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NATIONAL BUREAU OF STANDARDS REPORT

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PHYSICO-CHEMICAL CHANGES IN POLY (VINYL CHLORIDE) PLASTICS INDUCED BY ADSORPED SULFUR DIOXIDE

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U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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by

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Sponsored

by

Materials Durability and Analysis Section
Building Research Division
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ABSTRACT

The adsorption of sulfur dioxide by clear and pigmented poly(vinyl chloride) plastics was measured by use of gas chromatography. At room temperature and in the absence of light this adsorption was found to be somewhat dependent on relative humidity conditioning as well as on formulation variables. The adsorbed sulfur dioxide produced gross changes in tensile properties and chemical structure in reaction times of 1-7 days. These changes were measured by use of tensile tests and infrared spectroscopy. The additives which appear to be sensitive to sulfur dioxide are identified and the chemical reactions responsible for the structural changes are postulated.

1. INTRODUCTION

The effects of sulfur dioxide air contamination on the properties of plastic materials have not been assessed. Recent work by Wohlers and others, (1) Baker and Doerr (2) have shown that sulfur dioxide is adsorbed by various plastics as well as aluminum. It was found that a high percentage of the sulfur dioxide passed through vinyl tubing or piping was irreversibly adsorbed. No measurements were made of the physical or chemical changes caused by this adsorbed sulfur dioxide.

Many commercial formulations of vinyl plastics are used in applications that will expose these materials to air contaminants both in outdoor or in protected locations. Therefore, it will be of benefit to know what effects may be caused by sulfur dioxide adsorption and how these effects vary with humidity and the additives present in plastics.

Two formulations of "rigid" poly(vinyl chloride) were chosen. These varied only in that one contained a white opaque pigment and the other contained no pigment.

These materials were subjected to controlled exposure in sulfur dioxide atmospheres without light. Afterwards the sulfur dioxide adsorption and the tensile properties of the plastics were measured. The infrared spectra of the unpigmented vinyl were examined for chemical changes.

The changes due to the sulfur dioxide adsorbed were then evaluated and the controlling variables postulated.

2. EXPERIMENTAL

2.1 Materials

Two poly(vinyl chloride) plastics of "rigid" type were used in this study. The components and proportions of each are:

Material	Parts by Weight	
	PVC-A	PVC-B
Geon 103EP	100.0	100.0
Ti Pure R-101	10.0	-
Ethylene Bis-stearamide	1.0	1.0
Acryloid K-120	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
Cyasorb UV-9	-	0.5
Plaskon 103 (Chlorinated)	-	10.0

2.2 Exposure Conditions

Specimens of poly(vinyl chloride) materials, 2 x 12 x 0.025 cm, were subjected to controlled humidity conditions for approximately 72 hours. They were then placed in closed exposure tubes (see Figure 1) which were then assembled and flushed thoroughly with a 4.5% mixture of sulfur dioxide in air. (These exposure tubes were designed by Drs. Campbell and Wright.) The stopcocks were closed off and rubber septums

placed over the tube ends. The tubes were placed in the dark at laboratory temperatures. After timed intervals the exposure tubes were removed and the gases analyzed by gas chromatography to measure the adsorption of sulfur dioxide. The specimens were then subjected to tensile tests and specimens of the unpigmented material were analyzed by infrared spectroscopy to assess any chemical changes that may have occurred during the sulfur dioxide exposure.

2.3 Sulfur Dioxide Adsorption

The measurement of sulfur dioxide adsorption was made by use of gas chromatography. The chromatographic separation of air, moisture and sulfur dioxide was accomplished using a 6 foot glass column packed with Poropak Q porous polymer beads. Isothermal conditions were maintained for the injection port, column chamber and the thermal conductivity detector. The injection port and column were maintained at a temperature of 75°C, while the thermal conductivity detector was maintained at 85°C. The flow rate for the helium carrier gas was 50 ml/minute.

Gas samples were analyzed by injection of a 200 μl gas sample from the exposure tube into the chromatograph. Control exposure tubes containing no specimens were analyzed to provide a check of the response of the chromatograph. Only slight drift of the sulfur dioxide level in control tubes was noted after periods of seven days. This was caused by small losses through or into the fluorocarbon grease used at the two stopcocks and the ball joint.

2.4 Infrared Spectral Measurements

The infrared transmission spectra of the unpigmented vinyl (PVC-B) films were made, using a Model IR-8 Beckman Infrared Spectrophotometer. Transmission spectra of the components used in the formulation of PVC-B were made of either thin films on salt windows for liquids or suspended in potassium bromide pellets for the solids. All spectra were recorded on slow speed in the infrared region from 2.5 to 16 microns. For absorbance comparison purposes the background transmission was set on 90% at 5.0 microns by reference beam attenuation.

2.5 Tensile Tests of Vinyl Films

The specimens for tensile testing were cut to a "dogbone" shape with flat section dimensions of 1.0 cm width by 4.5 cm length. The thickness of the flat section was measured to the nearest 0.001 mm using a dial thickness gage. The overall specimen length was 12 centimeters.

The tensile tests were conducted using serrated grips and distance between grips of 6.35 cm. The crosshead speed was 0.2 cm/minute and the chart speed was 5.0 cm/minute.

The tensile test was continued until the load-elongation curve passed through a maximum load. This maximum was used to calculate tensile strength and per cent elongation. Duplicate tests and control specimens were measured for each exposure condition.

