NATIONAL BUREAU OF STANDARDS REPORT

9648

USE OF SULFUR DIOXIDE TO STUDY PHOTODEGRADATION RATES OF POLY(VINYL CHLORIDE) PLASTICS

by

V. E. Gray

NBS

U.S. DEPARTMENT OF COMMERCE

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1. Introduction

The photochemical degradation of poly(vinyl chloride) (PVC) has been studied extensively. Color changes (1), ultraviolet (2) and infrared spectral changes (3), oxygen absorption (4), hydrogen chloride evolution (5), and analysis of degradation products by mass spectrometry (3) have been used to detect changes caused by photochemical degradation. Nearly all of these measurements have limited applicability to commercial formulations.

Dr. J. R. Wright and this author (6) described a colorimetric technique which was useful for measuring the photodegradation of many commercial polyesters and PVC materials. This technique had several faults which became evident in the studies of PVC. Some of the pigments and heat stabilizers contained impurities which reacted with the colorimetric reagent. This led to less sensitivity in the method and to questionable values for photo-oxidation rates.

It was also found that the colorimetric method detected intermediate products and did not provide a good measure for total degradation products (7).

Therefore the search for quantitative methods to measure photodegradation rates has continued. The variability in the behavior of formulated plastics, when exposed outdoors, has also demanded a technique to assess the relative sensitivities of these materials toward photo-oxidation and/or photohydrolysis.

Many sensitive analytical tools and exposure techniques have been developed since 1962. This report describes the application of gas chromatographic techniques to the study of photodegradation of formulated PVC materials.

This is an extension of the work of several people. In 1964 Campbell and Wright (8) reported on a controlled-environment technique which they used to study the oxidation of asphalt by ozone. The rate of oxidation of the asphalt was measured by the change in the infrared absorption at 5.88μ.

In 1967 Mitchell and Perkins (9) reported on a technique by which they determined the hydroperoxide groups in oxidized polyethylene by absorption of sulfur dioxide. They then measured the infrared absorption of the adsorbed sulfur dioxide to determine hydroperoxide concentration.

Since the colorimetric method has been found to be a poor measure of photooxidation rate, a method to measure initial or final oxidation products was desirable. The idea of a controlled atmosphere exposure along with the use of sulfur dioxide to measure hydroperoxide was intriguing. This seemed to offer the possibility to measure initial reactions and final products in one experiment. The infrared absorption method of

Mitchell and Perkins was not applicable to most commercial materials because of the interference of pigments and other additions with the infrared absorption bands.

In 1966 O. L. Hollis (10) reported on a chromatographic technique which made use of porous polymer beads to separate and analyze mixtures of polar compounds. It was found that air, carbon dioxide, water and sulfur dioxide were easily separated by this technique.

This report covers the use of exposure tests in which plastics are exposed to controlled-atmospheres of air-sulfur dioxide mixtures and the gases then analyzed by gas chromatographic separation. The rate of photodegradation can be measured by sulfur dioxide adsorption or by carbon dioxide evolution. The application of this technique to plastics degradation study is examined using three formulations of PVC.

2. Experimental

2.1 Materials

Three rigid poly(vinyl chloride) formulations were used in this study. The compositions were:

	Parts by Weight		
Materials	A	B	C
Geon 103EP	100.0	100.0	100.0
Ti Pure R-101	10.0	---	---
Ethylene bis-stearamide	1.0	1.0	1.0
Acryloid K-120	15.0	15.0	15.0
Argus Mark 235 (BaCd)	3.0	3.0	---
Argus Mark C (Phosphite)	1.0	1.0	---
Argus Drapex 4.4 (Epoxy)	2.0	2.0	---
Admex 746 (Epoxy)	3.0	3.0	3.0

Materials	Parts by Weight A	 B	 C
Cyasorb UV-9	---	0.5	0.5
Plaskon 103 (Chlorinated)	---	10.0	---
Ferro Stabilizer 840	---	---	0.5
Thermolite 24	---	---	2.5
Thermolite 31	---	---	0.5

2.2 Exposure Conditions

Specimens of poly(vinyl chloride) materials, 2 x 12 x 0.25 mm, were placed in exposure tubes shown in Figure 1. (These were designed by Drs. Campbell and Wright.) The tubes were assembled and flushed with a 4.5% mixture of sulfur dioxide in air for 10 minutes at a flow rate of 100 ml./ minute. The glass stopcocks were closed and rubber septums used to cover the tube ends. The tubes were then placed on the drum of the weathering device.

