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1977 F R MAYO, T L NEMZEK

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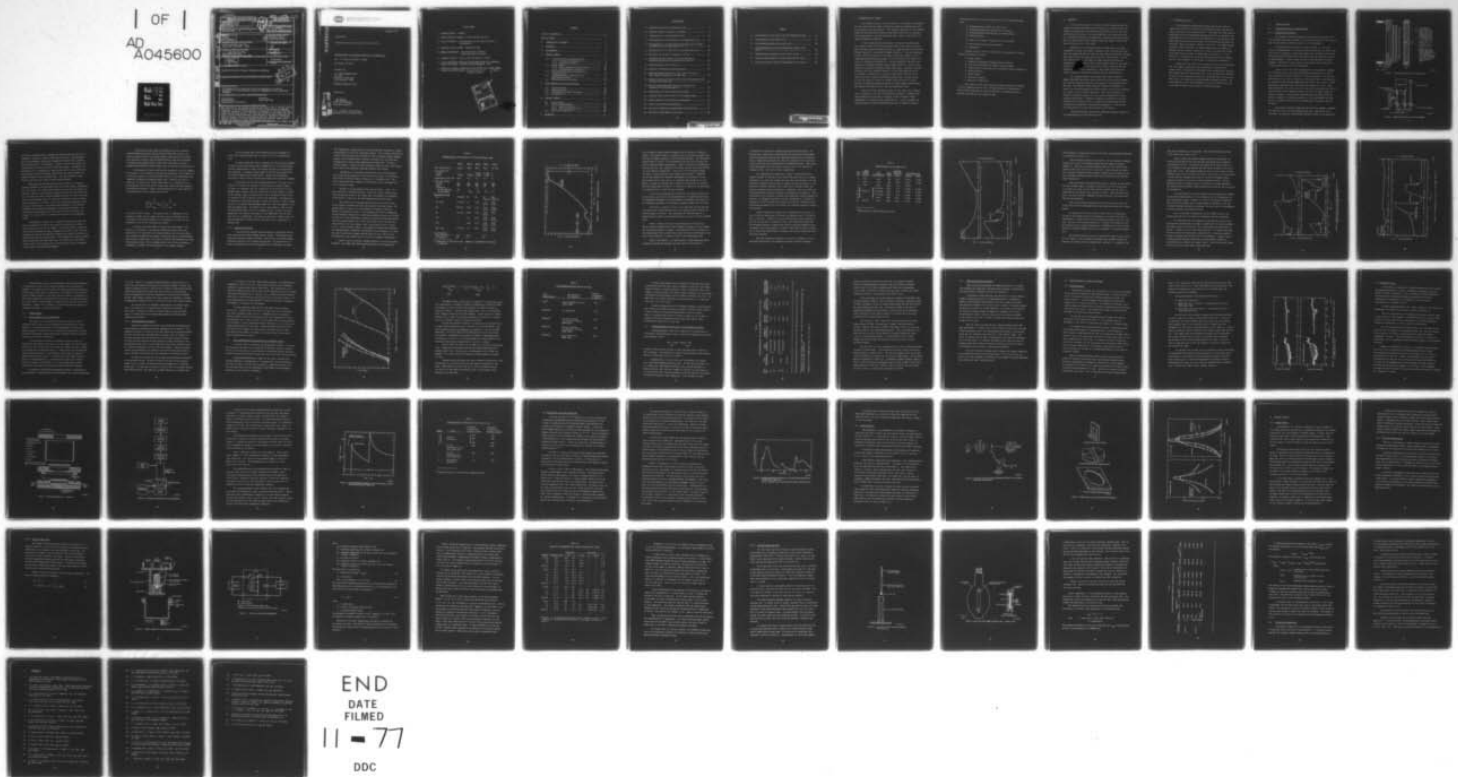
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Covering the Period 21 June 1976 to 20 June 1977

PHOTOOXIDATION AND ACCELERATED TESTING OF POLYPROPYLENE

By: F. R. Mayo and Thomas L. Nemzek

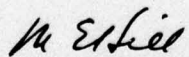
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1. INTRODUCTION AND SUMMARY

The ultimate objective of this research is to develop an accelerated test for predicting the useful lifetimes of stabilized polypropylene (PP) films exposed to sun and weather.¹ The immediate objectives of the research during the one-year period covered by this final report were to consider several approaches to the testing problem and to study in more detail the approach found most promising.

We have examined several methods for following reactions during the induction period (IP) and have grouped them in this report into three major sections: Chemical Methods (Section 4), Light Absorption and Emission Methods (Section 5), and Physical Changes (Section 6). The most promising and most practical approach to accelerated testing now appears to be the transducer-monitored pressure change, and we have studied this approach in detail, as described in Section 4.1. In our experimental work with this approach, we sometimes obtained results almost routinely; at other times, leaks in the system or transducer caused long delays. The major practical difficulty with this approach appears to be the long induction period (for example, illumination of a lightly stabilized film at 35°C is 25 hours) even with a powerful 2500W mercury-xenon lamp. Another problem is that the system is limited to testing of only one film at a time. However, we found that gamma-irradiation in oxygen before photooxidation can shorten or eliminate the IP, even with stabilized films.

Most of the other methods described in this report were examined only to establish if they had the sensitivity necessary to measure reactions during the IP and thus to determine if they warranted further examination for consistency and reproducibility. Of these methods, the following deserve further consideration but must be compared carefully

to determine which ones are most suitable for use in accelerated aging tests:

- Thermogravimetric analysis at 165 to 170°C
- Dinitrophenylhydrazine determination of ketones
- Triphenylphosphine determination of hydroperoxides
- Chemiluminescence

We ascribe only marginal usefulness to these methods:

- Fourier-transform infrared absorption
- Fluorescence

Methods found not sensitive enough with our equipment to warrant further investigation include:

- Weight changes
- Temperature-programmed thermogravimetric analysis
- Electron spectroscopy for chemical analysis (ESCA)
- Transmission or attenuated total reflectance infrared absorption
- Light scattering
- Contact angle
- Dielectric constant
- Electrical conductivity

The results in this report show that several methods are available to follow changes during the IP in the photooxidation of stabilized PP. After careful comparison for their suitability, a determined effort to develop a satisfactory test should be made.

2. BACKGROUND

In our previous work,² we started to follow changes in physical properties during photooxidation of PP films but we soon found that the changes were small until the induction period (IP) was over. The film was then close to failure. We then decided that only stabilized films are of practical interest and concentrated on measuring reactions during the IP in such films so that we might predict the length of the IP and hence the service life of the film.

During the IP in stabilized films, we would expect the total consumption of oxygen to be small, although several reactions may occur. About one oxygen molecule may react for each stabilizer molecule destroyed. Some chain reaction of oxygen with PP is also to be expected. For each free radical produced, the number of oxygen molecules reacting (or hydroperoxide groups formed, kinetic chain length) increases from about 0 initially to 100 at the end of the IP, which coincides with the exhaustion of one or more stabilizers. Water vapor and alcohol and carbonyl groups are formed from decompositions of hydroperoxides.

Our research proposal and previous final report (Contract DAHCO4-73-C-0035)² described earlier efforts to follow pressure changes and oxidation products during the early stages of the photooxidation of PP films. Our principal effort employed a sensitive transducer to measure the pressure changes that occurred while a PP film was irradiated in a small cell in an oxygen atmosphere. After the irradiation, we analyzed the gaseous products in a gas buret and examined the film by infrared spectroscopy. Although we encountered difficulties with the transducer and photolysis cell, we irradiated an unstabilized PP film and obtained one apparently satisfactory experiment.^{1,2} This work is the starting point for the work described in this report.

Carlsson and Wiles³ have recently published competent reviews of the photooxidation and stabilization of PP.

3. POLYPROPYLENE FILMS

The unstabilized polypropylene powder used in this work was supplied by Dr. Henry G. Schutze of Exxon Chemical Company and was the same as that used in the previous work.^{2 3} The powder was taken from the production line after deashing and washing but before any inhibitor had been added to it; it was dried in the laboratory in a vacuum oven at 50°. Exxon analyses showed that the polymer was 97.13% heptane-insoluble and contained 7 ppm Ti, 29 ppm Al, 33 ppm Cl, and no Fe. Its number-average molecular weight was 69,300; its weight-average molecular weight was 465,000, and its intrinsic viscosity in tetralin was 2.85 dl/g at 135°. This powder has been stored in vacuum since we received it. It was pressed into films about 75 to 100 μ m thick between sheets of aluminum foil in a CO₂ atmosphere at 185 to 200°, as described in Reference 1.

Stabilized films 100 to 125 μ m thick were supplied by Ciba-Geigy Ltd. The lightly stabilized films (designated L) contained 0.2% Irganox 1076. The moderately stabilized films (designated M) contained 0.2% Irganox 1076 and 0.25% Tinuvin 120. An M film supplied in mid-1975 was stored in the dark between sheets of waxed paper until used in early 1977, when it was found to have deteriorated (designated CG-M-75). New films supplied in early 1977 (designated CG-L-77 or CG-M-77) have been stored under nitrogen between sheets of interleaving paper.

4. CHEMICAL METHODS

4.1. Transducer-Monitored Pressure Change

4.1.1. Procedure and Apparatus

The original experimental procedure and problems associated with this technique have been described.^{1,2} We have since modified the photolysis cell and the glassware attaching the cell to the transducer.

The modified photolysis cell is shown in Figure 1. An O-ring groove of standard depth is used so that the cell will have the same volume each time it is assembled. Metal lock washers were originally used on the screws, but these oxidized badly in the water bath and have been replaced by rubber washers. A Mylar washer is used to keep the quartz disc from chipping. The Buna-N O-ring is given a thin coating of Dow Corning 970V silicone grease before the cell is assembled.

Figure 2 shows the latest configuration of the photolysis assembly. The transducer used is the all-welded Validyne modified AP-10, 0.2 psid model, described in earlier reports.^{1,2} When the assembly is in use, the photolysis cell, all three stopcocks, and the bottom half of the transducer are immersed in the constant temperature water bath. When a film is being photolyzed, stopcocks A and C are closed and stopcock B is open. Under these conditions, the volume on the cell side of the transducer was 4.76 cm³ and the volume on the reference side was 7.05 cm³, but these volumes are subject to change. This photolysis assembly gives reasonably stable behavior, although it is sometimes necessary to fill the assembly with gas and let it stand overnight to attain a steady rate of pressure change in the dark.

The rates of pressure change observed with this assembly, comparing the reference side to the nonirradiated cell side, range from 0 to 0.1 torr/hour. We attribute these pressure changes to leaks in the photolysis

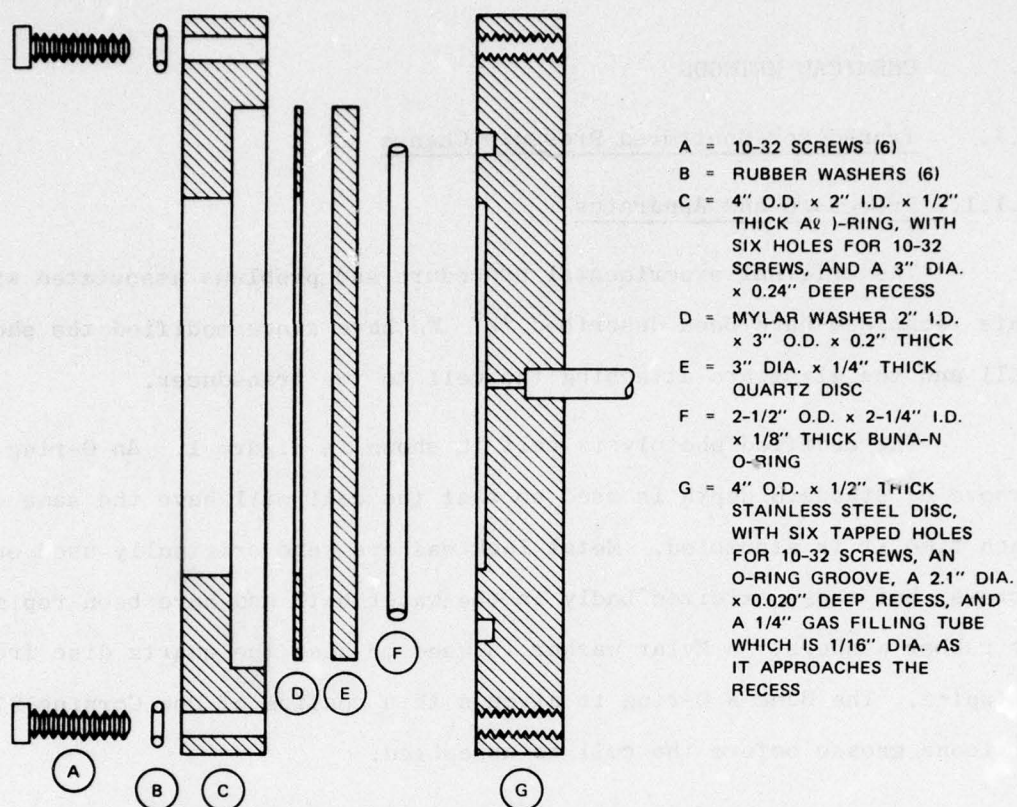


FIGURE 1 EXPLODED CROSS SECTION OF PHOTOLYSIS CELL

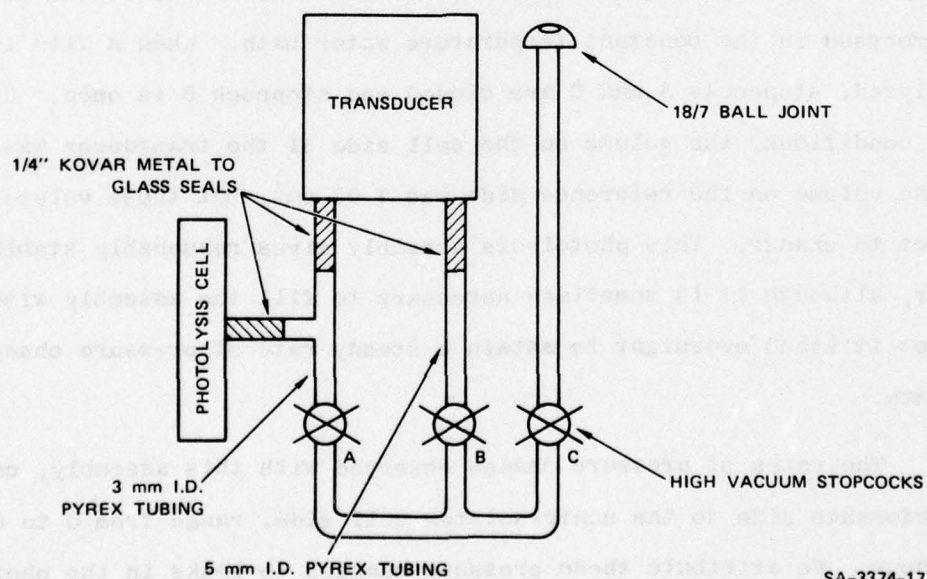


FIGURE 2 SCHEMATIC DIAGRAM OF PHOTOLYSIS ASSEMBLY

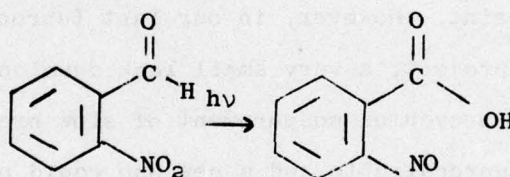
cell, since different rates of change are obtained each time the cell is assembled. The rate of change can be made very small if the photolysis cell is disassembled, cleaned, and reassembled several times, checking the rate each time. This procedure is tedious, however, and while it is taking place the PP film is at 35°C under pure oxygen. In general, the photolysis cell is assembled only once and used as is, since corrections can be made to account for small, steady leak rates when following the pressure changes of the irradiated cell. For long irradiation times, however, the leaks will affect the gas product balances.