3. EXPERIMENTAL RESULTS

3.1 Sulfur Dioxide Adsorption

The sulfur dioxide adsorption by vinyl plastics was measured for time periods up to seven days. By this time apparent equilibrium of tensile properties had occurred at all humidity conditions.

The sulfur dioxide adsorption of pigmented PVC was measured after conditioning specimens at 20, 50 and 100% R.H. at room temperature. Table I shows the sulfur dioxide adsorption and tensile test data for these series of experiments. It was found that the sulfur dioxide adsorption varied directly with relative humidity. A similar effect was found when unpigmented PVC (PVC-B) was exposed at 20 and 100% R.H.

Tables II and III give the sulfur dioxide adsorbed and tensile properties measured for vinyl samples conditioned at low and high relative humidities. In both cases the pigmented material adsorbed the larger amounts of sulfur dioxide. Assuming that titanium dioxide is more hydrophilic than vinyl resin, this increased adsorption could possibly be linked to the effect - noted above - of moisture-aided adsorption. This does not clear up the question - Does sulfur dioxide react with the pigment as well as the other components in the formulation?

3.2 Changes in Tensile Properties

The tensile properties of vinyl materials were tested as described in section 2.5.

Table IV shows the results of humidity conditioning tests on the pigmented and unpigmented vinyl. The humidity conditioning alone appears to cause insignificant change of tensile properties except in the case of PVC-B at 100% R.H.

An analysis of the tensile data is given in Table V. The data was taken from control specimens tested over a six week period and conditioned at 50% R.H.

The reproducibility of tensile tests is the same for the two materials, although the pigmented material has a slightly higher tensile strength.

In Figure 2 is plotted the tensile strength versus the amount of sulfur dioxide adsorbed. For both materials there appears to be a direct relationship between the decrease in tensile strength and the amount of sulfur dioxide adsorbed. In Figures 3 and 4 the tensile strength versus time of exposure to sulfur dioxide is shown. In these figures a decided leveling off of tensile strength is observed.

In Figures 2, 3 and 4 the data from low humidity conditioning usually shows the greatest decrease in tensile strength either for the same time of exposure (Figures 3 and 4) or for the same amount of adsorbed sulfur dioxide (Figure 2). From this it is apparent that humidity increases sulfur dioxide adsorption but does not directly influence the decrease in tensile properties.

From Figures 3 and 4 it is obvious that sulfur dioxide adsorption can cause decreases in tensile strength of vinyl materials. This decrease was 12% for pigmented and 13% for unpigmented materials.

3.3 Changes in Chemical Structure

The adsorption of sulfur dioxide and the gross physical changes produced thereby posed a question of the chemical nature of the adsorption process. Although relatively small amounts of sulfur dioxide were adsorbed, an examination of the infrared transmission spectra of unpigmented material showed that chemical changes had occurred. As shown in Figure 5, the vinyl material strongly absorbs infrared energy. The major change observed in the transmission spectrum of PVC-B was a pronounced decrease in the absorbance peak centered at a wavelength of 6.5 microns after seven days exposure to sulfur dioxide-air mixture (Figure 5). Figure 6 is the transmission spectrum of vinyl material exposed for seven days to sulfur dioxide-air mixture.

In order to isolate the component undergoing the chemical change responsible for the decrease in the absorbance at 6.5μ, reference spectra were made of the additives present in PVC-B. Only barium-cadmium carboxylates used as heat stabilizers were found to have a large absorbance peak at 6.5μ (see Figure 6). Treatment of this material with hydrochloric acid gave a carboxylic acid with the spectrum shown in Figure 7. Therefore hydrolysis of this component was responsible for the decrease in the 6.5 micron peak. Also the trans-

mission spectrum shown in Figure 5 can be used to explain the continued adsorption of sulfur dioxide. There is obviously some of the carboxylates still unhydrolyzed after this period.

4. DISCUSSION OF RESULTS

Other workers have noted the effects of sulfur dioxide on the physical properties of textiles, paper and paints. In 1949 Race (3) showed the loss of tensile strength of cotton was faster during winter exposure and was dependent on pH. He therefore postulated that this effect was due to the presence of more sulfur gases which lead to increased hydrolysis of the cellulose.

The adsorption of sulfur dioxide by paper has been extensively studied by Langwell (4) and also by Hudson and others(5). This work proved conclusively that sulfur dioxide was most strongly adsorbed by spots contaminated by iron, catalysts and other metal deposit.

The chemical reactions which occur during the processing of vinyl plastics have not been clearly defined. There have been some studies with the barium-cadmium heat stabilizers. Frye and Horst (6) studied the interaction of poly(vinyl chloride) with barium, cadmium, and zinc carboxylates and found evidence of ester formation during heating. Fields and Nielsen (7) have recently shown that zinc oxide reacts with acrylic acid polymers to produce products with increased tensile properties. The increase in tensile strength was found to be dependent on the amount of zinc dicarboxylate salt formed.

From the evidence above the results from this study of vinyl materials can be explained on the basis that sulfur dioxide is preferentially adsorbed at carboxylate sites, and hydrolyzes these to the carboxylic acid groups. This results in less units being cross-linked by the barium or cadmium atoms. Therefore the overall tensile strength would be lowered.