The weathering devices were maintained at 140°F (black panel temperature) and 120-125°F dry bulb temperature. This was a setting of 5A for the enclosed violet-arc and a 5700 watts input to the xenon lamps. Periodically the ultraviolet output of the sources was measured using the Toyo Rika Integrating actinometer.

After timed intervals the exposure tubes were removed and the gases analyzed by gas chromatography to measure evolution of carbon dioxide and adsorption of sulfur dioxide.

2.3 Analytical Techniques

Chromatographic analysis: The chromatographic separation of gases was accomplished using a 6 ft. glass column packed with Poropak Q porous polymer beads. Isothermal conditions were maintained for the injection port,

column, and thermal conductivity detector. The temperature of the injection port and column was maintained at 75°C, while the thermal conductivity detector was maintained at 85°C. It was found that a 200 ul gas sample allowed good separation of the carbon dioxide and air.

3. Results and Discussion

3.1 Carbon dioxide evolution

Samples of PVC-A, PVC-B, and PVC-C were exposed for periods of 24, 48, and 94 hours in the enclosed violet-arc. The rates of carbon dioxide evolution is shown in Figure 2. From this figure it is immediately obvious that the pigmentation of PVC-A caused a decreased rate of carbon dioxide evolution. The variation in the formulations of the clear PVC materials seemed to cause a slight change in the oxidation. PVC-B seemed to show an induction period as did pigmented PVC-A, while PVC-C appeared to evolve CO_2 at a steady rate from the start of exposure.

A comparison of the effect of sources on carbon dioxide evolution is shown in Figure 3. The rate of evolution appears to be slightly higher under xenon lamps exposure. This did not follow the result expected from ultraviolet intensity measurements. The carbon-arc radiant intensity was approximately three times as great as that from the xenon lamp (85 versus 32 units/minute).

It appears that oxidation is not strictly related to ultraviolet intensity. This is similar to the study by Martin, Campbell and Wright (11) which showed that the carbonyl formed during the photooxidation of asphalt is not strictly related to ultraviolet radiant energy when carbon-arc and xenon lamps are compared.

From the results it appears that carbon dioxide evolution is not sensitive enough to the formulation variables. The clear PVC-B and PVC-C materials are different but show little variation in carbon dioxide rates. The rate under variable radiant flux appeared to be temperature dependent as well as ultraviolet sensitive.

3.2 Sulfur Dioxide Adsorption

The rate of sulfur dioxide adsorption were also measured for the PVC materials and showed more promise for pointing up variations in photodegradation rates. Figure 4 shows the disappearance of sulfur dioxide during carbon-arc exposure. In this experiment PVC-A adsorbs sulfur dioxide at the lowest rate and it also gave off carbon dioxide most slowly. The sulfur dioxide adsorptiom by the unpigmented materials were quite different. PVC-B has the highest rate of adsorption and--if the reaction is similar to that postulated by Mitchell and Perkins--forms hydroper oxide groups at a greater rate.

Because of the permeability of plastics to gases and adsorption being possible because of several chemical reactions, control samples were exposed to sulfur dioxide atmospheres but no light for the same interval as those subjected to light exposure. Figure 5 shows the rate of sulfur dioxide adsorption for PVC-B with and without light exposure.

The "dark" reaction could be a result of peroxides formed during the formulation and fabrication of the PVC film. The initial rate of the "light" reaction would support this assumption. Referring to Figure 4 the initial adsorption rates of all materials were very rapid and declined after 24 hours to a steady lower rate. This lower rate probably is most valid for photodegradation measurement, as it appears to be the best parameter to gauge the effect of light on various formulations of PVC.

3.3 Color Changes

The color changes produced during exposure of poly(vinyl chloride) plastics have been used to measure visible degradation (1). Early in these exposure studies it became evident that sulfur dioxide accelerated the color changes produced during exposure to carbon-arc or xenon lamps radiant flux. Therefore the color of these materials was measured using a tristimulus colorimeter.

The color of PVC-A specimens which were exposed to xenon lamp in normal air and in sulfur dioxide-air atmospheres is shown in Table I. The data points up the gross effect of a sulfur dioxide-contaminated atmosphere. Normal air exposure for as long as 1000 hours caused only minor changes in the color of white PVC, whereas exposure in a sulfur dioxide-air atmosphere caused large color changes in only 24 hours.

In Table II the data from PVC-B material is shown. This clear material shows the same gross effect as the white material. Therefore the color changes are not due to the presence of pigment. In this same table we see that the effects of sulfur dioxide are similar whether the photodegradation is carried out in presence of a carbon-arc or xenon lamp source.