Beginning with the experiments listed in Table 2, we observed pressure increases in the photolysis cell in the dark between irradiations of our PP films. The observed dark behavior was for the cell pressure to increase (relative to the reference pressure) several torr and then level off. We found that these transient changes were due to a leak on the cell side of the transducer, which was repaired with several coats of Glyptol vacuum sealing paint. However, in our last (unrecorded) experiment near the end of this project, a very small leak developed in the transducer diaphragm, which prevented measurement of slow pressure changes. The welded cell was unrepairable and a new one could not be obtained soon enough to be useful, and so no further work was done on the transducer method.

Photolyses were done at 35°, through a Corning 7-60 filter with maximum transmission at 350 nm and limits of 310 and 390 nm, under an initial pressure of 600 torr of oxygen. The initial amount of oxygen in the photolysis assembly was 388 ± 3 μ moles in all cases. This value was determined by filling the photolysis assembly with oxygen at 600 torr and measuring the gas with the gas buret. This procedure was repeated several times and gave the same value each time. The variation in the stated volume is due to the reading error of the gas buret, and not to changes in the volume of the photolysis assembly.

To decrease the time needed for photolysis, we used a Hanovia 929 B9U 2500W mercury-xenon lamp in an Oriel model 6155 housing. We used this lamp for most of our runs, because it provides 10 to 20 times more intensity at 365 nm than the 200W PEK mercury lamp used previously. To prepare photooxidized films for many other experiments, we used a cheaper General Electric mercury street lamp, as described in Section 6.2.2.

To determine the absolute photon flux impinging on the film samples, we attempted to use a potassium ferrioxalate actinometer,^{1,4} but found that a one-minute exposure of the ferrioxalate solution to the 2500W Hg-Xe lamp completely consumed the complexing agent used to measure the extent of reaction. To measure this intense light source it is necessary to use an actinometer that can be used at higher light fluxes than the potassium ferrioxalate actinometer. ONBA (o-nitrobenzaldehyde) has been reported⁵⁻⁷ to photoisomerize with a quantum yield of 0.50



in the 280 to 410 nm region. The quantum yield is independent of the presence of oxygen and the reagent has been used at concentrations up to 0.033 M,⁵ but at high conversion it is necessary to correct for the absorbance of the nitroso isomerization product.⁷

A solution of 0.051 M ONBA in acetonitrile was prepared. This solution, in 2-cm-thick, 5-cm-diameter cylindrical quartz cells, was positioned in the water bath in the space normally occupied by the photolysis assembly and photolyzed through a 7-60 filter and a 1.8-inch-diameter mask, using the 2500W lamp. The extent of reaction was determined by liquid chromatography using a 50:50 H₂O:CH₃CN solvent mix, 254 nm uv detection, μ Bondapak C₁₈ columns, and p-nitrotoluene as an internal standard.

A 2-min exposure gave 9.21% conversion, which corresponds to 2.53×10^{20} incident photons and to a flux of 1.3×10^{17} photons $\text{sec}^{-1} \text{cm}^{-2}$.

For leak testing and routine evacuation of the photolysis assembly, we used a mercury-free vacuum line, equipped with an oil diffusion pump. Silicone vacuum grease is used on the vacuum line and on the photolysis cell stopcocks. A separate vacuum system is used for gas analyses with the mercury Toeppler pump and gas buret. During the gas analyses, a cold trap is used to prevent mercury from entering the photolysis assembly.

Gas analyses are done as described previously.² The cell is connected to the vacuum line through a U-trap cooled in liquid nitrogen. All gases not condensed there are transferred to the gas buret with the Toeppler pump, measured, and then forced into a Cu-CuO furnace at $\sim 290^\circ\text{C}$. In the furnace, oxygen is removed as CuO; CO is converted to CO_2 , and H_2 is converted to H_2O ; N_2 and CH_4 (if any) are unaffected. The gases from the furnace are then passed through a U-tube trap cooled in liquid nitrogen (-195°C), and residual noncondensable gases ($\text{N}_2 + \text{CH}_4$) are measured in the buret and pumped away. The furnace trap is then warmed to -100° (liquid nitrogen/acetone slush), and CO is measured as CO_2 . Finally, the CO_2 is pumped away, the furnace trap warmed to room temperature, and the water vapor from H_2 is determined. The trap near the cell is warmed to dry ice/acetone temperature to determine CO_2 , and then to room temperature to determine H_2O .

4.1.2. Experimental Results

In the photolysis assembly described above, we photolyzed four PP films and measured pressure changes and gas uptake. Unstabilized films showed small pressure changes initially, with the rate of pressure change increasing steadily as the irradiation proceeded. In earlier work,² in which an unstabilized PP film was photolyzed with a 200W lamp, we found

that stopping the irradiation for a few hours and then restarting it caused an acceleration in the rate of pressure change. In the present experiments, however, dark periods hardly affected the rate of pressure change, perhaps because of the increased light intensity available from the 2500W lamp, accompanied by a lower steady concentration of peroxides. We made a serious attempt to repeat the 200W experiment toward the end of the project, but a leak in the transducer diaphragm thwarted this attempt.

Photolysis of a moderately stabilized PP film, CG-M-75, showed very little pressure change for about the first 32 hours of irradiation, after which the pressure began to change at an increasing rate. Here also, starting and then stopping the irradiation did not accelerate the rate of pressure change.

Results of the gas analyses are given in Table 1. Runs 1 to 4 show results for irradiated PP films. Run 5 was a blank without film to find the impurity levels in the oxygen used; the assembly was evacuated, filled with O_2 at 600 torr, and then analyzed using the gas buret.

The results for the unstabilized films are all similar in that little oxygen is consumed and only small amounts of gas are formed. The product ratios in runs 2 to 4 are difficult to interpret since the amounts of gas found are small. The differing ratios may be complicated by lamp intensity variations or by differing impurity levels in the films. For runs 2 to 4 the differences in μ moles of initial and final gas are the same within experimental error, since these values result from the difference between two large numbers, each of which has an error of about $\pm 0.5\%$. A more accurate measure of gas uptake is obtained from the pressure changes during irradiation, as measured by the transducer. For runs 2, 3, and 4 the pressure changes observed were 11.3, 0.8, and 9.7 torr, corresponding to gas uptakes of 2.8, 0.2, and 2.4 μ moles, respectively.

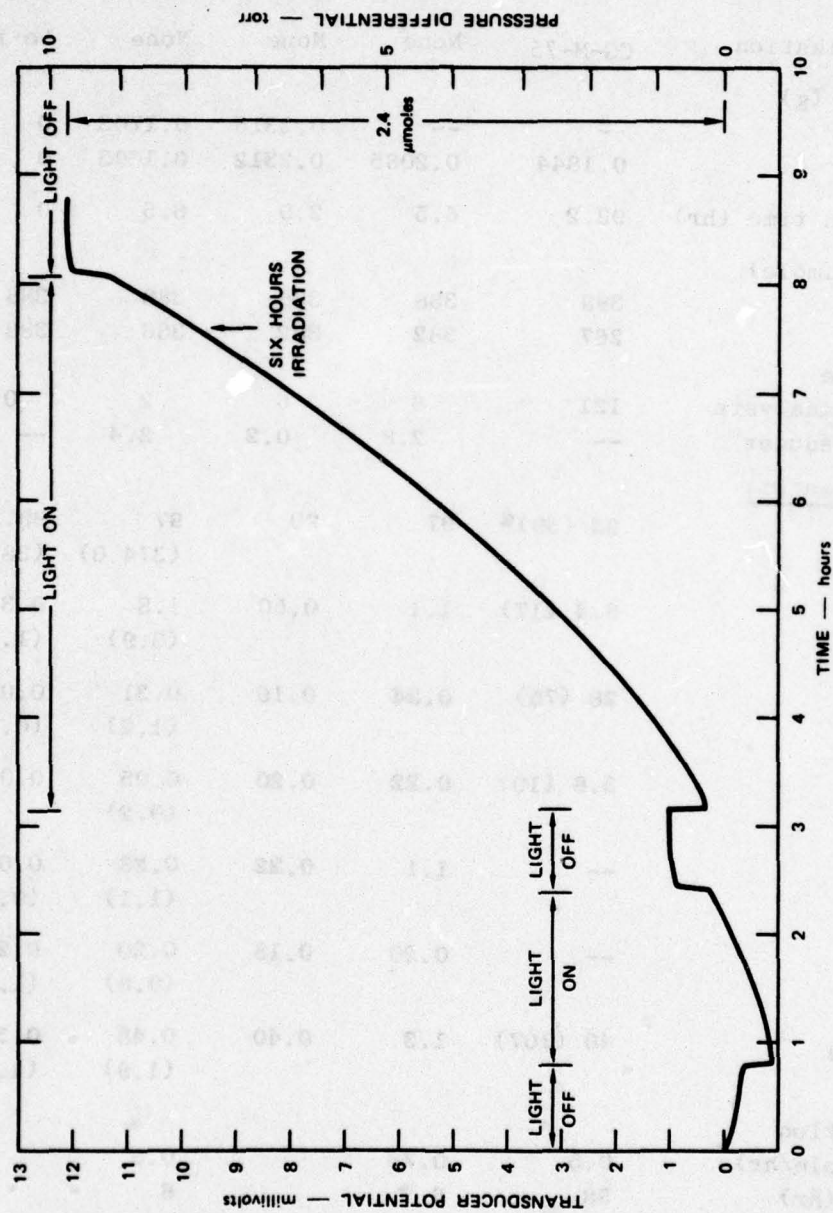
Figure 3 shows the pressure changes observed in run 4 with unstabilized PP. The 2500W lamp causes localized heating of the photolysis

Table 1

PHOTOOXIDATION OF PP FILMS AT 35° WITH 2500W Hg-Xe LAMP

	<u>Run 1</u>	<u>Run 2</u>	<u>Run 3</u>	<u>Run 4</u>	<u>Run 5</u>
Film stabilization	CG-M-75	None	None	None	No film
Film weight (g)					
Initial	--	--	0.2315	0.1703	0
Final	0.1844	0.2085	0.2312	0.1693	0
Illumination time (hr)	92.2	6.5	2.0	6.5	0
Total gas (μ mole)					
Initial	388	388	388	388	388
Final	267	382	382	386	388
Difference					
By gas analysis	121	6	6	2	0
By transducer	--	2.8	0.2	2.4	--
<u>Gas analysis^a (%)</u>					
O ₂	22 (59) ^a	97	99	97 (374.0)	99.3 (385.3) ^a
N ₂ + CH ₄	6.4 (17)	1.1	0.50	1.8 (6.9)	0.31 (1.2)
CO	28 (75)	0.24	0.16	0.31 (1.2)	0.06 (0.23)
H ₂	3.8 (10)	0.22	0.20	0.05 (0.2)	0.00
CO ₂	--	1.1	0.22	0.28 (1.1)	0.07 (0.27)
H ₂ O	--	0.20	0.18	0.20 (0.8)	0.25 (1.0)
H ₂ O + CO ₂	40 (107)	1.3	0.40	0.48 (1.9)	0.33 (1.3)
Gas absorption					
Rate (μ mole/hr)	0.5	0.75		0.6	
At time (hr)	38	6		6	

a Percentage of final total gas. Numbers in parentheses are μ moles in final gas.



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FIGURE 3 IRRADIATION NO. 4 — UNSTABILIZED PP FILM

cell, leading to abrupt pressure changes when the shutter is opened or closed. The pressure begins to change as soon as irradiation begins, and the rate of change increases as the irradiation proceeds. The dark period between hours 2.4 and 3.1 of the experiment does not seem to affect the rate of pressure change significantly. After 7.6 hours of the experiment, when the film has been irradiated for 6 hours, the net rate of gas absorption has reached 0.6 μ mole/hour. This rate is the difference between the rates of oxygen absorption and product gas evolution. Combining the net gas uptake from transducer measurements (2.4 μ moles) with the gas product data in runs 4 and 5, we calculate that during run 4, 11.3 μ moles of oxygen are consumed and 7.5 μ moles of other gases are evolved. Thus the oxygen uptake is about 4.7 times the 2.4 μ moles of net gas uptake by transducer and 1.5 times the gas evolution.

In run 1 with stabilized film (CG-M-75), the induction period was about 32 hours and the film was photooxidized for an additional 60 hours. No transducer measurement of gas consumption is available; when this film was irradiated overnight, the transducer pressure reading went off scale.

The extent of reaction in run 1 is so high that the rate may have been affected by oxygen depletion and by the product gases as well as by previous aging in the dark. This experiment was useful primarily in determining the length of the induction period for this film with the 2500W lamp.

Table 1 includes net rates of gas absorption for three runs. These rates were calculated from the transducer readings, the cell volume, and the initial pressure of oxygen. The stabilized PP film is similar to the unstabilized films in that 6 hours after the end of the 32-hour IP, the rate of gas absorption is similar to that of the unstabilized film.

Table 2 and Figures 4 to 6 show results of eight additional photo-oxidations, without gas analyses, and with tests of the ability of

γ -irradiation to shorten the induction period with stabilized PP. We expected that irradiating a stabilized PP film with γ -rays before photolysis would partially destroy the stabilizers and shorten the induction period. Moderately stabilized PP films were irradiated with γ -rays from a ^{60}Co source and then photolyzed with our 2500W Hg-Xe lamp. Three films were γ -irradiated for 6, 24, and 69.7 hours at 5.21×10^4 rad/hour to dosages of 0.31, 1.25, and 3.7 Mrad, respectively.

The experimental procedure was to place a stabilized PP film, roughly 2 inches in diameter, into a Pyrex tube under 600 torr of oxygen, γ -irradiate it, remove the treated film from the tube and place it in the photolysis assembly under 600 torr of oxygen, and then photolyze it. The photolysis assembly contains a cell volume and a reference volume, the pressure difference being monitored by a transducer. The two volumes can be equilibrated by opening a stopcock and equalizing the pressures. After equilibration, the stopcock is closed, and unexplained pressure changes are observed. A transducer potential of 10 mV corresponds to a pressure difference of 8.1 torr between the photolysis cell and the reference volume. As pressure decreases in the cell volume, the transducer potential becomes more positive.