5. SUMMARY AND CONCLUSIONS

The adsorption of sulfur dioxide by pigmented and unpigmented "rigid" vinyl materials has been found to be dependent on humidity conditioning. This adsorption was accompanied by a 12-14% decrease in the tensile strength of these materials as well as chemical changes observable by infrared spectroscopic examination.

A heat stabilizer component, barium-cadmium carboxylate, was found to be responsible for the infrared absorption changes which occur during the sulfur dioxide adsorption.

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6. REFERENCES

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(3) Race, E., J. Soc. Dyers and Colourists 65, 56-63 (1949).

(4) Langwell, W. H., Tech. Bull. Brit. Paper and Board Makers' Assoc. 30, 170 (1953).

(5) Hudson, F. L. and W. D. Milner, Nature No. 4533, 590 (1956).

(6) Frye, A.H. and R. W. Horst, J. Polymer Sci. 40, 419 (1959).

(7) Fields, J. E. and L. E. Nielsen, J. Appl. Polymer Sci. 12, 1041 (1968).

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TABLE I

Effect of Relative Humidity Conditioning on Sulfur Dioxide Adsorbed and Tensile Strength of White Poly(vinyl chloride)

	Conditioning Relative Humidity					
	20%		50%		100%	
Exposure Time (Hours)	SO_2 Adsorbed (mg/specimen)	Tensile Strength	SO_2 Adsorbed (mg/specimen)	Tensile Strength	SO_2 Adsorbed (mg/specimen)	Tensile Strength
0	0	478	0	484*	0	499
24	0.73	442	1.51	460	1.67	452
48	1.63	432				
72			2.59	449		
96	1.97	442			2.88	413
96	2.47	420				
168	2.45	435	2.99	428	3.55	423
168	2.99	411				

* Mean($\bar{x}$)= 484 (n = 22)

Estimate of variance (s) = 12.2

TABLE II

Sulfur Dioxide Adsorption and Resulting Tensile Properties of Poly(vinyl chloride) Plastics after Low Humidity Conditioning

	PVC-A (White)			PVC-B (Clear)		
		Tensile Properties			Tensile Properties	
Exposure Time (Hours)	SO_2 Adsorbed (mg.)	Tensile Strength (Kg/cm^2)	Elongation (%)	SO_2 Adsorbed (mg.)	Tensile Strength (Kg/cm^2)	Elongation (%)
0	0	484*	2.20*	0	438*	2.25*
24	0.73	442	2.08	0.50	416	2.14
48	1.63	432	1.91	0.85	391	2.10
96	1.97	442	1.95	1.64	405	2.04
96	2.47	420	2.12			
168	2.45	411	1.85	2.07	381	2.07
168	2.99	435	1.92			

* See Table V for Statistical Analysis

TABLE III

Sulfur Dioxide Adsorption and Tensile Properties of Poly(vinyl chloride) Plastics after High Humidity Conditioning*

	PVC-A (White)			PVC-B (Clear)		
		Tensile Properties			Tensile Properties	
Exposure Time (Hours)	SO_2 Adsorbed (mg.)	Tensile Strength (Kg/cm^2)	Elongation (%)	SO_2 Adsorbed (mg.)	Tensile Strength (Kg/cm^2)	Elongation (%)
0	0	499	2.34	0	456	2.26
24	1.67	452	1.99	1.52	427	2.15
96				2.26	394	1.89
120	2.88	413	1.80			
168	3.55	423	1.83	3.25	384	1.93

* Samples conditioned at 25°C and 100% R.H. for 48 hours prior to exposure to 4.4% SO_2 in air.

TABLE IV

Effect of Humidity Conditioning* on Tensile Properties of Poly (vinyl chloride)

	PVC-A		PVC-B	
	Tensile Properties		Tensile Properties	
Relative Humidity (%)	Tensile Strength (Kg/cm^2)	Elongation (%)	Tensile Strength (Kg/cm^2)	Elongation (%)
0	500	2.32	472	2.31
50	486	2.18	466	2.30
100	482	2.32	429	2.43

* Specimens conditioned at given R.H. for 3 days and tested within 30 minutes from time of removal.

TABLE V

Statistical Analysis of Tensile Property Measurements

	PVC-A		PVC-B	
	Tensile Strength	Per Cent Elongation	Tensile Strength	Per Cent Elongation
Mean ($\bar{x}$)	484	2.20	438	2.25
Estimate of variance (s)	12.2	0.05	13	0.05
Population (n)	22	26	16	16