The color changes found for the other clear material, PVC-C, showed the same trend as did PVC-A and PVC-B. The only change was that PVC-C did not show as much color change as PVC-B in the same exposure interval. The adsorption rate for sulfur dioxide had been found to be less for PVC-C (Figure 4). For all materials the color changes were directly related to amount of sulfur dioxide adsorbed as shown in Figure 6.

In a former report (12) photooxidation has been shown to cause a bleaching effect. The present report finds the same effect in normal air experiments with PVC-A, PVC-B and PVC-C. Sulfur dioxide eliminates this bleaching effect by its pronounced acceleration of color formation.

In the same report mentioned above it was shown that color formation was greatest in winter for a Cincinnati, Ohio site. One possible explanation could be a higher concentration of sulfur dioxide in the winter months.

The use of sulfur dioxide-air mixtures in exposure tests would produce color changes which are not valid for the exposure sites of Florida and Arizona but could show susceptability of plastics to sulfur dioxide contamination. Some of the outdoor exposure data which shows non-correlatable color changes could be examined again. The possibility of sulfur dioxide pollution and its effect on color changes should be examined. The direct relationship found in this report between color formation and sulfur dioxide adsorption could explain some of the color variations caused by industrial sites.

4. References

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Table I

Color Changes of PVC-A during Exposure to Xenon Lamp Radiant Flux

(with and without Sulfur Dioxide)

Exposure Time (Hours)	COLOR L	a	b	Evolved CO_2	Ads. SO_2
0	93.79	-0.5	2.3	0	0
24	92.60	-0.7	5.1	3	10.4
48	91.73	-0.4	7.6	9.2	14.9
1119	86.67	+1.2	16.4	25.6	38.9
(Without Sulfur Dioxide)					
0	93.74	-0.4	1.7	0	-
67	94.05	-0.3	1.4	0	-
110	93.98	-0.4	1.3	0	-
158	93.99	-0.3	1.3	10	-
204	94.08	-0.2	1.3	18	-
552*	93.38	-0.3	1.3		
1057*	93.42	-0.3	1.2		

*No exposure tubes used.

Table II

Color Change of PVC-B During Exposure to Carbon-arc or Xenon Lamp Radiant Flux

Exposure Time (hours)		COLOR		Evolved	Ads.
	L	a	b	CO_2	SO_2
(Carbon-arc, SO_2)					
0	91.73	-1.4	4.4	0	0
24	90.61	-1.1	7.0	8	15.5
48	87.51	-0.1	12.8	21	31.4
95	75.24	5.5	27.8	54	55.4
(Xenon-arc, SO_2)					
0	91.79	-1.5	4.2	0	0
30	89.58	-1.5	8.4	5	8.8
54	88.06	-0.8	11.5	9	33.5
126	81.82	+1.2	20.8	32	48.5
(Xenon-arc without Sulfur Dioxide)					
0	91.71	-1.4	3.9	-	-
102	91.87	-1.0	3.6	-	-
552	91.84	-1.2	3.5	-	-
1057	92.28	-1.1	3.8	-	-