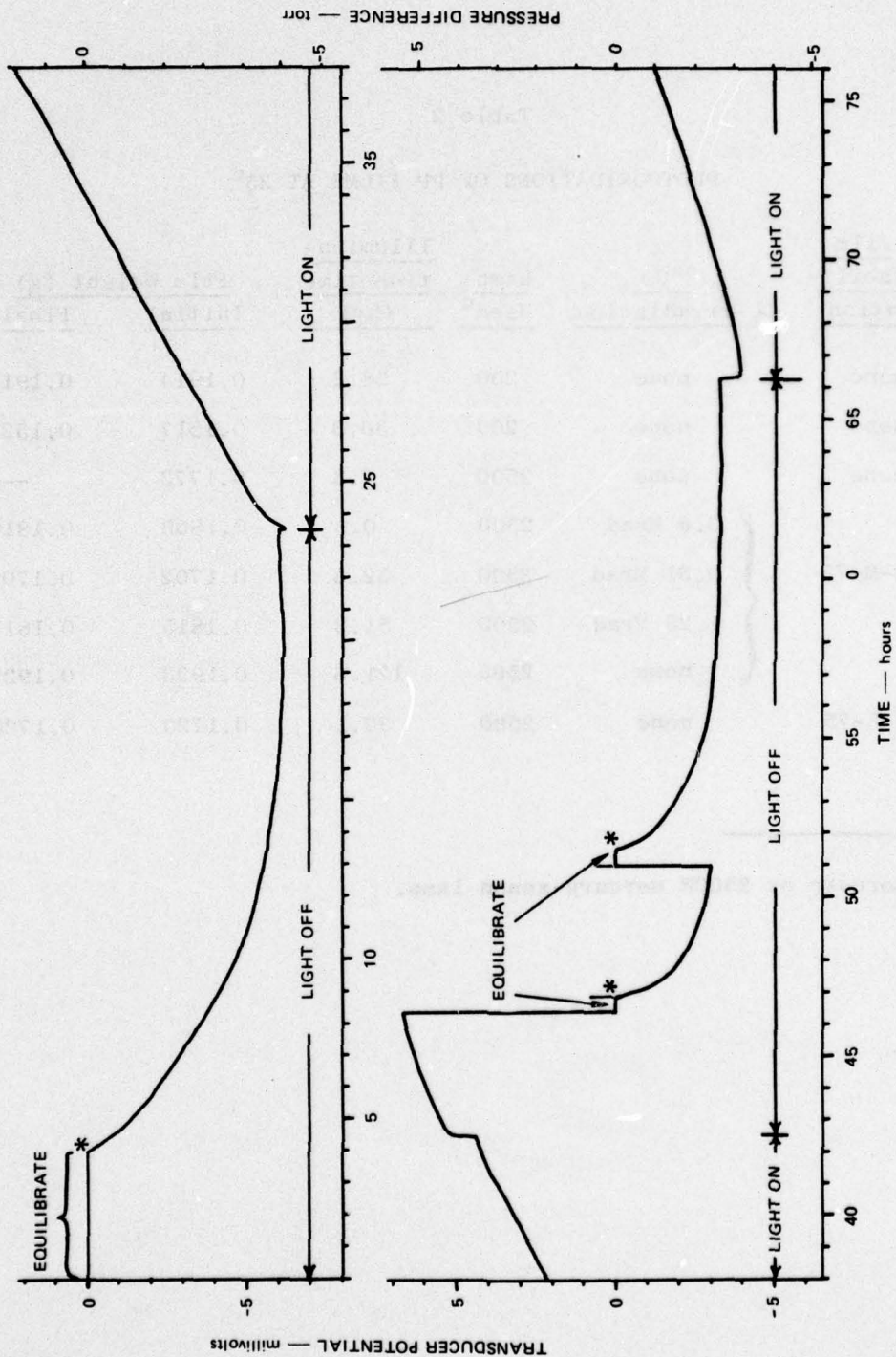
Table 2 compares the results for γ -irradiated films (runs 8, 10, and 11) with the photolyses of films not γ -irradiated (run 13 in Table 2, run 1 in Table 1). Figures 4 to 6 show the pressure changes observed in runs 13, 11, and 12 as a function of time. Our discussion assumes that the reference pressure is constant and that all pressure changes are due to changes in the cell pressure. We did not know that the film in runs 8, 10, 11, and 13 had deteriorated in storage, and no other stabilized films were then available.

When the volumes are isolated (as at hour 4 in Figure 4, run 13, moderately stabilized), the transducer potential typically decreases

Table 2
PHOTOOXIDATIONS OF PP FILMS AT 35°

<u>Run No.</u>	<u>Film Stabili- zation</u>	<u>⁶⁰Co γ-irradiation</u>	<u>Lamp Used^a</u>	<u>Illumina- tion time (hr)</u>	<u>Film Weight (g)</u>	
					<u>Initial</u>	<u>Final</u>
6	none	none	200	28.2	0.1914	0.1915
7	none	none	200	36.3	0.1517	0.1521
9	none	none	2500	7.3	0.1773	--
8	CG-M-75	3.6 Mrad	2500	0.9	0.1808	0.1810
10		0.31 Mrad	2500	32.8	0.1702	0.1709
11		1.25 Mrad	2500	51.3	0.1815	0.1811
13		none	2500	121.6	0.1923	0.1925
12	CG-L-75	none	2500	32.1	0.1720	0.1720

^a 200W mercury or 2500W mercury-xenon lamp.



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FIGURE 4 PHOTOOXIDATION 13 OF FILM CG-M-75 WITH 2500W LAMP AT 35°

*Indicates isolation of all volumes after equilibration.

(corresponding to increasing pressure in the cell) and eventually stabilizes, as mentioned in Section 4.1.1.

When illumination began (at hour 23.5), the cell pressure increased slightly as a result of localized heating and then began to decrease (Figure 4). The rate of pressure decrease slowed to 0.44 torr/hour and stayed at this rate from hour 25 to hour 42.5. When the lamp was turned off, localized temperature effects caused a sudden pressure change and the rate of pressure change decreased slowly from the previous rate observed under illumination.

When the volumes were equilibrated and then isolated (at hour 46.9), the cell pressure began to increase, as at hour 4, but the initial rate of increase was larger and the total pressure increase and the time to stabilization were smaller than at hours 4 to 23.5. Thus admitting fresh gas to the cell resulted in apparent net gas evolution in the dark rather than net gas absorption.

The rate of pressure change at hour 70 is less than at hours 25 to 42.5 and is slowly increasing rather than remaining constant, for reasons unknown.

We continued run 13 for a total of 121.6 hours of illumination. The end of the induction period is estimated to be at about 100 hours of illumination, at which time the rate of pressure change was about 1.5 torr/hour. The end of the induction period is, of course, not associated with any specific rate of pressure decrease but is defined as the time at which the rate of decrease changes from a slow or constant to a rapidly changing rate.

The induction period of run 13 is about three times as long as that of run 1 (Table 1) for a similarly stabilized film, probably because the lamp and its housing were moved between run 5 and run 8. In addition, the

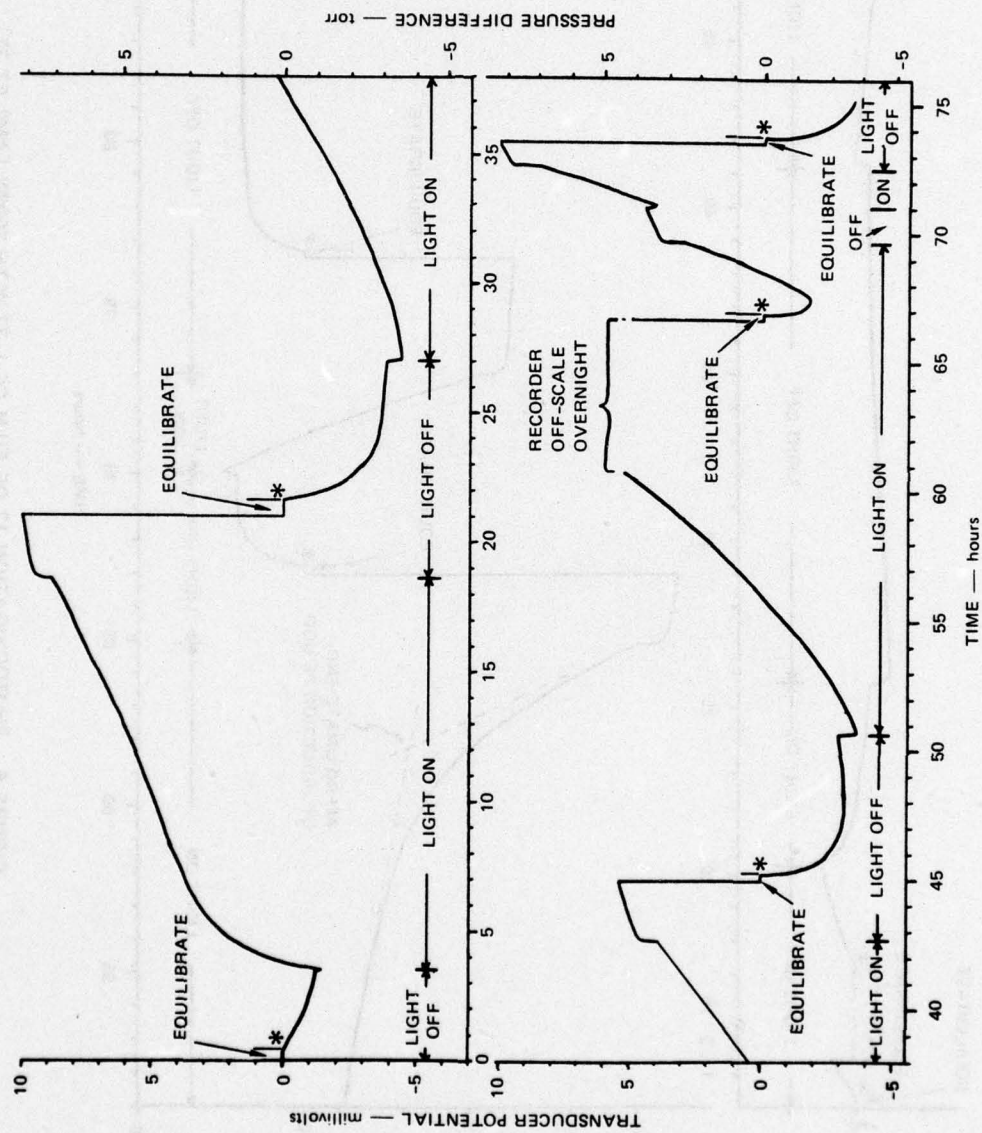
lamp output decreases as the lamp ages. The lamp and housing were kept in one position for runs 8 to 13.

Figure 5 shows the pressure changes observed on photolysis of a similarly stabilized PP film that had been pretreated with 1.25 Mrad of γ -irradiation (run 11). The initial gas uptake in the light (hours 3.5 to 5 of Figure 5) was much greater than that shown in Figure 4 for run 13 (hours 23.5 to 25). The pressure change at hour 5 of run 11 was 2.9 torr, compared with 0.9 torr at hour 25 of run 13. After hour 5, the rate slowed to 0.36 torr/hour (somewhat less than for run 13) and remained nearly constant from hour 6 to hour 18.6, when illumination ceased. Further photolysis (hour 27) caused the rate of reaction to increase gradually. The induction period probably ended between hours 60 and 65 (40 to 45 hours of illumination).

In run 8 (Table 2), with the highest γ -ray pretreatment (3.6 Mrad), the pressure changed rapidly (5.3 torr during 55 min of illumination) as soon as photolysis began. Because of a leak in the constant temperature bath, we did not continue this run long enough to determine if the rate of pressure change decreased or increased. We do not know if γ -irradiation entirely eliminated the induction period.

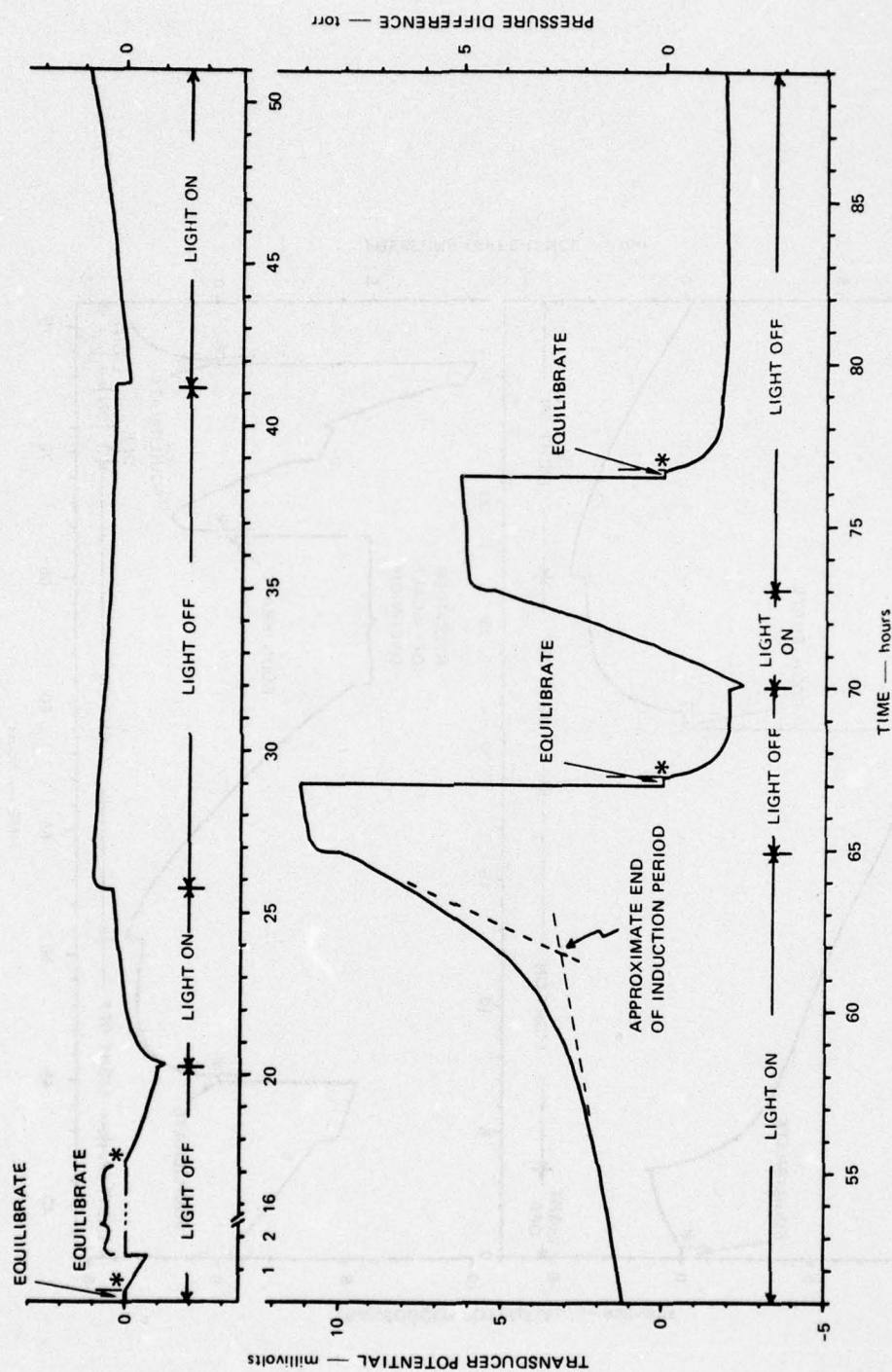
Run 10 (0.31 Mrad γ -irradiation) did not reach the end of the induction period after 32.7 hours of illumination and was terminated.

Our conclusion that the moderately stabilized PP films from mid-1975 may have deteriorated in storage is supported by the initial constant but rather large (0.44 torr/hour) rate of photolytic gas uptake seen in Figure 4. Figure 6, run 12, shows the photolysis of a lightly stabilized PP film received from Ciba-Geigy in February 1977. Little gas uptake is evident for roughly the first 15 hours of illumination. Figure 6 shows a nicely defined induction period and the same pressure increase on equilibration and isolation as Figures 4 and 5. Run 12 is the only irradiation we have done using fresh, stabilized film.



SA-5524-1

FIGURE 5 PHOTOOXIDATION 11 OF FILM CG-M-75 PRETREATED WITH 1.25 MRAD OF Y-RADIATION, WITH 2500W LAMP AT 35°



SA-5524-2

FIGURE 6 PHOTOOXIDATION 12 OF FILM CG-L-77 WITH 2500W LAMP AT 35°

The photolysis results are encouraging in that the photooxidation of stabilized PP films can be routinely followed with our photolysis assembly. γ -irradiation both shortens the induction period and causes an initial rapid oxygen uptake on photolysis. We thought at first that the pressure changes observed in the dark intervals between uv irradiation in both γ -preirradiated and untreated PP films were due to chemical reaction, but we now ascribe these changes to a small leak on the cell side of the transducer. Further work is needed on γ -ray pretreatment and possibly on thermal pretreatment of stabilized PP films.

