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NATIONAL BUREAU OF STANDARDS REPORT

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WEATHERABILITY OF PLASTICS
CONTROLLED-ATMOSPHERE TESTS OF PLASTICS FILMS

by

William F. Brucksch, Jr.

Sponsored by

Manufacturing Chemists' Association, Inc.

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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Controlled-Atmosphere Tests of Plastics Films

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I. Introduction

The subject of this report is a controlled-atmosphere exposure test. Plastics films of various types are confined in Pyrex vessels and exposed to light rich in ultraviolet. The gaseous atmosphere in the vessel is provided artificially, hence the name "controlled-atmosphere." This makes possible a study of known atmospheric components such as oxygen, ozone, water, nitrogen dioxide, sulfur dioxide, and sulfur trioxide. Small added amounts of these components can be injected to a known atmosphere and the effect evaluated.

Experiments with a few plastics and with a few specific gaseous contaminants are described.

This work was done at the National Bureau of Standards. It is part of a program on the subject "Weatherability of Plastics". The project objectives of this study are as follows:

A. Show which environmental factors determine the weatherability of plastics.
    1. Show the relative importance of each factor.
    2. Show the interaction of factors in different types of plastics.

B. Develop methods to reduce the time scale required for evaluation.

C. The ultimate aim is to develop improved methods of evaluating and predicting weatherability.

II. Discussion

A. Experimental

1. Apparatus

The device for exposure testing is designed to provide intense light on a sample of plastic film. The unit consists of an array of sample chambers mounted equidistant from a central light source on a circle of 8" diameter. Twelve individual film samples can be tested as one time. The "atmosphere" in each sample chamber can be provided at will. The whole device is fitted into a cylindrical chamber which has an exhaust blower at the bottom to remove ozone-containing air (Figure 1).

a. The Light Source

The light source is a mercury arc photochemical lamp[1,2,3]. This choice was made to provide most intense radiation in the visible and ultraviolet region of the spectrum and least intense in the infrared. Characteristics of the arc are as follows: Hanovia 673A, 550 watt, 145 volts, 4.4 amperes, arc length 4.5 inches. The lamp is powered by a ballast, reactive transformer core and coil, Hanovia 20651-1. Output of the lamp (radiated energy in watts over the spectral range) is provided by the manufacturer.[4]

The tubular light source is mounted vertically, inside a pyrex condenser. The condenser is chilled by refrigerated water at 17 °C, circulated continuously. Outside and a little beyond the condenser, the sample tubes were mounted. With this arrangement radiation from the lamp[2,3,5] is modified (1)

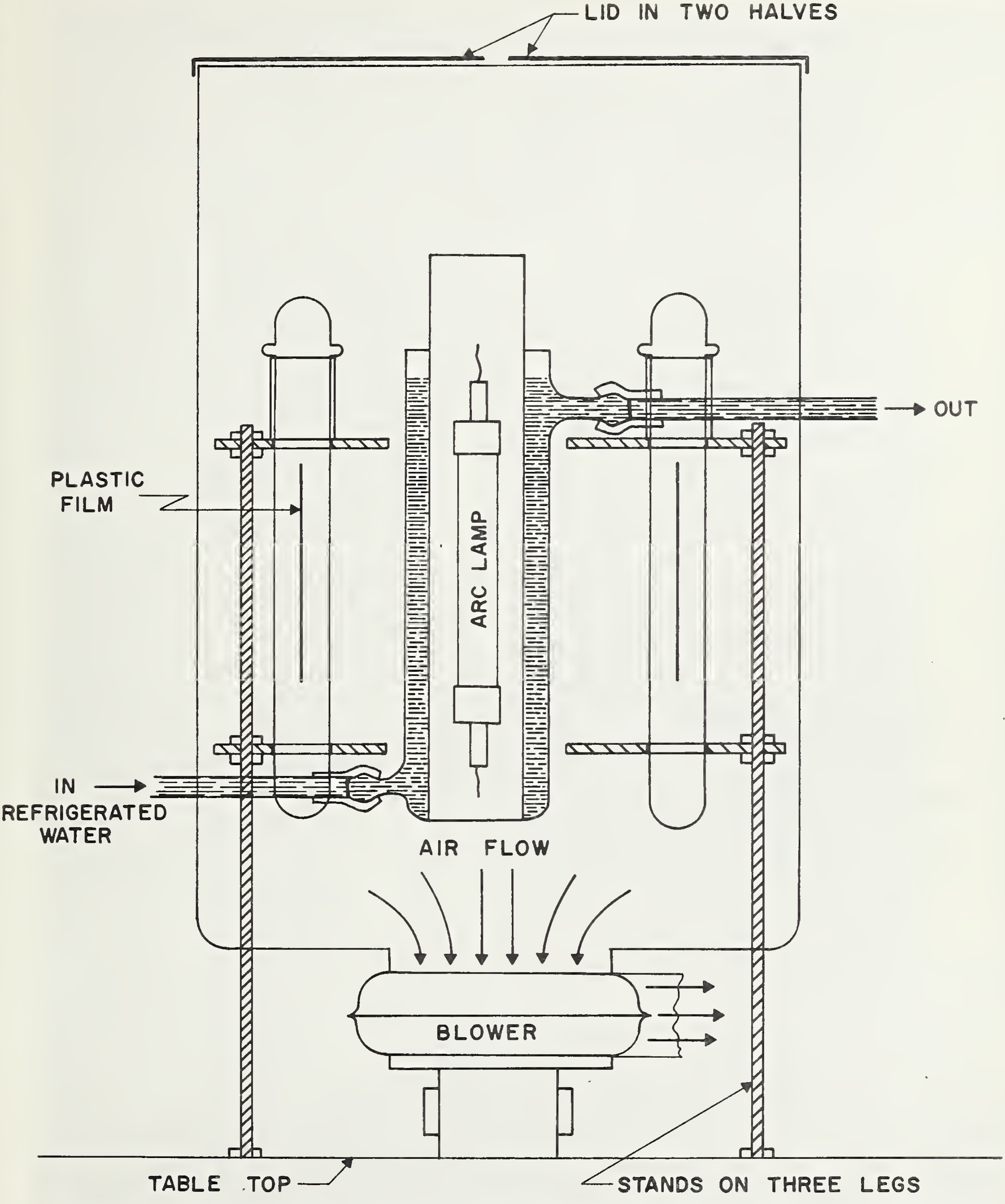

Figure 1. Apparatus for controlled-atmosphere testing. Plastic film samples were mounted in pyrex chambers; two are shown.

to remove infrared energy by passing through a "wall" of water 1 cm in thickness and (2) to limit transparency below 2900Å by passing through three layers of borosilicate glass (Pyrex)[3], two on the condenser and one on the sample chamber. The reason for filtering-out infrared energy is to avoid overheating the plastic film sample. Refer to the discussion of film temperature in the Appendix. The purpose of using radiation within the atmospheric limits, with emphasis on the ultraviolet, is to match incoming light to the spectral sensitivity range of many plastics.[6,7]

b. The Plastic Film Sample Chamber

The sample chamber which holds the mounted plastic film, is a transparent pyrex enclosure (Figure 2). The sample is enclosed to permit variation in the chemical content of the "atmosphere". The aim is to observe the effect of light on the film, as a function of "atmosphere". The atmosphere could be static or dynamic.

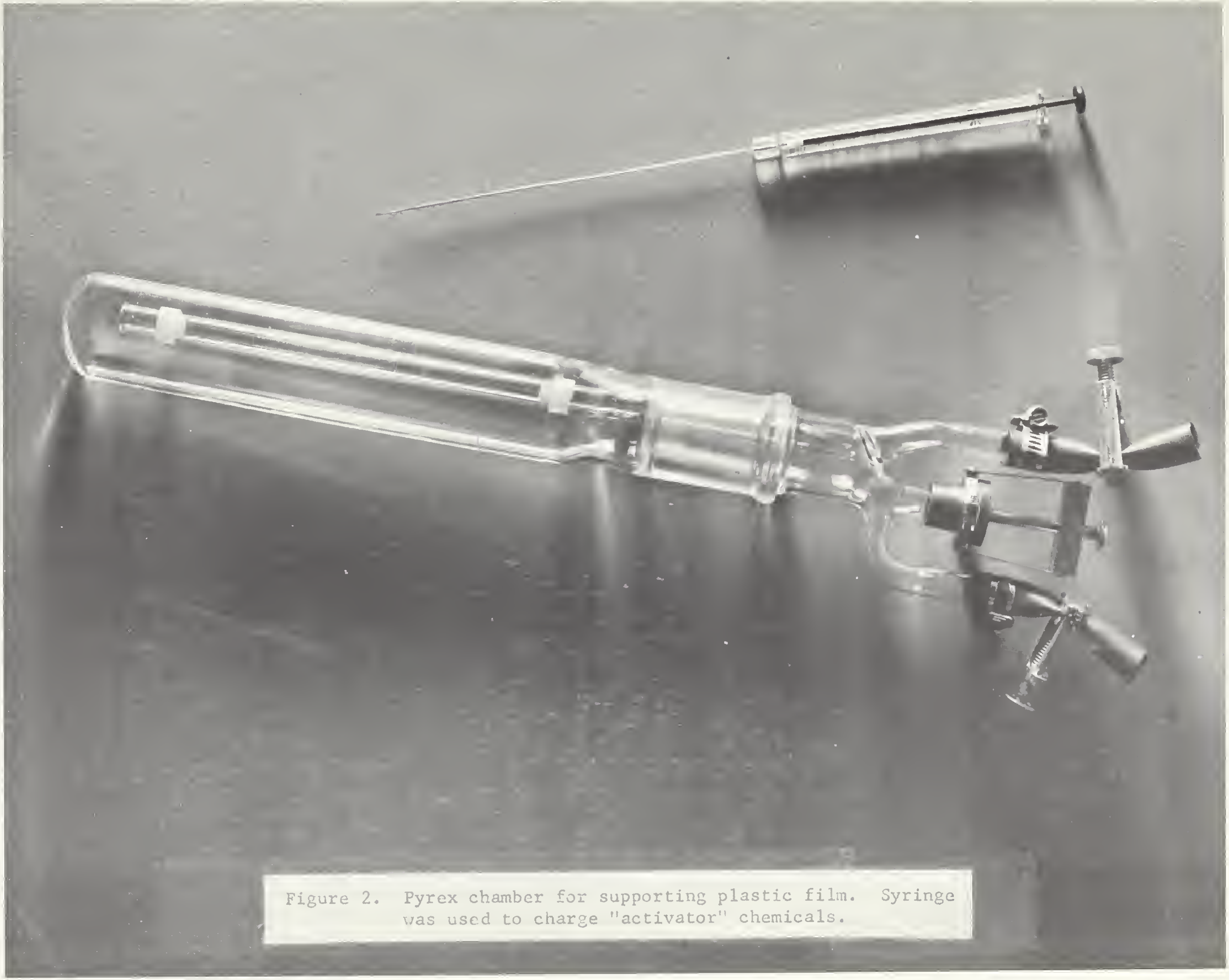

Figure 2. Pyrex chamber for supporting plastic film. Syringe was used to charge "activator" chemicals.

The original intent was to provide continuous flow of gas through the chamber. Actually, only ozone (ozonized oxygen) has been handled in this manner. In all other cases the vessel was purged with gas, sealed, then charged with "activator" chemicals by syringe.

The sample chamber was cylindrical in cross-section. Later in the study flat-walled vessels were adapted. Although these are more fragile, optical transmission is higher over the area of the film sample and more uniform.

Each chamber has an inlet tube, coaxial, to the bottom and an outlet tube near the top for purging and filling with gas. The sample of film, 1-1/8" x 5" was stretched inside the tube vertically against the inlet tube. Film was held top and bottom by Teflon sleeves. The film was planar. The distance from the plane of the film to the light source was 3.3".

The following were improvements made in chamber design. The purpose was to make the procedure more reproducible and to permit analysis of the gaseous contents. Also, reactive materials and components were replaced, to attain inertness to chemical attack and to radiation.

a. Flexible tubing on inlet and outlet ports was used to connect vessels in series, for charging with oxygen or helium.

Tubing of fluoroelastomer (PLV tubing, Pelmor Laboratories, Inc.) was used to replace flexible PVC (plasticized). The PVC was unsatisfactory on the basis of dissolving "activator" gases (SO_2, NO_2, Br_2).

Fluorocarbon elastomer components, tubing and stoppers, were pretreated. The purpose was to minimize reactions which might consume or be a source of carbon dioxide:

1. Residual alkaline polyamine vulcanizing agent might combine with CO_2 to form a solid carbonate.
2. Calcium carbonate filler, a compounding agent, might react with acid to form CO_2.

Tubing was boiled in aqueous hydrochloric acid, then boiled twice in distilled water, then dried thoroughly at 60 °C. The tubing was stiffened slightly by the treatment.