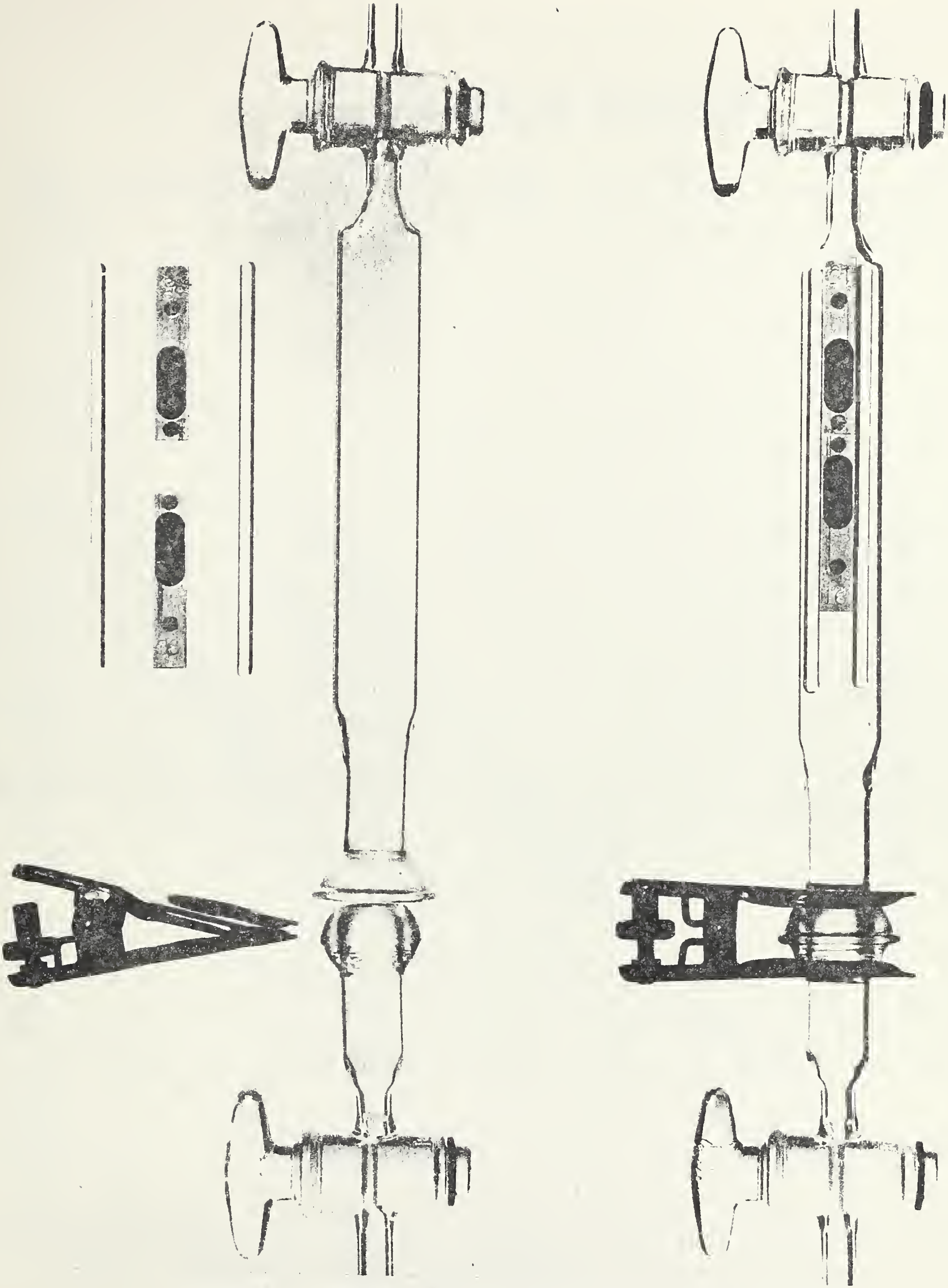

FIGURE 1. GLASS IRRADIATION TUBES AND ASPHALT SAMPLES.