4.2. Weight Changes

4.2.1. Weight Changes During Illumination

The weight of an oxidized PP film decreases when the film is irradiated under vacuum, and this decrease can be monitored by a microbalance.⁸ It should be possible to use a microbalance to follow the weight increase of a PP film as it is irradiated in oxygen and to obtain continuous measurements during irradiation, although the gaseous products would not be available for analysis.

If we estimate that during the induction period 1 mmole O_2 is absorbed for each mole of C_3H_6 units, and if we neglect the loss of gases such as CH_4 , CO_2 , and H_2O , then a 0.2-g PP film should increase in weight by 152 μg during the induction period. A weight change of this magnitude could be easily measured on a microbalance, except that the change is spread over many hours or days. To measure this slow weight change, we need a very stable balance on a vibration-free mounting in a location that is not subject to air drafts. If a very intense lamp is used, complications may arise from convection currents inside the balance.

We examined a Cahn RG Electrobalance and found it unsuitable for our experiments. This balance has a rated capacity of 1 g and a sensitivity

of 0.1 μg . However, it needed a 100- μf capacitor to reduce noise to a level that would permit the detection of microgram changes. Further, the balance reading drifted at a rate of 0.5 to 2 $\mu\text{g/hr}$ at night and fluctuated erratically during the day when there was activity in the laboratory. When an unstabilized PP film was irradiated for 35 hours with a 200W PEK mercury lamp through a Corning 7-60 filter under one atmosphere of oxygen, no appreciable change was seen in the rate of drift of the balance reading.

We conclude that for meaningful measurements, the balance would have to be remounted in a vibration-free, draft-free environment. It might also be necessary to speed the weight change by using the 2500W lamp or to reduce the noise by making measurements periodically after evacuating the balance.

4.2.2. Thermogravimetric Analysis

Grassie and Leeming⁹ have shown that irradiating polypropylene at 254 nm sensitizes subsequent isothermal degradation of the polymer. They degraded the polymer in vacuum so that they could trap the gaseous products. This section shows that thermogravimetric analyses (TGA) at steadily increasing temperatures under nitrogen do not distinguish among stabilized PP films that have and have not been exposed to light and oxygen but that photooxidized films start to lose weight much sooner than unoxidized films at a constant temperature of 165 to 170° under oxygen. These preliminary results are encouraging; they indicate that further experiments should be done to determine the potential of the technique in an accelerated test.

All TGAs were carried out with the Cahn RG Electrobalance described in the previous section. PP films of about 6 cm^2 were cut into squares roughly 3 mm on a side, and these sections were weighed onto a platinum balance pan. For each run, we used 40 to 50 mg of PP, but the small squares fused during heating, with large but variable reductions in surface area.

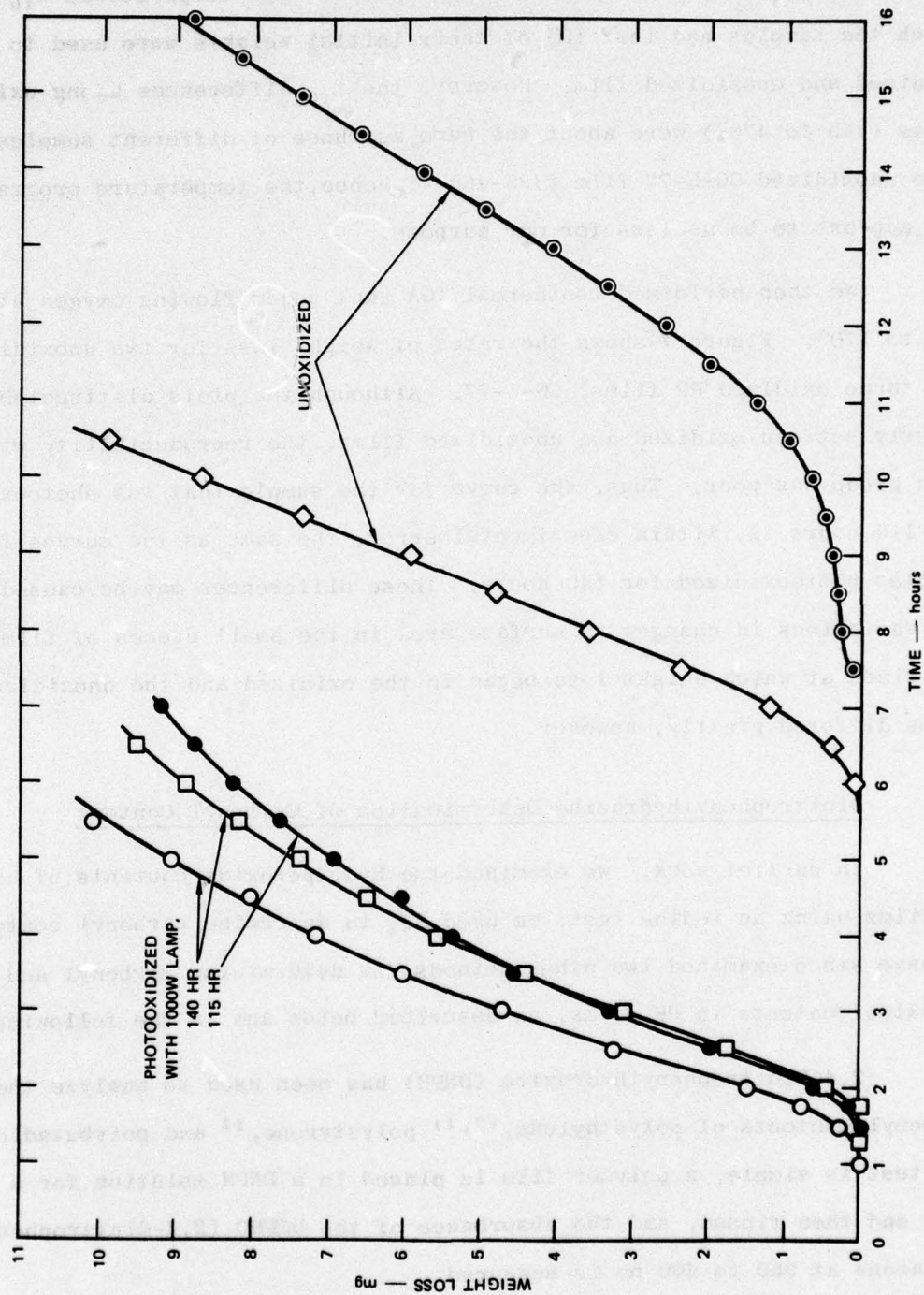
In a number of TGA runs under flowing nitrogen, the temperature was programmed to rise at $9.0^{\circ}/\text{min}$. Under these conditions, all PP samples exhibited a sudden weight loss at about 450°C . The temperatures t_{10} at which the samples had lost 10% of their initial weights were used to compare oxidized and unoxidized film. However, the t_{10} differences among oxidized films (445 to 470°) were about the same as those of different samples of the same unoxidized CG-L-77 film (435 - 460°); hence, the temperature programmed TGA appears to be useless for our purpose.

We then performed isothermal TGA runs under flowing oxygen at 165 to 170° . Figure 7 shows the rates of weight loss for two unoxidized and three oxidized PP films, CG-6-77. Although the plots distinguish clearly between oxidized and unoxidized films, the reproducibility within each group was poor. Thus, the curve for the sample that was photooxidized for 115 hours is, within experimental error, the same as the curves for the samples photooxidized for 140 hours. These differences may be caused by the variations in changes in surface area in the small pieces of film. The times at which weight loss began in the oxidized and the unoxidized films differed greatly, however.

4.3. Dinitrophenylhydrazine Determination of Carbonyl Content

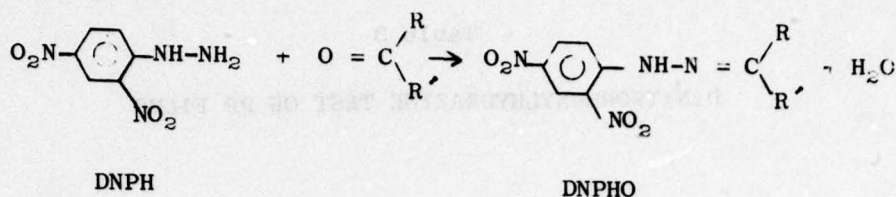
In earlier work,² we examined the hydroperoxide contents of oxidized PP films using an iodine test; we used SF_4 to determine carbonyl contents. We have since examined two other methods for determining carbonyl and hydroperoxide contents in PP films, as described below and in the following section.

2,4-Dinitrophenylhydrazine (DNPH) has been used to analyze the carbonyl contents of polyethylene,^{10,11} polystyrene,¹² and polybutadiene.¹³ The test is simple; a polymer film is placed in a DNPH solution for a set time and then rinsed, and the absorbance of the DNPHO (2,4-dinitrophenylhydrazone at 350 to 400 nm is measured.



SA-5524-4

FIGURE 7 TGA CURVES FOR PP FILMS IN OXYGEN AT 165-170°



The DNPHO formed in these tests is reported¹³ to have molar extinction coefficients of 10,000 to 14,000 for aldehydes and 15,000 to 17,000 for ketones, so that relatively small amounts of carbonyl groups can easily be detected. Reaction times ranging from 5 min to 4 hr have been used, along with both good and poor solvents. A poor solvent or a short reaction time is used if the carbonyl groups on the surface of a polymer film are of interest rather than those in the bulk.

We used the procedure of Kato:¹² a solution in the proportions of 1 g DNPH (recrystallized Eastman), 5 ml H₂O, 5 ml concentrated HCl, and 100 ml absolute ethanol was prepared just before use. Not all the DNPH dissolved. Films were placed in the solution for 15 min, then rinsed with ethanol. Measurements were made on a Beckman DU spectrophotometer by placing a wet film into a 1 mm path length cell, adding ethanol, and measuring transmittance compared with a 1 mm cell of ethanol.

Table 3 gives the results of the DNPH test on several polypropylene films. Significant differences were observed between photolyzed and nonphotolyzed films. These results are encouraging, and the DNPH test appears to be an easy method for detecting carbonyl groups in oxidized PP films.

Although large differences were seen in percent transmission, these differences do not correlate well with the degree of oxidation of the films. Specifically, the film from run 11 is more oxidized than the one from run 10 and would be expected to give a lower percent transmittance in the DNPH test.

Table 3
DINITROPHENYLHYDRAZINE TEST ON PP FILMS

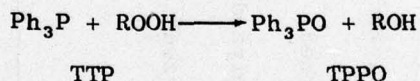
Film Stabilization	Photooxidation (cf. Table 2)	Percent Transmission at 360 nm
None ^b	Run 9 (exposed 7.3 hr to 2500W lamp)	64.1
Moderate ^c	not photolyzed	95.2
Moderate ^c	Run 10 (0.31 Mrad γ -irradiation; 32.8 hr 2500W lamp)	67.5
Moderate ^c	Run 11 (1.25 Mrad γ -irradiation; 51.3 hr. 2500W lamp)	70.9
Moderate ^c	Run 13 (121.6 hr 2500W lamp)	80.1

Further experimental work is necessary to determine the proper experimental conditions under which the DNPH test will give the correct relative amounts of carbonyl groups in lightly oxidized PP films. For example, a better solvent than ethanol would be helpful, and the reaction time should be long enough to allow the DNPH to penetrate the film. The DNPH test in its final form should be convenient since it is quick and uses only 1 to 2 cm² of film.

Because hydroperoxides are the primary products of photooxidation and ketones are secondary products, the DNPH test might be more useful if it were modified to determine hydroperoxides as well as ketones. Thus, if a photooxidized film were heated in vacuum to 150 to 200°C to pyrolyze peroxides, considerably more ketone might then be found, increasing the sensitivity of the test.

4.4. Triphenylphosphine Determination of Hydroperoxide Content

Triphenylphosphine (TPP) reacts rapidly with hydroperoxides to yield TPPO (triphenylphosphine oxide), which can be analyzed by gas liquid chromatography (glc)¹⁴:



A series of PP films was allowed to react overnight with a solution of TPP in benzene. Film composition, extent of photooxidation, and relative amounts of TPPO found are given in Table 4.

Experimentally, 0.1 gm of film, cut into pieces, was weighed into 5 cm³ glass-stoppered weighing vials. To each vial was added 4 ml of a fresh 0.01 M TPP (Matheson Coleman & Bell, vacuum sublimed) in benzene solution; the vials were wrapped in aluminum foil and placed in a covered beaker under flowing nitrogen gas, and the reaction was allowed to proceed overnight at room temperature. A 2-ml quantity of each

Table 4

TRIPHENYLPHOSPHINE TEST FOR HYDROPEROXIDE CONTENT OF PP FILMS

<u>Vial</u> <u>No.</u>	<u>Film</u> <u>Stabilization</u>	<u>Film</u> <u>Oxidation</u>	<u>Weight of</u> <u>Film Used (g)</u>	<u>Reaction</u> <u>Time (hr)</u>	<u>Relative</u> <u>Amount of TPPO</u>	<u>Relative Amount</u> <u>TPPO, Corrected^a</u>
1 } 2 }	CG-L-77	{ Not photolyzed Photolyzed ^b	0.1432 0.1517	14.63 13.47	1.77 79.6	0.47 45.3
3 } 4 }	None	{ Not photolyzed Photolyzed ^c	0.0874 0.1111	17.47 18.30	2.02 4.04	1.02 2.39
5	No film			12.63	1.00	0.0

^a Corrected by subtracting the blank (vial 5) and multiplying by the ratio of film weights.

^b Exposed 134 hr under oxygen to 1000W lamp. Film was brittle and showed strong carbonyl and hydroperoxy infrared absorbances.

^c Exposed 7.3 hr to 2500W Hg-Xe lamp (run 9 in Table 2).

reaction solution was then mixed with 2 ml of an internal standard solution (triphenylmethane in benzene) and the mixture was injected within 30 min into a Hewlett-Packard model 5700A gas chromatograph. A 6-ft column of 10% OV-17 on Gas Chrom Q was used, at 220°C with flame ionization detection. Each analysis took about 50 min.

When first made up, the TPP solution contained no detectable TPPO. The blank solution (Table 4, vial 5) however, contained a measurable amount of TPPO, presumably a result of oxygen being present when the TPP solution was first pipetted into the vial. The amount of TPPO in the blank is appreciable compared with the amounts in the reaction vials; therefore, merely storing the vials under nitrogen is not enough and a glove box should be used in future pipetting work.

The results in Table 4 show that the photolyzed films do yield larger amounts of TPPO, corresponding to higher film hydroperoxide content. However, the amount of TPPO in the blank (vial 5) was near the detection limit of the chromatograph detector. Also, the amounts of film that were used are close to the amounts customarily photolyzed during a run in our photolysis assembly. If less oxidized films or lower weights of film were used, the detector would not be able to record the TPPO produced.

The TPP test is not yet satisfactory but it may be sensitive enough to deserve further study. A more sensitive detector, such as an electron capture detector, should be used. All the film weights should be the same, to avoid correction to account for the amount of TPPO formed. All solutions should be prepared in a glove box. A different internal standard should be used, so that the analysis temperature can be raised to 240°C, which would reduce analysis time by 50%. Smaller vials and less TPP solution should be used in order to increase the concentration of TPPO.

