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Studies on the Photodegradation of Poly (Methyl Methacrylate)

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Jordan J. Baruch, ***Assistant Secretary for Science and Technology***
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, ***Director***

ABSTRACT

When poly (methyl methacrylate), PMMA, is exposed to sunlight, it gradually degrades and, after long-term exposures, may be unable to perform its intended functions. While the photodegradation of PMMA has been studied extensively using radiation sources below 300 nm, natural sunlight at the earth's surface does not extend below 292 nm. This study was performed in order to examine the effect of the radiation from the upper part of the ultraviolet, UV, and the visible regions on PMMA and to identify the mechanism(s) of degradation induced by the radiation.

Thin films of PMMA were irradiated in air with upper UV, upper UV-visible, upper UV-visible-near infrared and 436 and 546 nm radiation. Exposure to either the upper UV or visible radiation caused degradation of the polymer. The data show that both random scission and unzipping of the polymer chain are operative in the degradation. Unzipping becomes increasingly important with incident radiation of increasing wavelength.

Key Words: Degradation, IR; photodegradation; poly(methyl methacrylate); UV; visible.

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CONTENTS

1. INTRODUCTION

Poly (methyl methacrylate), PMMA, is an important polymer in the building industry as well as other industries [1]. However, despite its long history of use, little information is available from controlled tests about the stability of the polymer to long-term exposure to sunlight.

Studies of the degradation of PMMA when exposed to the 253.7 nm mercury line have been carried out [2-7]. The photolysis of PMMA under these conditions has been assumed to result in a random scission of the polymer backbone by a free radical process [1,6,8]. The main volatile products of the photolysis in air are methyl methacrylate, methyl formate, methanol, carbon monoxide, carbon dioxide and hydrogen. In contrast, the dominant product of thermal degradation is monomer which is liberated in high yield at 250°C. The mechanism of monomer formation is assumed to be the reverse of free radical polymerization [9]. After the initial chain homolytic scission generates radicals, the latter unzip to produce monomer [1,9].

Earlier [1] we reported the irradiation of PMMA with 253.7 and 300 nm mercury lamps and found that this radiation caused a rapid decrease in the molecular mass accompanied by a small amount of volatile products, characteristic of random scission degradation. Molecular mass and glass transition temperature data further showed that, while the intensity of 300 nm lamps at the 253.7 nm wavelength was about one tenth of that of the 253.7 nm lamps, the quantum yield was about one fourth [1]. That led us to conclude that ultraviolet (UV) radiation greater than 253.7 nm plays a role in the degradation. We also noted [1] that the mass loss data showed that exposure to 300 nm lamps resulted in a greater mass loss than exposure to 253.7 nm lamps. Finally we suggested that the longer wavelength radiation results in a different degradation mechanism than for 253.7 nm. We noted that the mechanism might be, at least in part, a thermal degradation.

When PMMA is exposed to sunlight for a long period of time it degrades. Since no 253.7 nm irradiation reaches the earth's surface, degradation studies above 300 nm were carried out in order to begin building a data base for understanding how the polymer degrades at longer wavelengths so that methods of stabilizing it might be developed.

For these reasons we proposed to study the effect of the following additional radiation sources on the degradation of PMMA:

a. Irradiation from 300 nm lamps filtered with a pyrex filter to eliminate the band at 253.7 nm.

b. Irradiation from 350 nm lamps, in which the spectrum is almost entirely between 300 and 400 nm.

c. Irradiation in the upper UV (300-400 nm) and the visible spectrum using a flood lamp and an infrared (IR) filtered Xenon arc lamp.

d. Irradiation with two different bands in the visible, 436 nm (blue) and 546 nm (green).

e. Irradiation from a Xenon arc lamp with borosilicate filters, simulating outdoor weathering and sunlight which contain the upper UV, visible and IR light.

Such studies, combined with earlier studies [1] were needed to characterize more fully the mechanisms of degradation under these different conditions. Once the degradation mechanisms are characterized, the feasibility of utilizing accelerated aging tests to predict the long-term performance of the polymer can be determined.

2. EXPERIMENTAL

2.1 Test Samples

Test samples of PMMA of two different mass average molecular masses (190,000 and 240,000) were provided by the Rohm and Haas Company*, these were identified as PMMA I and II, respectively. The polymer was purified and cast into thin films (20 ± 5 μ). For a detailed description of this method see [1].