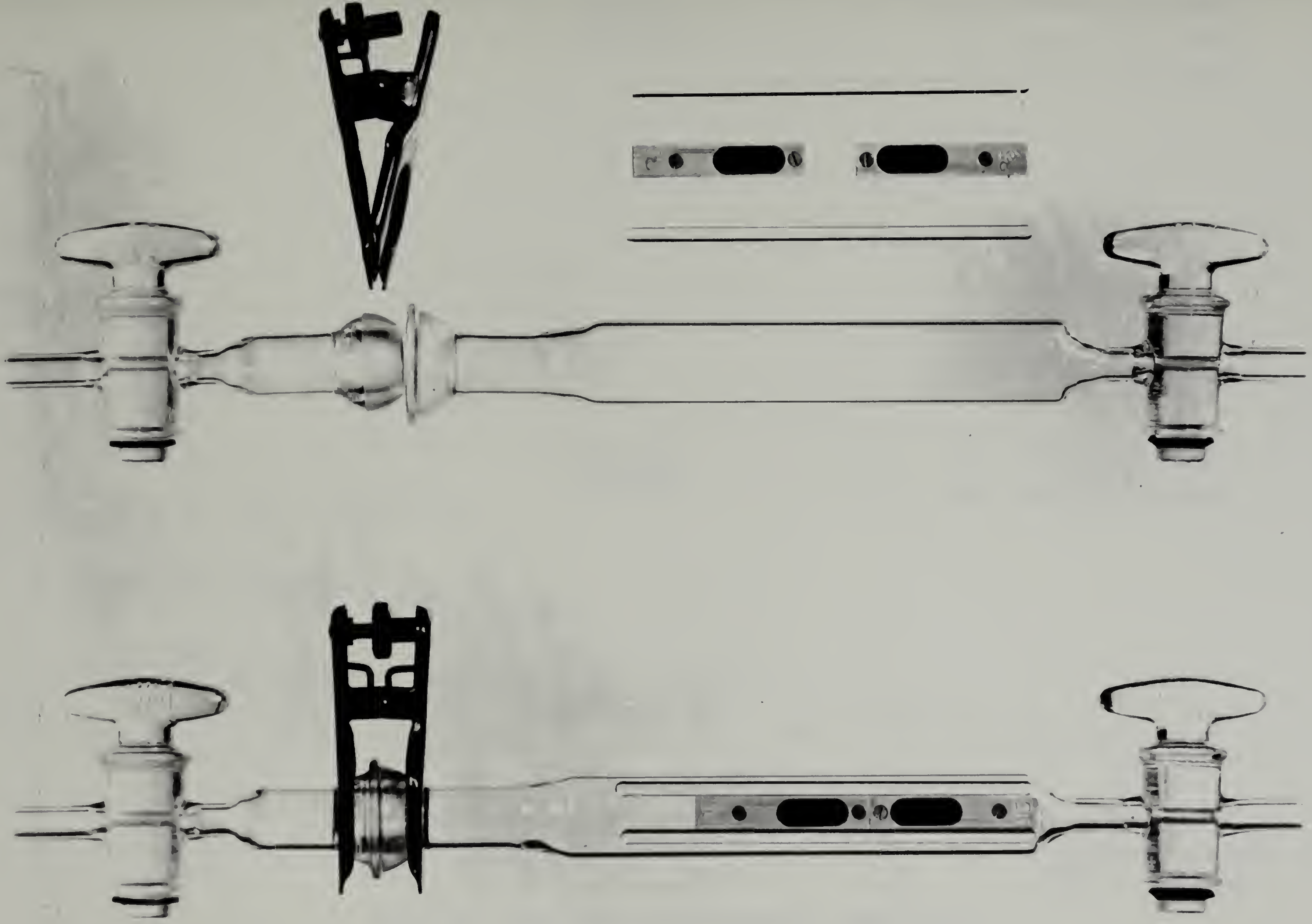

Figure 1. Glass irradiation tubes, unassembled and assembled with model samples.