4.5. ESCA and Electron Microscopy

ESCA (electron spectroscopy for chemical analysis) is a widely used technique for qualitative and quantitative studies of surfaces and has been applied to polymers by Clark and coworkers.¹⁵

To determine whether ESCA has the sensitivity to detect chemical changes occurring during the IP of PP photooxidation, we submitted a sample of nonirradiated unstabilized PP film and a sample of PP film that had been irradiated for 6.5 hours (run 2, Table 1) to Surface Science Laboratories in Palo Alto for ESCA analysis. The extent of PP oxidation was small and probably spread throughout the thickness of the film. The possibility existed, however, that most of the reaction occurred on the surface of the film, in which case ESCA might detect differences between the two films.

When the films were examined with a Hewlett-Packard model 5950 ESCA spectrometer to a depth of 40 to 50 Å, they were found to be the same within experimental error, the nonirradiated film having $1 \pm 0.2\%$ surface oxygen and the irradiated film having $0.7 \pm 0.2\%$ surface oxygen. The extent of reaction was too small to analyze the C(1s) peak for broadening due to ketone groups. We conclude that ESCA is less sensitive than our transducer-gas buret method for detecting oxidation and that our method of preparing films may result in some surface oxidation.

Electron microscopy has been used to examine the surface roughening and cracking that occurs as PP photooxidizes,^{16,17} but we have not yet tried to use this technique to determine if any changes in surface appearance occur during the early induction period.

5. LIGHT ABSORPTION AND EMISSION METHODS

5.1. Infrared Methods

Infrared spectroscopy (ir) potentially is one of the best methods for analyzing the products in photooxidized films. In previous work, we used ir to measure crystallinity, hydroxy-hydroperoxy content, and ketone content.² These measurements were hampered by interference fringes and by low optical densities. We attempted to eliminate interference fringes by wetting films in solvents (usually CCl_4) and pressing them between salt plates. The interference fringes decreased greatly, although we observed some solvent effect.²

We used SF_4 gas to distinguish between carbonyl and carboxyl absorption in the oxidized PP films.^{2, 18} And concluded that the absorbance in the 1750 cm^{-1} region was due primarily to carbonyl groups.

We examined three unstabilized PP films on a Perkin-Elmer model 467 infrared spectrometer, an unoxidized film, a film oxidized for 36-1/3 hours with 200W PEK mercury lamp in the photolysis assembly (Run 7, Table 2), and a film oxidized for five days in a Pyrex Petri dish 1.5 feet from a 1000W mercury street light. To examine the films, we used the wetted film technique, and the Attenuated Total Reflectance (ATR) method, with a 45 degree KRS-5 prism. No absorbance bands could be seen by either technique in the 3400 cm^{-1} (hydroxy-hydroperoxy) or the 1750 cm^{-1} (carbonyl) regions.

Fourier Transform Infrared (FTIR) spectra were obtained for several PP films by the Army Materials and Mechanics Research Center, Watertown, Massachusetts, through the courtesy of Dr. George Thomas, who arranged for the spectra to be made and analyzed by Dr. James Sprouse. A Digilabs FTIR spectrometer was used. Spectra were obtained by direct transmission (200 scans, 4 cm^{-1} resolution) and by ATR (45 degree KRS-5

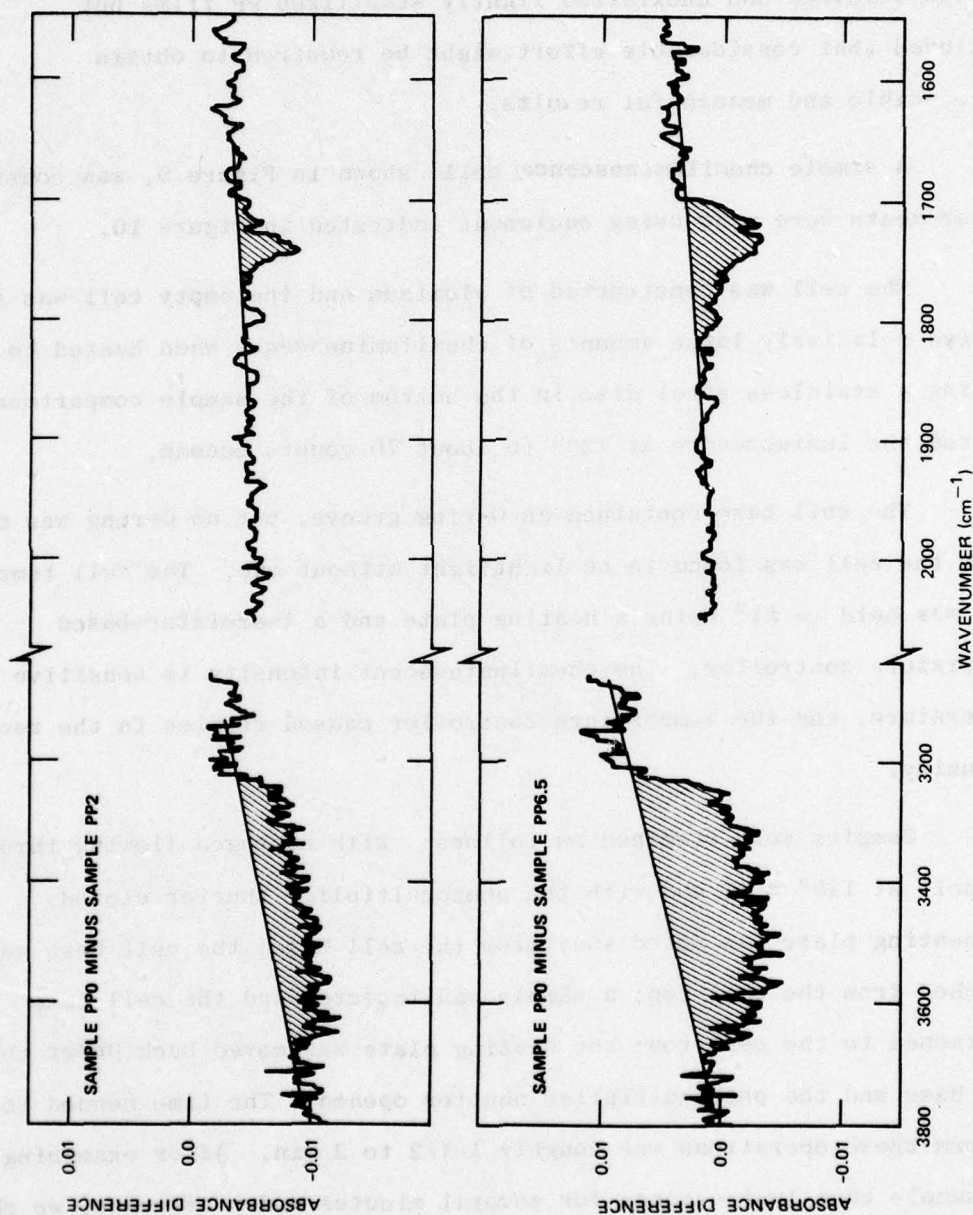
prism, 4 cm^{-1} resolution, 1200 scans of each film with the prism, 2000 scans of each film with the prism, 2000 scans of the prism alone). The spectra were normalized at the 1170 cm^{-1} C-C stretching band, and difference spectra were computed.

The unstabilized PP films examined by FTIR were:

- Sample PPO, unoxidized
- Sample PP2 (Run 3 in Table 1) = photooxidized 2 hr with 2500W Hg-Xe lamp.
- Sample PP6.5 (Run 2 in Table 1) = photooxidized 6.5 hr with 2500W Hg-Xe lamp.

The ATR FTIR spectra showed no significant differences between the three films in the regions around 3400 and 1750 cm^{-1} . The direct transmittance FTIR spectra showed small differences in these regions, which suggests that at these oxidation levels, products may form throughout the film rather than preferentially on the surfaces. Figure 8 shows the different spectra obtained in the regions around 3400 and 1170 cm^{-1} . The shaded areas may correspond to absorption by hydroperoxide and carbonyl groups, since they are in the proper spectral regions and increase in size with more photolysis of the films. The noise level is high and where to draw the baseline is uncertain, especially for the 3400 cm^{-1} band.

We conclude that at these levels of oxidation, direct observation of hydroperoxide and carbonyl group absorbances is not feasible with a conventional ir spectrometer and only marginally feasible with FTIR. Other workers use ir to follow hydroperoxide and carbonyl buildup in photooxidized PP films, but their films are oxidized almost to brittleness,¹⁹ whereas our films are only slightly oxidized.



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FIGURE 8 DIFFERENCE SPECTRA OBTAINED FROM THREE FTIR DIRECT TRANSMITTANCE SPECTRA,
ALL NORMALIZED AT 1170 cm^{-1}

5.2 Chemiluninescence

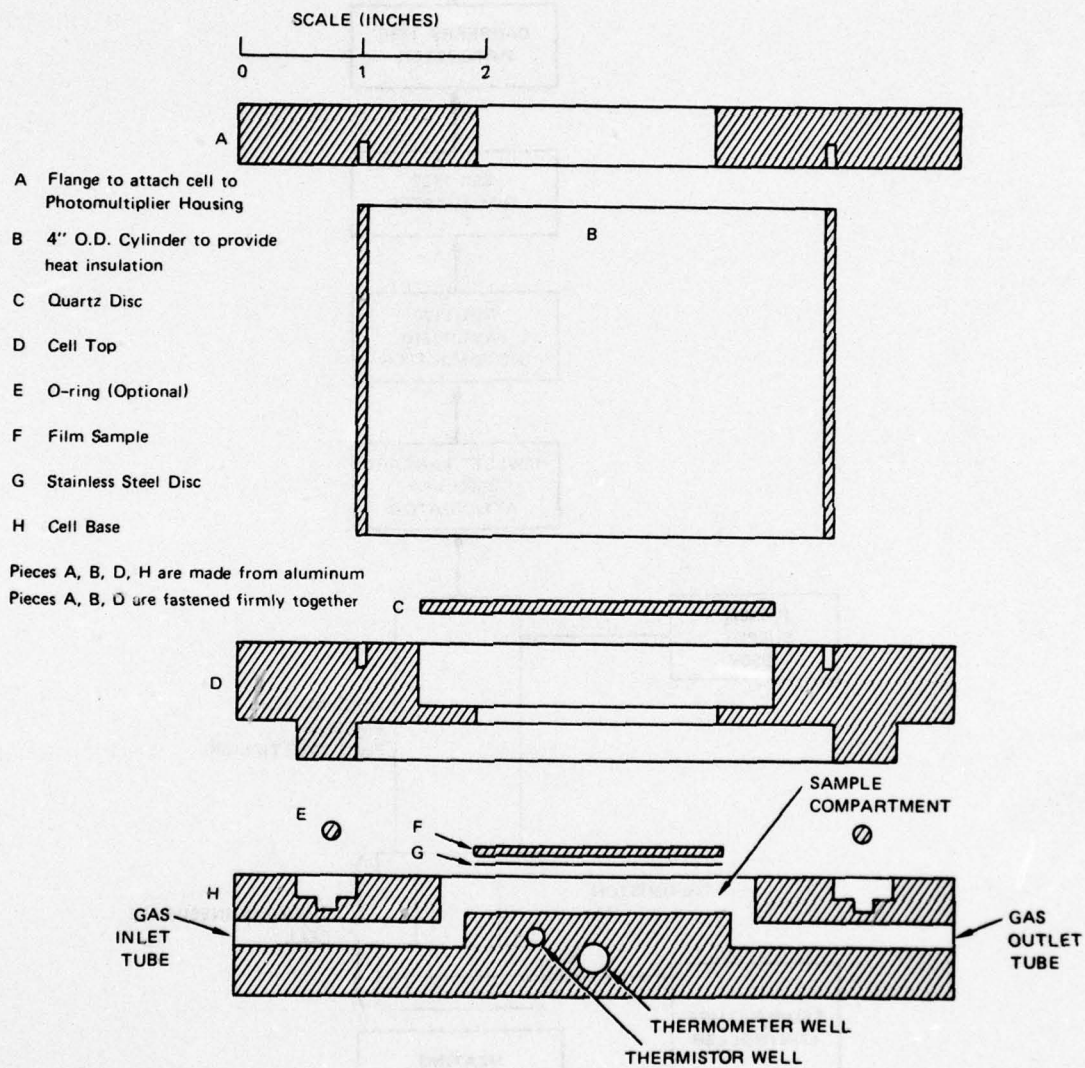
The oxidation of polymers at elevated temperatures can be followed by chemiluminescence,^{20,21} usually attributed to formation of excited ketones in chain termination. By this technique, we found differences between oxidized and unoxidized lightly stabilized PP films but concluded that considerable effort might be required to obtain reproducible and meaningful results.

A simple chemiluminescence cell, shown in Figure 9, was constructed. Measurements were made using equipment indicated in Figure 10.

The cell was constructed of aluminum and the empty cell was found to give relatively large amounts of chemiluminescence when heated to 120°. Putting a stainless steel disc in the bottom of the sample compartment lowered the luminescence at 120° to about 70 counts/second.

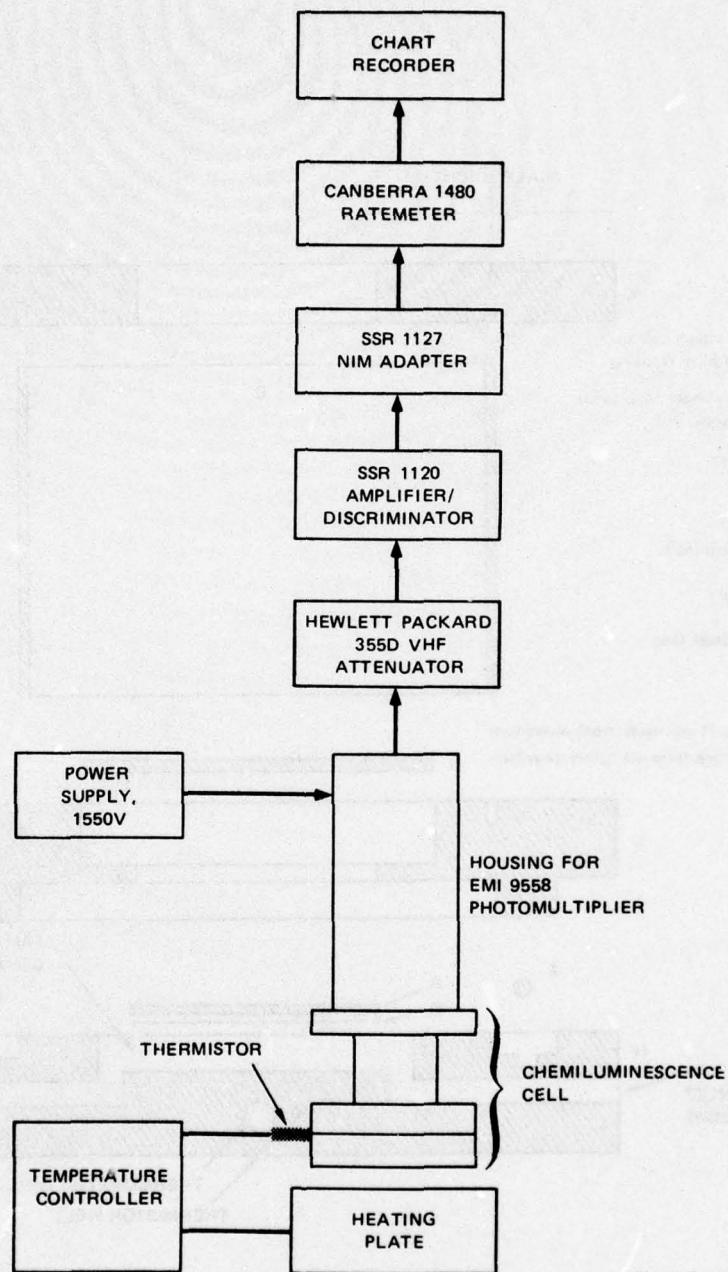
The cell base contained an O-ring groove, but no O-ring was used since the cell was found to be lighttight without one. The cell temperature was held to $\pm 1^\circ$ using a heating plate and a thermistor-based temperature controller. The chemiluminescent intensity is sensitive to temperature, and the temperature controller caused ripples in the recorded intensity.