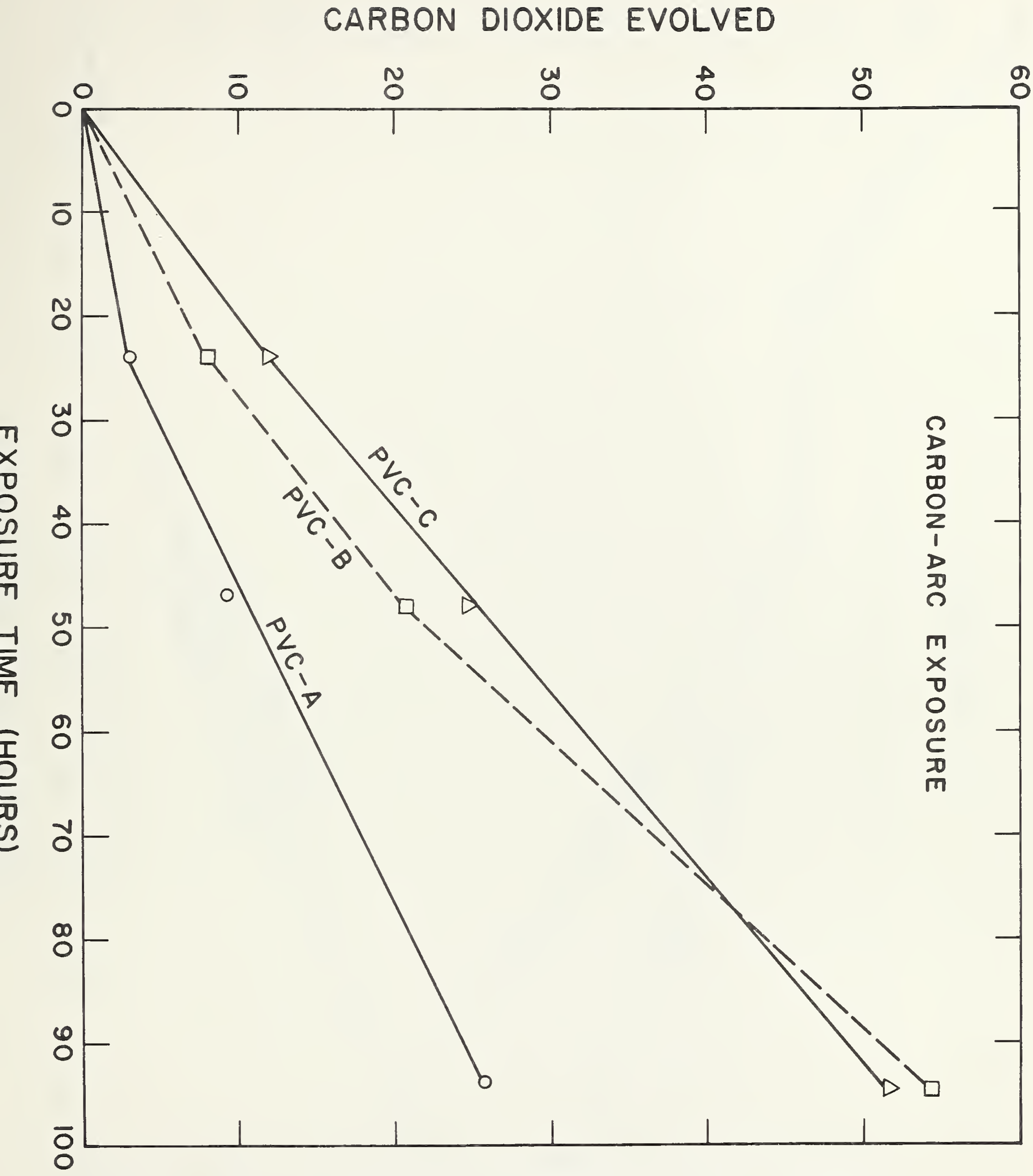

FIGURE 2. CARBON DIOXIDE EVOLVED DURING EXPOSURE OF THREE PVC MATERIALS TO CARBON-ARC RADIANT FLUX.