2.2 Light Sources

2.2.1 Mercury lamps

2.2.1.1 Photochemical reactor

The photochemical reactor has been described previously [1]. The lamps used in the irradiation of samples were the 300 nm and 350 nm lamps, the radiation from the former being filtered through pyrex. The spectral distribution of these two sets of lamps are shown in Figure 1 and 2, respectively.

2.2.1.2 Flood lamp

A high intensity mercury lamp with pyrex filters, operating at a constant power of 400 watts, was used to irradiate the sample. Exposures were performed with and without bandpass optical filters. Two different filters were used, one transmitted a band at 436 nm (blue) while the other transmitted a band at 546 nm (green). The spectral distribution

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* DISCLAIMER: Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

of the flood lamp alone and of the blue and green light are shown in Figures 3, 4 and 5, respectively.

2.2.2 Xenon-Arc Lamp

An Atlas Electric Weatherometer (Model M65) was used in irradiating the polymer. The Xenon arc lamp was operated at 650 watts and monitored at three different wavelengths 340, 420 and 580 nm. Infrared and borosilicate filters were used with this lamp. The spectral distributions of the Xenon arc lamp with these filters in the light path are shown in Figures 6 and 7. The temperature inside the weatherometer was monitored and did not exceed 50°C.

2.3 Polymer Irradiation

For the irradiations with the 300 and 350 nm lamps (Rayonet) see [1] When the flood lamp was used for irradiation, the PMMA samples were clipped to glass slides and placed 200 mm from the lamp. While in the case of the Xenon arc lamp the samples were mounted on an aluminum holder which was held vertically facing the lamp at a distance of 480 mm (see Figure 8). Samples of PMMA I and II were exposed to all of the different light sources for 1000, 2000, 3000 and 4000 hours respectively. In addition PMMA I and II samples were respectively exposed for 500 and 1500 hours to the flood and the Xenon lamp. Additional exposures of 4500, 6000 and 8000 hours were made with the Xenon lamp and borosilicate filters.

2.4 Experimental Methods

The molecular masses were measured using the gel permeation chromatography technique. The glass transition temperature (T_g) was measured by thermal mechanical analysis (TMA). The UV, IR spectra and the prcent mass loss were measured according to the normal technique. For a complete description of these methods see [1].

3. RESULTS AND DISCUSSION

The data obtained from the various experiments are shown in Table 1 through 14. The mass average molecular mass, $\bar{M}w$, of PMMA I and II decreased by 22.8 and 23.4 percent, respectively, after irradiation with the 300 nm lamps with pyrex filter for 4000 hours (Tables 1 and 2). While irradiation of the 350 nm lamps for 4000 hours, the $\bar{M}w$ of PMMA I and II decrease by 11.6 and 12.9 percent, respectively (Tables 3 and 4). The flood lamp with a pyrex filter was intense, and irradiated samples showed bigger decreases in $\bar{M}w$ of 33.9 and 33.1 percent respectively when each were irradiated for the the same number of hours. (Tables 5 and 6). When the polymer was irradiated for 4000 hours with the blue (436 nm) light the degradation was slow and $\bar{M}w$ respectively decreased by 7.9 and 8.1 percent for PMMA I and II (Tables 7 and 8), while with a 4000 hours exposure to the green (546 nm) light the $\bar{M}w$ decreased by 6.9 percent for both PMMA I and II (Tables 9 and 10).

In the case of the Xenon lamp with IR filters the exposure time was also 4000 hours and the $\bar{M}w$ decreased by 22.2 and 21.8 for PMMA I and II, respectively (Tables 11 and 12). While with borosilicate filters, PMMA I and II was exposed for 8000 hours and $\bar{M}w$ decreased by 34.9 and 37.5 percent, respectively (Tables 13 and 14).

From these data, the percent degradation was calculated as the mass average molecular mass as percent of the original for PMMA I and II when irradiated with different light sources. The data are summarized in Table 15 and Figures 9 and 10. An examination of the data shows that irradiation with the upper part of the UV region (300-400 nm) from the 350 nm lamps causes degradation of PMMA. Similarly degradation was caused by irradiation of PMMA with 436 nm (blue) light and 546 nm (green) light. As shown in Figures 9 and 10, the rates of degradation caused by the optical bands are much slower than that by the higher-energy light sources.

