chloride	2.0	30	19.5	1-20

The disadvantages of KRS-5 that are most noted are its softness and the toxicity of the salts. The plates scratch very easily when rubbed even with acetone soaked cotton and cleansing tissues. This necessitates frequent polishing to maintain highly polished surfaces.

The refractive index of KRS-5 (2.4) and Ziegler type polyethylene (1.54) (17) gives a relative index of refraction of 1.59. This high ratio places the index of the crystal well above the "critical" index below which total internal reflection would cease. The "safe" index (25) has been defined as 0.2 below the "critical" index. Thus, the prism provides freedom from excessive band distortion.

Review of the Literature

There have been a number of theoretical studies made of surface reactions and phenomena by attenuated total reflectance and multiple reflection techniques. Harrick(7) mentions work that has been done with chemisorbed molecules on metal surfaces, oxide growth, gas surface adsorption and electric field effects on adsorption. Fused salts have also been studied(1). Sharpe(21) studied molecular interactions in oriented monolayers of ethyl and hydrogen octadecanoate in a germanium parallelopipe.

Some of the more practical applications of this technique include the evaluation of paint vehicles by extraction(15). The diluted extracts were dried on the F.M.I.R. plate for analysis. Harris and Svoboda(10) made quantitative determinations of alkyd resins using phthalic anhydride, isophthalic acid, vinyl toluene and styrene. Parker(18) used a water reference cell with solutions of glycyl-L-alanine at acid and base pH's using 45° and 50° angles of incidence. Deley, Gigi, and Liotti(2) used F.M.I.R. to determine the spectra of acrylic, polyvinyl chloride-polyvinyl acetate, silicone, polyethylene, polystyrene and paraffin coated papers as well as organic dye impregnated papers. Katlofsky and Keller(11) reported the spectra of various organic acids, amines, amides, phenols and inorganic salts in aqueous solution as well as polyvinyl acetate and acrylic resin emulsions. Goulden and Manning(5) studied concentrated aqueous solutions with F.M.I.R. and found the technique to be advantageous. Wilks and Iszard(29,30) demonstrated the spectra of various commercial materials, i.e. cellophanes, coated cellophanes, vinyl floor tile, coated metals, polyethylene and various natural and synthetic F.M.I.R. techniques.

The technique has been used for identifying many materials that previously had been elusive of analysis or had required tedious separation techniques. Although F.M.I.R. has been used to identify oxidation products of polyethylene, no study relating carbonyl intensity with power of corona treatment has been published.

I. R. Spectrum of Polyethylene

The theoretical aspects of infrared spectroscopy are generally available in college texts. Only a brief description of an atomic oscillator will be given to identify the source of the absorption bands in the polyethylene spectrum. The energy of a molecule consists of translational, rotational, vibrational, and electronic components. Infrared spectroscopy consists of the study and measurement of the vibrational and rotational energy of the molecule. The absorption of energy of vibration will be considered in the medium infrared spectrum of polyethylene.

The mechanical analogy of molecular vibrations can be visualized by considering a series of steel spheres suspended to the same level by strings(22). The spheres are connected to each other by helical springs each having the same or different frequencies of vibration. An oscillating eccentric source is physically connected to an end sphere by means of a wire or other material capable of transmitting sonic vibrations. As the speed of the device increases, it disturbs the model. When the disturbing frequency is the same as the vibrational frequency of the helical springs, it incites the normal mode of vibration in the spring and energy is absorbed. The mass of the sphere and length of the spring affect the spring frequency. The classical simple harmonic oscillation will be possible.

Similar but somewhat more complex phenomena occur with molecular structures in polymeric films. A theoretical model for diatomic, one dimensional chain has been presented by Zbinden(24). When radiant energy having the same frequency as a bond type contacts the oscillator, vibration is established at that frequency and the energy is absorbed. The energy absorbed is related to the area and peak height of the absorption bands of spectra.

The vibrational energy consists of bending and stretching. Components of bending consist of in-plane "scissoring" and "rocking." Out-of-plane bending consists of "twisting" and "wagging"(23). Less energy is required to produce bending so absorption from this motion occurs at lower frequencies. The two types of stretching are symmetric and asymmetric and absorption occurs at higher frequencies than bending.

Polyethylene is a polymethylene with terminal methyl groups. Because of the chain transfer phenomena during polymerization, a small amount of branching occurs. It has been reported that for most polyethylene only two types of branches are present--ethyl and butyl(24). The occurrence of degradation products, i.e. carbonyl and unsaturation, will be observed to some degree due to extrusion and environmental conditions or deliberate treatment. Commercial films would also have additives, i.e. plasticizers, stabilizers, anti-block and anti-static agents as well as slip agents. If these are not removed, the infrared absorption of these materials will be present in the spectra.

The major absorption bands of polyethylene have been identified in Table II. The band numbers correspond with those in Figure 1.

TABLE II

IDENTIFICATION OF POLYETHYLENE ABSORPTION BANDS(16, 19)

Band No.	Wavelength (Microns)	Oscillation(s)
1	3.42	Asymetric methylene stretch.
2	5.82	Carbonyl stretch.
3	6.10	Carbon-carbon double bond stretch.
4	6.80	Methylene deformation, methyl and methylene bend.
5	7.25	Symmetrical methyl CH bend; methylene wag.
6	7.65	Symmetrical methyl CH deformation.
7	9.25	Skeletal deformation.
8	10.35	Trans RCH=CHR.
9	11.28	RCH_3
10	13.72	Butyl, methylene rock.

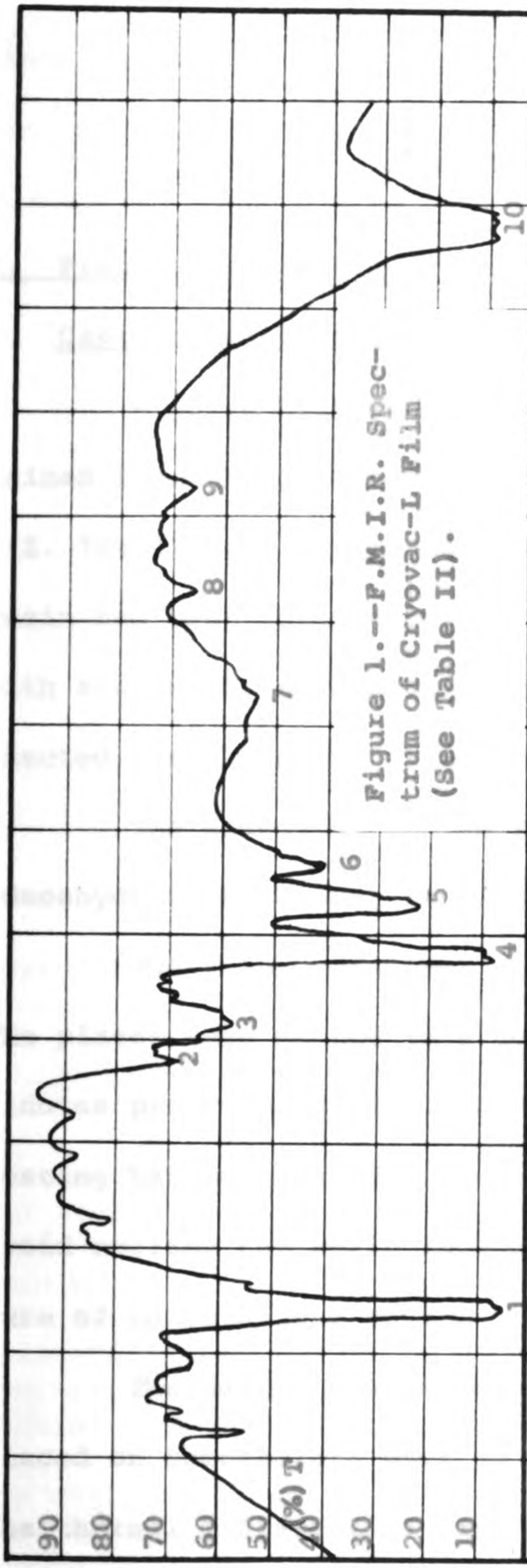


Figure 1.--F.M.I.R. Spectrum of Cryovac-L Film (See Table II).

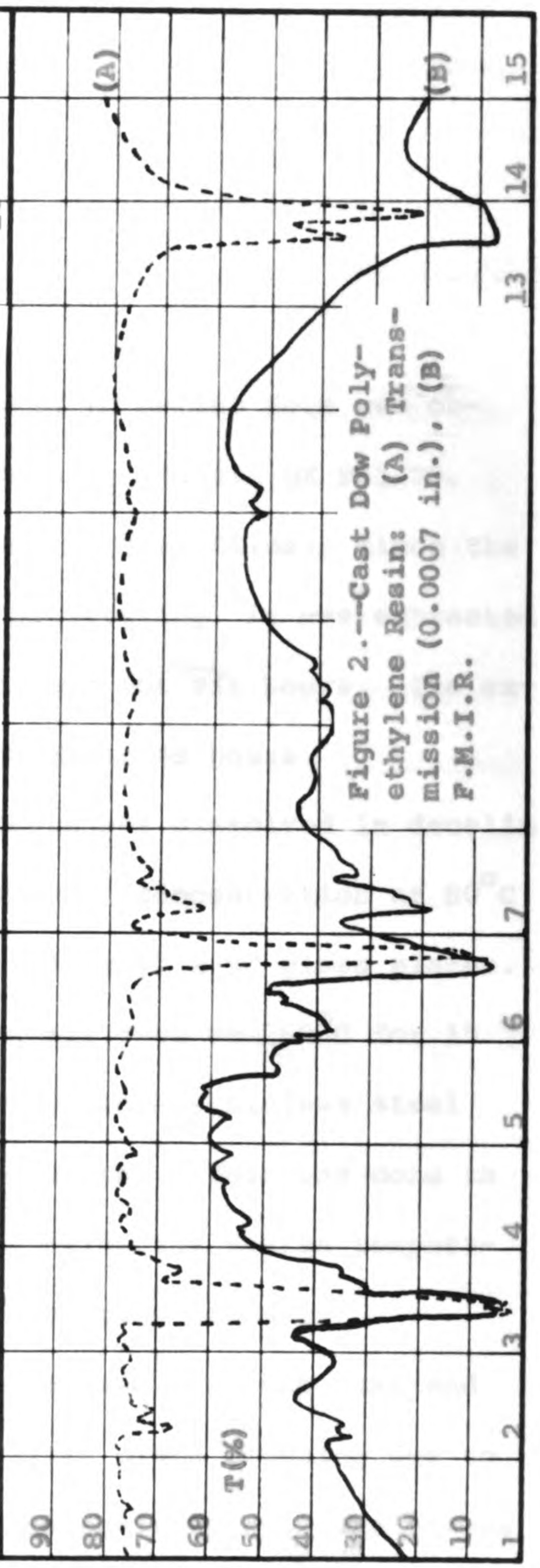


Figure 2.--Cast Dow Polyethylene Resin: (A) Transmission (0.0007 in.). (B) F.M.I.R.