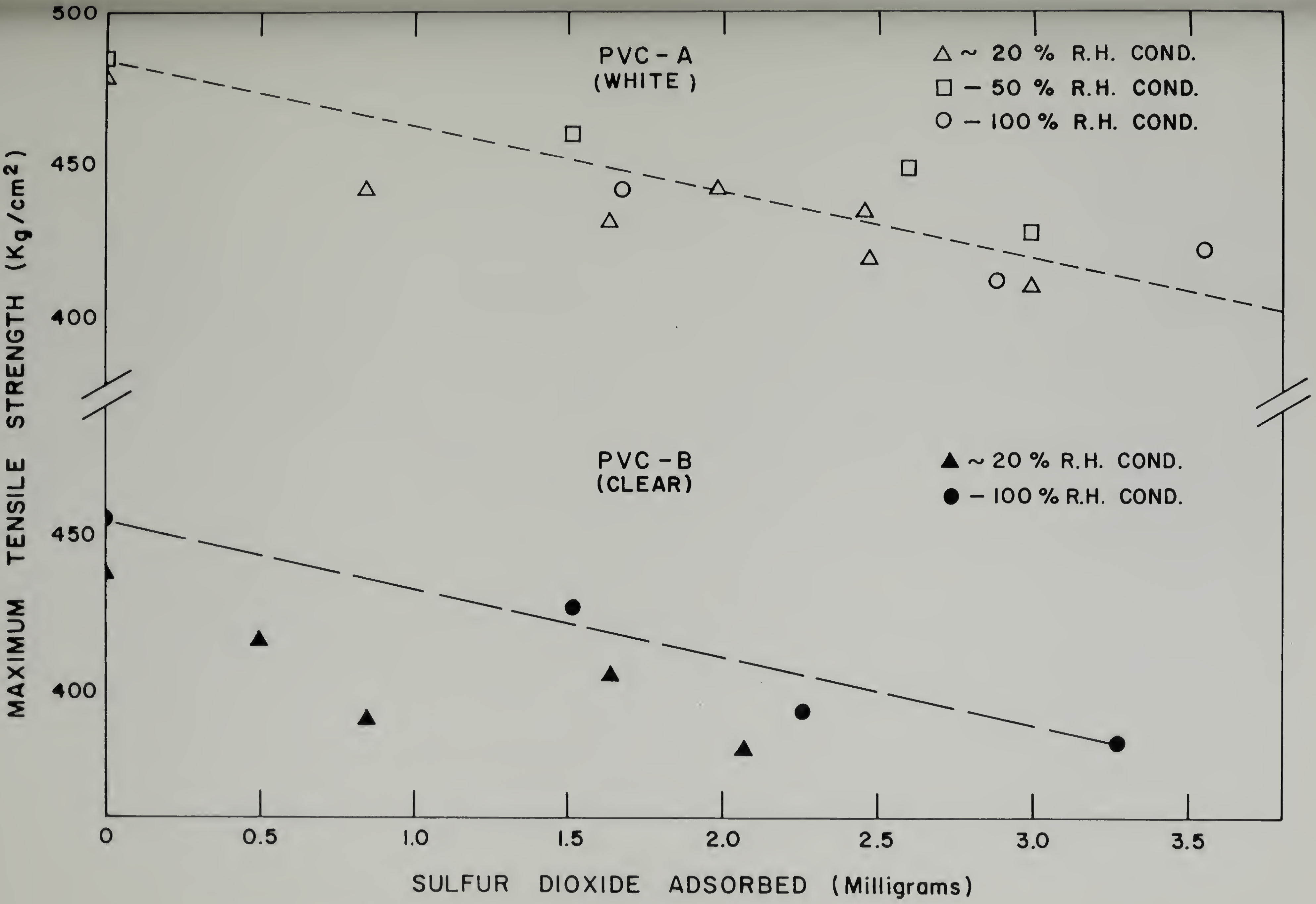

Figure 2. The tensile strength of PVC plastics after adsorption of various amounts of sulfur dioxide.

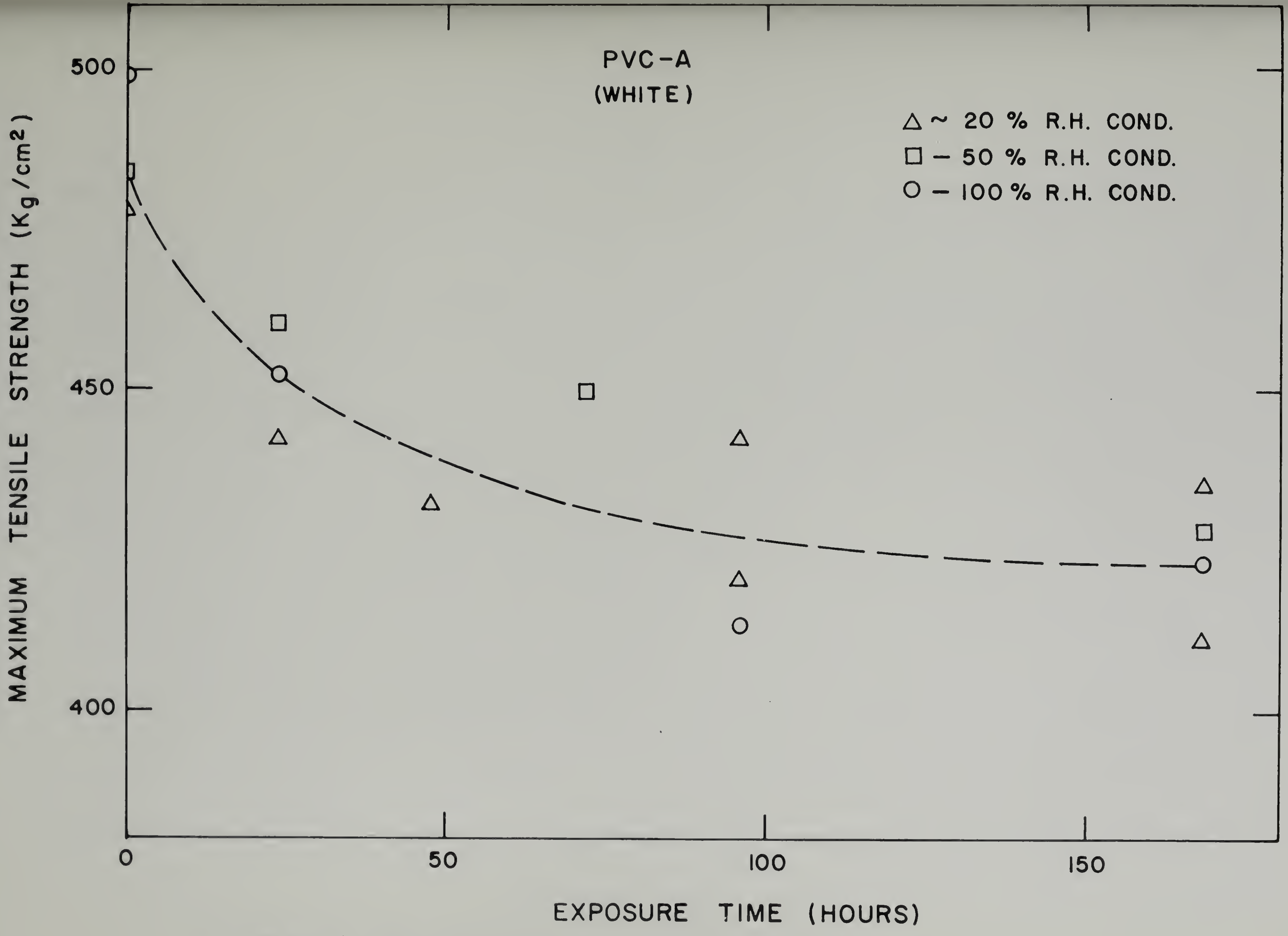

Figure 3. The Tensile Strength of pigmented PVC plastics after conditioning at different R.H. levels and then exposure to SO_2 in air for various periods of time.