Samples were examined as follows: with nitrogen flowing through the cell at $119^\circ \pm 1^\circ$ and with the photomultiplier shutter closed, the heating plate was moved away from the cell base; the cell base was detached from the cell top; a sample was inserted and the cell base reattached to the cell top; the heating plate was moved back under the cell base and the photomultiplier shutter opened. The time needed to perform these operations was roughly 1-1/2 to 2 min. After examining the sample chemiluminescence for several minutes under nitrogen, we changed the flowing gas to oxygen.



SA-5524-5

FIGURE 9 CHEMILUMINESCENCE CELL — SIDE VIEW



SA-5524-6

FIGURE 10 EQUIPMENT FOR MEASURING CHEMILUMINESCENCE

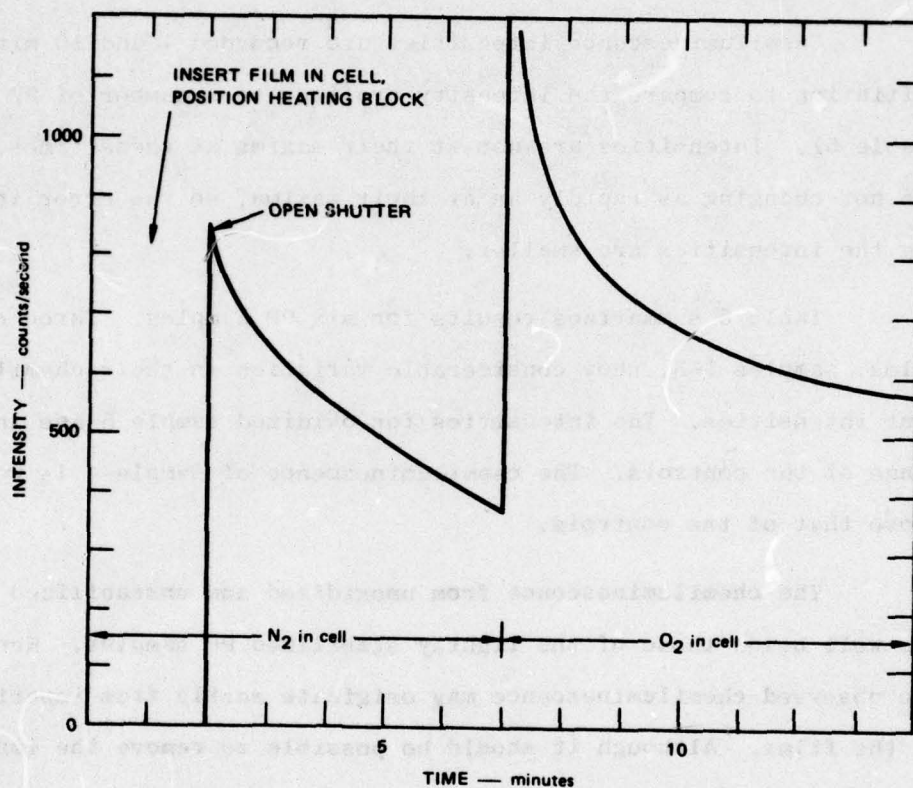
A typical plot of sample chemiluminescence versus time is given in Figure 11. Chemiluminescence decreases with time under both gases, and there is a short, intense increase in luminescence when oxygen is added, for reasons that are not clear. The chemiluminescence observed under nitrogen may be due to reaction of residual oxygen or of impurities trapped in the film. The intense burst of luminescence when oxygen is admitted may be caused by reaction of easily oxidizable compounds on the film surface.

Chemiluminescence intensities are recorded 4 and 10 minutes after initiation to compare the intensity profiles of a number of PP samples (Table 5). Intensities are not at their maxima at these times, but they are not changing as rapidly as at their maxima, so the error in determining the intensities are smaller.

Table 5 summarizes results for six PP samples. Three control films, samples 1-3, show considerable variation in their chemiluminescent intensities. The intensities for oxidized sample 5 are in the range of the controls. The chemiluminescence of sample 4 is well above that of the controls.

The chemiluminescence from unoxidized and unstabilized sample 6 was well below those of the lightly stabilized PP samples. Hence, the observed chemiluminescence may originate mostly from impurities in the films. Although it should be possible to remove the impurities by solvent extraction, in these preliminary studies we have left the impurities in the film and used appropriate controls.

Our chemiluminescence results indicate that this technique may be feasible for examining PP films at moderate oxidation levels. Further work would entail remodeling the sample cell so that samples could be inserted more rapidly, using a lens to increase the light intensity reaching the photomultiplier, and using cartridge heaters and insulation on the cell to attain better temperature regulation.



SA-5524-7

FIGURE 11 CHEMILUMINESCENCE INTENSITY AT 119° OF PP FILM CG-L-77 AFTER 70-HOUR PHOTOLYSIS WITH 1000W LAMP

Table 5

CHEMILUMINESCENT INTENSITIES OF PP FILMS AT 119°

Sample	Film	Intensity ^a (counts/sec) at time = 4 min	Intensity ^a (counts/sec) at time = 10 min
1	CG-L-77, unoxidized	640	430
2		240	260
3		820	480
4	CG-L-77, photolyzed 97.5 hr with 1000W lamp	1770	1220
5	CG-L-77, photolyzed 70 hr with 1000W lamp	560	680
6	Unstabilized, unoxidized	40	120

^a Intensities have been corrected for background noise.

5.3. Fluorescence and Light Scattering

Carlsson and Wiles^{17,22-25} and Allen et al.²⁶ have studied the fluorescence and phosphorescence of oxidized and unoxidized PP films. A sample of oxidized pure PP film should exhibit photoemission only because of the presence of aliphatic carbonyl groups. In practice, films contain impurities and rapidly become contaminated with polynuclear aromatic molecules when exposed to urban air.^{22,24,25} Because polynuclear aromatics absorb and fluoresce more strongly than aliphatic carbonyls, a small proportion of such aromatic groups can mask the fluorescence of aliphatic carbonyl groups.²³ Under such conditions, phosphorescence is expected to be more useful than fluorescence in analyses to determine carbonyl groups.^{23,26}

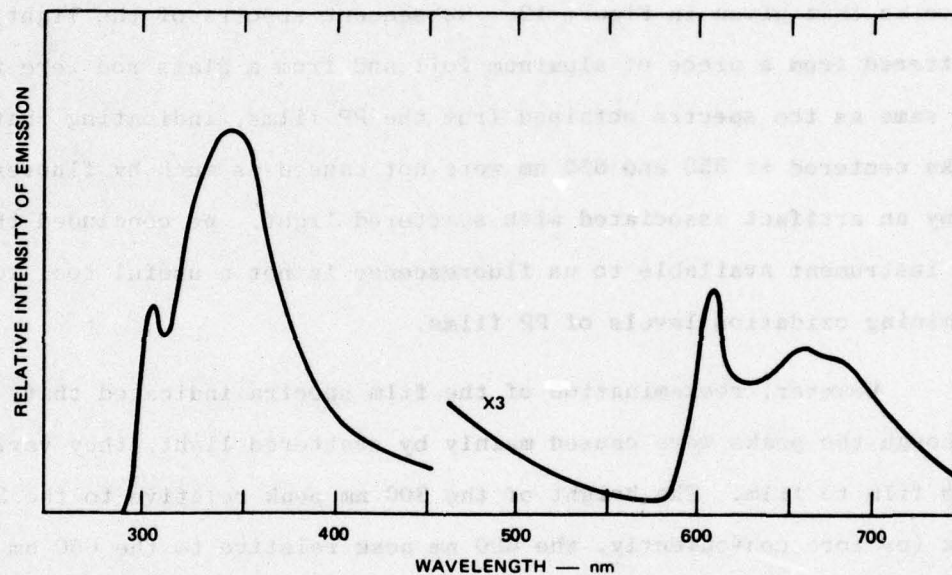
We wished to compare the emissions from oxidized and unoxidized PP films but the only instrument available, an Aminco-Bowman Spectrophotofluorometer, had no phosphorescence accessory. We then decided to measure the fluorescence spectra of several films, even though we doubted the usefulness of such spectra.

We used a 150W Xe lamp as light source. The exciting light passed through a monochromator and a Corning 7-54 filter. The emitted light passed through a monochromator and either a Corning 0-53 filter or a Pyrex filter. Films were placed in "picture frame" holders¹⁹ cut from 0.004-inch thick stainless steel and painted black. The holders were inserted diagonally into a cell block designed for 1 cm square cells, and the film was positioned across the cell so that one side of the film was illuminated while the emission was viewed through the back of the film. This arrangement reduced the amount of reflected light reaching the emission monochromator. Wavelengths of excitation were about 300 nm. Spectra were recorded with the films at room temperature.

The emission spectrum of a typical film is shown in Figure 12. The sharp peaks at 300 and 600 nm are caused by scattered light leaking through the Pyrex filter and being passed at the second and first orders of the grating in the emission monochromator. We assume that the peak between 300 and 400 nm is a result of fluorescence, whereas the broad peak between 600 and 750 nm is a result of the 300 to 400 nm peak being passed through and distorted by the first order of the grating in the emission monochromator.

All the films tested showed the same general shape of emission curve as that given in Figure 12. Subsequent spectra of the light scattered from a piece of aluminum foil and from a glass rod were roughly the same as the spectra obtained from the PP films, indicating that the peaks centered at 350 and 650 nm were not caused as much by fluorescence as by an artifact associated with scattered light. We concluded that with the instrument available to us fluorescence is not a useful tool for examining oxidation levels of PP films.

However, reexamination of the film spectra indicated that, although the peaks were caused mainly by scattered light, they varied from film to film. The height of the 300 nm peak relative to the 350 nm peak (or more conveniently, the 600 nm peak relative to the 650 nm peak) increased with oxidation. The correlation of these ratios with film oxidation seemed to be real, although difficult to reproduce. The ratios also vary with changes in the excitation wavelength, with the filters used, with film positioning, and with lamp flicker. Reproducibility of film positioning was greatly improved by constructing the "picture-frame" film holders from two pieces of 1 mm thick Al plate. To ensure representative spectra however, it is necessary to run an oxidized film and an unoxidized control film alternately, taking several spectra of each film. This rather tedious procedure could be shortened if the lamp did not flicker.



SA-5524-8

FIGURE 12 EMISSION SPECTRUM OF PP FILM CG-L-77 AFTER PHOTOOXIDATION FOR 134 HOURS WITH 1000W LAMP

Excitation at 302 NM through a Corning 7-54 filter; emission through a Pyrex filter.

We conclude that studying scattered light intensities with the spectrophotofluorometer is a potential method for comparing PP film oxidation levels, but that considerable additional work would be needed to test the method.

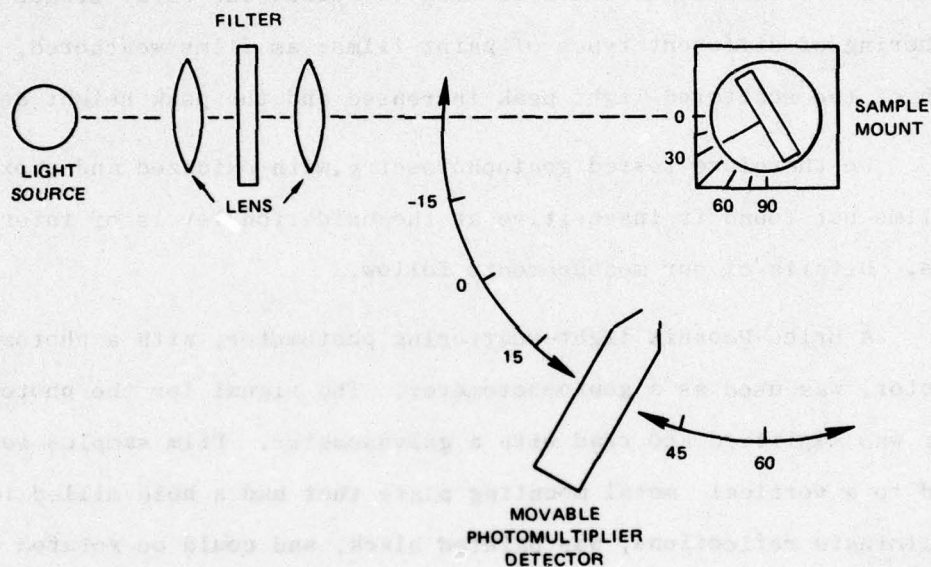
5.4. Goniophotometry

Goniophotometry, the measurement of the angular dependence of light scattered from a surface, has been used to follow the deterioration of paint films.²⁷⁻³⁰ It was found that plots of scattered light intensity versus reflectance angle could be used to follow the early stages of weathering of different types of paint films; as films weathered, the width of the scattered light peak increased and the peak height decreased.

We therefore tested goniophotometry with oxidized and unoxidized PP films but found it insensitive at the oxidation levels of interest to us. Details of our measurements follow.

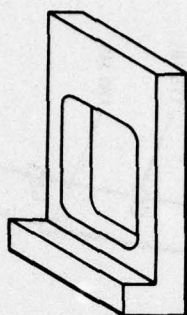
A Brice-Phoenix light-scattering photometer, with a photomultiplier detector, was used as a goniophotometer. The signal for the photomultiplier was amplified and read with a galvanometer. Film samples were taped to a vertical metal mounting plate that had a hole milled in it to eliminate reflections, was painted black, and could be rotated relative to the incident light beam. For simplicity, only one angle of incidence, roughly 30 degrees, was used. The light scattering photometer and the sample mount are shown in Figures 13 and 14.

We found that for heavily oxidized PP films, plots of scattered light intensity versus reflectance angle showed the expected broadening along with a decrease in the peak maximum intensity, as illustrated in Figure 15A. For moderately oxidized PP films, however, the scattered light profiles were not appreciably different from the profiles of unoxidized films, as shown in Figure 15B.