EXPERIMENTAL

I. Preparation of Film

Cast Polyethylene

A polyethylene base resin in pellet form was obtained from the Dow Chemical Company (Code: QX 945.79, S.I. 784727) for the preparation of cast films. Since the resin had been formulated for pelletizing, it was extracted with acetone in a Soxhlet extractor for six hours. The extracted resin was air dried for about 48 hours.

The dried, extracted resin was dissolved in decalin (decahydronaphthalene) in a 10%(w/v) concentration at 80°C.

The films were cast on 13" x 6" x ¼" glass plates. The plates were heated in a hot air oven at 160°C for 15 minutes prior to casting. A 0.006 inch stainless steel casting bar was heated with the plates. This was done to avoid cooling the resin lacquer below the fusion temperature of polyethylene during the casting process.

The heated plates were removed from the oven and placed on cheesecloth mats to avoid plate cracking due to the thermal differential with the environment. The plates were transferred to a fume hood for casting. The casting bar was placed at one end of the casting plate parallel to the width. The lacquer was poured onto the plate so as to fill the bar reservoir. The bar was then drawn the length of the plate to form the film.

The cast lacquer was allowed to set until the top surface had hardened. Fusion was accomplished by placing the plate in the hot-air oven for twenty minutes at 160 degrees.

The fused films were air-cooled to room temperature. They were removed from the plates by submerging in acetone for about 3 to 5 minutes and lifting them from the plates. Films were air-dried overnight (ca. 16 hours) to remove residual acetone.

Extruded Polyethylene

The preliminary work was done with 0.0013, 0.0016 and 0.0030 inch Union Carbide polyethylene film. The major work with extruded film was done with Cryovac L film (Type D925, 75 gauge). A 40" x 8" strip of film was cut in the machine direction from an 18 inch roll. It was extracted for eight hours with acetone in the Soxhlet extractor to remove additives. It was then air-dried overnight (ca. 16 hours) before being sampled for F.M.I.R. analysis.

II. Sample Preparation

Sample Cutting

A 40" x 6" x ¼" glass plate was etched with a diamond point Electric Marker (Cat. No. 11-100) by Ideal Industries, Inc., to form a 37" x 3" overall pattern (Figure 3). The overall dimensions were subdivided into four quadrants, each having six sample cells of 5-4/5" x 39/50". These cells were subdivided into three sections each of which fit a side of the one-millimeter matched KRS-5 plates (2" x 39/50"; 97/50" x 39/50" and 92/50" x 39/50").

The cast films were placed over quadrants I and II because of their shorter length. The extruded film covered the entire plate. The films were fastened firmly to the plate with pressure-sensitive tape.

The cast film samples were cut in a consecutive order from quadrant I-A-1 to II-D-1; from quadrant I-A-2 to II-D-2, etc. The extruded film samples were cut in a random order as listed in Table XII.

Sample Loading

The cast film samples were loaded onto a one-millimeter matched pair of KRS-5 F.M.I.R. plates. The three sections of the sample were cut from a sample

Figure 3.--F.M.I.R. Sample Cutting Plate.

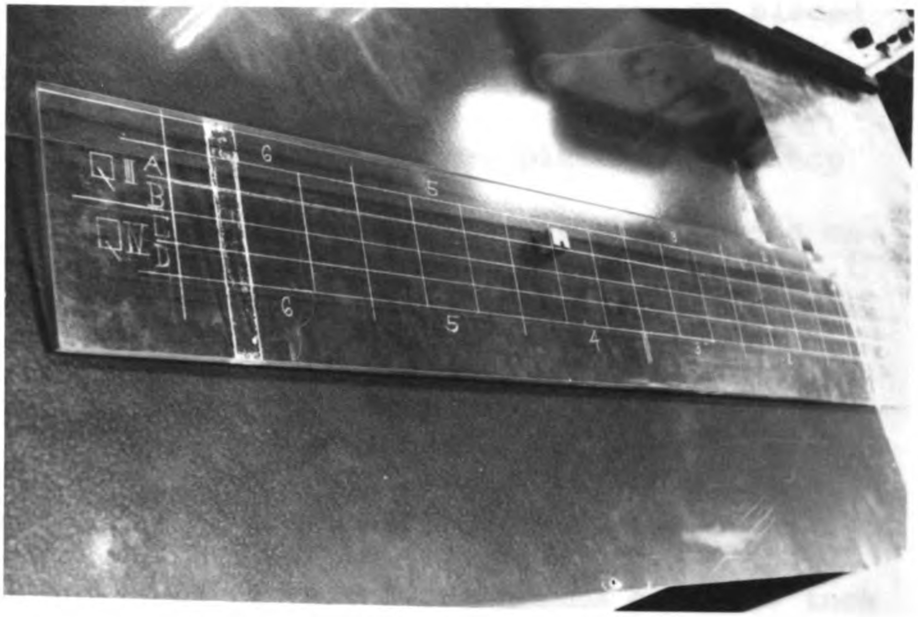
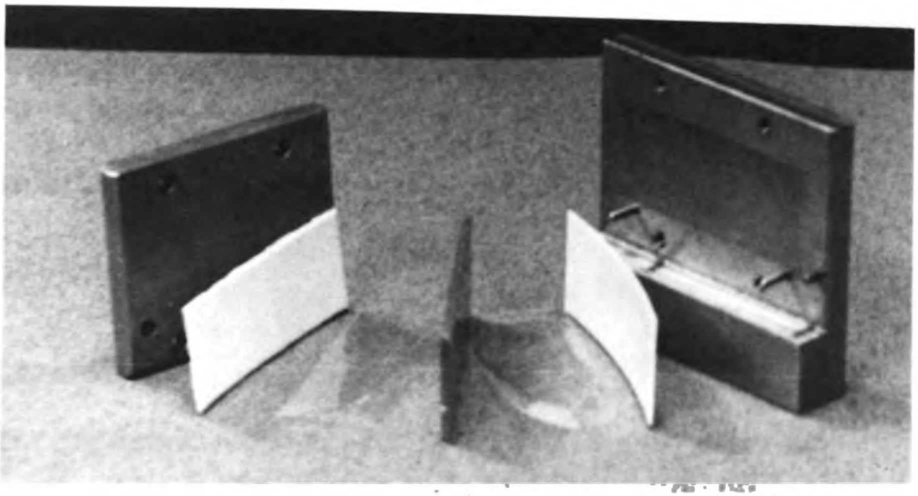


Figure 4.--F.M.I.R. Solid Sample Holder and Loading Sequence.



section of the cutting plate with a straight edged rule and a razor blade. The smallest section was placed on the top of the small plate and the largest section was placed on the bottom of the large plate of the matched pair. The middle sized section of the sample was placed on the top of the large plate. The smaller plate was then placed on top of the larger plate. The side of the cast films that were next to the casting plate were placed against the KRS-5 plates.

Surface contact of the sample section with the plates was accomplished by use of two pieces of 0.015 inch extruded polystyrene foam. One piece was placed between each section of the plate holder and the outside sample sections of the loaded matched plates (See Figure 4).

The extruded film samples were loaded onto a two millimeter KRS-5 plate in the same manner as for the cast films. The sample holder was tightened by means of Allen-head screws.

Sample Bromination

The interference observed in the 6.0-6.4 micron range suggests various types of unsaturation. In an effort to reduce this, bromination was attempted. The extruded film samples were brominated in a 5% bromine-in-carbon-tetrachloride solution for six hours according to the method of Lomonte(14). The samples were soaked in carbon tetrachloride for two to four hours to remove remaining bromine. They were air dried at least 16 hours before running them. The sample used for a study of bromination with time was treated according to the same method. The cast polyethylene films were not brominated because of the lower interference and because of changes observed by treatment of the controls.

Corona Treatment

A Lepel High Frequency Spark Generator, Model HF SG-2 was the power source used for corona treatment of the samples (Figure 5). The unit has a spark gap energized primary circuit with a tuned secondary output circuit. The frequency of the output voltage is about 450 kilocycles(32).

The treatment was applied on a 12 inch diameter variable speed rotating drum. The drum surface was covered with ten layers of 0.001 inch Mylar film to provide uniform charge distribution. The discharge was distributed to the sample by means of two six-inch aluminum bars mounted in parallel across the drum. The power range and vernier of