The stoppers were not so treated since it was necessary to maintain a resilient quality for needle puncture.

b. Flexible tubing was fastened onto inlet and outlet glass tubes by miniature worm gear clamps (Chemical Rubber Company).

c. In a similar manner, it was necessary to change stoppers through which chemicals were injected by needle syrings. Stoppers of fluorocarbon elastomer appeared to combine inertness to chemicals and to intense untraviolet light. The change to fluorocarbon (Viton 458 black S-42, West Company) was made after unsuccessful trials of natural rubber and of butyl rubber. Butyl rubber was cracked in UV light exposure in a stream of ozonized oxygen after only thirty minutes. Elastomer stoppers were used "as received" to preserve resilience. Earlier, stoppers were treated in boiling aqueous HCl (see under "a") but the material was hardened severely.

d. One undesired source of CO_2 in the sample vessel was from oxidation of material other than the plastic film. The adhesive used to fix the film in place was a source of CO_2 generated linearly from zero time. The adhesive was replaced by mechanical clamps. Thereafter, the blank (polystyrene film in oxygen) held zero value for at least seventy (70) hours.

e. Clamps were made from inert fluorocarbon (Fep Teflon) tubing, selected to fit over the inside glass tube snugly. A short cylinder was cut in half from the side and from the top, in the form of a chair. Two clamps were placed along the tube 5" apart. The film was fastened by clamp at both top and bottom, held against the glass.

f. One change was made which eliminated two sources of leakage:

   1. A button of teflon was pressed mechanically against the needle-puncture zone of the stopper (Figure 3). The button was removed when ever a sample of gas was withdrawn, then replaced at once.

   2. The mechanical device used a yoke around the stopper, ensuring a close fit on the glass tubing. There were several instances where leakage was noted and the yoke was not screwed tightly around the stopper.

g. Frequency of sampling from the chamber was reduced from once in 24 hours to once in 100 hours.

h. Fluorocarbon lubricant (KEL-F No. 90 Grease, 3M Company) was used to replace silicone on the ground joint.

i. Ports at the head of the sample chamber were relocated. The stopper port was placed closer to the vessel and aligned vertically so that a long needle (5" length) could pass through to the chamber below.

j. SO_2 gas was charged by syringe more precisely by using a dilute (1%) "solution" in helium.

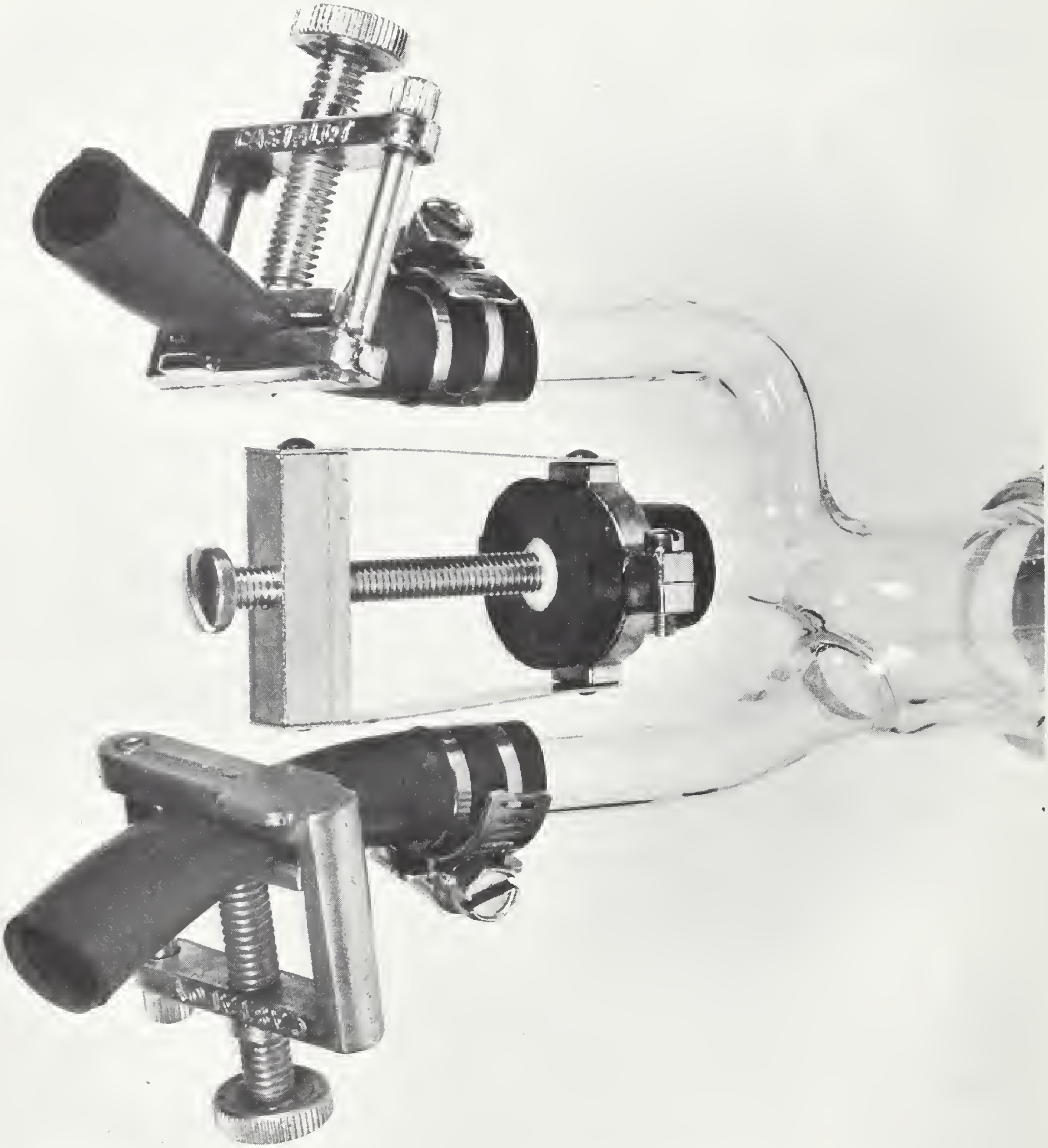

Figure 3. Head of plastic film chamber, showing yoke and button to minimize gas leakage.

2. Materials

A variety of plastics has been accumulated for "controlled-atmosphere" testing. Most are in the form of thin films, where possible in one mil thickness. Thin, transparent films were used for the rollowing reasons:

1. To provide large surface/volume ratio. Surface effects are of first importance in weatherability.
2. For easier observation of infrared and UV spectra.
3. To detect brittleness readily.
4. To observe discoloration

3. Procedure

An experiment in controlled-atmosphere testing consists of the following steps:

1. Affix the plastic film in place inside the pyrex sample vessel.
2. Connect the vessels in series, using short lengths of "Viton" tubing. Flush with the gas desired, at one atmosphere pressure from a cylinder.
3. Close off individual traps by screw clamps one inch beyond the "Viton" - pyrex joint.
4. Inject the desired "activator" gas by hypodermic syringe, either through the wall of the "Viton" tubing or through a bottle stopper (Fisher 3-225), or disconnect a "Viton" tube momentarily to charge $H_2 SO_4$ (containing SO_3) by eye dropper.
5. Install twelve sample tubes in the exposure can and start the lamp.

6. After exposure, the gases are analyzed by gas chromatography to measure the carbon dioxide, water and other gases evolved or absorbed during exposure.
7. Observe samples for discoloration or brittleness. Take the infrared absorption spectrum.

B. Results

This report describes some of the results from controlled-atmosphere experiments with plastics films. This is a continuation of earlier work, which showed the pronounced activity of certain atmospheric agents (SO_2, NO_2, SO_3). Photoactivation by the presence of added halogen was considered also. Details and conclusions from these preliminary experiments are listed in the appendix. Refer to Tables II-VIII, inclusive.

The objectives of work since were the following:

1. To adapt some of the reactions (above) to "Early-Detection-of-Failure" tests.
2. To re-examine the reactions with ozone in continuous-stream gas flow experiments.
3. To establish a connection between oxidation and SO_2-activated reactions in light.
4. To seek a method for photo-oxidation more applicable broadly to plastics.
5. To examine the reactions of hydrolysis of whole plastics and of components.
6. To improve the method of radiation-exposure testing plastics films, seeking better control of temperature of the substrate.

1. Photo-Oxidation Experiments

a. Photo-Oxidation in Oxygen Alone

Polystyrene film reacted slowly with oxygen during the exposures to light. Increased carbonyl content, onset of brittle quality and appearance of anions[8] in the film surface were noted after 130 hours exposure (Figure 4).

b. Photoactivation by SO_2

The pattern of reactivity of a plastic film could be seen in a series of short exposure tests, as follows:

1. Polystyrene film was not very reactive in oxygen alone. It was very reactive in the added presence of sulfur dioxide (Figure 5).

   The degree of oxidation was proportional to the concentration of sulfur dioxide (Figure 6).
2. Light was necessary for the reaction in (1). Even in the presence of sulfur dioxide there was no reaction in the dark in the oven at 50 °C (Figure 7).
3. The effect with added sulfur trioxide in oxygen was like that with sulfur dioxide in oxygen (Figure 8).
4. The effect of oxidation was like that produced by ozonized oxygen. (Figures 12, 13 and 14).

The above results were consistent with the findings that SO_2, dilute in air, reacts with oxygen:

$$SO_2 + 2O_2 \xrightarrow{h\nu} SO_3 + O_3$$

This reaction proceeds in ultraviolet light.[9,10]

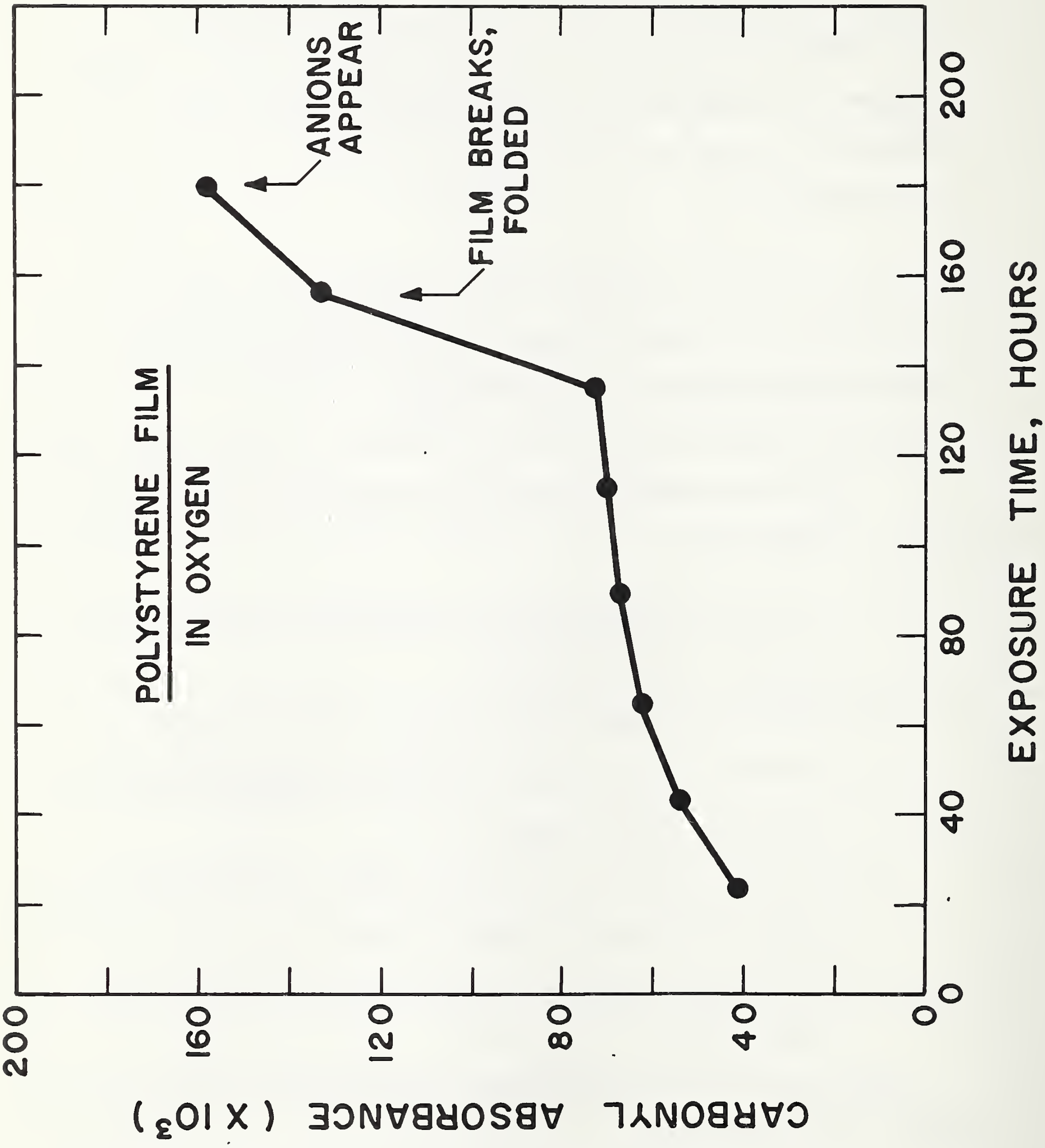

Figure 4. Irradiation of polystyrene film. Increase of carbonyl content with exposure time.