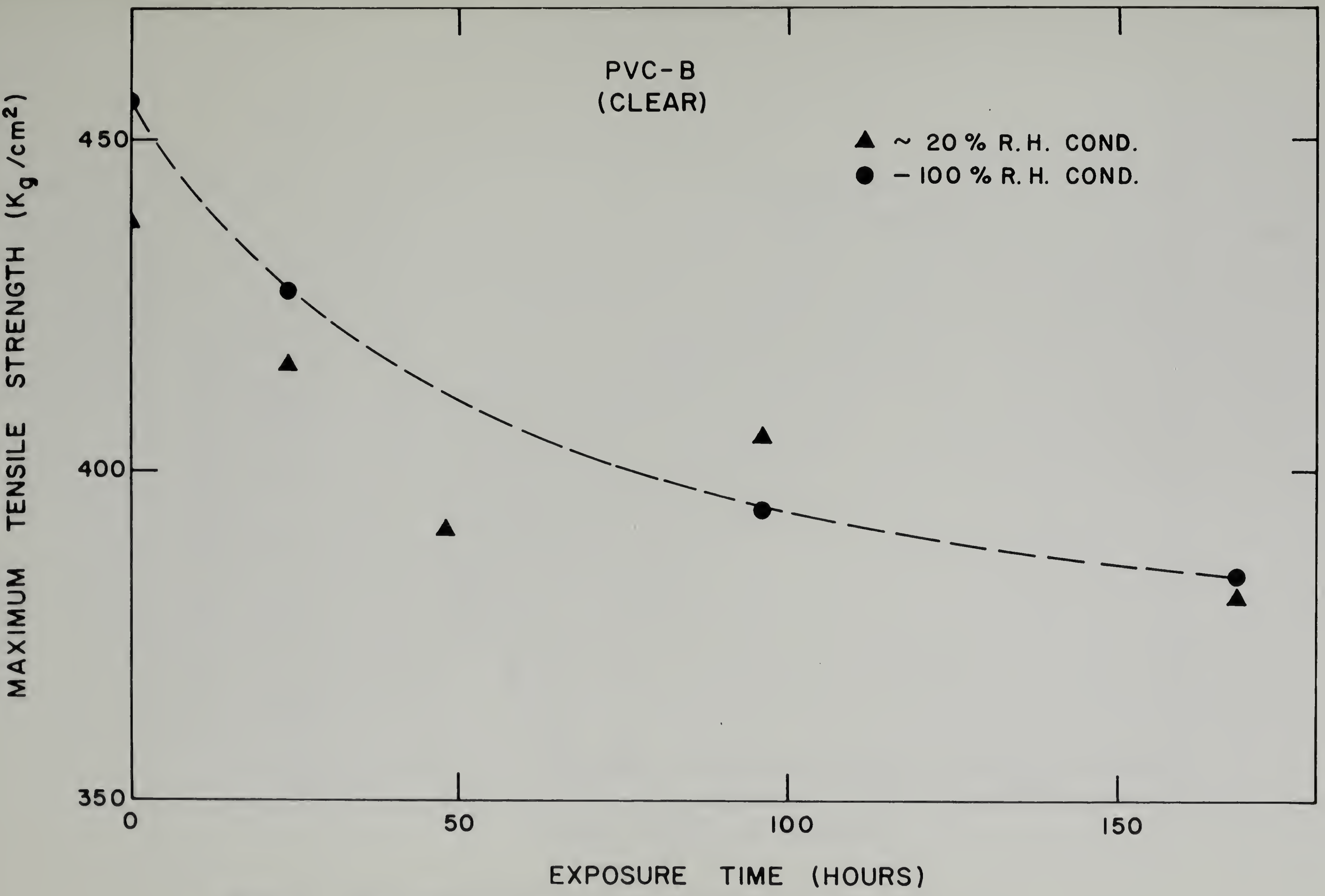

Figure 4. The tensile strength of unpigmented PVC plastics after conditioning at two R.H. levels and then exposure to SO_2 in air for various periods of time.