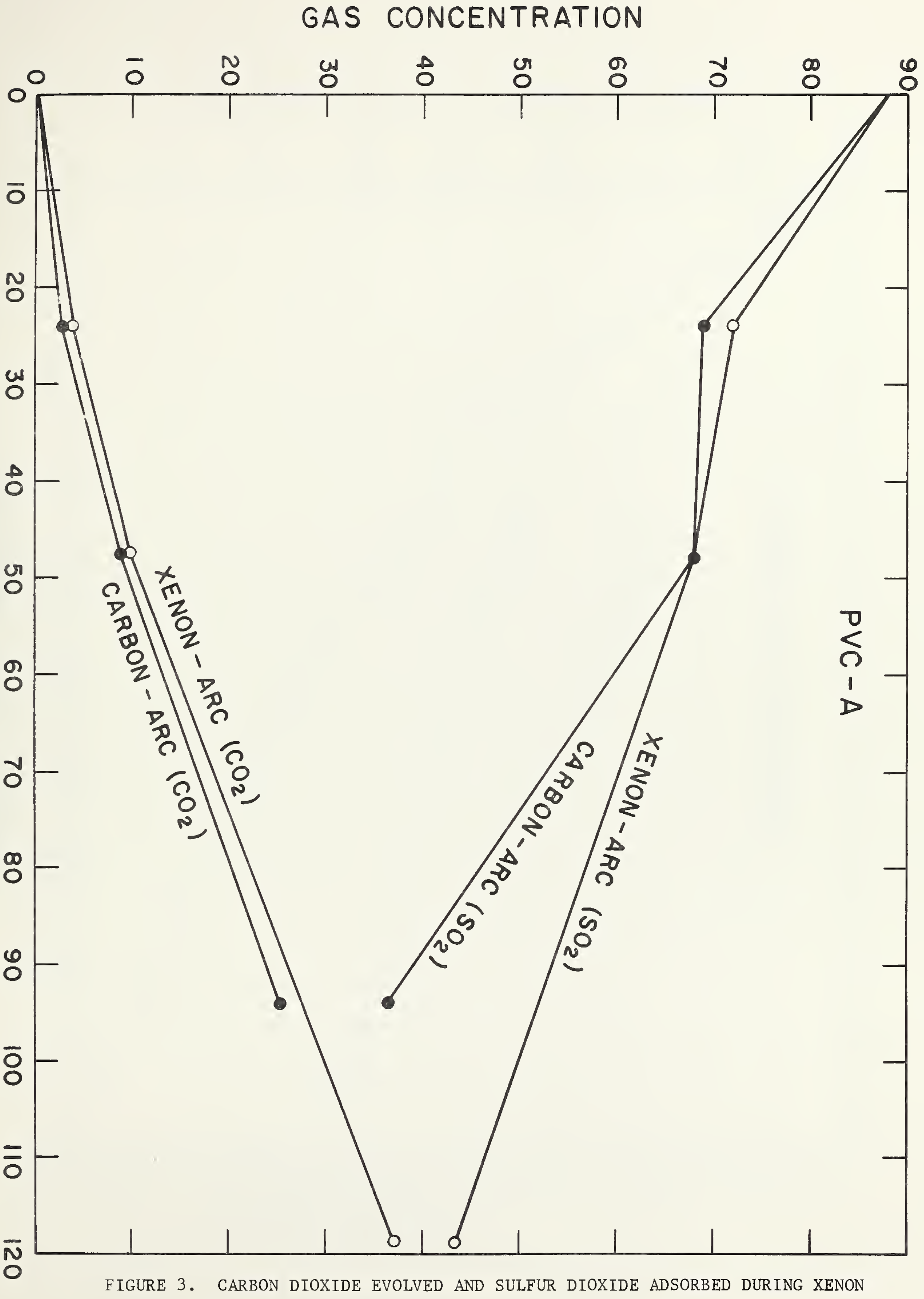

FIGURE 3. CARBON DIOXIDE EVOLVED AND SULFUR DIOXIDE ADSORBED DURING XENON AND CARBON-ARC EXPOSURE OF WHITE PVC.