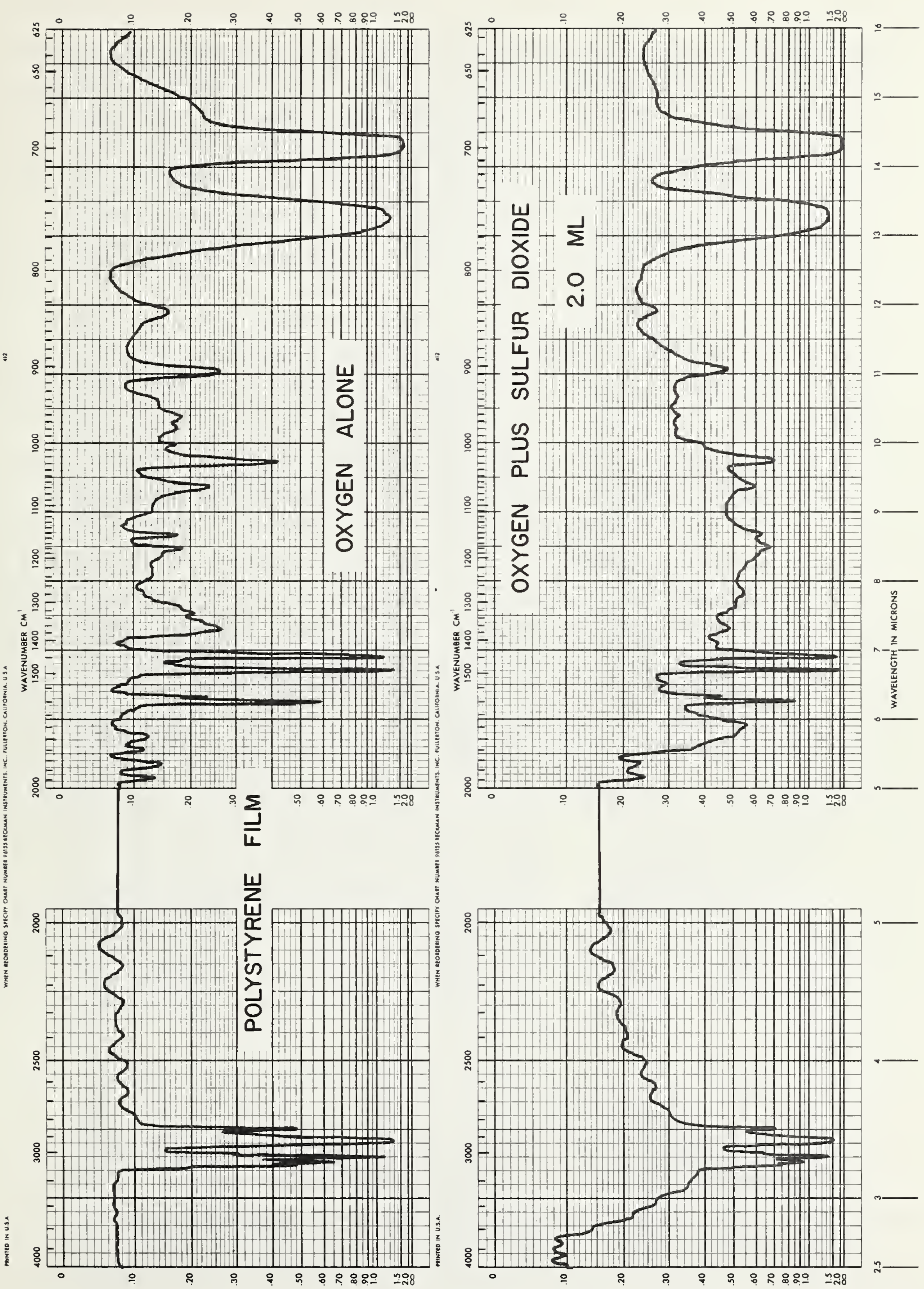

Figure 5. IR spectrum of irradiated polystyrene film. Upper curve is with oxygen (146 ml) alone, exposed 42.6 hours. Lower curve is with oxygen (146 ml) plus added SO_2 (2 ml), exposed 39.4 hours.

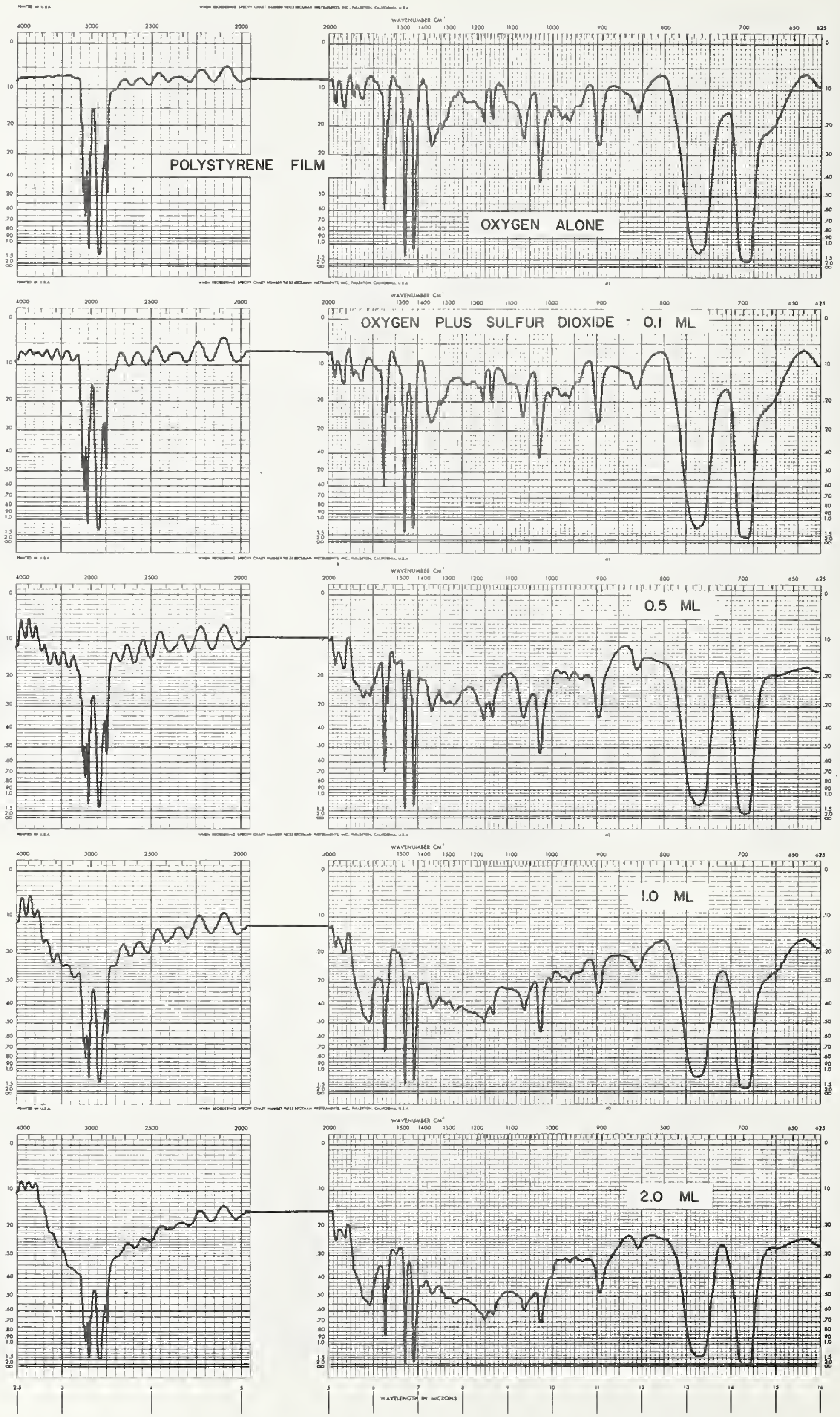

Figure 6. Progressive change in IR spectrum of irradiated polystyrene, with SO_2 charged to the vessel. All exposures were 42.6 hours except the last, 39.4 hours.

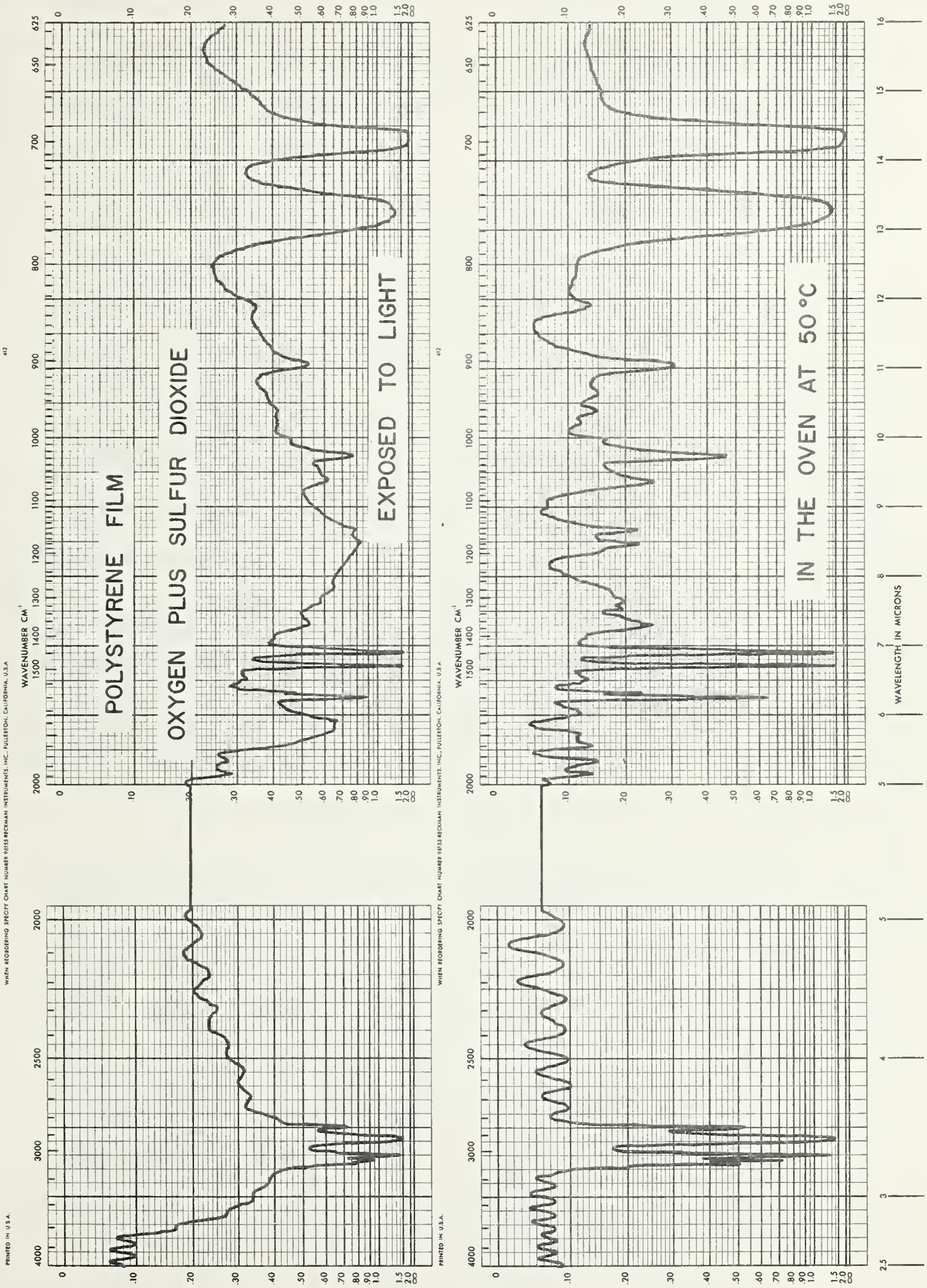

Figure 7. The effects of light on oxidation of polystyrene, "activated" by the presence of SO_2 (2.0 ml) in O_2 (146 ml). Exposure periods were 70.7 hours in light; 71.2 hours in the 50°C, oven.