Percent mass loss and changes in the T_g of PMMA I and II caused by irradiation with different light sources are summarized in Tables 16 and 17, respectively. The percent mass loss and the T_g are plotted vs. percent degradation for PMMA I and II in Figures 11, 12, 13 and 14 and 15, 16, 17 and 18, respectively.

The percent mass loss was the highest when PMMA I and II were irradiated with the Xenon lamp with borosilicate filters: 2.83 and 2.97, respectively (Tables 13 and 14). The smallest percent mass loss (0.49 and 0.51 percent) was due to the green (546 nm) light. The rest of irradiation caused a mass loss in between these extremes.

By examining Figures 11 and 12 we observe that for the same percent degradation, the percent mass loss is higher for PMMA exposed to the Xenon lamp with borosilicate filters than all other light sources. Figures 13 and 14 show the percent degradation vs. percent mass loss for PMMA I and II, respectively, irradiated with 253.7 nm, 300 nm [1], 300 nm with pyrex filter and 350 nm lamps as well as the Xenon arc lamp with borosilicate filters. We can see clearly that for the same percent degradation the irradiation with 253.7 nm lamps caused the lowest mass loss, followed by the 300 nm lamps without a filter. As noted before (Figures 11 and 12), irradiation with the Xenon lamp with borosilicate filters shows the highest mass loss, while all of the other sources causes losses between the extreme values.

The irradiation of PMMA causes an increase in the UV absorption of the thin film, as shown in Figures 19 and 20. Increase in the absorption between

260 and 320 nm previously observed [1] was also observed here. This absorption is in the region usually associated with carbonyl chromphores and is believed to result from carbonyl groups in the polymer chain itself rather than in the low molecular mass photolysis products.

The only changes in the IR spectrum of PMMA during the irradiation were a broadening of the carbonyl band at 5.71 μm (1750 cm^{-1}) and the appearance of small new bands at 6.19-6.10 μm (1610-1640 cm^{-1}). The latter bands are attributed to olefinic unsaturation produced during the photolytic chain scission. It should be noted that substantial degradation has to occur in order to form enough fragments with unsaturated groups, or containing carbonyl chromophore to cause changes in the UV and IR spectra.

It is interesting to note that the Xenon lamp with the borosilicate filters is the only light source with a substantial portion of radiation in the IR regions (Figure 7). While most of the other light sources emit radiation which falls in the upper part of UV (300-400 nm) and the visible (400-700 nm), (Figures 1-6), only the 253.7 nm and the 300 nm lamps without a filter, emit primarily in the UV region [1].

It is known that with random scission the amount of volatile products are very small, while with unzipping, is much larger. From the percent mass loss vs. percent degradation and the information about the light sources one can conclude that in addition to the random scission mechanism proposed for the photodegradation of PMMA at 253.7, unzipping of the polymer chain is also occurring. Moreover, the unzipping increases with increasing incident wavelength, which is seen by the increase of the percent mass loss in this direction.

Although the percent mass loss as a result of irradiation with IR-component lamps was relatively small in the case of the high molecular mass polymers used in this study, the IR-induced mass loss may become significant in polymers of lower molecular masses.

From Figures 15-18 one can see that for the same percent degradation there is good aggreement in the change in the glass transition temperature with irradiation, no matter what the light source is. One can also notice that the initial rate of decrease in the glass transition temperature is high compared to the rate at later stage of degradation which it does agree with the general relationship between molecular mass and glas transition temperature (Figures 17 and 18).

4. CONCLUSIONS

The test data show that the irradiation of PMMA with visible light causes degradation of the polymer. This has not been reported before. Also, the irradiation of PMMA with UV radiation above 300 nm wavelength alone causes the polymer to degrade.

The data also reveal that the percent mass loss for the same percent degradation increases with increasing incident wavelength up to and including the IR region. This leads to the conclusion that in addition to the random scission mechanism proposed for the photodegradation of PMMA, unzipping of the polymer chain plays an important role in the degradation. This role increases with increasing wavelength of incident radiation.