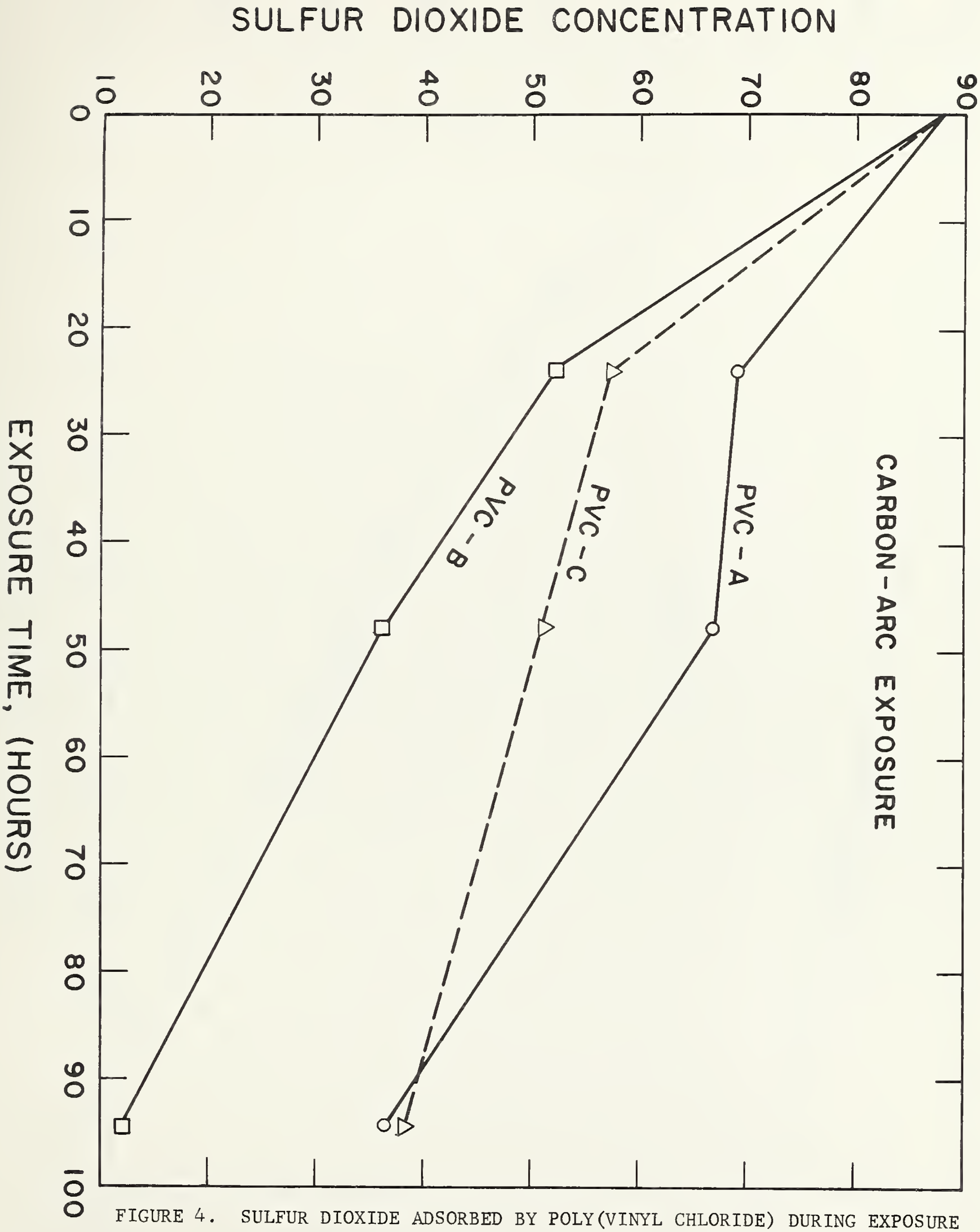

FIGURE 4. SULFUR DIOXIDE ADSORBED BY POLY(VINYL CHLORIDE) DURING EXPOSURE TO CARBON-ARC RADIANT FLUX.

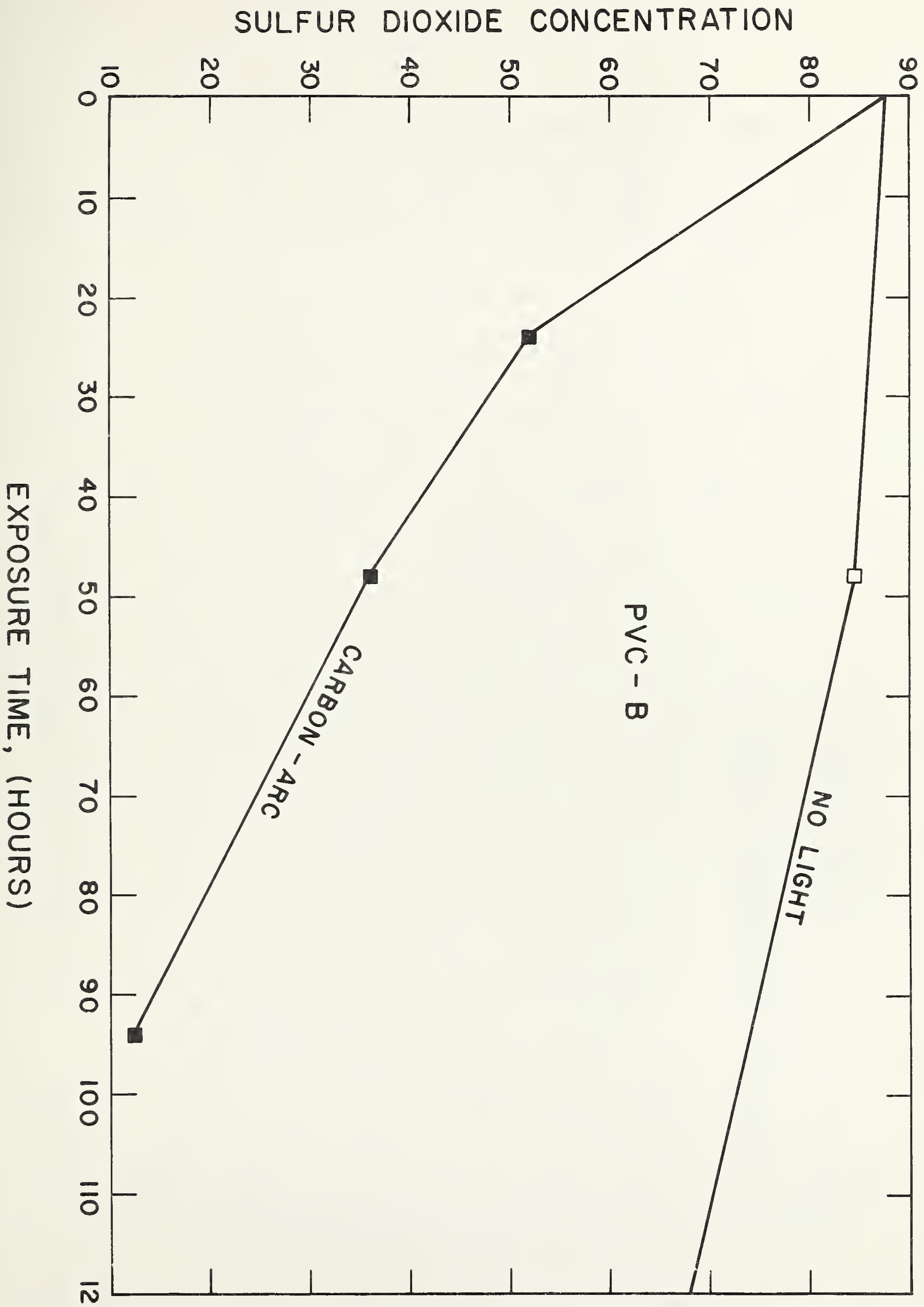

FIGURE 5. SULFUR DIOXIDE ADSORBED BY POLY(VINYL CHLORIDE), FORMULATION PVC-B, WITH AND WITHOUT CARBON-ARC RADIANT FLUX.