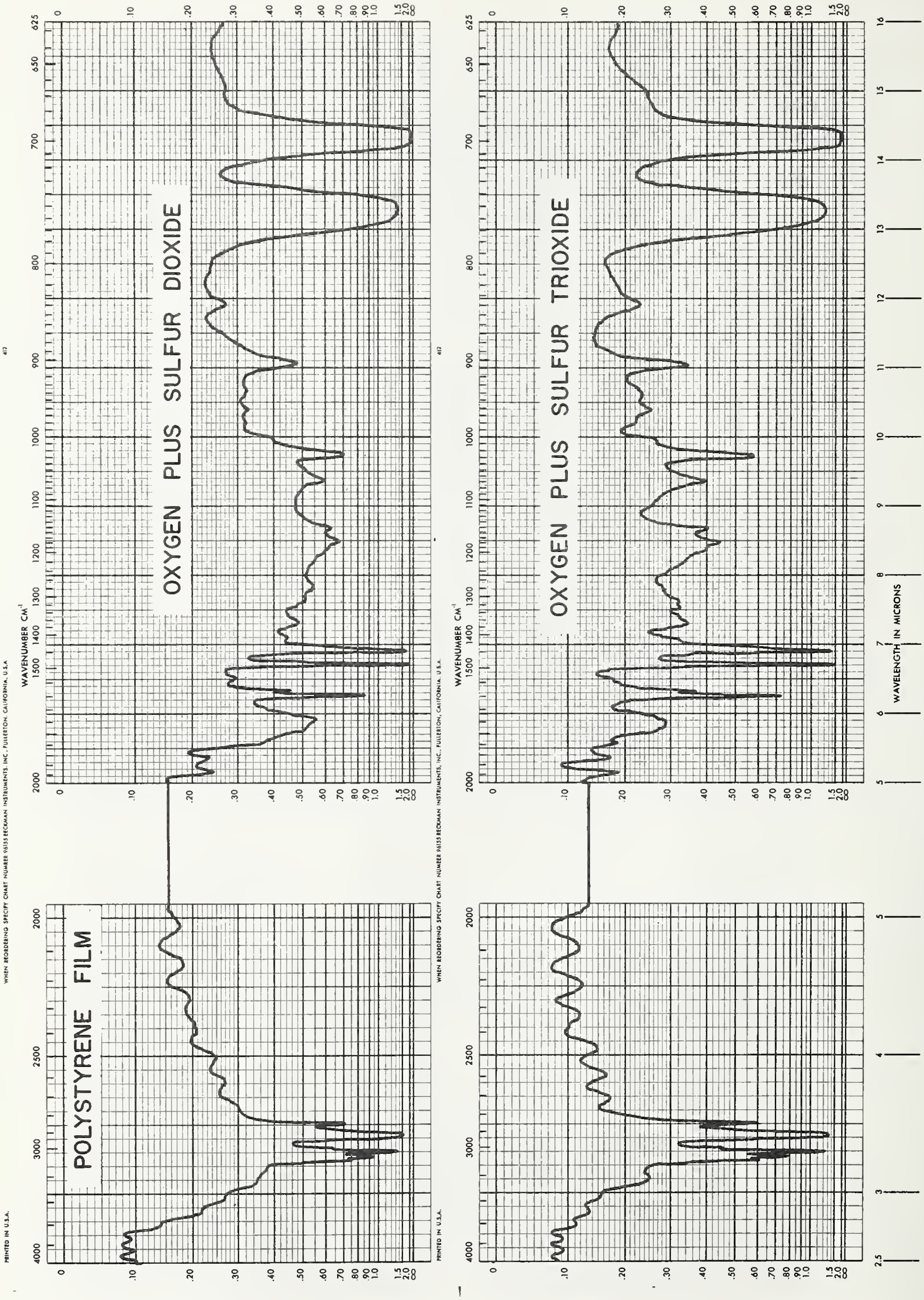

Figure 8. IR spectrum of irradiated polystyrene with SO_2 (2 ml) as "activator" (upper curve) versus SO_3 (1 drop H_2SO_4, fuming) as activator (lower curve). The carrier gas was oxygen (146 ml). Exposure periods were 39.4 and 42.6 hours, respectively.

c. CO_2 - Evolution as an Oxidation Index

Films of polystyrene in oxygen are literally "burned" in light. Carbon dioxide and water are generated, a reaction hastened by the presence of SO_2. The experiment was suited very well to the controlled-atmosphere vessel. Samples of gas were withdrawn by syringe, then fractionated in the chromatographic column. With helium gas carrier, peaks are observed for O_2, CO_2 and H_2O. This effect has been reported for asphalt[11]/and for paint[12]/films.

Here is an alternate test for oxidation index, more generally applicable to plastics. In this experiment there was no limitation to materials which are transparent at 5.8 microns, as with carbonyl in the infrared.

A few experiments were done with oxygen alone and with increased levels of SO_2. The results showed the general pattern: For exposure periods up to 100 hours, the CO_2 generated was proportional to the level of SO_2 charged (Figure 9).

For longer term exposures, results were erratic. With 0.25 ml SO_2, the level of CO_2 increased to an apparent maximum, then faltered and stepwise was decreased (Figure 10). Here multiple punctures of the stopper was the source of a serious gas leak. The first three points were reliable, usually. Since each point was determined from three samples of gas withdrawn from the chamber, three points meant that the stopper was punctured nine times. This was the limit of reliability before leakage developed.

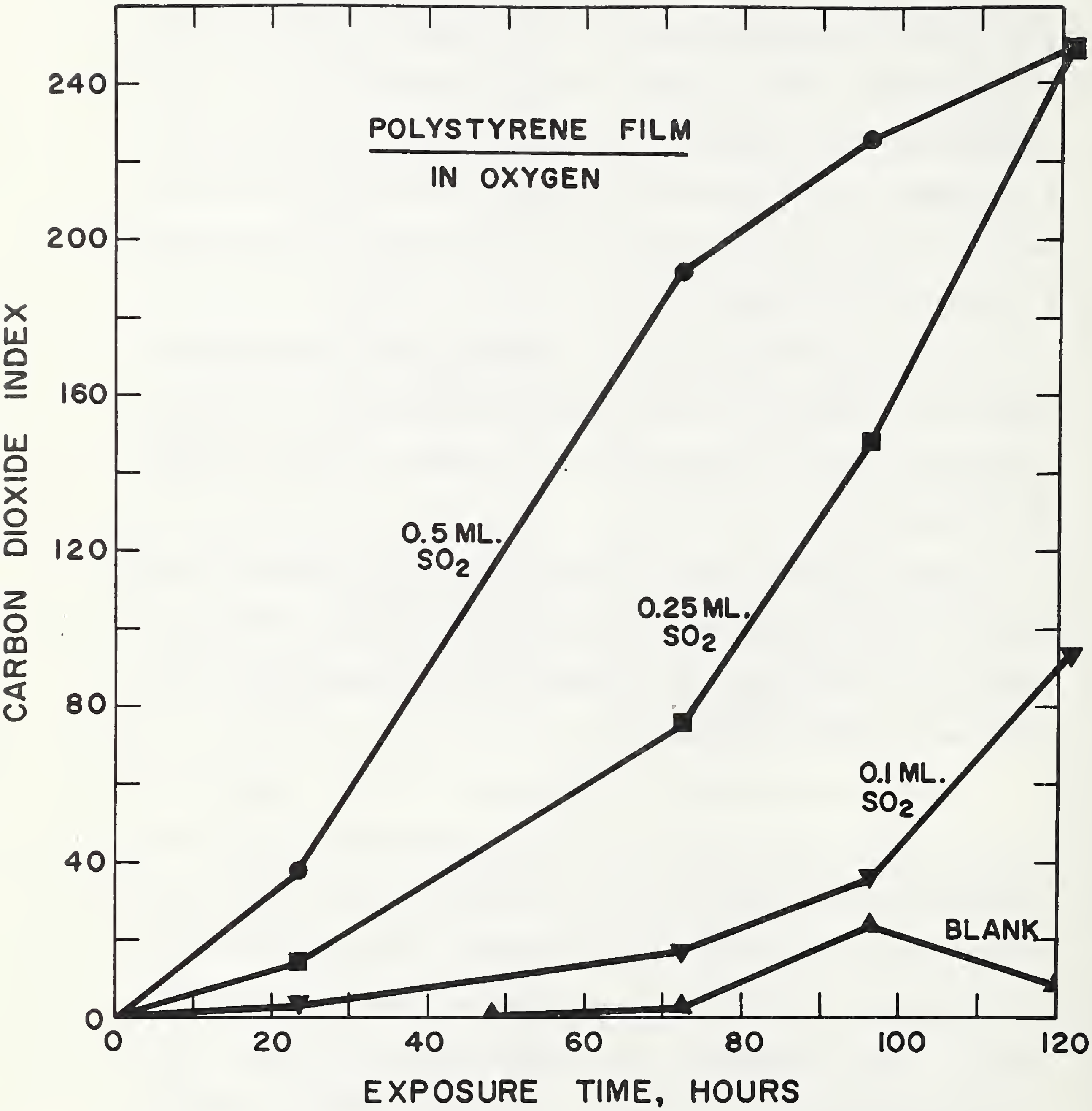

Figure 9. Irradiation of polystyrene film in oxygen (146 ml). Carbon dioxide gas generated as a function of SO_2 gas charged (at the start of exposure).

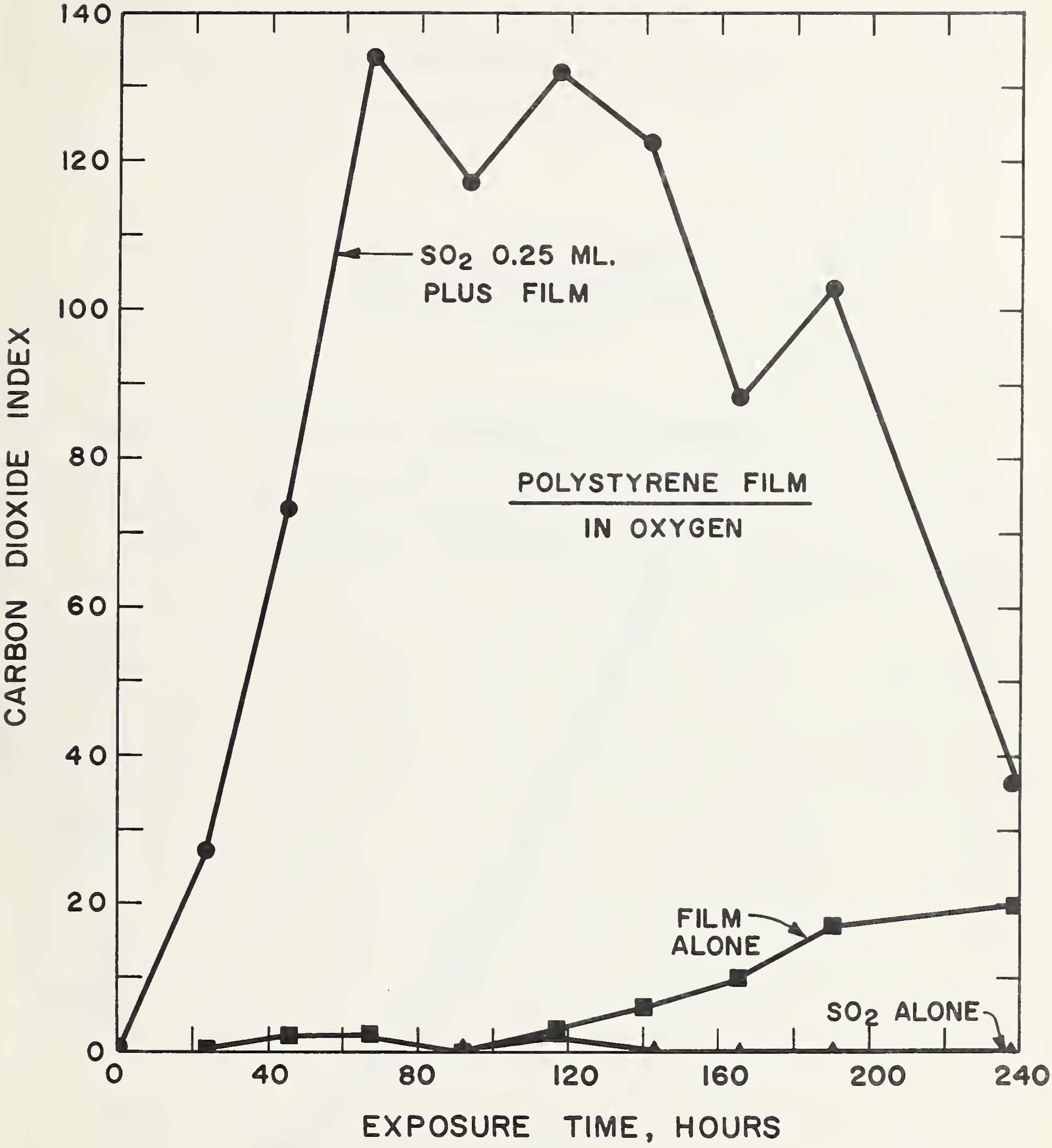

Figure 10. Irradiation of polystyrene film in oxygen (146 ml). Where SO_2 was present, film generated carbon dioxide, high values which fall away due to gas leaks.

In the same period a blank film (no SO_2) increased slowly from zero after 100 hours. With no film, but with 0.25 ml SO_2, the blank held zero for 240 hours, i.e., CO_2 was not generated in the vessel. This was done to show that CO_2 was not generated from the elastomer in the presence of SO_2.

After these experiments, changes were made to eliminate sources of leakage and improve reliability of method. Refer to the section on Apparatus, page 5.

With improved apparatus and technique it was possible to overcome the downward trend of CO_2 level (Figure 11). Note that the exposure was continued for 500 hours without down-turn. Samples were taken at intervals of 100 hours.