Lepel High Frequency Power Source and Corona Treating Drum

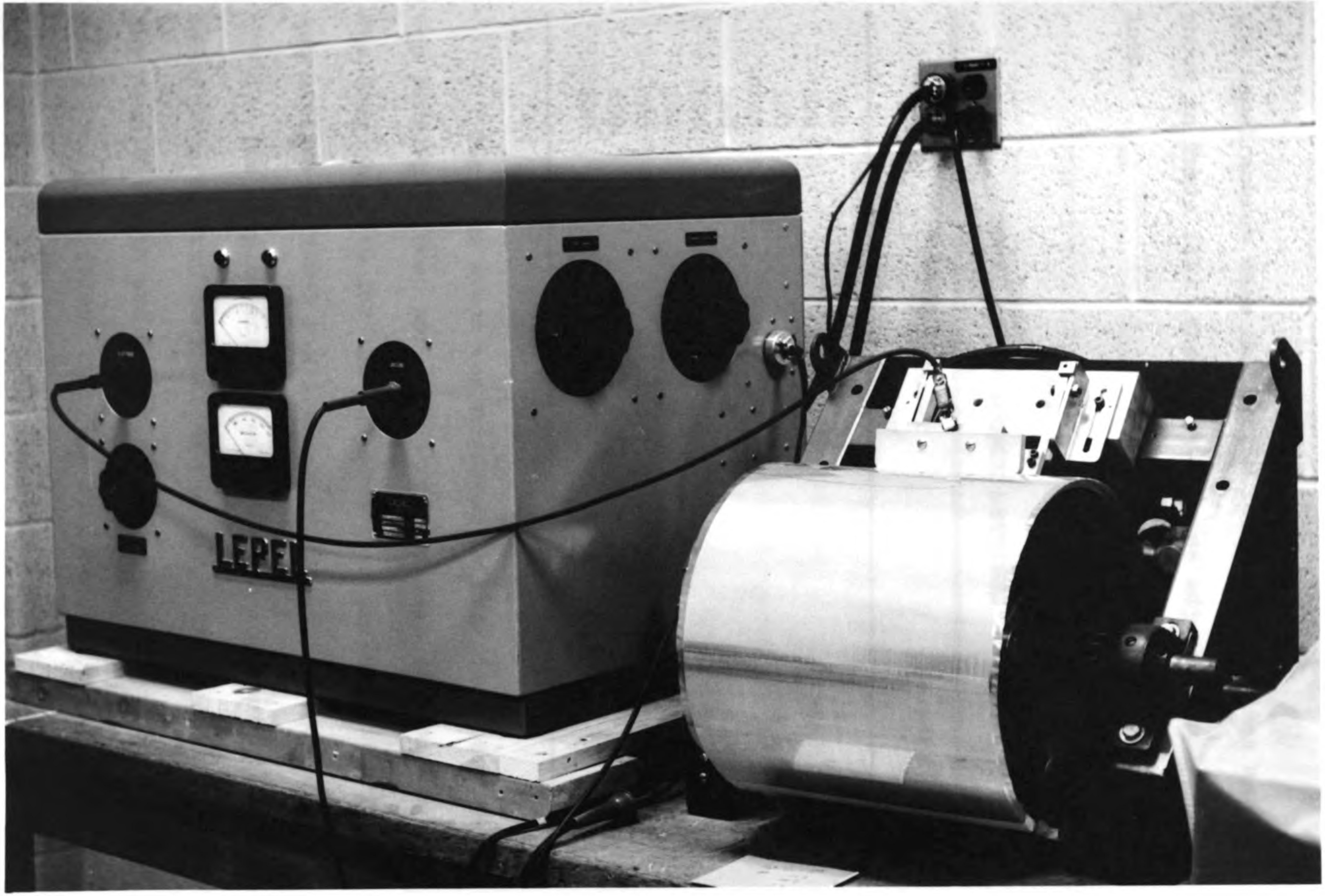


Figure 5.

the Lepel source were calibrated for power settings as shown in Table III. The spark gap was adjusted to 1/16 inch.

TABLE III

LEPEL POWER SOURCE SETTINGS

Watts	Power Range	Vernier
60	2	4
100	3	9
150	4	1
200	4	7
260	5	4
310	5	8
350	6	2
400	6	4
450	6	6
520	6	8

The drum speed was adjusted to provide a peripheral web rate at 86 feet per minute for the cast film series. The drum web rate for the extruded film series using the two millimeter KRS-5 F.M.I.R. plate was 66 feet per minute.

The sample sections were aligned together on the Mylar covered drum in front of the first treatment bar. The sample length was directed along the drum circumference. For cast films, the film surface next to the casting plate was exposed to corona discharge. Both sides of the sample that was between the two matched plates were exposed to treatment.

The drum was started and the sample surfaces exposed to one revolution of corona discharge. The discharge was triggered by means of a button trigger. The exposed pieces were removed with tweezers and loaded onto the prisms.

III. Spectra Recording

The spectra of the samples run in this work were obtained with a Beckman IR-4 infrared spectrophotometer equipped with Tracking Accuracy Control and Variable Scale Expansion accessories. The spectrophotometer was also equipped with a dry-air purge system. The functional unit of the purge system was a Gilbarco Model HF220, 115v, 60 cycle Heatless Fractionater manufactured by Applied Penumatic Division of Gilbert and Barker Manufacturing Company.

The F.M.I.R. system consisted of a model 9, Single Beam MIR attachment manufactured by the Wilks Scientific Corporation. A Wilks MIR-11 Beam Attenuator was used in the reference beam of the double beam spectophotometer.

The spectra for the work were run at the following instrument settings:

Speed: 0.2
Scale: 2 inches per micron
Gain: 1.80
Period: 2
Slit: 0.37 mm. @ 9.0 microns

Most working spectra were run between 5.0 and 9.0 microns. Attenuation of the reference beam was set at 94% transmission at 8.4 microns for the cast film and at 5.4 microns for the extruded film. The slit width was programmed independent of scanning speed.

Tracking Accuracy Control Speed Suppression was used for all samples to provide better resolution. It was set at the same wavelengths as was the attenuation.

The samples were run by placing the loaded sample holder in the MIR-9 attachment, adjusting the slit width and reference beam attenuator to the preselected values and starting the scanning device.

The effect of treatment on surface transmission was done by setting attenuation at 94% transmission for an acetone extracted control sample. After running the spectrum, the sample was brominated and re-run without adjusting the attenuation. This procedure was repeated for the sample after corona treatment. Data for each treatment were recorded.

IV. Spectra Reading and Data

The baseline technique was used for reading all spectra bands. The difference in height between the center of the baseline across the shoulders of the analytical absorption band and the bottom of the band is proportional to the amount of absorbing oscillator present in the sample. The shoulders at 6.5 and 5.5 microns were used for drawing the baseline for the carbonyl band at 5.8 microns and the olefinic unsaturation band at 6.1 microns. The shoulders at 6.5 and 8.1 microns were used for drawing the baseline for the methyl deformation band at 7.6 microns.

The methyl CH symetrical bending absorption recorded at 7.25 microns was measured on the extruded Cryovac film spectra to compare results with those obtained with the deformation band that was used as reference. The shoulders at 7.1 , and 7.5 microns were used to draw the baseline for this band.

An integration technique was also used with the cast film to compare the two methods. This procedure consisted of transferring the outline of the absorption bands to a one millimeter square grilled paper. The squares within the band outline and the drawn baseline were counted.

To avoid discrepancies resulting from film-to-prism contact variances that occur between samples, a ratio between the analytical bands and the methyl reference bands was used. The band heights were all measured as 50ths of an inch. The ratios of the analytical bands to reference bands were plotted as ordinates against energy of treatment calculated as watt-hours per one-thousand square feet (See Appendix).

DATA

Reproducibility of Reference Band

The reproducibility of an absorption band to use as reference for the carbonyl and olefinic unsaturation bands was observed. Three uncoded Union Carbide films of 0.0013, 0.0016, and 0.0030 inch thicknesses were used. Sixteen samples of the first film and eight samples of the latter two films were run with the one-millimeter matched KRS-5 plates. The methyl deformation band at 7.6 microns was measured by the baseline method. A mean of 100 (as 50ths of an inch) with a standard deviation of ±5 was obtained for the peak height of the three films. This data is tabulated in Table IV.

TABLE IV

REPRODUCIBILITY OF METHYL DEFORMATION BAND AT 7.6 MICRONS WITH ONE MILLIMETER MATCHED KRS-5 PLATES*

Film Thickness (inch)	No. of Runs	Peak Height Averages (50ths of Inch)			
		Band (microns)	5.8	6.1	7.6
0.0013	16		112	140	100
0.0016	8		72	92	102
0.0030	8		107	126	100

*For band at 7.6 microns: $\overline{X}=100, \sigma=\pm 5$ for the 32 measurements.

Effect of Treatment on Surface Transmission

The effect of treatment on surface transmission was checked to determine whether absorption bands would be affected by bromination and corona discharge. The data obtained for the effect on the carbonyl and olefin unsaturation ratio to the methyl deformation band at 7.6 microns is recorded in Table V. It is plotted in Figure 7 with ratios of carbonyl and unsaturation as ordinate and sample treatment spaced as abscissa. The hyphenated lines in Figure 7 represent the ratios resulting from re-adjustment of the reference beam to the 93% transmission set for the control sample.

TABLE V

EFFECT OF CORONA TREATMENT ON SURFACE TRANSMISSION*
(MATCHED KRS-5 PLATES)

Sample	Band Height (50th of inch)			Band Ratios	
Band(microns)	5.8	6.1	7.6	5.8/7.6	6.1/7.6
1. Control	87	80	63	0.915	1.10
2. Brominated	86	78	63	0.930	1.04
3. Brominated plus 130 Watt-Hours	73	67	54	1.08	1.11
4. Brominated and treated; atten. readjusted to 93%T	120	109	94	1.28	1.16

*Initial attenuation set at 93% transmission.

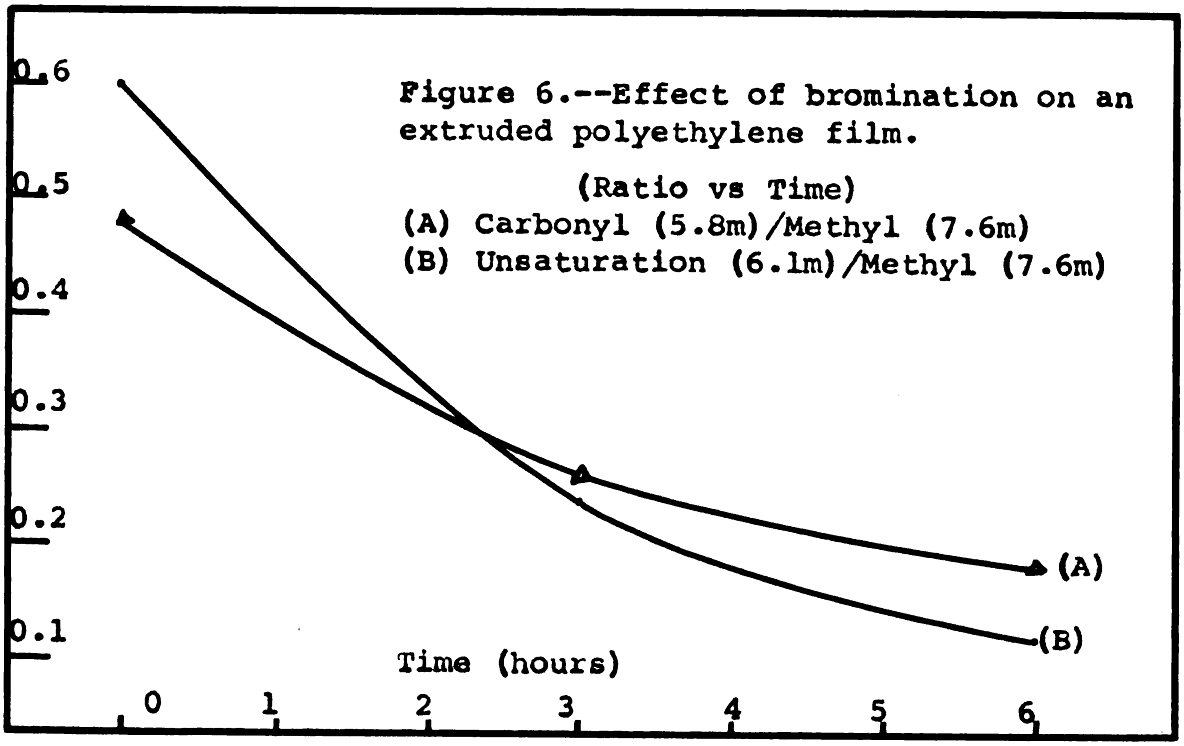


Figure 6.--Effect of bromination on an extruded polyethylene film.