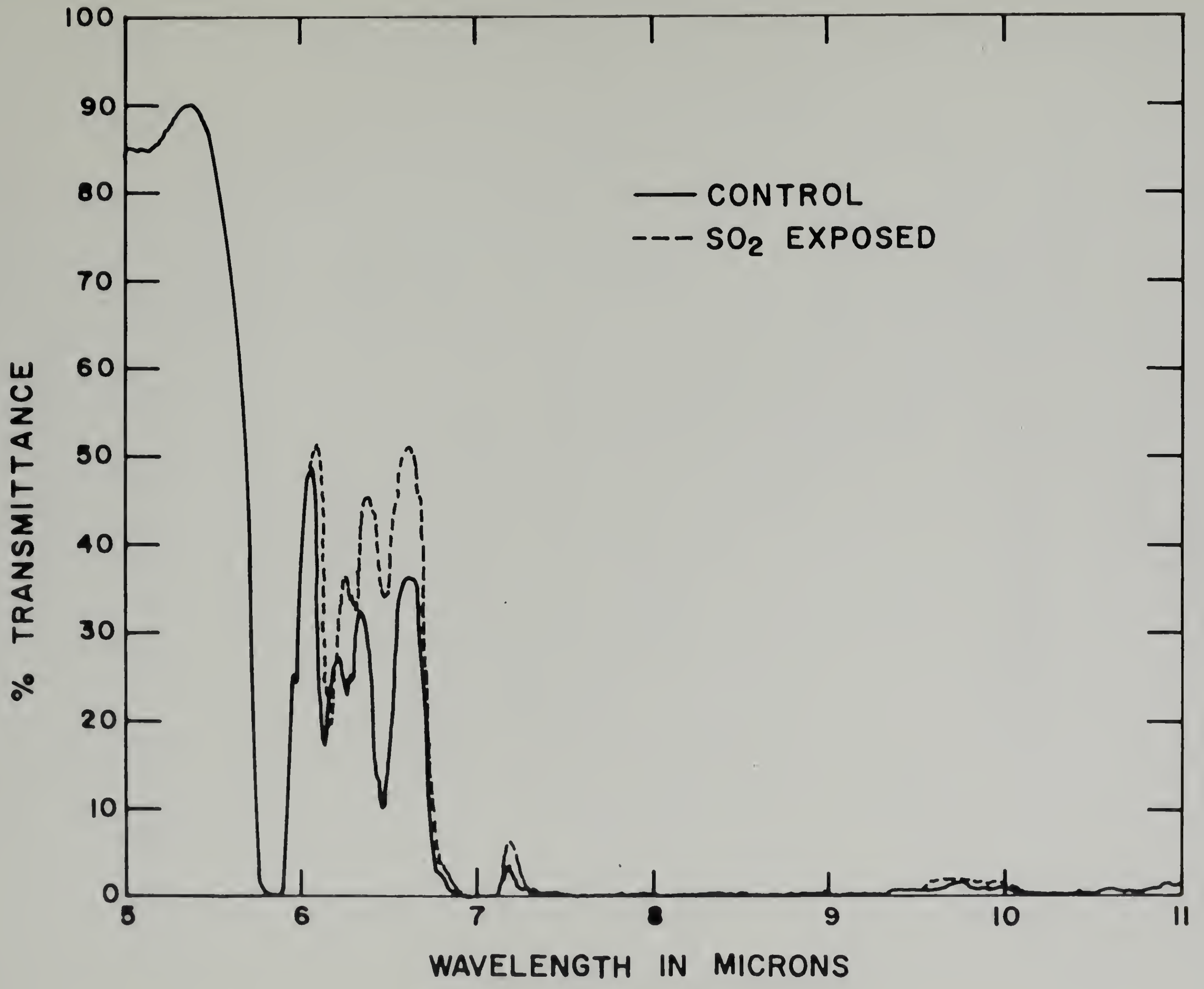

Figure 5. The infrared transmission spectra of clear PVC plastic before and after exposure to SO_2 in air for 7 days.