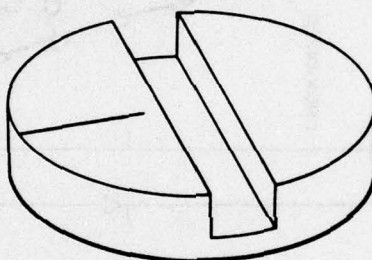


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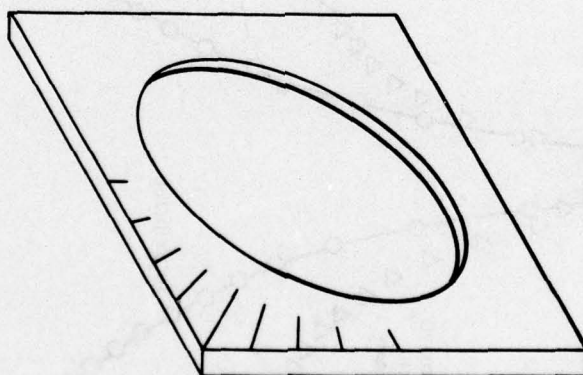
FIGURE 13 SKETCH OF LIGHT-SCATTERING PHOTOMETER, SHOWN AT 30° INCIDENCE AND REFLECTANCE ANGLES



(a) BLOCK TO WHICH PP FILM IS TAPED



(b) ROTATING BLOCK WITH ONE ALIGNMENT SCRATCH



(c) PLATE WITH ALIGNMENT SCRATCHES EVERY 15°
SA-5524-10

FIGURE 14 SAMPLE MOUNT FOR LIGHT-SCATTERING PHOTOMETER

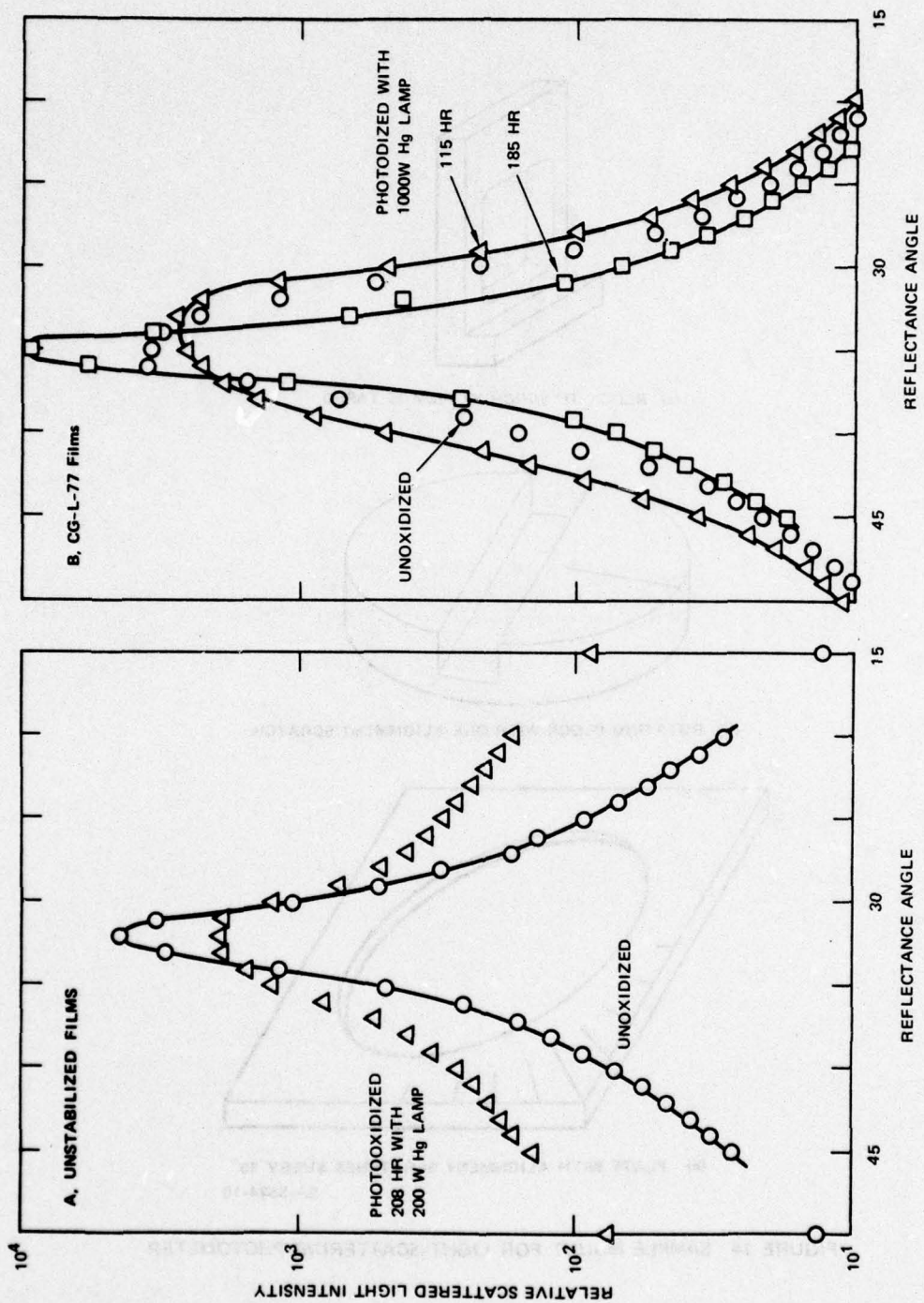


FIGURE 15 SCATTERED LIGHT FROM PP FILMS AT 30° INCIDENCE ANGLE

6. PHYSICAL CHANGES

6.1. Contact Angles

Photooxidation of a polymer is expected to lead to changes in its surface properties and may lead to significant changes in the surface wettability. Fox and coworkers³¹ examined changes in contact angle for various polymer films at differing degrees of photooxidation. They found that the contact angle changed as the polymer was irradiated and that the amount of change depended on both the polymer and the wetting liquid.

We measured contact angles to see if this technique could be useful in monitoring the photooxidation induction period of unstabilized PP films. Water was used as the first wetting liquid, and the measurements were made on a Rame-Hart Model A-100 NRL Contact Angle Goniometer. The measured angle for unirradiated unstabilized PP film was 100 degrees and the angle for a piece of this film that had been irradiated for 6.5 hours (run 4, Table 1) was 97 degrees. The 3 degree difference is too small to use contact angles as a measure of the degree of PP oxidation when water is the wetting liquid.

In a second effort, unoxidized films were compared with a film that had had a longer exposure to the same lamp (28 hours, Run 6, Table 2), and a syringe was used to ensure uniform drop sizes. Contact angles of water on two different pieces of unoxidized PP film were 99.5 and 95 degrees. The angle on the photooxidized film was 94 degrees; thus, the angle changes when the film is photooxidized but at this level of oxidation, the change is small and is comparable to differences among films, often due to surface roughness. We conclude that angle changes are not sensitive enough to follow our PP photooxidations.

Glycerol and n-hexadecane were also examined on a piece of unoxidized PP film to determine their usefulness as wetting agents. Glycerol tended to give irregularly shaped drops with variable contact angles. n-Hexadecane gave flat drops that had a small contact angle and were difficult to measure accurately. Water gave the most consistent results and had the largest contact angle of the three liquids. Water should therefore exhibit the largest angle change when polar groups are introduced into the PP film, but this change is not large enough.

6.2. Dielectric Measurements

When PP is photooxidized, nonpolar bonds are converted to polar carbonyl and hydroperoxide bonds. These changes should be accompanied by changes in the conductivity and dielectric properties of the films.

Dielectric measurements have been used to examine oxidized polyethylene³² and PP films.^{33 35} For polystyrene films, it is reported that photooxidation can be followed more easily by dielectric measurements than by oxygen uptake.³⁶ Changes were observed in all three films as they oxidized but it is not clear how early in the oxidation these changes occurred.

Dielectric measurements on thin films can be made either by the liquid displacement technique³⁷ or by a parallel plate cell fitted with a guard ring. In a serious effort to obtain some useful measurements at low extents of oxidation, we tried both techniques, but neither was sensitive enough for our purposes. Our results are described in the two subsections below.

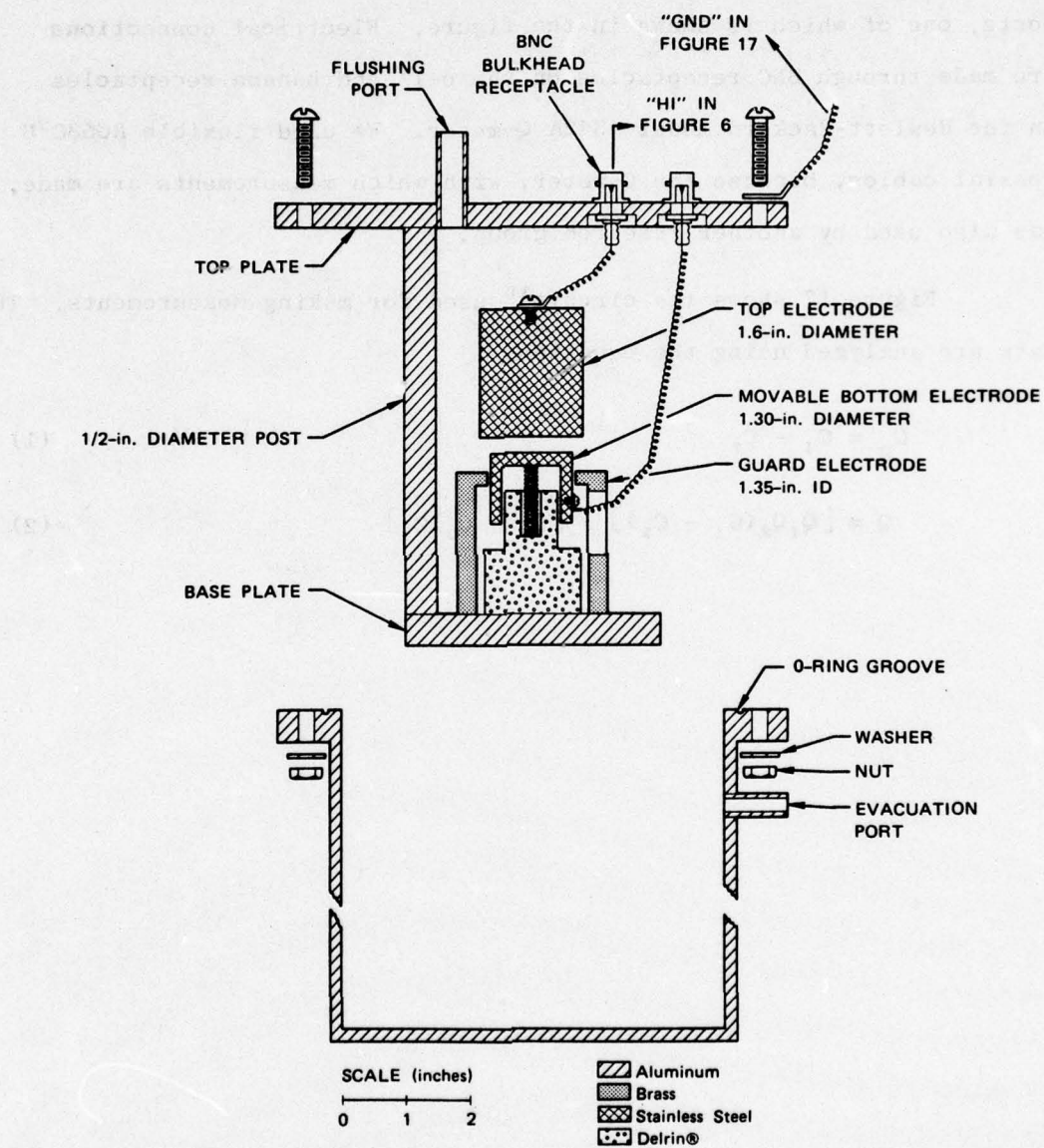
6.2.1. Parallel Plate Cell.

The design of our spring-loaded parallel plate cell^{36,38} is shown in Figure 16. The cell can be fitted into a cylindrical can for evacuation or, if necessary, for operating under an inert gas. The base plate is attached to the top plate by three 0.5-inch-diameter posts, one of which is shown in the figure. Electrical connections are made through BNC receptacles on the cell and banana receptacles on the Hewlett-Packard model 4342A Q-meter. We used flexible RG58C/U coaxial cables, because the Q-meter, with which measurements are made, was also used by another research group.

Figure 17 shows the circuit³⁹ used for making measurements. The data are analyzed using the equations

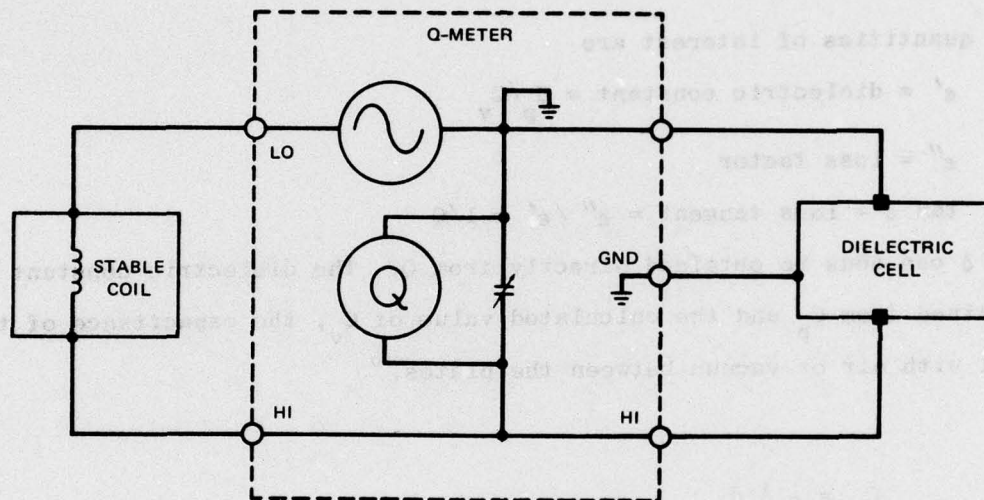
$$C_p = C_1 - C_2 \quad (1)$$

$$Q = [Q_1 Q_2 (C_1 - C_2)] / [Q_1 - Q_2) C_1] \quad (2)$$



SA-3374-21

FIGURE 16 SPRING LOADED CELL FOR DIELECTRIC MEASUREMENTS



■ = BNC Connections

○ = Banana Connections

Q-METER = Hewlett Packard Model 4342A Q-Meter

STABLE COIL = Boonton Radio Corporation Type 103A Inductors

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FIGURE 17 CIRCUIT FOR DIELECTRIC MEASUREMENTS

where

C_p = effective parallel capacitance of cell

C_1 = measured capacitance of a stable reference coil

C_2 = measured capacitance of the cell and the coil in the parallel circuit of Figure 6

Q = Q value of the cell

Q_1 = measured Q value of a stable reference coil

Q_2 = measured Q value of the cell and the coil in the parallel circuit of Figure 6

The quantities of interest are

$$\epsilon' = \text{dielectric constant} = C_p / C_v \quad (3)$$

$$\epsilon'' = \text{loss factor}$$

$$\tan \delta = \text{loss tangent} = \epsilon'' / \epsilon' = 1/Q \quad (4)$$

$\tan \delta$ can thus be obtained directly from Q . The dielectric constant is obtained from C_p and the calculated value of C_v , the capacitance of the cell with air or vacuum between the plates.⁴⁰

$$C_v = \epsilon_0 A/d \quad (5)$$

where

$$\epsilon_0 = 0.0885 \text{ pf/cm}$$

A = area of the smaller parallel plate

d = distance between plates

The parameter of greatest interest is $\tan \delta$ because it, as well as ϵ'' , is expected to increase rapidly as PP is oxidized.⁵

Qualitative dielectric measurements were made on oxidized and unoxidized PP films. The purpose of these experiments was to estimate the usefulness of dielectric loss measurements at our low levels of film oxidation.

Several unoxidized samples were cut from Ciba-Geigy lightly stabilized PP film (Code CG-Feb 77-1 in Table 2). The oxidized film was from Run 12, Table 2. Film thicknesses were 0.104 ± 0.003 mm (0.0041 ± 0.0001 inch). The film samples were stored in a vacuum desiccator for several days before being measured. Measurements were made at ambient temperature in normal room air. No conductive layers were applied to the film surfaces; the films were merely placed between the stainless steel electrodes of the cell shown in Figure 16.

The values for C_2 and Q_2 were determined with a piece of PP film between the two electrodes. The values for C_1 and Q_1 should be determined with the top electrode disconnected from the BNC receptacle. For any further studies, a switch⁴¹ should be installed between the top electrode and the BNC receptacle. For these experiments, we found that when we placed an insulating block (1.9 cm high) between the two electrodes, we obtained the same C_1 and Q_1 values as when we physically disconnected the top electrode.