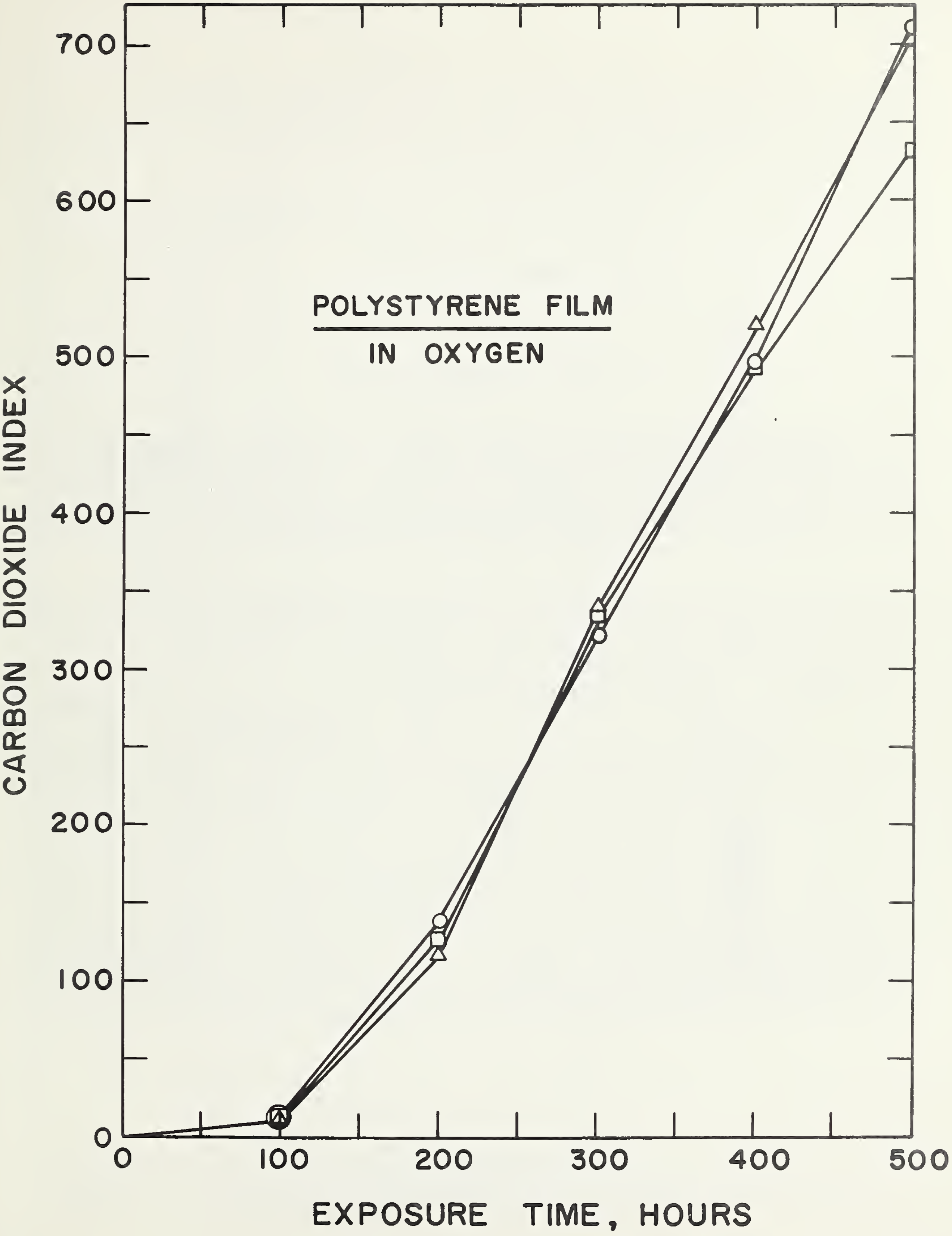

Figure 11. Irradiation of polystyrene film in oxygen. Reproducibility of experiments with improved apparatus.

d. Photoactivation by Ozone

Plastics films exposed to light were slow to react with oxygen. This was in an exposure of seventy (70) hours. The infrared spectrum of film was like the original. However, with added ozone in oxygen, oxidation of the film was observed. Polyethylene (Figure 12), polypropylene (Figure 13) and polystyrene (Figure 14) all generated

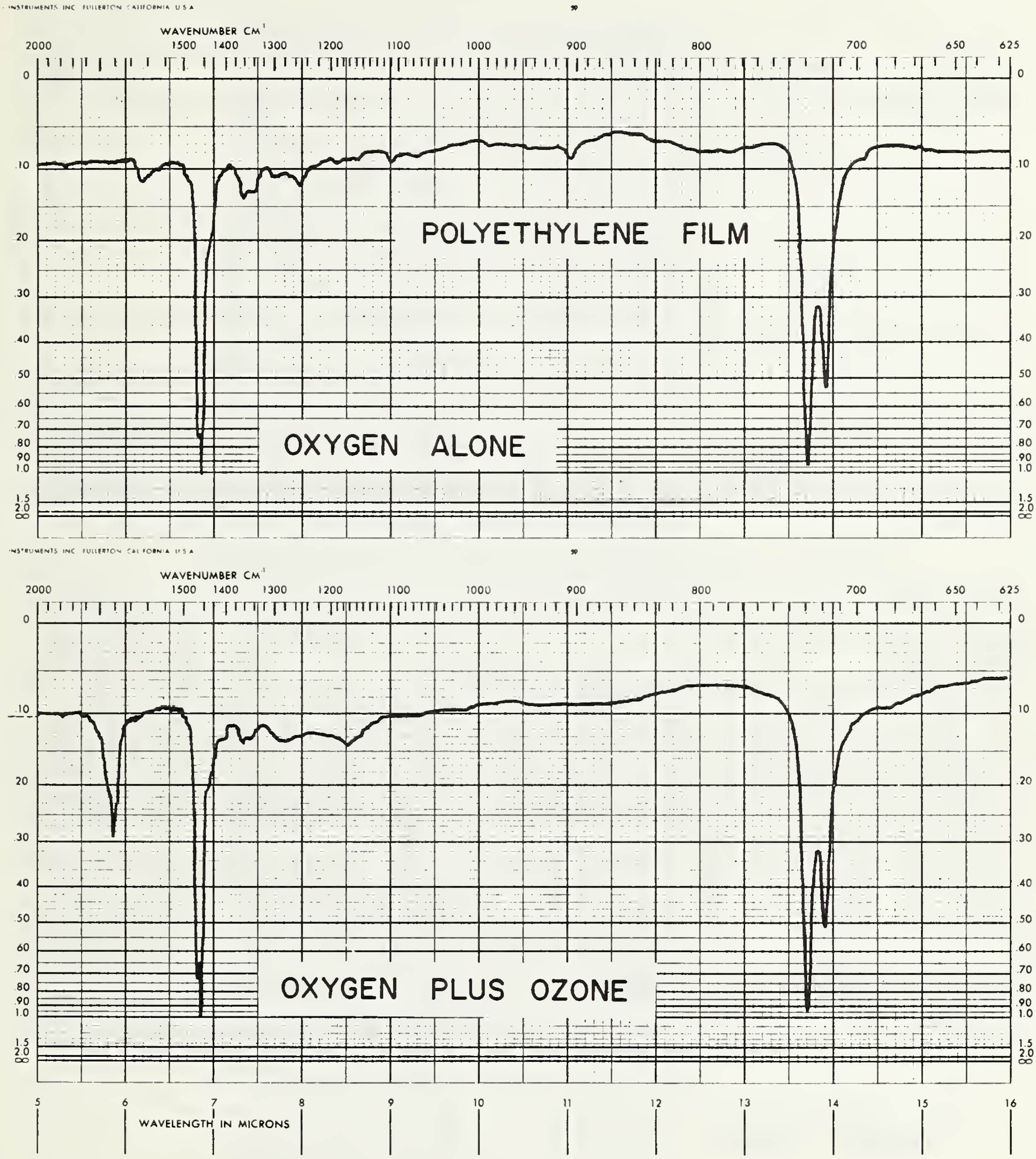

Figure 12. IR spectrum of polyethylene film irradiated in oxygen and in ozonized oxygen.

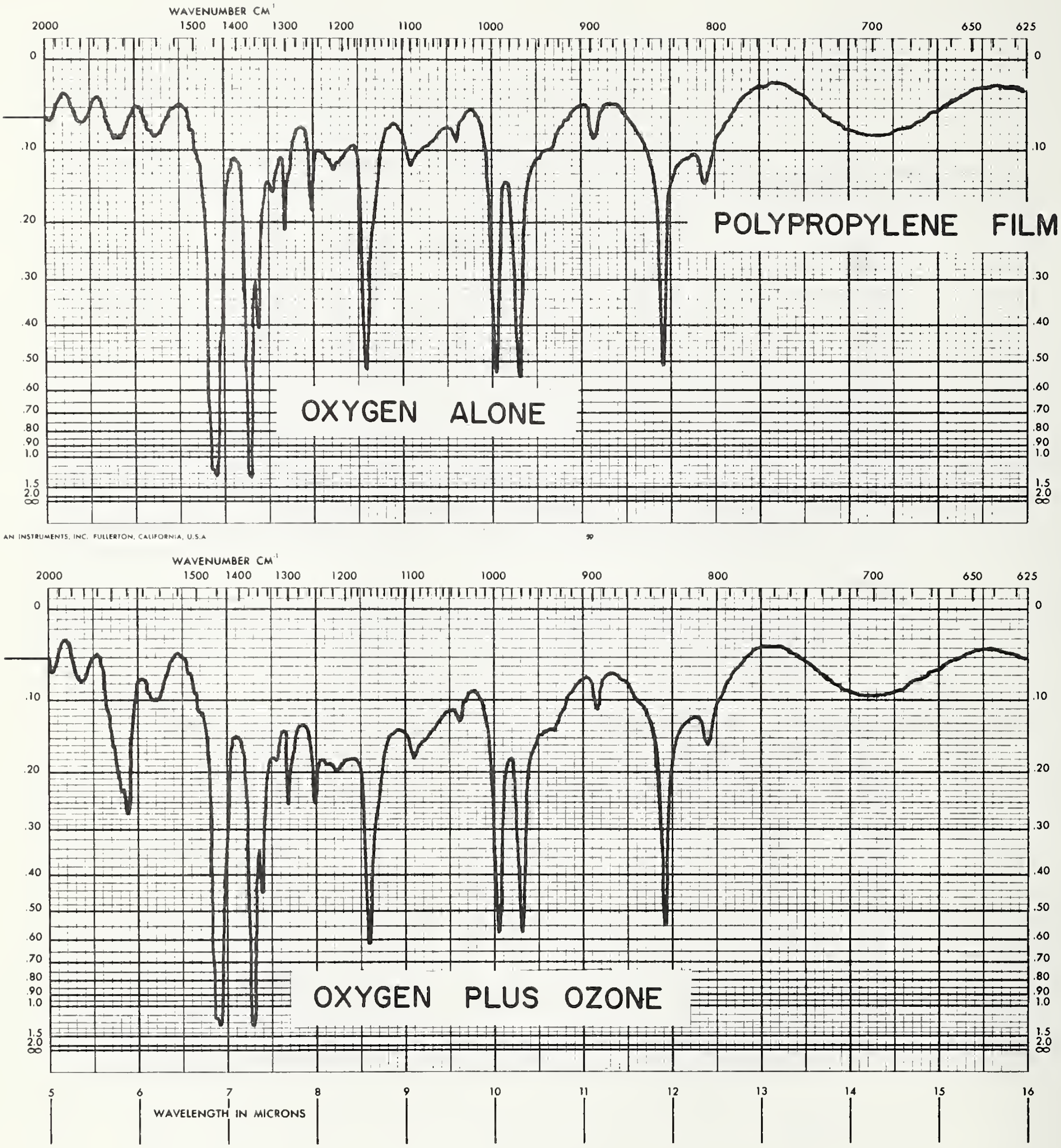

Figure 13. IR spectrum of polypropylene film irradiated in oxygen and in ozonized oxygen.