(Ratio vs Time)

(A) Carbonyl (5.8m)/Methyl (7.6m)

(B) Unsaturation (6.1m)/Methyl (7.6m)

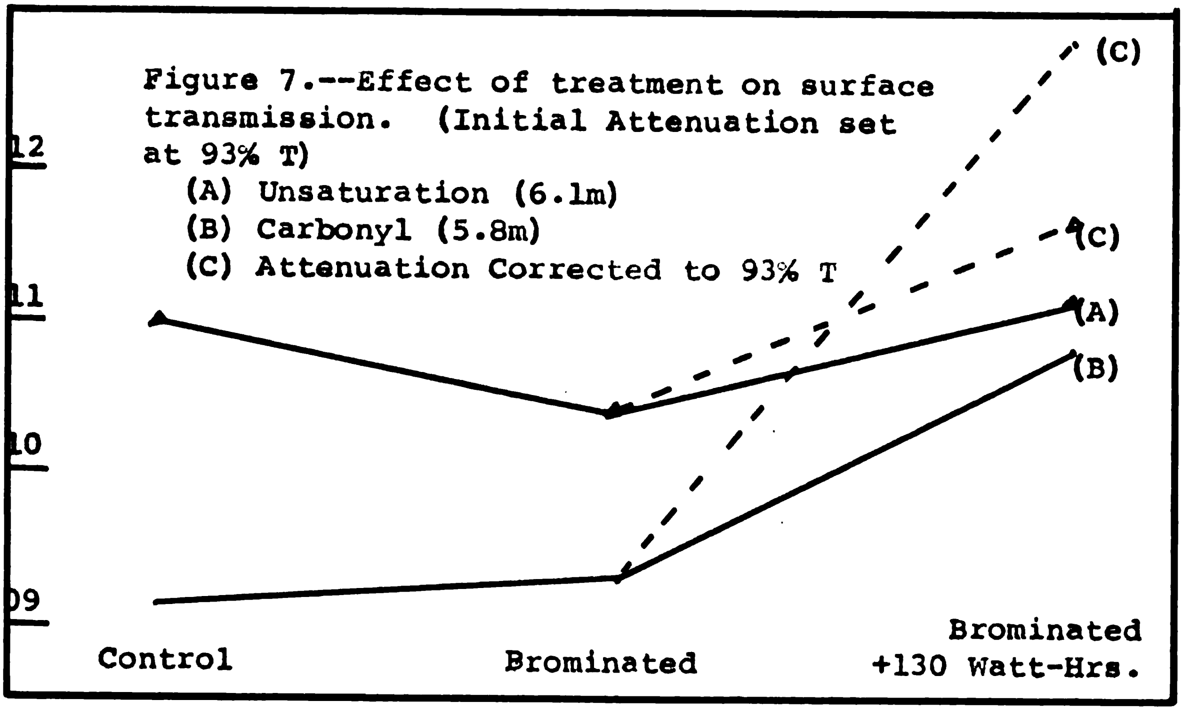


Figure 7.--Effect of treatment on surface transmission. (Initial Attenuation set at 93% T)

(A) Unsaturation (6.1m)

(B) Carbonyl (5.8m)

(C) Attenuation Corrected to 93% T

Bromination Rate

The rate of bromination of a 0.0030 inch Union Carbide film was studied to determine if there was a reasonable time in which interference in the 6.0-6.4 micron region could be eliminated. The original sample was run before acetone extraction to show the effect of the extraction. The extracted sample served as the control. Two consecutive three hour brominations were run to give the three and six-hour samples. The ratios obtained by the baseline method for carbonyl and olefinic unsaturation changes are recorded in Table VI and plotted in Figure 6.

TABLE VI

EFFECT OF BROMINATION OF AN EXTRUDED POLYETHYLENE FILM WITH TIME*
(MATCHED KRS-5 PLATES)

Sample Treatment	Band Ratio (microns)	
	5.8/7.6	6.1/7.6
Original	1.42	1.75
Acetone	0.482	0.600
Brominated 3 hours	0.260	0.233
Brominated 6 hours	0.182	0.114

*Union Carbide (0.0030).

Cast Polyethylene Film

The initial work with cast polyethylene film was with the use of the matched one-millimeter KRS-5 plates.

Seven levels of power were used for this series. The peak heights and ratios obtained for the sample controls and the treated samples are tabulated in Tables VII and VIII respectively. The measurements were obtained by the baseline method. The band ratios are plotted as ordinate against watt-hours per 1000 square feet as abscissa in Figure 8.

TABLE VII

CAST POLYETHYLENE FILM—CONTROLS
(BASELINE METHOD; ONE MILLIMETER MATCHED KRS-5 PLATES)

Treatment Control		Peak Height (50ths of inch)			Band Ratio	
Watts	Watt-hours	Band5.8	6.1	7.6	5.8/7.6	6.1/7.6
60	23	19	44	88	0.215	0.500
100	39	22	42	86	0.256	0.488
150	58	25	38	62	0.403	0.613
200	78	26	49	59	0.441	0.830
260	100	22	40	41	0.537	0.975
310	120	19	60	63	0.302	0.952
350	136	20	59	63	0.317	1.000
			Average		0.353	0.765

TABLE VIII

CORONA TREATED CAST POLYETHYLENE FILM
(BASELINE METHOD; ONE MILLIMETER MATCHED KRS-5 PLATES)

Treatment		Peak Height (50ths of inch)			Band Ratio	
Watts	Watt-hours	Band 5.8	6.1	7.6	5.8/7.6	6.1/7.6
60	23	27	50	95	0.284	0.526
100	39	34	45	75	0.453	0.600
150	58	35	40	61	0.547	0.656
200	78	38	60	56	0.679	1.07
260	100	40	62	63	0.653	0.984
310	120	40	64	64	0.625	1.00
350	136	40	64	55	0.727	1.16

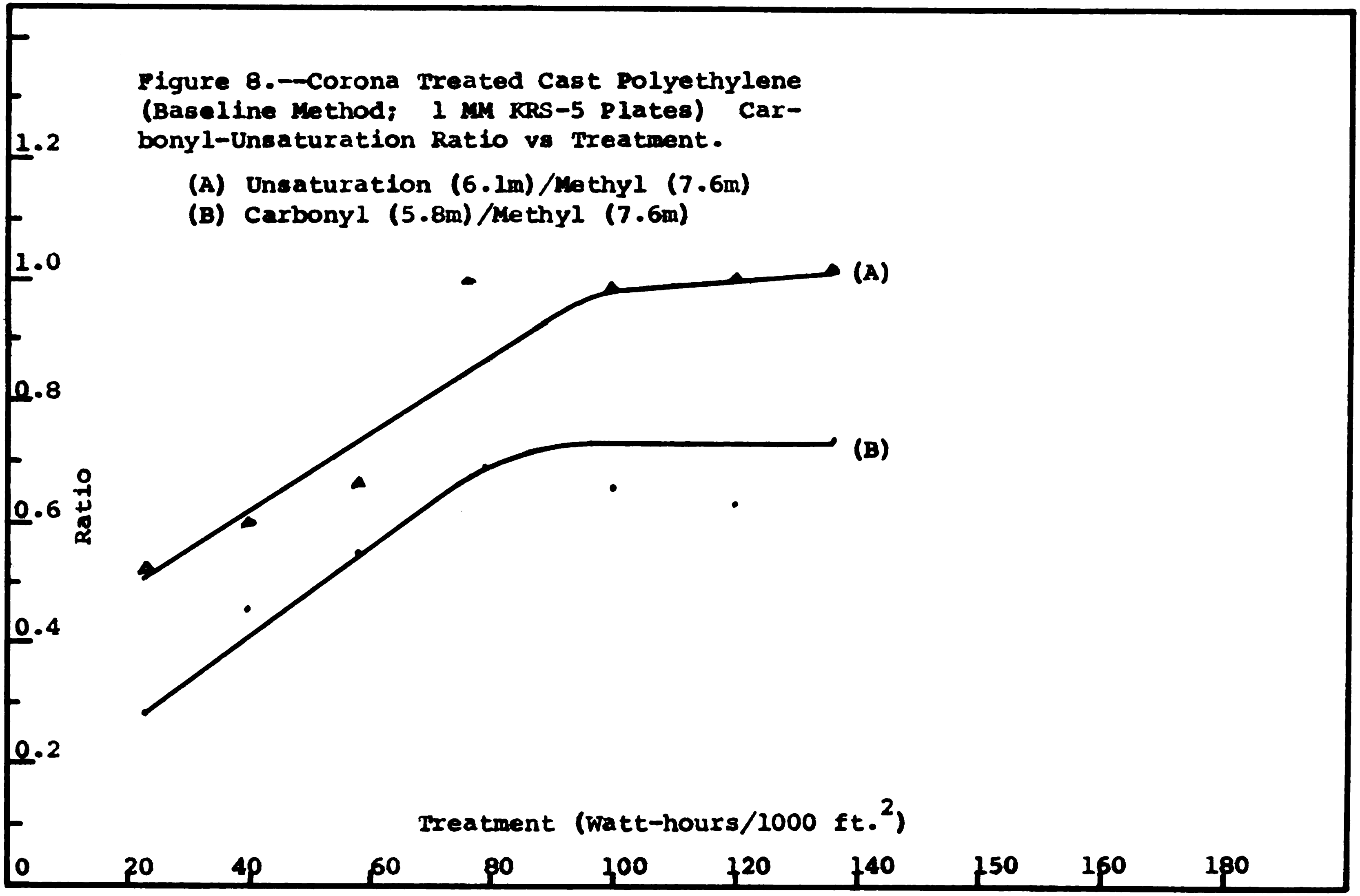


Figure 8.—Corona Treated Cast Polyethylene (Baseline Method; 1 MM KRS-5 Plates) Carbonyl-Unsaturation Ratio vs Treatment.

(A) Unsaturation (6.1m)/Methyl (7.6m)
(B) Carbonyl (5.8m)/Methyl (7.6m)

The same peaks were measured by integration for the purpose of comparing the two methods of measurement. These data are tabulated in Tables IX and X.