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Table 1. PMMA I Exposed to 300 nm Lamps, with Pyrex Filter, in Air

Exposure Time in Hrs.	$\bar{M}_w \times 10^{-3}$ [a*]	$\bar{M}_n \times 10^{-3}$ [a*]	$\bar{M}_w$ as % of Original	T_g °C [b*]	% Mass Loss
0	189	152	100	115	0
1000	176	139	93.1	113	.32
2000	165	129	87.3	111	.71
3000	156	121	82.5	110	1.02
4000	146	112	77.2	109	1.24

[a*] The molecular mass averages were determined by gel permeation chromatograhy.

[b*] The glass transition temperatures were determined by thermal mechanical analysis.

Table 2. PMMA II Exposed to 300 nm Lamps, with Pyrex Filter, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	248	197	100	115	0
1000	230	181	92.7	114	.39
2000	214	166	86.3	112	.87
3000	204	156	82.3	111	1.12
4000	190	144	76.6	110	1.46

Table 3. PMMA I Exposed to 300 nm Lamps, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	189	152	100	115	0
1000	183	147	96.8	115	.22
2000	177	141	93.7	114	.40
3000	172	137	91.0	113	.57
4000	167	132	88.4	112	.75

Table 4. PMMA II Exposed to 300 nm Lamps, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	248	197	100	116	0
1000	239	189	96.4	116	.24
2000	231	182	93.1	115	.42
3000	223	175	89.9	114	.61
4000	216	169	87.1	114	.78

Table 5. PMMA I Exposed to the Flood Lamp with Pyrex Filter, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	189	152	100	115	0
500	176	139	93.1	114	.43
1000	167	131	88.4	112	.71
1500	159	123	84.1	111	.98
2000	148	115	78.3	110	1.29
3000	136	104	72.0	108	1.72
4000	125	93	66.1	106	2.20

Table 6. PMMA II Exposed to the Flood Lamp with Pyrex Filter, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	248	197	100	115	0
500	233	181	94.0	115	.42
1000	224	170	90.3	113	.65
1500	213	159	85.9	112	.97
2000	204	150	82.3	111	1.32
3000	186	133	73.4	109	1.71
4000	166	120	66.9	107	2.22

Table 7. PMMA I Exposed to 436 nm Light From the Flood Lamp, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	189	152	100	115	0
1000	185	149	97.9	115	$\sim$0
2000	182	146	96.3	114	.22
3000	178	142	94.2	114	.39
4000	174	137	92.1	113	.53

Table 8. PMMA II Exposed to 436 nm Light From the Flood Lamp, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g °C	% Mass Loss
0	248	197	100	116	0
1000	243	193	98.0	116	~ 0
2000	239	189	96.4	115	.24
3000	234	184	94.4	114	.41
4000	228	178	91.9	114	.55

Table 9. PMMA I Exposed to 546 nm Light From the Flood Lamp, in Air

Exposure Time in Hrs.	$\overline{Mw} \times 10^{-3}$	$\overline{Mn} \times 10^{-3}$	$\overline{Mw}$ as % of Original	T_g°C	% Mass Loss
0	189	152	100	115	0
1000	186	150	98.4	115	~0
2000	183	147	96.8	114	.20
3000	179	143	94.7	113	.36
4000	176	140	93.1	113	.49

Table 10. PMMA II Exposed to 546 nm Light From the Flood Lamp, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g°C	% Mass Loss
0	248	197	100	116	0
1000	244	194	98.4	115	$\sim$0
2000	240	190	96.8	115	.21
3000	236	186	95.2	114	.38
4000	231	181	93.1	114	.51

Table 11. PMMA I Exposed to Xenon Lamp with IR Filters, in Air

Exposure Time in Hrs.	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w$ as % of Original	T_g °C	% Mass Loss
0	189	152	100	115	0
500	184	147	97.4	114	.19
1000	178	141	94.2	114	.35
1500	172	135	91.0	113	.55
2000	168	130	88.9	113	.78
3000	159	123	84.1	112	1.09
4000	147	111	77.8	110	1.41

Table 12. PMMA II Exposed to Xenon Lamp with IR Filters, in Air

Exposure Time in Hrs.	$\overline{Mw}$ x 10^{-3}	$\overline{Mn}$ x 10^{-3}	$\overline{Mw}$ as % of Original	T_g°C	% Mass Loss
0	248	197	100	116	0
500	243	191	98.0	116	.18
1000	236	184	95.2	115	.32
1500	230	177	92.7	114	.51
2000	223	170	89.9	114	.73
3000	209	157	84.3	113	1.15
4000	194	143	78.2	111	1.49