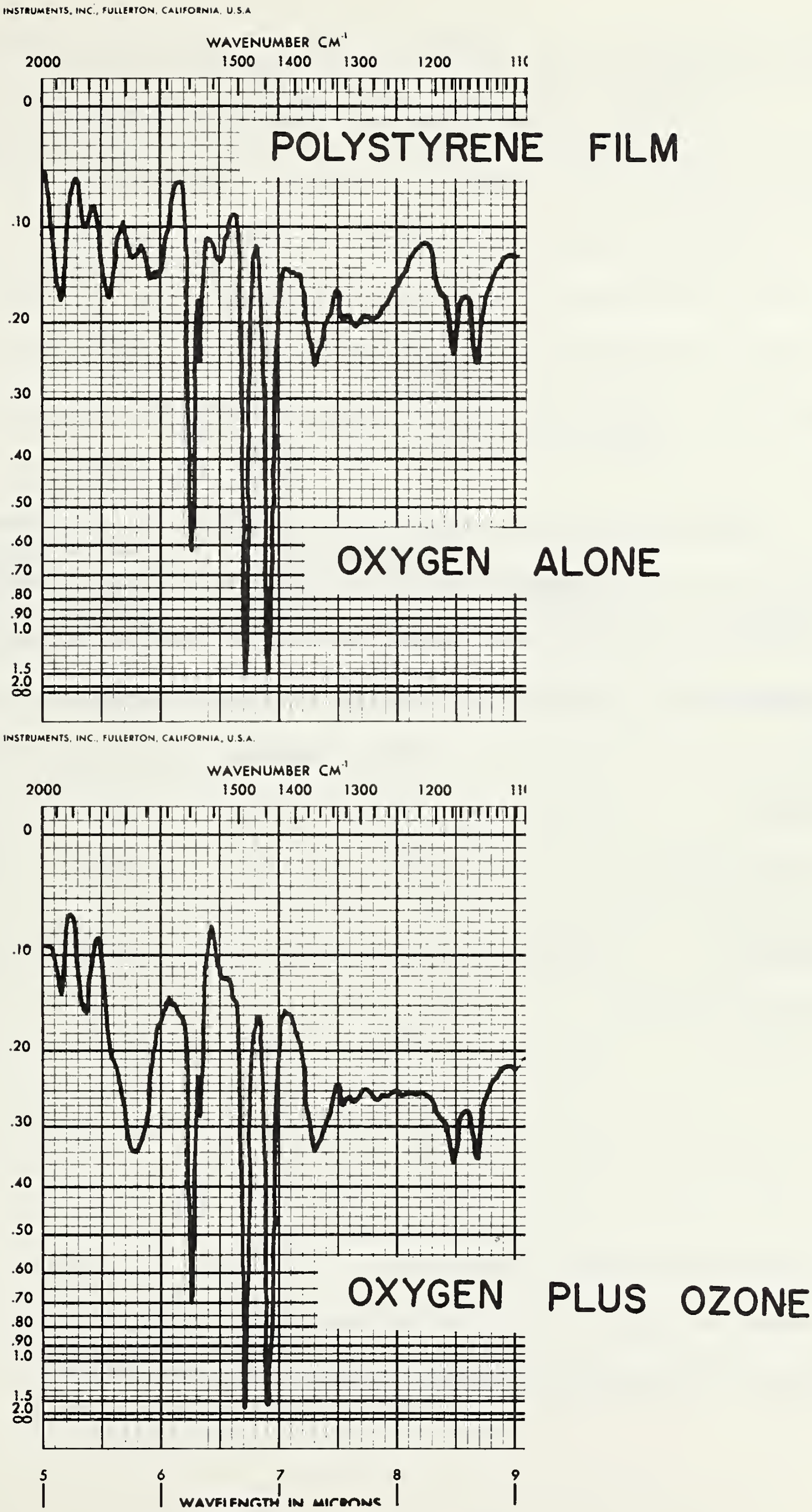

Figure 14. IR spectrum of polystyrene film irradiated in oxygen and in ozonized oxygen.

carbonyl absorption at 5.8 microns in the infrared after a similar exposure. In contrast, there was little change in carbonyl content of polyvinyl fluoride, polyvinylidene fluoride and polychlorotrifluoroethylene (Table I).

TABLE I

Exposure of Plastics Films, 70 Hours

Plastic	Film Thickness (mils)	Film Temp, Ave. °F In Oxygen	Film Temp, Ave. °F In Ozonized Oxygen	Carbonyl Absorption After Exposure In Oxygen	Carbonyl Absorption After Exposure In Ozonized Oxygen
Polypropylene	1.0	98	99	.046	.226
Polyethylene	1.0	110	102	.010	.192
Polystyrene	1.0	106	112	.099	.218
Polyvinylfluoride	1.0	110	110	.053	.055
Polyvinylidene Fluoride	1.0	113	111	.0005	.0003
Polychlorotrifluoroethylene	2.0	108	109	.058	.041

During the test, the temperature of the film in the chamber was continuously measured by thermocouple. Note that film temperatures were comparable (100 ° - 110 °F) to those which used reduced concentrations of air pollution chemicals (Table IX).

These tests were done with oxygen gas flowing continuously through the pyrex test chamber. The flow rate was 25 ml. per minute.

Two films of the same plastic were tested at once. Over the first, a stream of oxygen was passed. Thereafter, the stream was ozonized by passing through an electric discharge generator (Ozone Research and Equipment Corporation). The ozonized oxygen was then flowed continuously through the tube containing the second plastic film sample. The ozone content of the oxygen was 350 ppm.

In polystyrene, anionic sites were generated in the surface, judged by absorption of cationic dyes from solution.[8] The film showed no absorption of dye when exposed in oxygen alone for the same period. The presence of anionic sites has been noted, however, after prolonged exposure in oxygen (refer to Figure 4).

2. Experiments to Induce Hydrolysis

Certain plastics films were degraded by conditions which induce hydrolysis. The conditions necessary were the combined presence of water vapor and of an acidic catalyst.

Hydrochloric acid was a powerful catalyst; sulfurous acid H_2SO_3 (7.14% SO_2) was more moderate yet very effective.

A number of experiments used H_2SO_3 as catalyst since it is a known component of polluted air.

In cases where the acidic catalyst was a photosensitizer (SO_2), the process was accelerated by light (Figure 15). Experiments were done to show the presence of light was both necessary and critical.

The effect was demonstrated with polymeric esters and amides and also with plastics which contained ester or inorganic salt protective additives. See details in the Appendix, Tables X-XIV.

When plastics films were subjected to conditions for hydrolysis, two effects were seen: (1) If the materials were linked primarily by ester or amide groups, physical breakdown was complete. The exposed film disintegrated or became very brittle. This was true of polyamides (6 and 6-6), cellulose acetate-butyrate and polyethylene terephthalate (see Table X). Exposure was in light 69 hours, in air, in the presence of aqueous HCl, 37%, 0.28 grms. (2) If the material contained minor proportions of hydrolyzable additive (s), the effect was moderate. Exposure generated a blanched or white opaque coating (Figure 16).

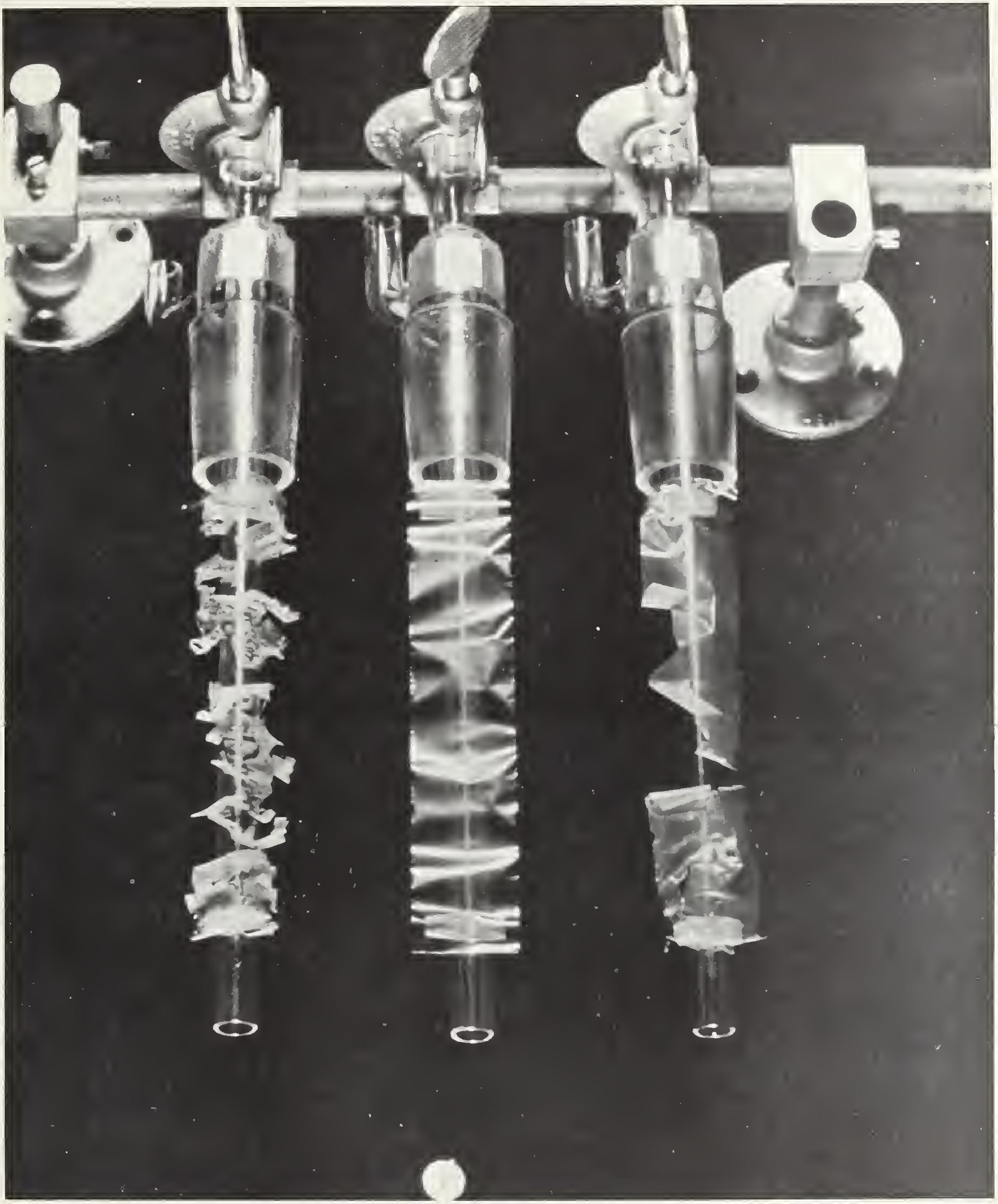

Figure 15. Hydrolysis of poly (hexamethylene adipamide), 1 mil thickness, in air:

Film	Added H_2SO_3 Gm.	Exposure	Hours
1 (left)	0.28	light	68.2
2	0.28	oven 50°c	67.8
5 (right)	0.055	light	68.2

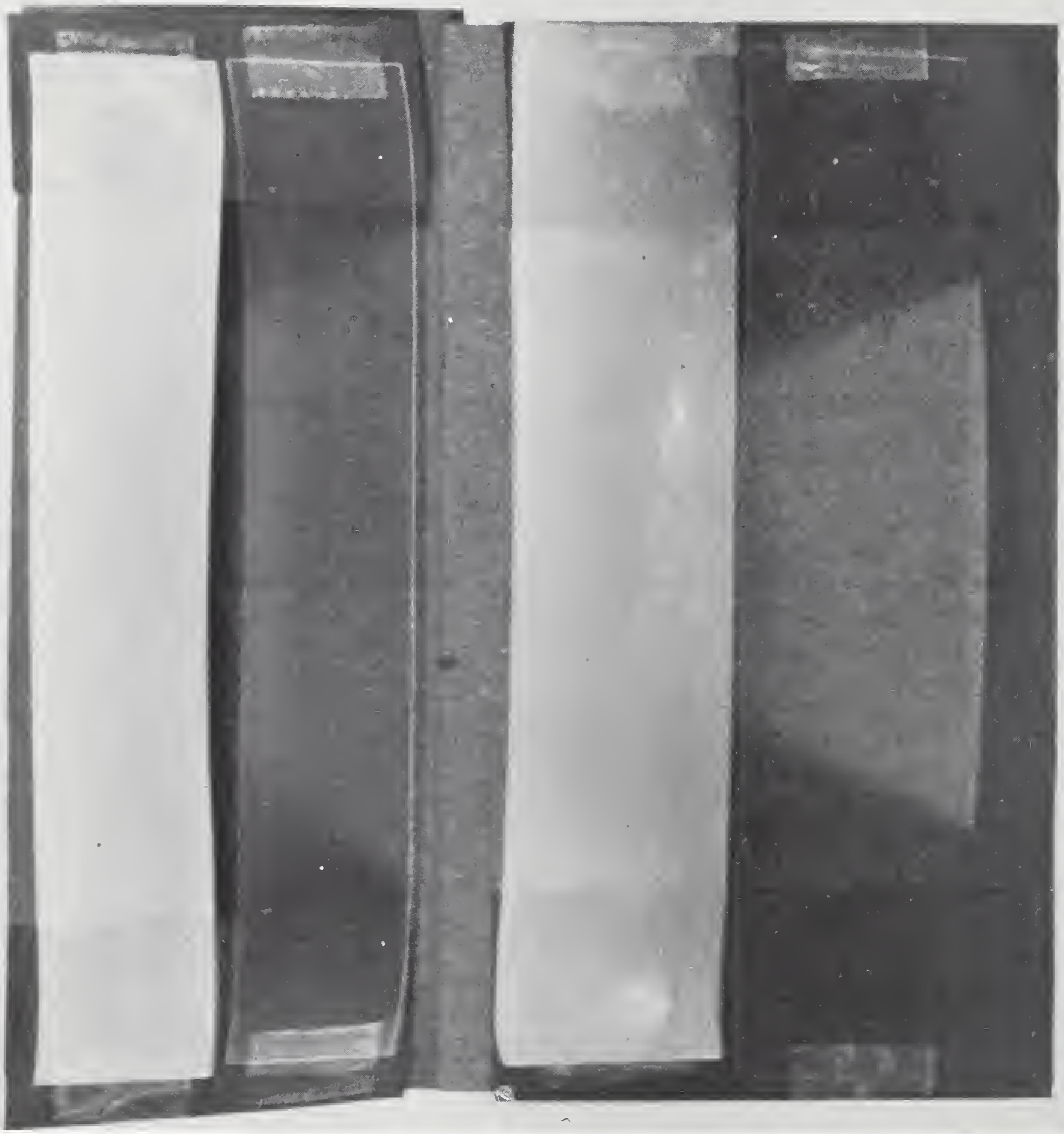

Figure 16. Hydrolysis of poly(vinyl chloride), two different rigid compounds, exposed in the presence of added H_2SO_3, 0.28 gms. Sample on left (compound B, 4 mils) shows cloudiness developed in light (70.0 hours), compared with the unexposed blank. The second pair (2 mil thickness) show an example of cloudiness developed in the oven at 50 °C, (69.5 hours), also compared with the unexposed blank.