TABLE IX

CAST POLYETHYLENE FILM-CONTROLS
(INTEGRATION METHOD; ONE MILLIMETER MATCHED KRS-5 PLATES)

Treatment Control		Peak Height (Square Millimeter)			Band Ratio	
Watts	Watt-hours	Band 5.8	6.1	7.6	5.8/7.6	6.1/7.6
60	23	97	266	903	0.107	0.294
100	39	77	358	900	0.085	0.397
150	58	143	345	555	0.257	0.621
200	78	108	456	602	0.179	0.757
260	100	104	404	390	0.266	1.04
310	120	77	559	690	0.111	0.810
350	136	90	560	605	0.148	0.925

TABLE X

CORONA TREATED CAST POLYETHYLENE FILM
(INTEGRATION METHOD; ONE MILLIMETER MATCHED KRS-5 PLATES)

Treatment		Peak Area (Square millimeter)			Band Ratio	
Watts	Watt-hours	Band 5.8	6.1	7.6	5.8/7.6	6.1/7.6
60	23	122	386	1100	0.110	0.350
100	39	168	402	744	0.225	0.536
150	58	182	339	555	0.327	0.610
200	78	156	503	494	0.315	1.02
260	100	204	611	555	0.367	1.10
310	120	206	604	618	0.333	0.977
350	136	260	640	559	0.465	1.14

A second series was run with cast polyethylene using the two millimeter KRS-5 plate. The band ratios obtained are listed in Table XI. Figure 9 contains plots of the band ratios of carbonyl and olefinic unsaturation as ordinate against watt-hours of corona exposure per 1000 square feet as abscissa.

TABLE XI

CORONA TREATED CAST POLYETHYLENE FILM
(BASELINE METHOD; TWO MILLIMETER KRS-5 PLATES)

Treatment Watts	Watt-hours	Band Ratio 5.8/7.6	Band Ratio 6.1/7.6
150	57	0.500	0.676
260	100	0.773	0.845
350	136	0.885	0.959
450	175	1.06	1.15

Extruded Polyethylene Film

The study of the formation of carbonyl and olefinic unsaturation with change in treatment of an extruded polyethylene was done with a Cryovac-L film. Sixteen controls were run using the two millimeter KRS-5 F.M.I.R. plates. Four power levels and four samples at each level were run. The latter sets of four came from the controls.

The sequence of the sample locations in which the controls were taken from the sample cutting plate are

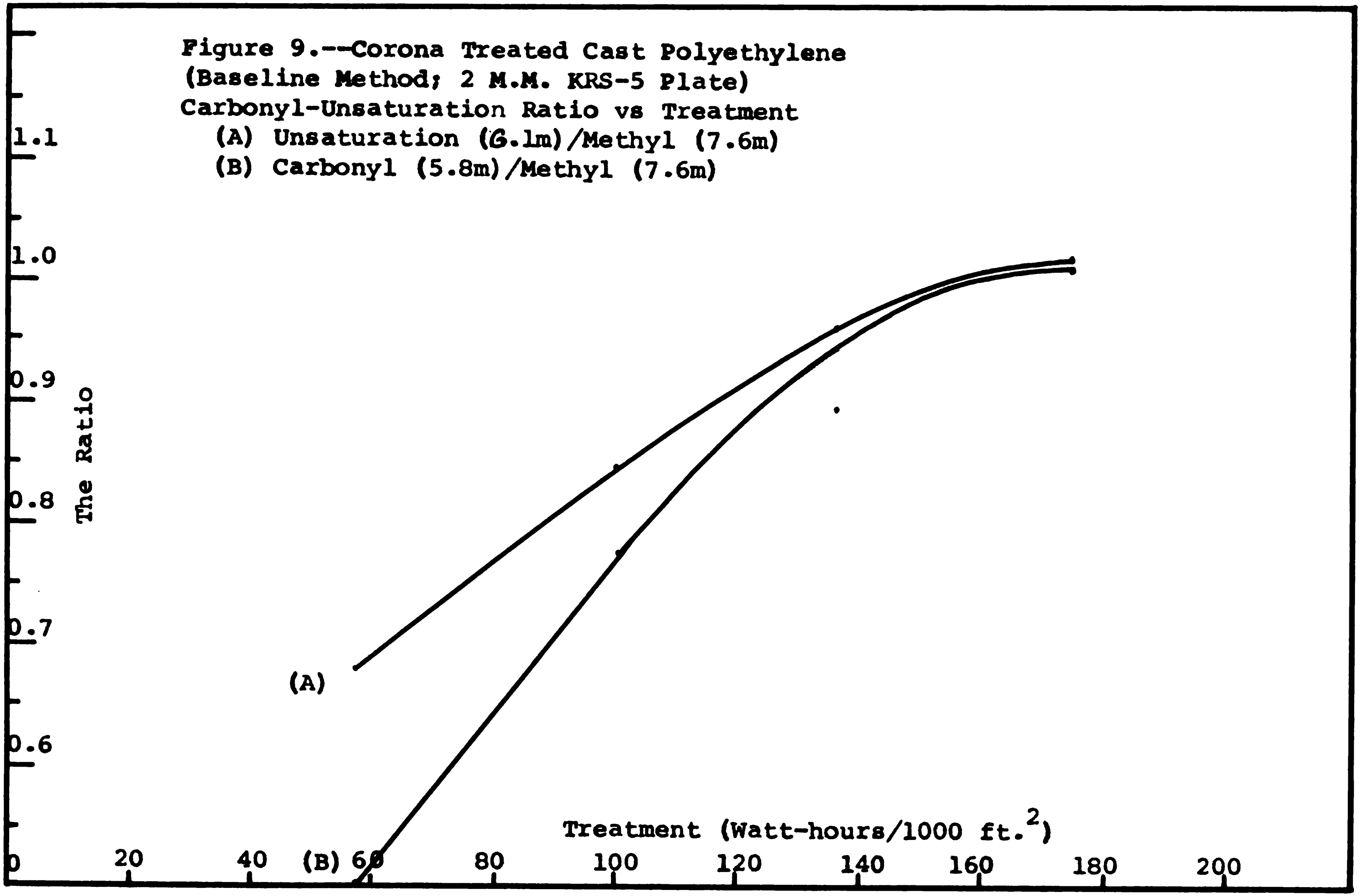


Figure 9.—Corona Treated Cast Polyethylene
(Baseline Method; 2 M.M. KRS-5 Plate)
Carbonyl-Unsaturation Ratio vs Treatment
(A) Unsaturation (6.1m)/Methyl (7.6m)
(B) Carbonyl (5.8m)/Methyl (7.6m)

tabulated in Table XII. The peak heights and band ratios obtained are also listed.

TABLE XII

EXTRUDED POLYETHYLENE FILM-CONTROLS
(BASELINE METHOD; TWO MILLIMETER KRS-5 PLATE)

Sample	Treatment		Peak Height (50ths of in.)			Band Ratio	
	Watts	Watt Hours	5.8	6.1	7.6	5.8/7.6	6.1/7.6
QI-A-2	100	50	105	90	99	1.06	0.909
QII-C-3	100	50	99	86	98	1.01	0.878
QIII-B-4	100	50	103	91	95	1.08	0.957
QIV-D-5	100	50	108	85	88	1.23	0.965
QI-A-3	200	101	111	79	97	1.14	0.814
QII-C-2	200	101	106	79	96	1.10	0.823
QIV-D-6	200	101	98	71	109	0.899	0.651
QII-C-1	200	101	103	95	90	1.14	1.06
QII-D-4	300	152	113	88	96	1.18	0.917
QIII-B-5	300	152	98	83	92	1.07	0.902
QIII-B-6	300	152	102	80	92	1.11	0.870
QI-B-2	300	152	101	75	94	1.07	0.798
QII-D-3	400	202	120	145	89	1.35	1.63
QIV-C-4	400	202	76	96	99	0.792	0.970
QIII-A-5	400	202	75	75	106	0.708	0.708
QIV-C-6	400	202	107	79	100	1.07	0.790

The four samples used for each treatment level and the corresponding data obtained from them are tabulated in Table XIII. Each group of four samples with a single treatment level corresponds with the controls (Table XII). The averages of each group of four controls that were used for treatment are listed in Table XIV. The averages for the same sets after treatment are listed in Table XV. The ratios of carbonyl and olefinic unsaturation obtained by use of the symmetrical methyl CH bend at 7.25 microns as the reference band are also tabulated in Table XV.

TABLE XIII

EXTRUDED POLYETHYLENE FILM-CORONA TREATED
(BASELINE METHOD; TWO MILLIMETER KRS-5 PLATE)

Sample	Treatment		Peak Height (50ths of in.)			Band Ratio	
	Watts	Watt Hours	5.8	6.1	7.6	5.8/7.6	6.1/7.6
Q1-A-2	100	50	84	78	104	0.808	0.750
QII-C-3	100	50	95	85	104	0.913	0.817
QIII-B-4	100	50	117	86	94	1.24	0.914
QIV-D-5	100	50	124	97	93	1.33	1.04
QI-A-3	200	101	145	95	100	1.45	0.950
QII-C-2	200	101	127	109	100	1.27	1.09
QIV-D-6	200	101	108	104	105	1.03	0.990
QII-C-1	200	101	139	125	103	1.35	1.21
QII-D-4	300	152	149	100	100	1.49	1.00
QIII-B-5	300	152	121	102	103	1.17	0.990
QIII-B-6	300	152	147	116	98	1.50	1.18
QI-B-2	300	152	154	120	101	1.52	1.19
QII-D-3	400	202	153	126	95	1.61	1.33
QIV-C-4	400	202	124	100	102	1.22	0.980
QIII-A-5	400	202	123	111	105	1.17	1.06
QIV-C-6	400	202	161	131	101	1.59	1.30

TABLE XIV

AVERAGES OF CORONA TREATED EXTRUDED POLYETHYLENE FILM CONTROLS (BASELINE METHOD; RATIOS OF 5.8 AND 6.1 MICRONS TO 7.25 AND 7.6 MICRONS)

Control for		Band Ratios			
Watts	Watt-hours	5.8/7.25	6.1/7.25	5.8/7.6	6.1/7.6
100	50	0.708	0.600	1.10	0.928
200	101	0.696	0.551	1.14	0.902
300	152	0.640	0.503	1.05	1.08
400	202	0.618	0.653	0.980	1.02
	Averages	0.666	0.577	1.07	0.982

TABLE XV

AVERAGES OF CORONA TREATED EXTRUDED POLYETHYLENE FILM (BASELINE METHOD; RATIOS OF 5.8 AND 6.1 MICRONS TO 7.25 AND 7.6 MICRONS)

Treatment		Band Ratios			
Watts	Watt-hours	5.8/7.25	6.1/7.25	5.8/7.6	6.1/7.6
100	50	0.674	0.552	1.07	0.880
200	101	0.901	0.749	1.28	1.06
300	152	1.01	0.77	1.42	1.09
400	202	0.978	0.815	1.40	1.17

The comparison between the form of the curves obtained with the two reference bands are seen in Figures 10 and 11. Figure 10 shows the difference between the 5.8 micron carbonyl band while Figure 11 contains plots of the olefinic unsaturation band at 6.1 microns.