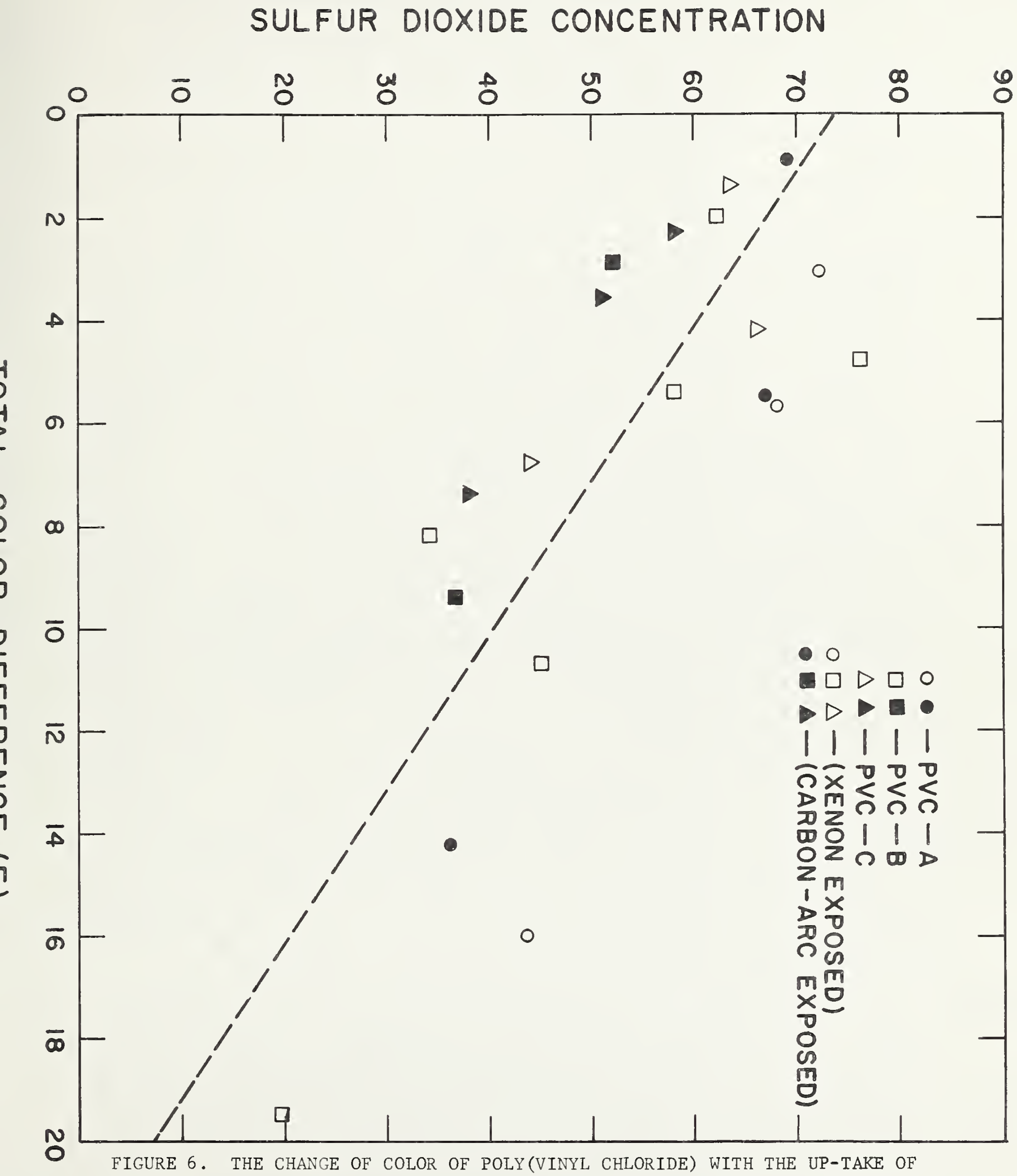

FIGURE 6. THE CHANGE OF COLOR OF POLY(VINYL CHLORIDE) WITH THE UP-TAKE OF SULFUR DIOXIDE DURING RADIANT ENERGY EXPOSURE.

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