Table 13. PMMA I Exposed to Xenon Lamp with Borosilicate Filters, in Air

Exposure Time in Hrs.	$\overline{Mw} \times 10^{-3}$	$\overline{Mn} \times 10^{-3}$	$\overline{Mw}$ as % of Original	T_g°C	% Mass Loss
0	189	152	100	115	0
500	182	146	96.3	114	.24
1000	178	141	94.2	113	.47
1500	175	138	92.6	113	.62
2000	165	130	87.3	112	1.08
3000	156	122	82.5	110	1.42
4500	144	111	76.2	109	1.84
6000	132	100	69.8	108	2.48
8000	123	92	65.1	107	2.83

Table 14. PMMA II Exposed to Xenon Lamp with Borosilicate Filters, in Air

Exposure Time in Hrs.	$\bar{M}w \times 10^{-3}$	$\bar{M}n \times 10^{-3}$	$\bar{M}w$ as % of Original	T_g °C	% Mass Loss
0	248	197	100	116	0
500	242	191	96.3	115	.22
1000	235	182	94.8	114	.49
1500	228	176	92.6	113	.77
2000	219	167	88.3	112	1.05
3000	206	156	83.1	111	1.61
4500	192	143	77.4	110	1.93
6000	176	129	71.0	109	2.45
8000	155	113	62.5	108	2.97

Table 15. Mass Average Molecular Masses as Percent of Original of PMMA I and II During Irradiation with Different Light Sources in Air

Exposure Time in Hours	300 nm Lamps with Pyrex Filter		350 nm Lamps		Flood Lamp with Pyrex Filter		436 nm Light		546 nm Light		Xenon Arc Lamp			
											IR Filters		Borosilicate Filters	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
500	--	--	--	--	93.1	94.0	--	--	--	--	97.4	98.0	96.3	96.3
1000	93.1	92.7	96.8	96.4	88.4	90.3	97.9	98.0	98.4	98.4	94.2	95.2	94.2	94.8
1500	--	--	--	--	84.1	85.9	--	--	--	--	91.0	92.7	92.6	92.6
2000	87.3	86.3	93.7	93.1	78.3	82.3	96.3	96.4	96.8	96.8	88.9	89.9	87.3	88.3
3000	82.5	82.3	91.0	89.9	72.0	73.4	94.2	94.4	94.7	95.2	84.1	84.3	82.5	83.1
4000	77.2	76.6	88.4	87.1	66.1	66.9	92.1	91.9	93.1	93.1	77.8	78.2	76.2*	77.4*
6000	--	--	--	--	--	--	--	--	--	--	--	--	69.8	71.0
8000	--	--	--	--	--	--	--	--	--	--	--	--	65.1	62.5

*Exposure for 4500 hours.

Table 16. Percent Mass Loss for PMMA I and II Exposed to Different Light Sources in Air

Exposure Time in Hours	300 nm Lamps with Pyrex Filter		350 nm Lamps		Flood Lamp with Pyrex Filter		436 nm Light		546 nm Light		Xenon Arc Lamp			
											IR Filters		Borosilicate Filters	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
500	--	--	--	--	.43	.42	--	--	--	--	.19	.18	.24	.22
1000	.32	.39	.22	.24	.71	.65	∼0	∼0	∼0	∼0	.35	.32	.47	.49
1500	--	--	--	--	.98	.97	--	--	--	--	.55	.51	.62	.77
2000	.71	.87	.40	.42	1.29	1.32	.22	.24	.20	.21	.78	.73	1.08	1.09
3000	1.02	1.12	.57	.61	1.72	1.71	.39	.41	.36	.38	1.09	1.15	1.42	1.61
4000	1.24	1.46	.75	.78	2.20	2.22	.53	.56	.49	.51	1.41	1.49	1.84*	1.93*
6000	--	--	--	--	--	--	--	--	--	--	--	--	2.48	2.45
8000	--	--	--	--	--	--	--	--	--	--	--	--	2.83	2.97

*Exposure for 4500 hours.