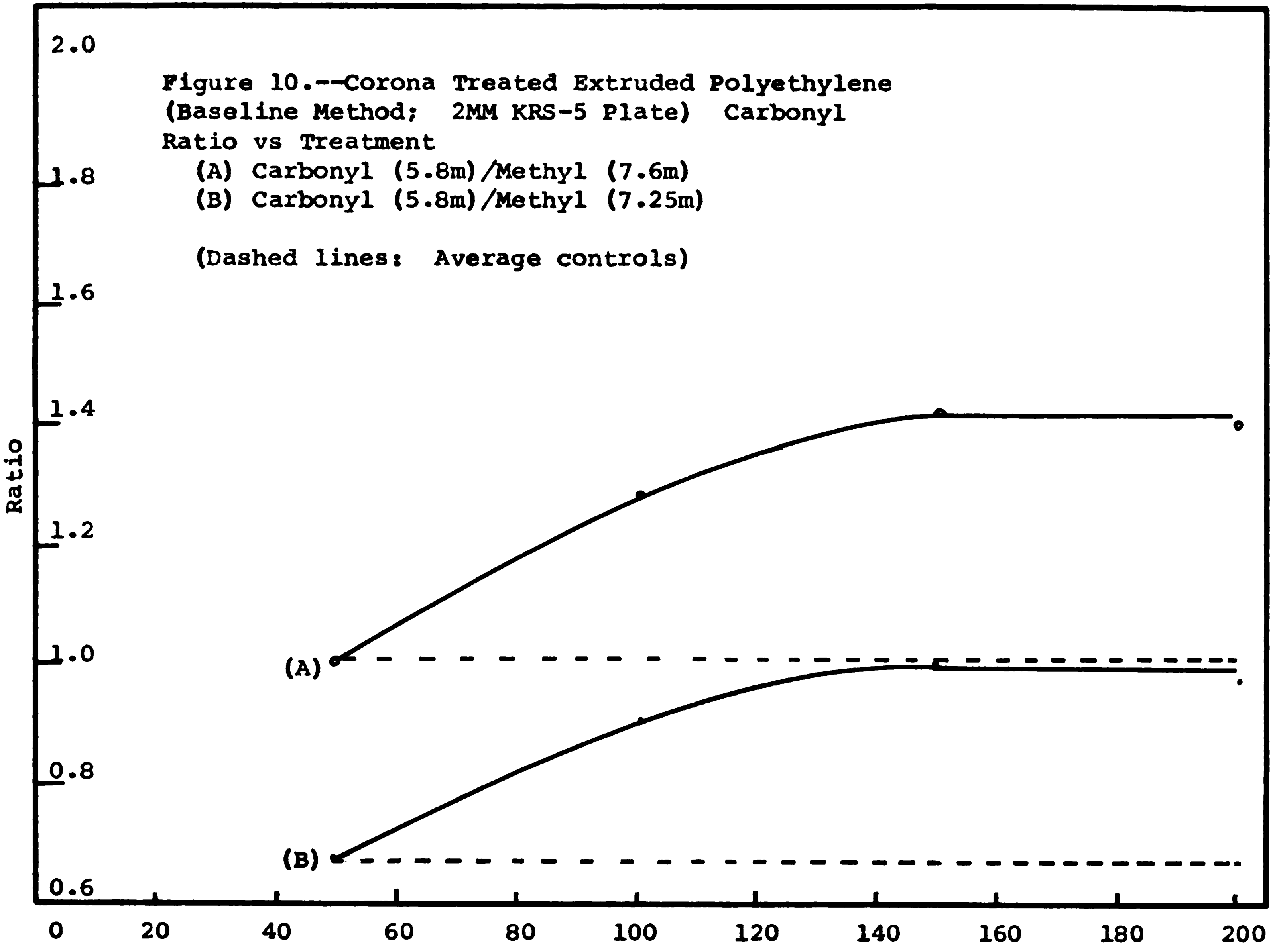


Figure 10.--Corona Treated Extruded Polyethylene (Baseline Method; 2MM KRS-5 Plate) Carbonyl Ratio vs Treatment
(A) Carbonyl (5.8m)/Methyl (7.6m)
(B) Carbonyl (5.8m)/Methyl (7.25m)

(Dashed lines: Average controls)

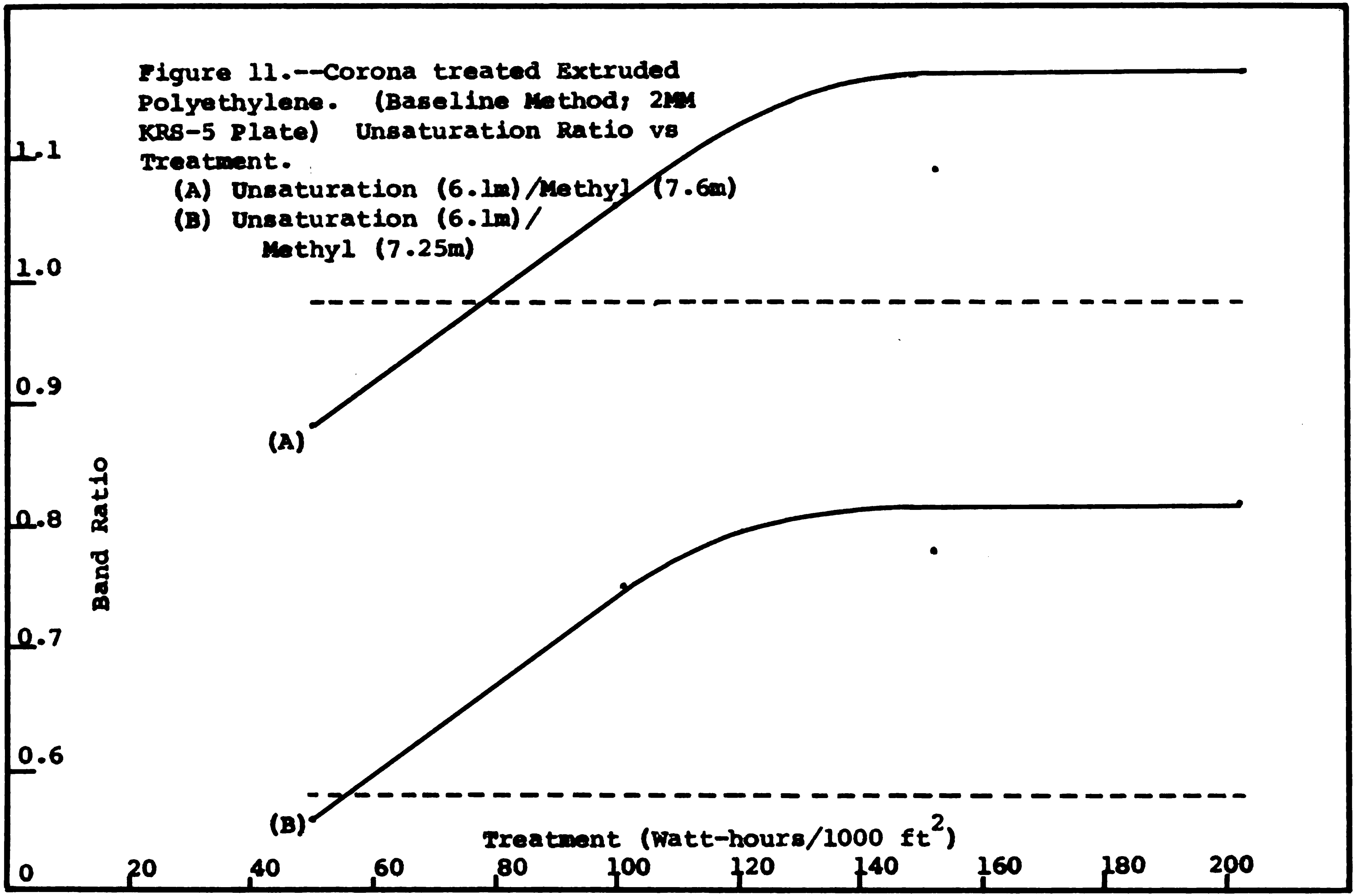


Figure 11.--Corona treated Extruded Polyethylene. (Baseline Method; 2MM KRS-5 Plate) Unsaturation Ratio vs Treatment.

(A) Unsaturation (6.1m)/Methyl (7.6m)

(B) Unsaturation (6.1m)/ Methyl (7.25m)

DISCUSSION

Sample Preparation

The presence of oxidation products in polymeric films can begin with the polymerization process. This is particularly noticeable when peroxide initiators are used. In cases where there is residual initiator in the resin and it is of a free radical nature, the extrusion temperature is often of sufficient magnitude to cause their rapid decomposition. The result is that oxidation artifacts are present within the polymeric film as it comes from the extruder die.

A second source of oxidation products is the reaction of atmospheric oxygen with the hot polymer tube surface as it leaves the die. This is probably the source of some of the carbonyl found on the surfaces of the controls.

It is well known that ultraviolet light causes free radical formation of unsaturation and other oxidation products in films. This is the reason for the incorporation of "U. V. absorbers" in plastics. Even with these materials within the bulk of the film, it is possible that surface oxidation does occur by the light environment of the film. It is another source of oxidation products on film surfaces.

The technique used in preparing the cast polyethylene films afforded little protection from oxidation by environmental exposure. Any residue in the film capable of liberating free-radicals at fusion temperature were allowed to do so. The surfaces of the films next to the casting plates were placed next to the F.M.I.R. plates to reduce the amount of oxidation in the controls. A dry box filled with an inert atmosphere would reduce oxidation during the casting process. The use of an oven with a similar atmosphere would reduce oxidation during the fusion of the films.

The presence of crystalline areas in polyethylene could be a source of variation between film samples and different lots. It was noticed during the early part of the work that differences in the shapes of absorption bands occurred between samples cut in the machine direction and transverse direction.