Table 6 shows the C and Q values measured on the Hewlett-Packard Q-meter. C_p , Q, $\tan \delta$, and ϵ' values were calculated from equations (1) to (4). For film thicknesses of 0.104 mm, equation (5) gives $C_v = 72.8$ pf. Correction for fringing at the guard gap⁴⁰ changes C_v by less than 0.5 pf. The accuracy of the values obtained leaves much to be desired, and the numbers are regarded as being merely indicative. At low frequencies (80 kHz and 124 kHz), the Q values of the films and the block were the same to within 0.5 Q units, which is the accuracy of the meter in this range. Thus, $\tan \delta$ values are 10^{-5} or less. The C_p values were less for oxidized than for unoxidized films. At high frequencies (3.5 MHz and 22 MHz), measured values depended on the position of the coaxial cables and of nearby objects. These values thus contain considerable error.

Table 6

DIELECTRIC MEASUREMENTS^a ON LIGHTLY STABILIZED PP FILMS

Sample ^a	Frequency (Hz)	Measured		Calculated			
		C (pf)	Q	C _p (pf)	Q	tan δ	ϵ
block	80 k	286	120	--	--	--	--
III	80 k	109.5	120	176.5	--	--	2.42
IV	80 k	99.5	120	186.5	--	--	2.56
oxidized	80 k	120.5	120	165.5	--	--	2.27
block	124 k	221	162.5	--	--	--	--
I	124 k	49.5	162.5	171.5	--	--	2.36
II	124 k	40	162.5	181	--	--	2.49
III	124 k	45.5	162.5	175.5	--	--	2.41
IV	124 k	39.5	162.5	181.5	--	--	2.49
oxidized	124 k	53.8	162.5	167.2	--	--	2.30
block	3.5 M	294.5	190	--	--	--	--
II	3.5 M	82	125	212.5	264	0.00379	2.92
III	3.5 M	73	122	221.5	256	0.00390	3.04
IV	3.5 M	67	118	227.5	240	0.00416	3.12
oxidized	3.5 M	71.2	120	223.3	247	0.00405	3.07
block	22 M	288	8.1	--	--	--	--
III	22 M	135	70	153	4.87	0.206	2.10
IV	22 M	135	69	153	4.88	0.205	2.10
oxidized	22 M	135	67.5	153	4.89	0.204	2.10

^a"Block" = 1.9 cm high insulating block used to measure C₁ and Q₁; "I-IV" = samples of unoxidized film; "Oxidized" = film sample from Run 12, Table 3.

Although C_p is often lower for oxidized than for unoxidized films in the low frequency measurements, the differences among blanks are greater than the effects of oxidation.

We then tried to work at lower frequency and to determine the effect of applying silver conducting paint on the films. A general Radio Type 1608A Impedance Bridge was used to make measurements at 1 kHz. We examined samples of lightly stabilized, unoxidized PP film (CG-L-77) as well as one sample of oxidized, lightly stabilized PP film (Run 12, Table 2). The five unoxidized samples had capacitances ranging from 133 to 148 pF; the oxidized film had a capacitance of 140 pF. The precision measurement for each film was about ± 3 pF. The dissipation factor, D, could not be determined with the bridge, except that it was less than 0.001. Since $Q = \frac{1}{D}$, the Q values for these films are greater than 1000.

Silver conducting paint was applied to the films in an attempt to improve the reproducibility. A circle about 1.6 inch in diameter was painted on one side of each film. On the other side was painted a circle about 1.3 inch in diameter and a ring of about 1.4 inch inside diameter. The films were dried for several days in a vacuum desiccator at room temperature. The painted unoxidized films had capacitances ranging from 154 to 163 pF, whereas the oxidized film had a capacitance of 157 pF. The precision was roughly ± 3 pF. Again, D was less than 0.001.

Thus, coating the films with silver conducting paint did not improve the reproducibility of measurement. The coated films had higher capacitances than the uncoated films, possibly because the paint filled in rough spots on the films, reducing the effective thickness.

We conclude that for the cell, Q-meter, and impedance bridge used, there is no measurable difference in dielectric constant between unoxidized and slightly oxidized PP films.

6.2.2. Liquid-Displacement Cell

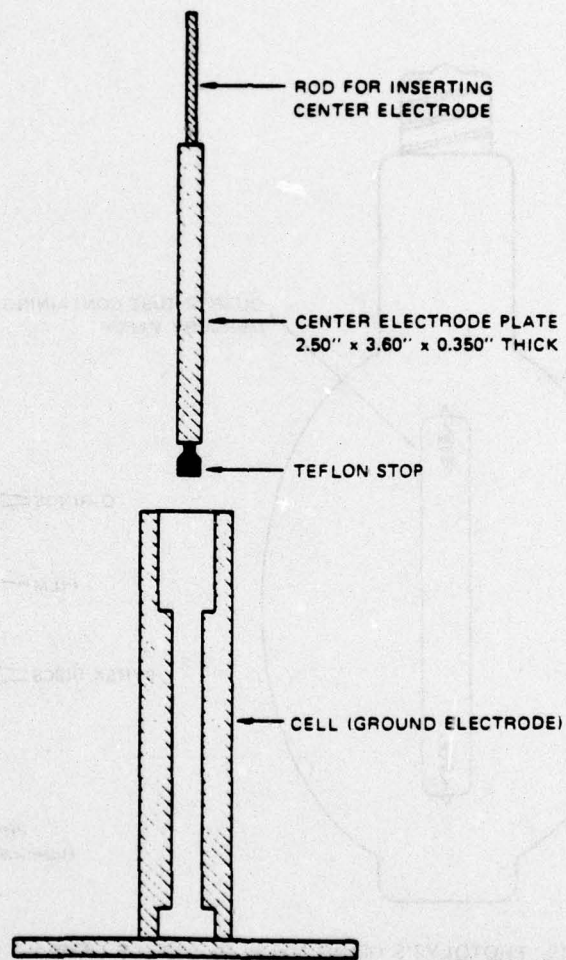
The cell used, depicted in Figure 18, was constructed of gold-plated brass with a spacing on either side of the center electrode of approximately 0.010 inch.⁴² The cell will hold two 2.5 inch x 3.6 inch films, one on each side of the center electrode. Smaller films can be used, although the measurements will be less accurate.

The liquid used in the cell was Dow Corning 200 fluid, a dimethyl-polysiloxane with 1 cs viscosity. Measurements were made at 1 kHz using an ESI (Electro Scientific Industries) Model 290A Impedance Bridge and an ESI Model 860A AC Generator-Detector. With this apparatus, capacitance can be measured to five significant figures and D can be obtained down to ± 0.0002 .

For best accuracy, measurements should be made using a pair of identical films, one placed on either side of the center electrode. The films should be slightly larger than the area (2.5 inch x 3.6 inch) of the center electrode or as close to this size as possible.

Our usual photolysis assembly (Section 4.1) uses one 2-inch diameter film. To obtain a pair of larger, oxidized films, we constructed several Pyrex photolysis cells. These cells consisted of a pair of 4-inch diameter 1/4-inch thick Pyrex discs held together by a pair of 6-inch OD x 3 1/4-inch ID aluminum rings. A 3-inch diameter film was placed between the discs, along with two concentric O-rings. The inner O-ring held the film in place; the outer O-ring was greased to maintain cell pressure.

To oxidize the films, we placed them in the cells under 760 torr of oxygen and photolyzed them 9 inches from a General Electric H1000 A36-15 1000W mercury street lamp. Two cells can be irradiated simultaneously, as shown in Figure 19. Periodically, the cells were opened,



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FIGURE 18 SIDE VIEW OF ASTM LIQUID DISPLACEMENT DIELECTRIC CELL

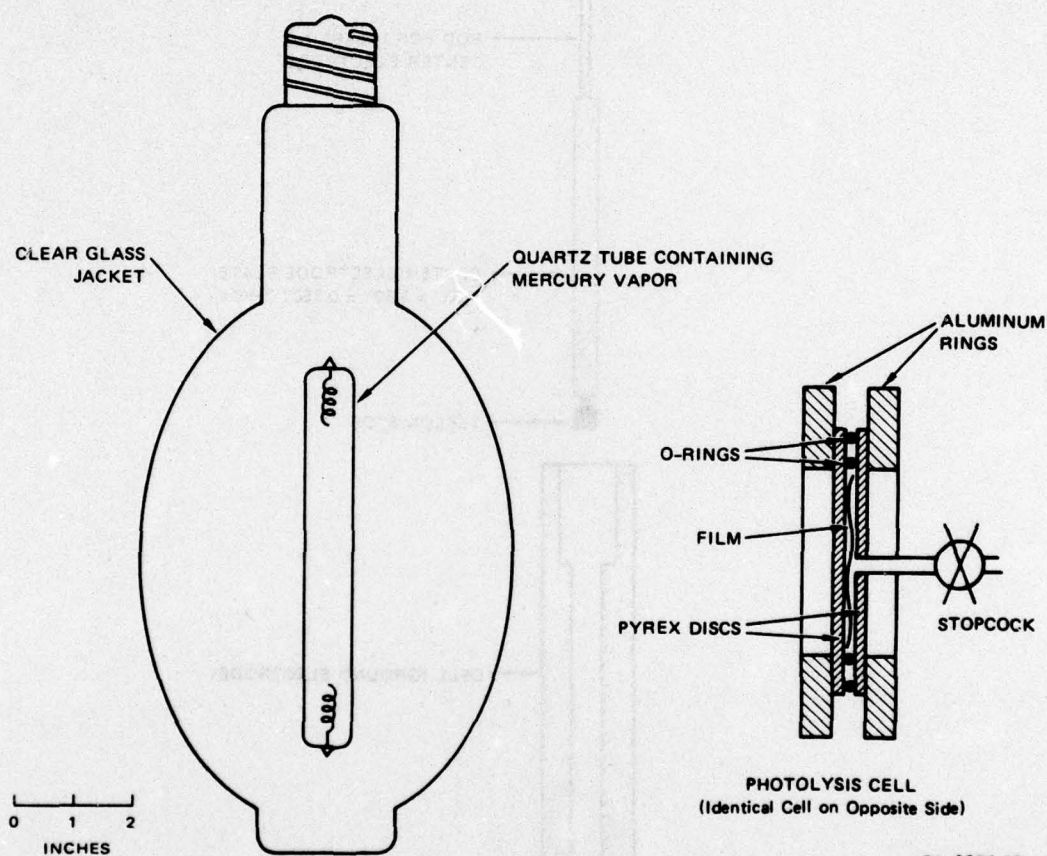


FIGURE 19 PHOTOLYSIS USING 1000W Hg STREET LAMP — Roughly to Scale

a small piece of film cut off, and an infrared spectrum taken. CG-L-77 PP films were irradiated. The first film tested was irradiated for a total of 134 hr, at which time it was brittle and had pronounced carbonyl and hydroperoxide absorbance in the infrared. This film was used in the TPP test for hydroperoxides (Section 4.4).

A pair of films was then irradiated. After 101 hr of irradiation, there was a slight hissing noise (indicating oxygen depletion inside the cell) when the cells were opened, although no carbonyl or hydroperoxide absorption was observed in the infrared. After 125 hr irradiation, we again heard the hissing noise when we opened the cells but observed no carbonyl or hydroperoxide absorbances in the infrared. The irradiation was stopped at 125 hr so as not to oxidize the films too heavily.

Pieces of 2.2-inch x 2.3-inch film were cut from each of the oxidized films. Pieces of the same size were cut from unoxidized PP for use as controls.

Series capacitance, C , and dissipation factor, D , were measured for the cell filled with air, with fluid, and with fluid plus film. The capacitance varied with temperature, so that the fluid alone was measured between each measurement of fluid plus film.

The equations used for analyzing the data were obtained from Reference 37. The actual plate separation, d , was obtained from

$$C_{\text{air}} = 2 A N / d$$

where $A = \text{plate area} = 2.50 \times 3.60 = 9.00 \text{ in.}^2$

$$N = 0.2250 \text{ pF/in.}$$

The measured capacitance of the cell filled with air, C_{air} , was 418.05 pF, giving a plate separation of 0.009688 inch.

Table 7

LIQUID DISPLACEMENT DIELECTRIC MEASUREMENTS ON PP FILMS

Film Code	Oxidation	Temperature C	C _{fluid} (pF)	ϵ' _{fluid}	d _{film} (inches)	C _{fluid + film}	(pF) ϵ' _{film}
CG-M-77	{ none	20.5	946.36	2.2638	0.00414	939.48	2.2421
		20.8	946.06	2.2630	0.00419	939.87	2.2438
		21.2	945.80	2.2624	0.00414	938.78	2.2403
CG-L-77	{ none	21.5	945.42	2.2615	0.00413	939.45	2.2427
		22.0	944.99	2.2605	0.00402	938.47	2.2394
		125 hr 1000W lamp					

To obtain the dielectric constant of the fluid, ϵ'_{fluid} , we used the measured capacitance of the cell filled with fluid, C_{fluid} , and the equation

$$C_{\text{fluid}} = \epsilon'_{\text{fluid}} \frac{2 NA}{d}$$

The dielectric constant of the films, ϵ'_{film} , was obtained from

$$\epsilon'_{\text{film}} = \epsilon'_{\text{fluid}} + \left[C_{\text{fluid} + \text{film}} - C_{\text{fluid}} \right] \frac{Ad}{A_{\text{film}} d_{\text{film}} C_{\text{air}}}$$

where

$C_{\text{fluid} + \text{film}}$ = measured value of cell containing fluid plus films

A_{film} = measured area of a piece of film =
2.2 x 2.3 in.²

d_{film} = measured film thickness in inches

The results of the liquid displacement measurements are given in Table 7. Within the instrumental reading error, the D values were the same (0.0026) for the cell containing fluid and the cell containing fluid plus films. The dielectric constant of the oxidized film is not very different from that of the unoxidized samples.

We conclude that the reproducibility and accuracy of the liquid-displacement cell are much better than those of the spring-loaded cell. However, the capacitance (dielectric constant) changes on mild oxidation are not large enough to measure the extent of oxidation. The changes in the Q value are too small to be observed with the instruments available to us.

6.3. Electrical Conductivity

The specific conductivity of poly(ethylene oxide) is nine orders of magnitude greater than that of polyethylene.⁴³ It therefore seemed possible that chemical changes during the IP in the photooxidation of

PP would lead to useful changes in electrical conductivity. However, the experiments described in this section show that slight photooxidation of stabilized PP has no measurable effect on the conductivity of PP film. Some details follow.

Conductivities were measured by placing films, roughly 2 inches in diameter, in the dielectric cell shown in Figure 17. To ensure electrical shielding, we placed solder wire in the O-ring groove of the cell. Coaxial cables were used between the cell, a 300V battery, and a Keithley 610A electrometer.

The electrometer was used to measure current flow through the circuit. The conductivity can be calculated from the current, the voltage, the film thickness (0.0040 in.), and the electrode diameter (1.30 in.).

We did not wash the films with solvent⁴⁴ nor did we coat them with layers of conducting materials.⁴³ Since the presence of water vapor has a large effect on conductivity, we stored the films overnight in a vacuum desiccator before use. After placing a film in the dielectric cell, we evacuated the cell for more than one hour before connecting the battery to the cell and performing the measurements. Because of leakage through the electrical connectors, the cell could be evacuated to a pressure of only 0.5 torr.

We measured two CG-L-77 PP films, one was unoxidized and the other had been photooxidized for 185 hr with the GE 1000W lamp.

Conductivities decreased with time after voltage had been applied.^{43,44} Two minutes after voltage application, both films showed a current flow of about 5×10^{-13} A corresponding to conductivities of $2 \times 10^{-18} \text{ ohm}^{-1} \text{ cm}^{-1}$. This value is about that expected for polypropylene.⁴³

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