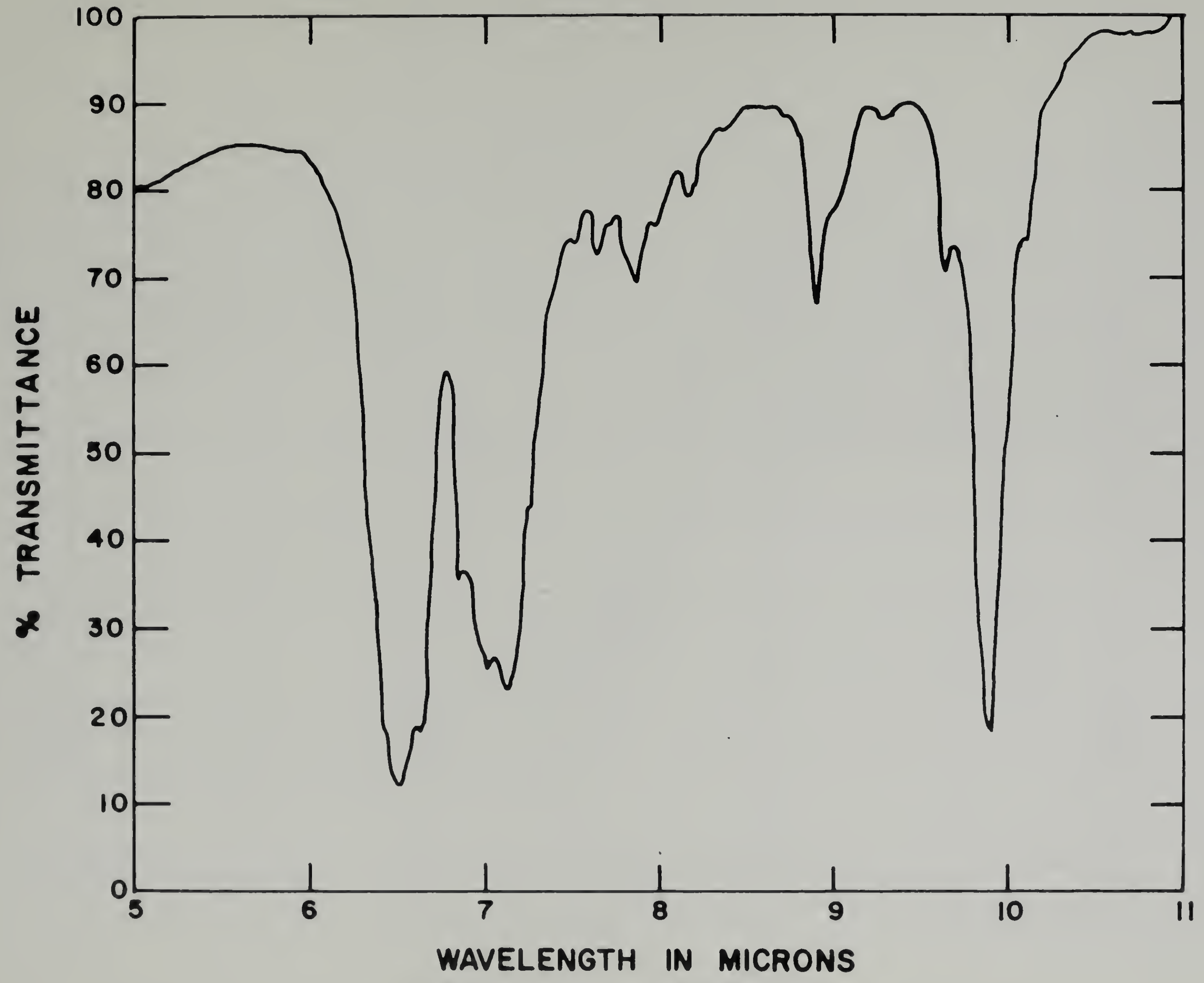

Figure 6. The transmission spectrum of barium-cadmium heat stabilizer used in PVC plastics.

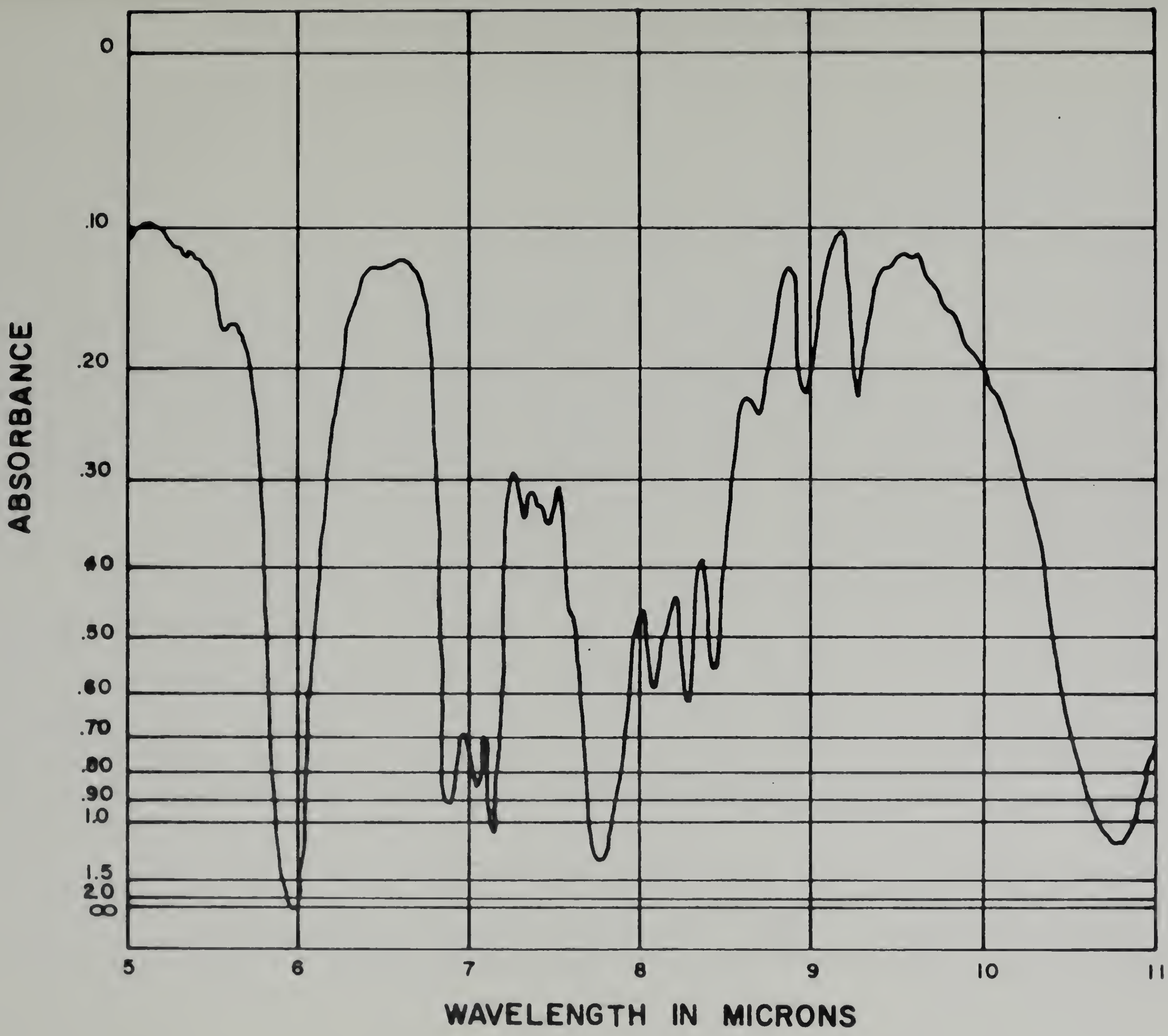

Figure 7. The infrared transmission spectrum of acid hydrolyzed barium-cadmium heat stabilizer.


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