To reduce variations thought to be due to crystallinity, two things were done. With the cast films, the differences of cooling rates between the top film surface and the surface next to the plate would cause differences in crystal size. Differences in reflection and in the measured effect of treatment could result. The surfaces next to the casting plates were placed next to the KRS-5 plate to provide continuity of surface throughout the work.

The extruded films were blown. Differences in crystal and amorphous molecular orientation between the machine and transverse directions would cause variations in results. Continuity in technique was obtained by using samples cut in the machine direction.

The contribution in additives containing carbonyl functional groups is noticed in the data of Table VI. A large reduction in the ratio of the 5.8 micron carbonyl band was observed as a result of acetone extraction.

Choice of Internal Standard

The sensitivity of the surface of the F.M.I.R. plates to sample contact provides a means of obtaining absolute values for absorption bands. Constant area contact and angle of incidence from sample to sample must be maintained. The nature of flexible films prevents the reproducibility in area contact required for obtaining absolute values without the use of reference absorption bands. Internal or external standards provide these reference bands.

An example of an external standard would be to have a standard material placed in a second KRS-5 plate holder located in the reference beam of a double beam instrument. Another example would be to use the single beam attachment. A second plate holder containing the reference standard would be placed in the attachment and the spectrum run separately for comparison with the unknown. This would be comparable to the "in-out" technique used with transmission spectrophotometry.

The difficulty that would occur with this work if these techniques were to be used would be from: 1) variability of the original oxidation level in the control film, 2) the variability of interference in the 6.0-6,4 micron region, 3) variations in orientation and crystallinity between films, and 4) possible changes in angles of incidence required between types of films.

Other means of obtaining absolute values include: 1) use of O^{18}, 2) neutron activation of O^{16}, and 3) transfer of surface oxidation products to a solvent so that liquid carbonyl standards could be used. The first two techniques require equipment that was not available while the latter technique was not tried.

The common practice in use of internal standards in transmission spectrophotometry is to add a compound having the desired reference band to the sample. With polymers, this could be approached in two ways. A high boiling liquid or a solid would be added to a lacquer of the resin and films cast from the lacquer or copolymers and blends containing the desired bands could be prepared.

The disadvantage of the first approach is that the migration of the added standard to the film surface would not be readily known. This approach would be better for transmission studies of films. The use of copolymers and blends present additional difficulties. The refractive index of these films may be sufficiently different from the sample films as to limit reliability. The molecular weight distribution may be such that in a casting process, fractionation would occur during film formation. The distribution of the standard functional group throughout the film would not be known.

The only alternative for a reasonably reliable internal standard would be to use an absorption band that represents an inherent structure of the homopolymer. Although this technique provides only a relative value, it is a simple means of following changes in the analytical bands with change in corona treatment.

The choice of a reference band requires that it be located at a wavelength near that of the analytical band. Changes in wavelength could cause a change in one band while not changing the other. It is desirable to use a band that represents a single oscillating species that will not change during the work. For analytical curves, it is desirable to use a reference band that gives a ratio of 1.0 near the center of the working curve.

Methyl groups are relatively stable and are constant in number for a great number of polyethylene films. These groups have a symmetrical CH bend absorption at 7.25 microns that is strong. They have a deformation band at 7.6 microns. The latter band's height relative to the carbonyl and olefinic unsaturation bands was a reason for investigating the reproducibility of the 7.6 micron band.

The reproducibility of the peak height of the band between three films of differing thickness was found to be ±10% with 95% confidence (Table IV). It was assumed that the films were made from resin produced by the same process since Union Carbide is a producer of polyethylene resin. From this data, it was believed that this band would suffice as a reference for following changes in carbonyl and olefinic unsaturation for this study. It was not intended that this band would be of the same height in all films.

Effect of Treatment on Surface Transmission

The ability to determine changes in concentrations of surface functional groups suggests that changes in surface transmissions may occur at the same time as corona treatment is applied. The data tabulated in Table V are from a brief study of this hypothesis.

The decrease in the transmission of Cryovac-L film caused by bromination was slight. The effect of 130 watt-hours per 1000 square feet of corona discharge indicated a definite effect on the transmission of the film and the ratio of the analytical bands. The reference beam attenuation was readjusted to the 94% transmission used with the control. The definite increase in carbonyl ratio is noted in the plot of this data (Figure 7). The large increase in the carbonyl ratio and the lesser increase in the olefinic unsaturation ratio suggests that the treatment affects transmission more in the 5.8 micron region that at longer wavelengths. As a result of this, the reference beam was readjusted to the same level as the controls on all series.

Bromination Rate

In the F.M.I.R. spectra of all polyethylene films run, interference was noticed in the 6.0-6.4 micron region (See Figures 1 and 2). A study of the effect of bromination was made to determine whether this treatment would eliminate the interference in a reasonable period of time. This data has been plotted in Figure 6.

The decrease of the ratio of the 6.1 micron band would suggest that bromination does occur. That it does occur, was observed at the 10.35 micron "trans" unsaturation band in Cryovac-L film. Figure 1 shows this band. After bromination for six hours, it had disappeared.

The similar decrease of the 5.8 micron carbonyl band places some doubt upon the validity of the assumption that bromination is the only phenomenon occurring at the 6.1 micron region. The knowledge that oxidation products can be removed by rubbing the film surface and that carbon tetrachloride is a solvent for polyethylene suggests that the interference may have been removed by dissolving some of the surface with each three-hour treatment. The time required to remove all interference was impractical.

The bromination step was not used with the cast films when it was found that changes with treatment could be observed without it. Because of the prominence of unsaturation in the Cryovac-L film, it was brominated before applying corona treatment.

F.M.I.R. System

The Wilks Model 9 MIR attachment provides adequate versatility for qualitative and routine observations. Because of the modifications necessary for the adaptation to the spectrophotometer, accurate control of the angle of incidence radiation is not possible. This situation reverts the control of this angle to the angle at which the prism ends are cut and the location of the holder pins on the attachment.

The greatest problem encountered with the mechanical set-up were the holders for the reference beam attenuator and the MIR attachment. The holder tracks do not provide a snug fit. To circumvent this, metal strips were fitted between the attachment and the tracks of the holders.

The attachment holder fits on a rail on the IR-4 instrument. Because of the nature of the fit of the holder, the attachment would rock out of line each time the sample holder was replaced. The latter problem could have contributed to some variability in spectrum transmission but not to reproducibility.

The KRS-5 crystal provides an excellent wavelength range of transmission. The sensitivities of the plates are restricted by the number of reflections possible. A calculation of the theoretical number of reflections possible in the two millimeter plate gave a value of 25 and for the one millimeter matched plates it is 99 (See Appendix).

An approximation of the penetration depth in polyethylene was calculated to be about seven microns (See Appendix). The effective path length of the two millimeter plate would be about 228 microns (0.12 mm.) and for the matched plates it would be about 663 microns (0.49 mm.). The approximation of the depth of flame treatment was estimated to be less than 0.00001 inch(12). If this is the case with corona treatment, then the penetration depth of our system is picking up absorption by carbonyl and unsaturated structures below this level.

The major difficulty encountered with the KRS-5 plates was their softness. The highly polished surfaces began to be lost after 3-5 samples. This loss is believed to be due to two factors, 1) normal wear due to the surface of the sample and 2) effects of soaking and wiping the plates with solvent soaked facial tissues.

It was found necessary to soak and actually rub the plate surface lightly with decalin soaked tissue to remove plate residue. A portion of the treated film surface remained on the plate surface. The amount left seemed to be directly related to the amount of treatment given the sample. As treatment increased, the adhesion of the film to the plate surface increased. The part remaining on the plate absorbed radiation in the 5.0 to 9.0 micron region. A spectrum of a two millimeter KRS-5 plate with this residue is shown in Figure 12. The slight loss of surface polish reduces the plate transmission. It would be best to give the plates a brief repolishing with Barnsite with each 3-5 runs.

Data and Curves

The spectrum of a polyethylene was explained in the Introduction. Figure 1 shows the F.M.I.R. spectrum of the Cryovac-L film used in the work. A comparison between the transmission spectrum of the cast Dow polyethylene resin and its F.M.I.R. spectrum is shown in Figure 2.

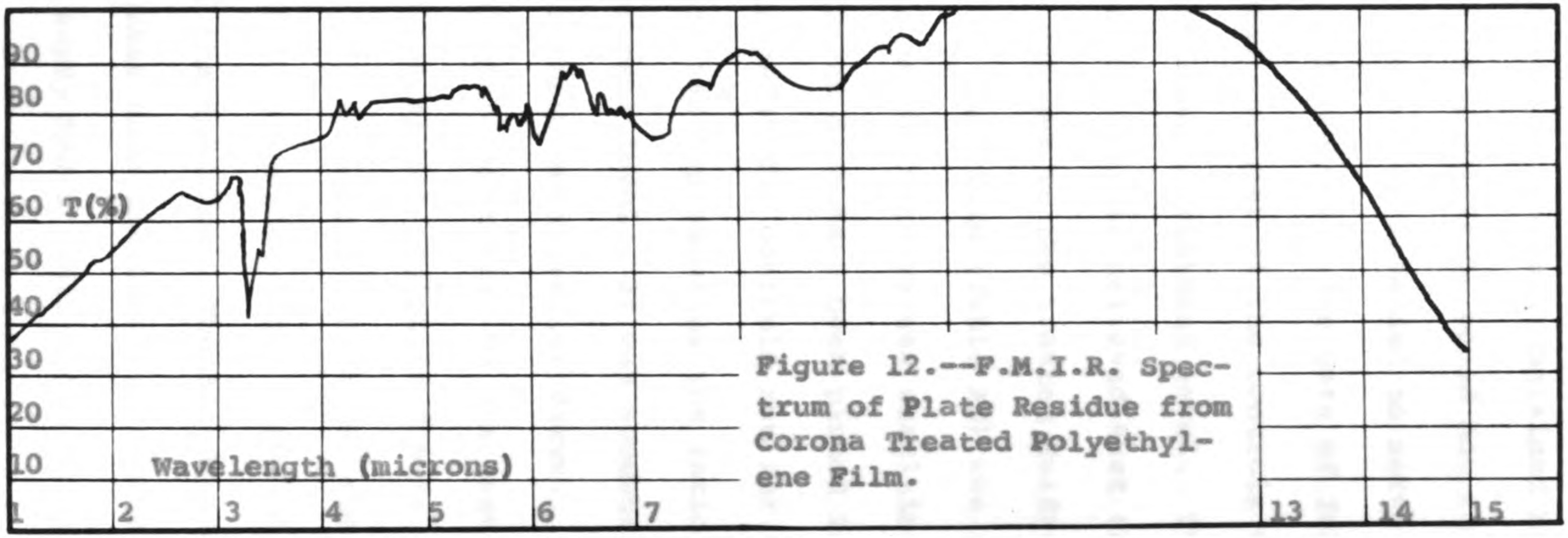


Figure 12.--F.M.I.R. Spectrum of Plate Residue from Corona Treated Polyethylene Film.