The experiments were performed in controlled-atmosphere vessels. Films were mounted and the chemical components provided, then exposed to radiation for a short period of hours. To accelerate the effect, concentrations of acid catalyst used were larger than present in the atmosphere.

After exposure to hydrolysis conditions a remarkable effect was observed. While the vessel is still closed, the plastic films appeared to be intact. When the vessel was opened and there was some loss of water vapor, the film disintegrated within a matter of seconds to minutes. This effect was observed a number of times.

Polyamide 1 mil film was hydrolyzed by the combined action of SO_2 and water, in light. In controlled - atmosphere tests, the atmosphere within the vessel was altered stepwise to provide dry air, added water and added sulfur dioxide gas. Half the number were exposed to light and half held in the oven at 50°C.

With only one or two components or in the absence of light, the film remained intact (Table XII). When both SO_2 and water were provided, in light, the film was disintegrated (sample 4).

A rigid polyvinyl chloride compound was treated similarly (Table XII). There was discoloration (sample 11) with sulfur dioxide (as reported previously). With added water to sulfur dioxide in light (sample 12) the effect was quite different. Discoloration was less and there was a definite whitening (blanching) of the piece. The sample was more opaque. The effect of blanching without disintegration was consistent with change in a minor component.

Conditions to induce hydrolysis were tested also in other polyvinyl-chloride (PVC) compounds. In two rigid stocks, the one with barium-cadmium stabilizer was blanched. With tin stabilizer the stock remained clear. Both were subjected to light (66.8 hours) in air (146 mil) in the presence of H_2SO_3 (5 drops, 0.28 gms). It is probable that the white coating on PVC compounds could be an hydrolysis product of barium-cadmium stabilizer, the insoluble inorganic hydrous oxide. Light was not necessary for blanching in all cases. In one PVC rigid compound, whitening was produced in the oven at 50°C. in the dark 69.5 hours (Figure 16).

C. Discussion of Results

In the foregoing experiments, plastics films showed a range of chemical activity. Some were oxidized and some were hydrolyzed. In a closed vessel, these effects were accelerated by providing known atmospheric components.

These experiments can form the basis for a test method for plastics films. The test would feature radiation exposure on multiple samples each enclosed in a "controlled" atmosphere. After exposure, chemical and physical changes would be noted: in the sample and also in the content of the atmosphere. Twelve samples could be evaluated simultaneously.

Composition of the atmosphere could be made up as desired. Both major and minor constituents could be provided, at will.

Controlled-atmosphere testing permits evaluation of single and combined factors in relatively short-term tests. As such, the method can be used to assess durability to factors in the weather. Also, the tests form the basis for development of a laboratory standard test of weatherability.

The controlled atmosphere method of testing has an interesting advantage. In the laboratory device with multiple chambers, the effect of different types of weather can be observed. Whereas plastics materials will be exposed in service at different sites in different kinds of weather, it is appropriate to test the material in a variety of types of weather.

This is quite different from the usual test of weatherability. Today's weather tests consist of a laboratory exposure to a single weather pattern plus outdoor exposures: usually one at the "home" site and one or two at preferred test sites (Florida, Arizona).

III. Acknowledgment

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V. APPENDIX

Controlled - Atmosphere Experiments With Plastics Films

Conclusions From Earlier Work

First experiments with plastics films used the mercury arc as a light source. Exposure times were short (40 to 70 hours) and concentrations of activator gases were high, relatively. The conclusions of that work are set forth below:

1. Plastics reacted with oxygen alone rather slowly, too little to be detected readily.
2. In contrast, there was a pronounced reactivity of certain plastics to the air-pollution chemicals SO_2, NO_2 and SO_3 used in amount $10^4 - 10^6$ times the normal concentration (in oxygen).[13]

    With SO_2, some were discolored (polystyrene, polycarbonate, polyvinyl fluoride, polyvinyl chloride, polyvinylidene chloride, polypropylene and polyethylene).

    Some were rendered brittle (polystyrene, polycarbonate, polyethylene terephthalate, polypropylene, cellulose acetate).

    Some which were transparent in the infrared showed oxidation by the appearance of carbonyl absorption (polystyrene, polypropylene, polyethylene, polyvinyl fluoride).

    With SO_2 reactions, light appeared to be a necessary factor.

With NO_2, pale green discoloration resulted, sometimes accompanied by brittleness. In the infrared there was the characteristic absorption of the nitro functional group.

With either SO_2 or NO_2 and polystyrene, oxygen did not appear to be necessary.

With SO_3, some were discolored (polystyrene, polycarbonate, polypropylene, polyethylene, polyvinyl fluoride, polyvinyl chloride, and polyvinylidene chloride). Some reactions of SO_3 proceeded at room temperature and did not require light.

3. The perfluorinated plastics tested showed no response to oxygen-SO_2 under radiation. Nor was there any response to oxygen alone nor to ozonized oxygen.
4. Photo-oxidation rates (polyethylene, polypropylene) could be accelerated many-fold by addition of chlorine or bromine, 2.7% in oxygen. The combination of halogen, oxygen and light was necessary to produce the effect.

TABLE II

Reactivity of SO_2 and NO_2 with Polypropylene Film

SERIES III

Film Thickness, 10 mil

		Change After Exposure 63.3 Hours		
Experiment	Condition	In Color	In Flexibility	In the IR Spectrum ***
1	Blank	Colorless	* *	None
2	Helium	Colorless	* *	None
3	Static Air	Colorless	* *	Slight
4	O_2	Colorless	* *	Slight increase at 5.85 (over Exp. 3).
5	$O_2 + H_2O$	Colorless	* *	Slight increase at 5.85 (over Exp. 4).
6	$O_2 + SO_2$*	Dark color	Very Brittle	Pronounced increase at 5.85, also at 3.0 and at 7-9.
7#	$O_2 + SO_2$* $+ H_2O$	Pink-orange, Light brown	Brittle	More moderated than above, but still quite positive at 6.0, also at 3.0 and at 7-9.
8	$O_2 + NO_2$*	Pale yellow-green	Brittle	Considerable change at 5.7-6.7 (5.85, 6.15, 6.5).
9	$O_2 + NO_2$* $+ H_2O$	Colorless	* *	Effect is nullified back to exactly like oxygen. Slight increase at 5.85. Slight absorption at 6.15.

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* 17.7% By volume. Gas, 31.5 ml was connected to sample vessel 146 ml.

* * Not Brittle; turns white when bent (folded).

*** After exposure, the infrared spectrum was taken to note any changes in regions of interest:

Functional Group	Microns	Evidence of
Carbonyl	5.8	Oxidation
Hydroxyl	3	Oxidation
Nitro	6.1, 6.5	Nitration
Sulfonic	7-9(broad)	Sulfonation

\# During Expt. 7 the "U" tube containing SO_2 became disconnected. Even so, note that the sample became brittle.

TABLE III

SERIES VII, XV

Polystyrene Film With SO_2, SO_3 and NO_2

Experiment	Carrier Gas	Added Chemical	Exposure	Change After Exposure 65.2 Hours: In Color	In Flexibility	In the IR Spectrum
VII-2	Oxygen	--	Light	None	None	Very little different from the unexposed "blank".
3	Oxygen	SO_2, 2 ml	Light	Light Brown	Brittle	Pronounced changes at 3.0, 5.8, and 7-10.
4	Oxygen	SO_2, 2 ml	On shelf, 25 °C	None	None	--
5	Oxygen	SO_2, 2 ml	In oven 39 °C	None	None	Not too different from the unexposed "blank".
6	Oxygen	SO_3*	Light	Black	--	--
7	Oxygen	NO_2, 2 ml	Light	Pale Amber-green	Brittle	Differences at 5.8, 6.1 and 6.5. Also broadening in the range 7.5-13.
9	Helium	NO_2, 2 ml	Light	Pale Amber-green	None	Very much like VII-7, the only difference is at 6.1, less nitration than with oxygen.
10	Helium	SO_3*	Light	Black	--	--
11	Helium	SO_2, 2 ml	Light	Light Brown	Brittle	Considerable difference at 3.0, 5.9 and broadening at 2.7-3.2, 7-10.
12	Helium	--	Light	None	None	--
XV-9	Oxygen	SO_2, 2 ml	Light (70.7 hrs)	Light Brown	Brittle	Pronounced changes at 3.0, 5.8 and 7-10.
10	Oxygen	SO_2, 2 ml	In oven 50 °C (71.2 hrs)	None	None	Very much like the unexposed film.

*H_2SO_4 Fuming, 1 ml.

Various Types of Plastics With SO_2

The following experiments showing different plastics exposed to light in oxygen - SO_2 are listed in Series IV and V. Similar experiments but with thinner films are listed in Series VI. This table compares a few plastics showing the effect of oxygen - SO_2 versus that of oxygen alone (4,2), (5,6), (11,10), and (8,12).

TABLE IV

SERIES IV

Different Plastics Exposed to SO_2

All Vessels Contained Oxygen (146 ml), SO_2(2.0 ml)

				Change After Exposure 45 Hours		
Experiment	Material	Carrier Gas	Added Gas	In Color	In Flexibility	In the IR Spectrum
1	Polystyrene (10)*	O_2	SO_2	Very discolored (Rich orange-brown.)	More brittle	Pronounced changes at 2.9, 5.8, 7-9.
2	Polyhexamethylene Adipamide (11)	O_2	SO_2	Colorless, but blanched opaque	Crease White on folding	None
3	Poly(vinyl chloride)(B) (8.5)	O_2	SO_2	Slight (Light amber)	None	Only slight differences, 3.0.
4	Poly(vinyl chloride)(C) (10.5)	O_2	SO_2	Slight (Amber)	None	Differences at 2.8-3.3
5	Polyethylene terephthalate (10)	O_2	SO_2	Slight (Pale, amber), Surface fogged.	Crease White on folding	None
6	Polyethylene terephthalate (5)	O_2	SO_2	Slight (Amber)	None	Only slight differences at 3-4.
7	Polyethylene (10)	O_2	SO_2	Discolored (Lt. tan)	None	Pronounced changes at 3.0, 5.8, 8-10.
8	Polypropylene (10)	O_2	SO_2	Discolored (Lt. tan)	Brittle	Pronounced changes at 3.0, 5.8, 7.5-10.
9	Polystyrene (1)	O_2	SO_2	Discolored (Dark brown)	Very Brittle	Pronounced changes at 3.0, 5.8, 7-10.
10	Poly(vinyl fluoride)(4)	O_2	SO_2	Discolored (Tan color)	None	Pronounced change at 5.8, also a change at 2.9.
11	Polychlorotrifluoroethylene (5)	O_2	SO_2	None	None	None
12	Fluorinated ethylene/propylene (5)	O_2	SO_2	None	None	None

* Values in parenthesis ( ) are thicknesses (mils).

TABLE V

SERIES V

Different Plastics Exposed to SO_2
All Vessels Contained Oxygen (146 ml), SO_2(2.0 ml)

Experiment	Material	Carrier Gas	Added Gas	Change After Exposure 66.6 Hours: In Color	In Flexibility	In the IR Spectrum
1	Poly(vinyl fluoride (4)	O_2	SO_2	Discolored (Buff) Lt. brown	None	--
2	Polyethylene terephthalate (10)	O_2	SO_2	Surface fogged (slight)	Brittle on folding	--
3	Polyethylene terephthalate (5)	O_2	SO_2	Discolored yellow-white from pale green	None	--
4	Polyethylene (5)	O_2	SO_2	Discolored (Amber lt. brown)	None	Pronounced differences at 3.0, 5.85 and at 7-12.
5	Polyethylene (9.6)	O_2	SO_2	Discolored (Lt. brown	None	Some difference at 3.0, pronounced differences at 5.8 and at 7.5-11.
6	Poly(vinyl chloride) (B) (8.5)	O_2	SO_2	Discolored (Pale buff, from very pale green)	None	--
7	Polypropylene (10)	O_2	SO_2	Discolored (Pale amber)	Brittle on folding	Pronounced differences at 3, 5.85 and at 7.5-10.
8	Poly(vinyl chloride) (C) (10.5)	O_2	SO_2	Discolored (Pale buff from pale green	None	--
9	Polychlorotrifluoroethylene (5)	O_2	SO_2	None	None	None
10	Polyhexamethylene Adipamide (11)	O_2	SO_2	Blanched white from pale amber	None	--
11	Polystyrene (10)	O_2	SO_2	Discolored (Orange-brown)	Brittle	--
12	Polycarbonate (5)	O_2	SO_2	Discolored (Dark orange-brown)	Very Brittle	--

TABLE VI

SERIES VI

Light Exposures of Different Plastics

All Vessels Contained Oxygen (146 ml)
Some had added SO_2(2.0 ml)