Table 17. Glass Transition Temperatures of PMMA I and II During Irradiation with Different Light Sources in Air

Exposure Time in Hours	300 nm Lamps with Pyrex Filter		350 nm Lamps		Flood Lamp with Pyrex Filter		436 nm Light		546 nm Light		Xenon Arc Lamp			
											IR Filters		Borosilicate Filters	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
500	--	--	--	--	114	115	--	--	--	--	114	116	114	115
1000	113	114	115	116	112	113	115	116	115	115	114	115	113	114
1500	--	--	--	--	111	112	--	--	--	--	113	114	113	113
2000	111	112	114	115	110	111	114	115	114	115	113	114	112	112
3000	110	111	113	114	108	109	114	114	113	114	112	113	110	111
4000	109	110	112	114	106	107	113	112	113	114	110	111	109*	110*
6000	--	--	--	--	--	--	--	--	--	--	--	--	108	109
8000	--	--	--	--	--	--	--	--	--	--	--	--	107	108

*Exposure for 4500 hours.

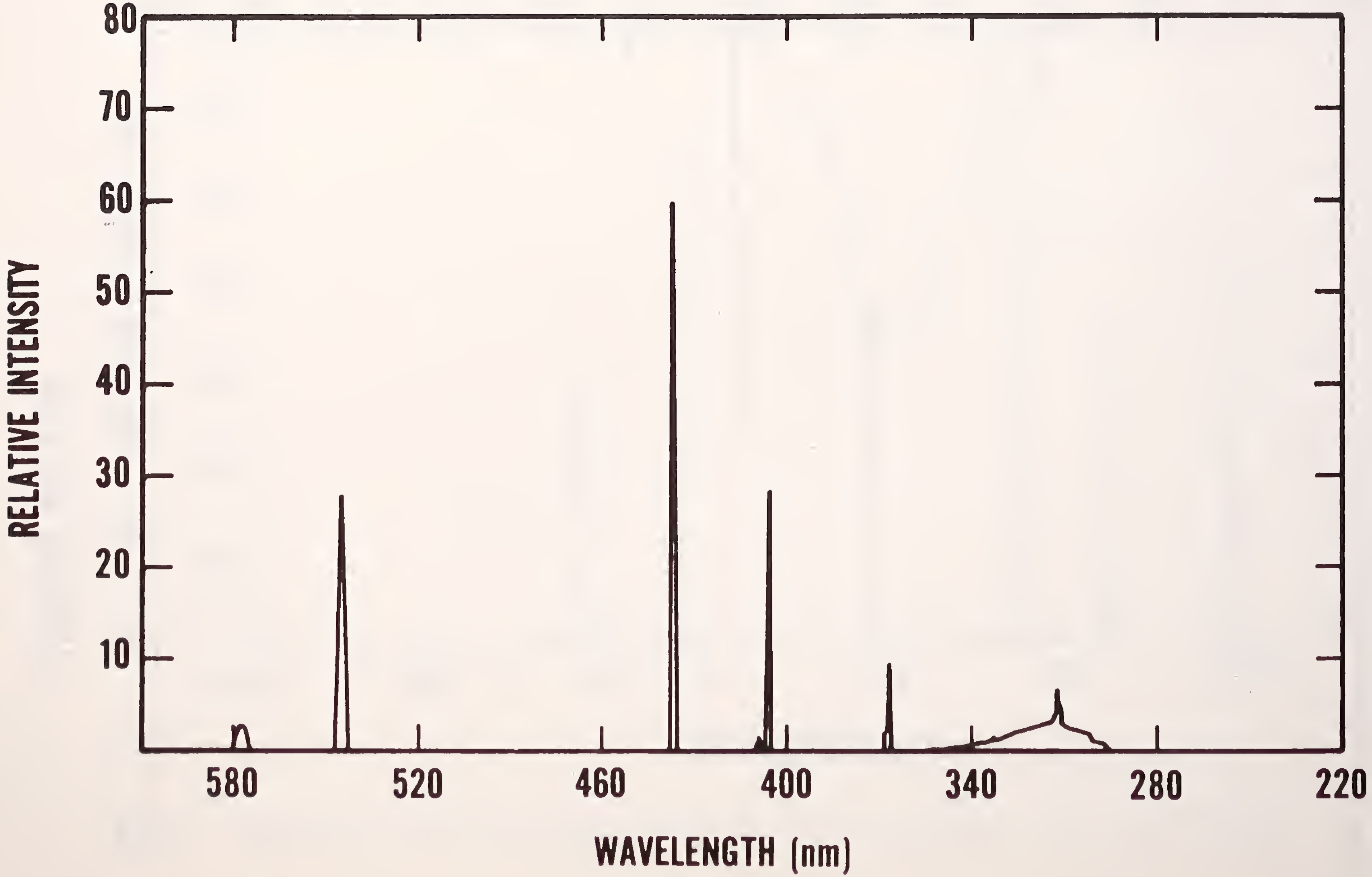

Figure 1. Spectral distribution of the 300 nm lamps with Pyrex filter used in the test reactor.