All of the film controls contained bands at 5.8 and 6.1 microns. Since bromination would not remove the interference, the controls were intended to serve as baselines for the treated film curves. The data of Tables VII and VIII show that the averages of the controls were higher than the ratio of lowest treatment level. The data are plotted in Figure 8. It was believed that the cause of this was due to changes in the treated surface. The four point series of the cast film (Table XI) was run without controls because of the high values resulting from the first series. These data have been ploted in Figure 9.

The average of the controls run for the extruded Cryovac-L film series approximates the ratio obtained for the initial treatment level. It was somewhat above this value for the olefinic unsaturation curve.

It is possible that some of the apparent interference in the 6.0-6.4 micron region is due to different forms of unsaturation and carbonyl, i.e. cross-chain, cyclic, aldehydic, ketone, and acid. Water vapor absorbs in the working area of the spectrum. The air-drying system fitted to the IR-4 reduces this interference considerably. The spectrum of an empty KRS-5 plate shows moisture to be very small. Drying film samples at 80°C for two hours did not reduce the interference. Water was not considered to be a significant contributing factor to this interference.

The level of corona treatment used in commercial production is dependent upon many factors including film formulation, web rate, the number of electrodes, the spark gap, and the geometrical form of the electrode. Leeds(13) described the minimum power required to obtain good ink adhesion with the films he used. With convex electrodes the minimum treatment required to obtain good ink adhesion was 23 watt-hours per 1000 square feet. The Packaging Division of the Dow Chemical Company, Cleveland, Ohio, uses about 20 watt-hours per 1000 square feet(26).

The lowest treatment level used in this work was 23 watt-hours per 1000 square feet. The one-millimeter plates were used. It is believed that if the plates are kept highly polished between runs, sensitivity to at least 15 watt-hours would be possible. Interference could be the restricting factor to sensitivity.

The data obtained from the corona treated series do not allow a correlation of limits. Neither the lowest limits detectable nor the highest level of significance was obtained with certainty. From the curves that were plotted, the one millimeter plates provide the best sensitivity. The change of ratio with increase of corona treatment does appear to approach an upper limit. With both plates and films used, there appears to be a portion of the curve that would serve as an analytical working curve. The increase in the two analytical bands in the working portion of the curves are listed below.

Series	Carbonyl Increase	Unsaturation Increase	Power Range (Watt-hours)
Cast (1 MM KRS-5)	260%	190%	113
Cast (2 MM KRS-5)	200	150	118
Extruded (2 MM KRS-5)	135	130	150

The extruded Cryovac-L film series shows a nearly equal increase in both analytical bands. This corresponds with the work of Rossman(20) showing the relation of carbonyl formation to unsaturation.

The use of the symmetrical methyl CH bend absorption band at 7.25 microns gives lower ratios than obtained with the deformation band at 7.6 microns. The form of the curve, however, is the same. No significant error is believed to have been introduced by the use of the latter band for a reference.

Curve Form

The curves obtained in the work appear to be approximately of the same form. Because the curves of Figure 10 were drawn with averages of four runs, they were used to determine a mathematical approximation for the curve.

The ratio of carbonyl to methyl deformation represents concentration. If concentration is dependent entirely on power per area, the equation for increase in ratio with power would be

$$R=R_o e^{P/K}$$

where R is the carbonyl to methyl deformation; K, is the area which was constant and R_o is the initial ratio. The curve would show a decrease in available oxidation sites. The fraction of available sites with increase in power would be expressed as $e^{-P/K}$. The number of sites used with power would be $(1 - e^{-P/K})$. The expansion series

$$R = R_o + (1 - e^{-P_1/K}) + (1 - e^{-P_2/K}) + \ldots$$
$$\ldots + (1 - e_n^{-P/K})$$

also approximates the curve well. The form suggests a discontinuity in the treatment process. Both equations fall within the limits of the standard error of estimate of ± 0.18 (See Appendix). The data calculated with these equations is listed below.

Power (Watts)	R (obs.)	$R_o e^{P/K}$	Expansion $R_o + (1 - e^{-P/K})$
0	1.07	----	0.00
100	1.07	1.12	1.12
200	1.28	1.19	1.22
300	1.42	1.25	1.36
400	1.40	1.31	1.54

It is believed that a proper treatment of the data would require investigation of: 1) the pattern of the spark discharge from the Lepel unit with gap distance, 2) the area coverage of the discharge per treatment electrode, 3) microphotography of the film surface, and 4) consideration of the film surface with respect to available oxidizable structures.

CONCLUSIONS AND RECOMMENDATIONS

The background of the methods for treating polyethylene surfaces and testing for levels of treatment have been discussed. The desirability of a single method for correlating surface treatment with ink adhesion and heat seal was mentioned.

The principles of attenuated total reflectance have been discussed. A literature survey of applications of the technique to surface phenomena was made to show that these principles could be applied in the attempt to follow changes in polyethylene surface oxidation with the changes in corona treatment of the film.

The type of vibrations causing the major absorption bands of the infrared and F.M.I.R. spectra were presented to provide an understanding of the absorption bands involved with surface oxidation.

The data obtained show that a differentiation between corona treatment levels was obtained. The form of the curves derived from the data was essentially the same and are approximated by an expansion series. This expression suggests a discontinuity in the oxidation process that may be related to the characteristics of the corona discharge and the availability of polymeric sites capable of being oxidized at the power levels used.

The work indicates that analytical working curves can be established that would be useful in correlating the surface characteristics of ink adhesion and heat sealability of polyethylene.

It is believed that work could be done to develop the theoretical description of the corona treatment process and to develop a practical correlary with ink adhesion and heat seal.

To develop these aspects, the following characteristics of the corona treatment should be investigated: 1) the geometric pattern of the spark at the point of contact with the film surface and 2) the heat energy transferred to the film at its point of contact with the spark. The relation of the above to (1) electrode geometry, (2) the size of the gap between electrode and film surface, and (3) the effect of changes of power and film surface relief should be observed.

The more practical aspects would include studies of the effect of additives with oxidation levels and changes in power; the study of surface reactions with components of printing inks; and changes in film surface orientation with corona treatment and applied heat.

APPENDIX

Appendix

Sample Calculation of Watt-Hours per 1000 Square Feet

Formula

1. Surface Treated per Hour

   Feet/minute x Electrode width x minutes/hour

   86 ft./min. x 0.5 ft. x 60 min./hr.

   = 2580 ft.^2/hour

2. Energy per Thousand Square Feet

   Watts Applied x 1/ft.^2/hr.

   60 watts x hour/2580 = 23 watt-hours/1000 ft.^2

Appendix

Estimation of Reflections Within KRS-5 Internal Reflection Plates

The calculations are based on the geometry of the F.M.I.R. plates. The plates have ends cut at 45° angles which accounts for two right triangles with sides equal to the plate thickness and the bases equal to twice the plate thickness. The energy enters the plate normal to the angled ends. The distance between the end triangles represents the "effective length." Each triangle within the rectangle of dimensions, plate thickness x "effective length," is:

$$\text{Number of triangles along plate base} = \frac{\text{effective length}}{2\,[(\text{plate thickness})\tan\theta]}$$

where the denominator represents the base of the triangle of a reflection. Since within this rectangle, there are the same number of triangles with bases along the top of the rectangle as along the bottom surface, the expression is multiplied by two. The extra reflection represented by the two ends is added to the expression to give:

$$\text{Number of reflections} = 2\left[\frac{\text{effective length}}{2(\text{plate thickness})\tan\theta}\right] + 1$$

One Millimeter Matched Plates

Effective length: 48.3 mm.

$$\text{Number of reflections} = 2\left[\frac{48.3}{2(1)(1)}\right] + 1 = \underline{49.2}$$

Since there are two plates, the number of reflections is 98.4 or approximately <u>99 reflections</u>.

Two Millimeter Matched Plates

Effective length: 48.3 mm.

$$\text{Number of reflections} = 2\left[\frac{48.3}{2(2)(1)}\right] + 1 = 24.1 + 1 = \underline{25 \text{ reflections}}$$

Appendix

Estimation of Energy Penetration Depth in Polyethylene Film

The formula is that from Harrick(7).*

$$x_{\frac{1}{2}} = \frac{0.693 \times \text{wavelength}}{2(\sin^2\theta - n_{12}^2)^{\frac{1}{2}}}$$

Wavelength = 5.8 microns

$$\theta = 45^\circ$$

$$n_{12} = (n_1/n_2) = (1.54/2.4) = \underline{0.642}$$

$$x_{\frac{1}{2}} = \frac{0.693(5.8\ \text{microns})}{2[(0.707)^2 - (0.642)^2]^{\frac{1}{2}}} \mp \underline{\underline{6.7\ \text{microns}}}$$

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*n_1 = Refractive index of polyethylene.

n_2 = Refractive index of KRS-5.

Appendix

Calculation of Standard Error of Estimate for Cryovac-L Film Carbonyl (Table XIII)

Power (watts) X	Ratio (Obs.) Y	Ratio (Curve) Y_E	$(Y - Y_E)$	$(Y - Y_E)^2$
100	0.808	1.01	-0.202	0.041
100	0.913	1.01	-0.097	0.009
100	1.24	1.01	+0.23	0.053
100	1.33	1.01	+0.32	0.102
200	1.45	1.28	+0.17	0.029
200	1.27	1.28	-0.01	0.000
200	1.03	1.28	-0.25	0.062
200	1.35	1.28	+0.07	0.005
300	1.49	1.42	+0.07	0.005
300	1.17	1.42	-0.25	0.062
300	1.50	1.42	+0.08	0.006
300	1.52	1.42	+0.10	0.000
400	1.61	1.40	+0.21	0.044
400	1.22	1.40	-0.18	0.032
400	1.17	1.40	-0.23	0.053
400	1.59	1.40	+0.19	0.036
			Σ	0.539

$$S.E. = \sqrt{\frac{(Y - Y_E)^2}{N}}$$

$$= \sqrt{0.539/16}$$

$$= \underline{\underline{\pm 0.184}} = \sigma$$

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