				Change After Exposure 42.6 Hours		
Experiment	Material	Carrier Gas	Added Gas	In Color	In Flexibility	In the IR Spectrum
1	Polychlorotrifluoroethylene (2)	O_2	-	None	None	None
2	Poly(vinyl fluoride) (1)	O_2	-	None	None	Only slight changes.
3	Poly(vinyl chloride)(B)(4)	O_2	SO_2	Slight discoloration (amber)	None	Only slight changes.
4	Poly(vinyl fluoride) (1)	O_2	SO_2	Discolored (dark amber)	None	Pronounced absorption at 5.8.
5	Polycarbonate (1)	O_2	SO_2	Discolored (dark amber)	Very brittle	Pronounced changes at 3.0, 5.8-7.7, 8.8-11.7.
6	Polycarbonate (1)	O_2	-	Almost equal to original	None	Only slight changes.
7	Polypropylene (1)	O_2	SO_2	None	None	More absorption at 5.8.
8	Polyethylene (1)	O_2	SO_2	Almost equal to original	None	Only very slight absorption at 5.8.
9	Polyethylene terephthalate (1)	O_2	SO_2	None	Brittle	Broad absorption at 2.7-3.7, otherwise similar to blank.
10	Polystyrene (1)	O_2	-	None	None	Only slight changes at 5.8.
11	Polystyrene (1)	O_2	SO_2	Discolored (dark amber)	Very brittle	Pronounced differences at 2.8-4, 5.9, 7-10.
12	Polyethylene (1)	O_2	-	None	None	None

TABLE VII

SERIES IX

Discoloration by Sulfur Trioxide

Oxygen 146 ml. - $H_2 SO_4$, Fuming 1 drop

		Change in Color	
Experiment	Material	Irradiated 39.4 Hours	Overnight (21 Hrs) at R.T.
2	Polycarbonate (1 mil)	Med. umber brown	-
3	Polypropylene (1 mil)	Med. umber brown	Umber brown
4	Polyethylene (1 mil)	Med. umber brown	Greenish yellow
9	Polyethylene terephthalate (1 mil)	Colorless Clear	-
11	Poly(vinyl fluoride) (1 mil)	Dark umber brown	Deep Blue
12	Poly(vinyl chloride) (B) (4 mils)	Med. umber brown	Green
	Polyvinylidene chloride (1 mil)	-	Blue to green to dark brown

In separate experiments, polypropylene film was discolored severely at room temperature, whether in helium or oxygen. One mil film was exposed for 42.5 hours. The amount of H_2SO_4 used was greater, 2 drops.

TABLE VIII

Photoactivation by Chlorine or Bromine

Polypropylene, 1 mil

Experiment	Carrier Gas, ml	Added Gas, ml	Exposure Condition	Exposure Time (Hrs)	Carbonyl Absorption In the IR
XVI - 7	146 O_2	4.0 Cl_2	Radiation	42.1	Pronounced
XVI - 8	146 O_2	4.0 Cl_2	Oven 50°C	42.1	Slight
XV - 14	146 O_2	4.0 Cl_2	Radiation	67.1	Pronounced
XVI - 1	146 He	4.0 Cl_2	Radiation	42.1	Slight
XVI - 2	146 He	4.0 Cl_2	Oven 50°C	42.1	None
XV - 15	146 O_2	4.0 Br_2	Radiation	67.1	Pronounced
XVI - 3	146 He	4.0 Br_2	Radiation	42.1	Slight
XVI - 4	146 He	4.0 Br_2	Oven 50°C	42.1	None
XIV - 7	146 O_2	I_2 *	Radiation	44.4	Slight
XV - 16	146 O_2	I_2 *	Radiation	67.1	Trace
XIV - 12	146 O_2	-	Radiation	44.4	Slight
XIV - 13	146 O_2	-	Radiation	334.5	Slight
XV - 13	146 O_2	H_2O_2**	Radiation	67.1	Trace

* Two small crystals to provide vapor.

** Fifteen drops of 3% aqueous.

Temperature of the Plastic Film Sample

One important consideration of irradiation testing is the temperature of the sample. In nearly all of the experiments described here, air-cooling limited the temperature of the sample to no less than 100 to 115 ^{o}F, usually nearer to 110 ^{o}F. This condition prevailed for moderate levels of air pollution activator chemical (Table IX) or with ozonized oxygen (Table I). Even in the course of hydrolysis (polyhexamethylene adipamide), the temperature was 103 ^{o}F, relative to the standard, polystyrene at 101 ^{o}F.

Film temperature was measured by thermocouple, cemented at beneath the center of the film. A record of the temperature was taken continuously throughout the exposure.

In cases where the sample was discolored severely, film temperature approached a value much higher than at the start. The temperature attained during exposure and the degree of film darkening were parallel (Table IX). Compare the stepwise decrease in this value as the level of SO_2 was decreased. Where the level was 0.5 ml or less the maximum value was the same as the original value.

TABLE IX

Temperature of Film by Thermocouple

Polystyrene, 1 mil

Experiment	Oxygen Gas, 146 ml, Plus	Maximum Temperature Attained During Irradiation	Discoloration After Exposure
VII - 2	Blank	114 °F	None
VII - 3	SO_2, 2.0 ml.	153 °F	Dark
VIII - 6	SO_3, 1 Drop H_2SO_4, Fuming	144 °F	Dark
VIII - 5	NO_2, 0.5 ml.	115 °F	Slight
VIII - 2	SO_2, 1.0 ml.	132 °F	Medium
VIII - 3	SO_2, 0.5 ml.	111 °F	Slight
VIII - 4	SO_2, 0.1 ml.	112 °F	None

Better control of film temperature was made possible in an improved apparatus. A device was constructed in which both light source and film chamber were immersed in water. The water bath was refrigerated.

The purpose was to attain better cooling by liquid contact than by circulating air. In this apparatus it was possible to perform air irradiation experiment with less overheating of the plastic. A clear polystyrene film in the sample chamber was thermostatted at 50 °F., during irradiation from an arc one inch distant. Temperature of the bath was 42 °F. In the same experiment, two PVC stocks were 54° F. (white pigmented) and 85° F. (black pigmented)

TABLE X

Hydrolysis of Plastics Films

Vessels Air-Filled, 146 ml

Series XVIII			After Light Exposure 69 Hours		
No.	Plastic	Hydrolysis Catalyst *	Effect on Color	Clarity	Integrity
5	Polycaprolactam, 1 mil	HCl, Conc.	-	-	Film Completely Depolymerized
6	Polyhexamethylene Adipamide, 1 mil	"	-	-	Completely Disintegrated**
7	Poly(vinyl chloride) Rigid, 1 mil	"	Amber	Clear	Flexible
8	Poly(vinyl chloride) Rigid, 2 mils	"	Amber	Clear	Flexible
9	Poly(vinyl chloride) 13% Plasticizer, 1 mil	"	Lt Brown	Clear	Flexible
10	Polyethylene Terephthalate, 1 mil	"	None	Clear	Brittle
11	Cellulose-Acetate-Butyrate, 1 mil	"	None	Clear	Disintegrated
12	Polycarbonate, 1 mil	"	Only Slight	Clear	Flexible

* 5 drops, 0.24 Gms.

** Only 20% of original film remained.

TABLE XI

Hydrolysis of Plastics Films

Vessels Air-Filled, 146 ml

Series XIX			After Light Exposure 68 Hours		
No.	Plastic	Hydrolysis Catalyst *	Effect on Color	Clarity	Integrity
1	Polyhexamethylene Adipamide, 1 mil	H_2SO_3	-	White Translucent	Completely Disintegrated
2	Polycaprolactam, 1 mil	H_2SO_3	-	White Translucent	Completely Disintegrated
3	Polycarbonate, 1 mil	H_2SO_3	Dark Brown		Completely Disintegrated
4	Poly(vinyl chloride) Rigid, 1 mil	H_2SO_3	Dark Brown	Clear	Flexible
5	Poly(vinyl chloride) 13% Plasticizer, 1 mil	H_2SO_3	Light Brown	Translucent	Flexible
6	Poly(vinyl chloride), 2 mils	H_2SO_3	Dark Brown	Translucent Blanched	Flexible
7	Polyethylene Terephthalate, 1 mil	H_2SO_3	Slight	Translucent	Brittle
8	Polyethylene Terephthalate, 1 mil	HCOOH 90.5%	None	Clear	Flexible
9	Polyethylene Terephthalate, 1 mil	Mono Chlor Acetic Acid	None	Clear	Flexible
10	Polyethylene Terephthalate, 1 mil	Acetic Acid Glacial	None	Clear	Flexible
11	Poly(vinyl chloride) Rigid, 1 mil	Acetic Acid Glacial	Lt Amber	Clear	Flexible
12	Poly(vinyl chloride) Rigid, 1 mil	-	Lt Amber	Clear	Flexible

* 5 drops (0.28 Grams in the case of H_2SO_3)

Samples 8-12 inclusive had additional water, 5 drops.

TABLE XII

Hydrolysis of Plastics Films

Vessels Air-Filled, 146 ml

Series XXII					After Exposure		
No.	Plastic	Hydrolysis Catalyst, SO_2, ml	Water, Gms.	Type Exposure	Effect on Color	Clarity	Integrity
1	Polyhexamethylene Adipamide, 1 mil			Light	None	Clear	Flexible
2	"		0.10	"	None	Clear	Flexible
3	"	2.0		"	None	Clear	Flexible
4	"	2.0	0.10	"	None	Opaque	Disintegrated
5	"			Oven	None	Clear	Flexible
6	"		0.10	"	None	Clear	Flexible
7	"	2.0		"	None	Clear	Flexible
8	"	2.0	0.10	"	None	Clear	Flexible
9	Poly(vinyl chloride) Rigid, 1 mil			Light	None	Clear	Flexible
10	"		0.10	"	None	Clear	Flexible
11	"	2.0		"	Dark Brown	Clear	Flexible
12	"	2.0	0.10	"	Dark Brown	Translucent Blanched	Flexible
13	"			Oven	None	Clear	Flexible
14	"		0.10	"	None	Clear	Flexible
15	"	2.0		"	None	Clear	Flexible
16	"	2.0	0.10	"	None	Clear	Flexible

In light - 72.0 hours.
In oven - 72.0 hours.

TABLE XIII

Hydrolysis of Plastics Films

Vessels Air-Filled, 146 ml

Series XX					After Exposure		
No.	Plastic	Hydrolysis Catalyst H_2SO_3	Water, Gms.	Type Exposure	Effect on Color	Clarity	Integrity
1	Polyhexamethylene Adipamide, 1 mil	*		Light	None	Opaque	Completely Disintegrated
2	"	*		Oven	None	Clear	Flexible
3	"		0.25	Light			
4	"		0.25	Oven			
5	"	* *		Light	None	Translucent	Partly Disintegrated
6	Polycapro-Lactam 1 mil	*		Light	None	Opaque	Completely Disintegrated
7	"	*		Oven	None	Clear	Flexible
8	"		0.25	Light			
9	"		0.25	Oven			
10	"	* *		Light	None	Opaque	Partly Disintegrated
11	Poly(vinyl chloride) Rigid 1 mil	*		Light	Dark Brown	Clear	Flexible
12	"	*		Oven	None	Clear	Flexible
13	"	* *		Light	Light Brown	Translucent	Flexible
14	Polyethylene Terephthalate, 1 mil			Light	None	Translucent	Brittle
15	"		0.25	Light	None	Clear	Flexible
16	Poly(vinyl chloride) 13% Plasticizer, 1 mil	*		Light	Light Brown	Translucent	Flexible
17	Poly(vinyl chloride) Rigid, 2 mil	*		Light	Dark Brown	Translucent	Flexible

* 5 drops, 0.28 Gms.
** 1 drop, 0.055 Gms.
Time: In 50 °C oven - 67.8 hours; in light - 68.2 hours.

TABLE XIV

Hydrolysis of Plastics Films

Vessels Air-Filled, 146 ml (Except 6, which used Oxygen)

Series XXI

				After Exposure		
No.	Plastic	Hydrolysis Catalyst	Type Exposure	Effect on Color	Clarity	Integrity
6	Polyhexamethylene Adipamide, 1 mil	H_2SO_3 0.28 gm.	Light	None	Opaque	Completely Disintegrated
7	Poly(vinyl chloride) Compound B, 4 mils	"	"	Amber	Translucent Blanched	Flexible
8	Poly(vinyl chloride) Compound B, 8.5 mils	"	"	Amber	Translucent Blanched	Flexible
9	Poly(vinyl chloride) Compound C, 10.5 mils	"	"	Amber	Translucent	Flexible
10	Cellulose Triacetate, 1 mil	"	"	Light Brown		Brittle Disintegrated
11	Cellulose-Acetate-Butyrate, 1 mil	"	"	Light Brown	Translucent	Completely Disintegrated
12	Styrene Methylmethacrylate Copolymer, 1 mil	"	"	Very Slight Discoloration	Clear	Flexible
13	Polycarbonate, 1 mil	"	Oven	None	Clear	Flexible
14	Polyethylene Terephthalate, 1 mil	"	"	None	Clear	Flexible
15	Poly(vinyl chloride), 2 mils	"	"	None	Translucent Blanched	Flexible
16	Poly(vinyl chloride) 13% Plasticizer, 1 mil	"	"	None	Clear	Flexible

In light - 66.8 hours.
In oven - 69.5 hours.

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