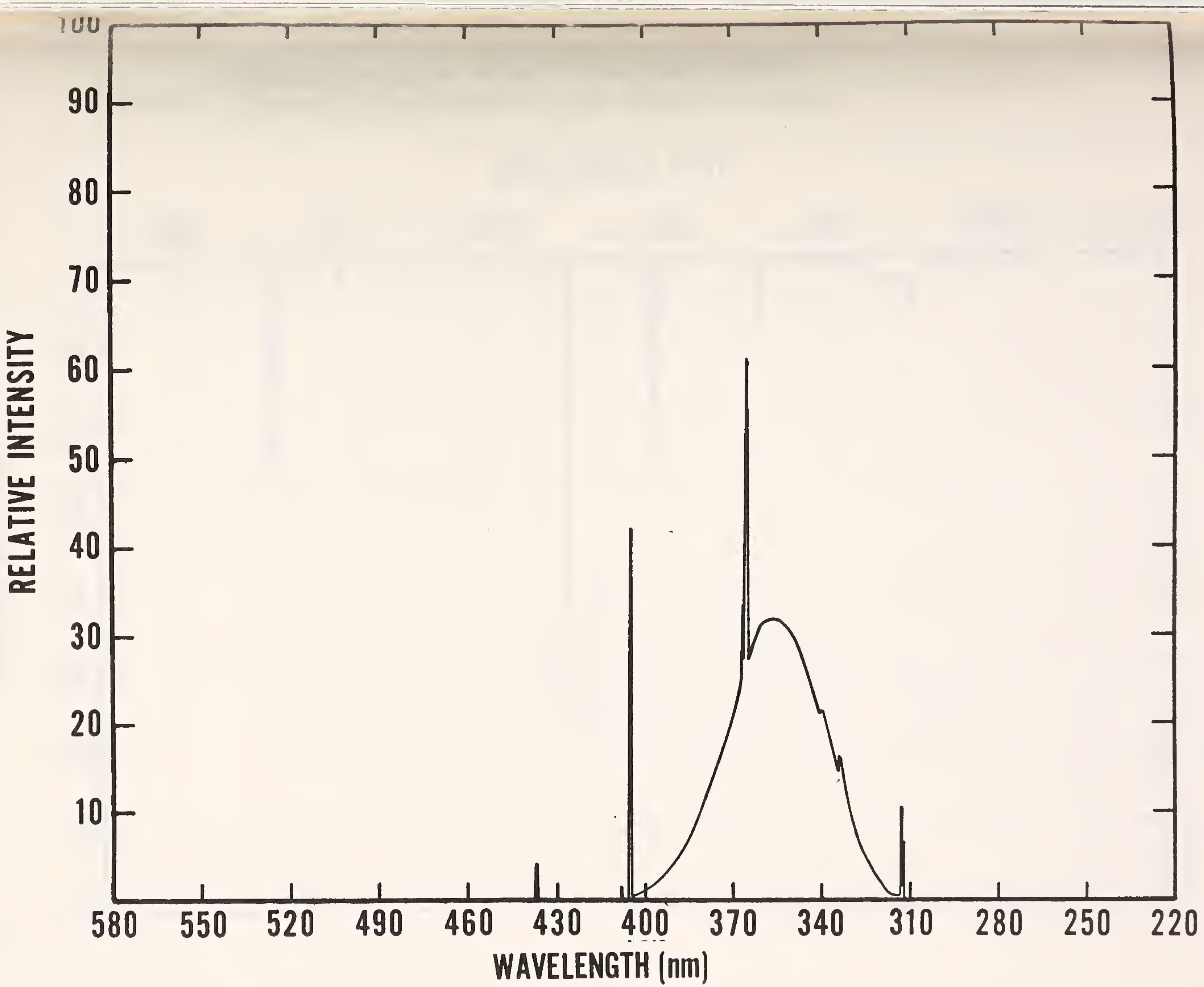

Figure 2. Spectral distribution of the 350 nm lamps used in the test reactor.

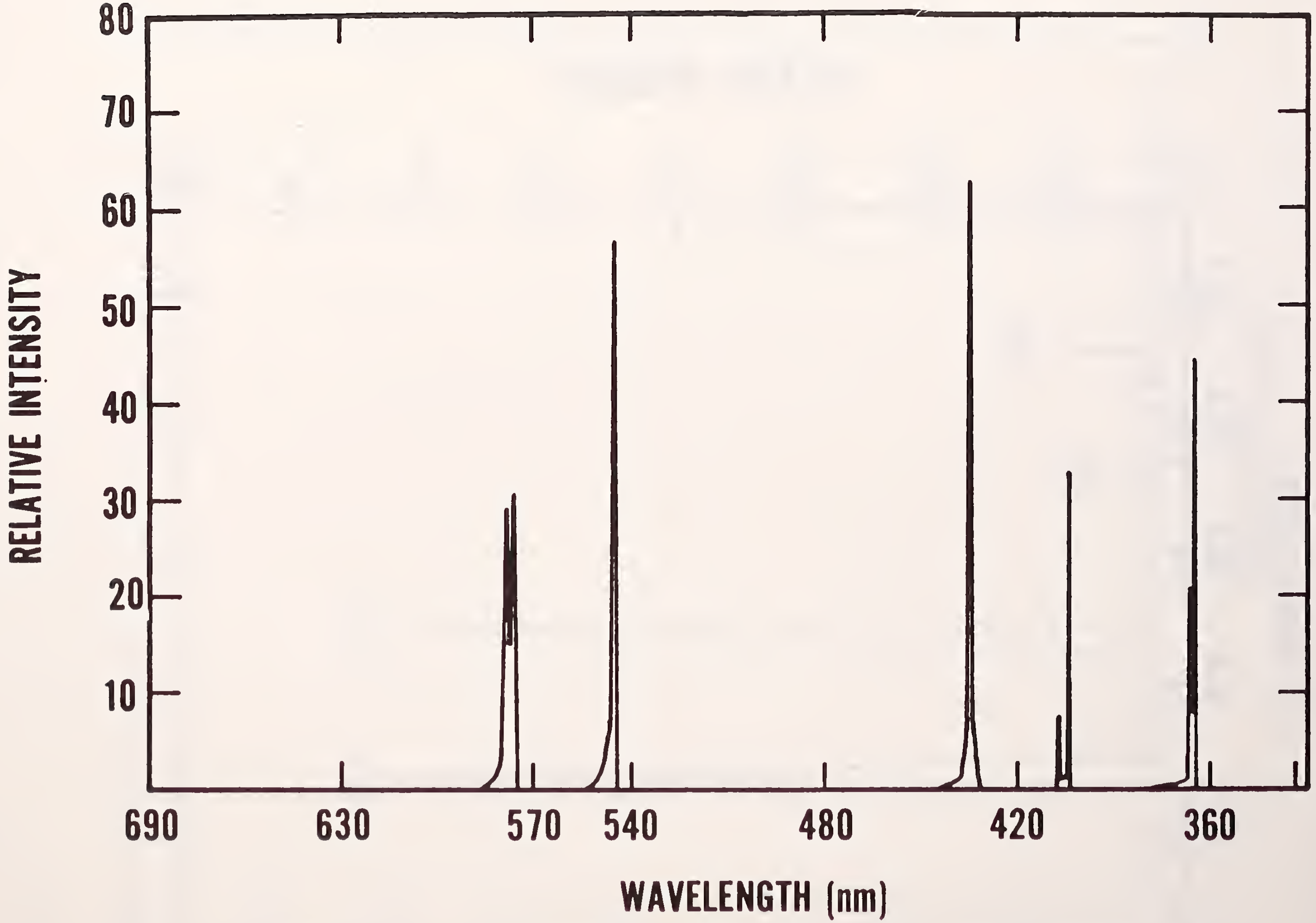

Figure 3. Spectral distribution of the flood lamp with Pyrex filter.

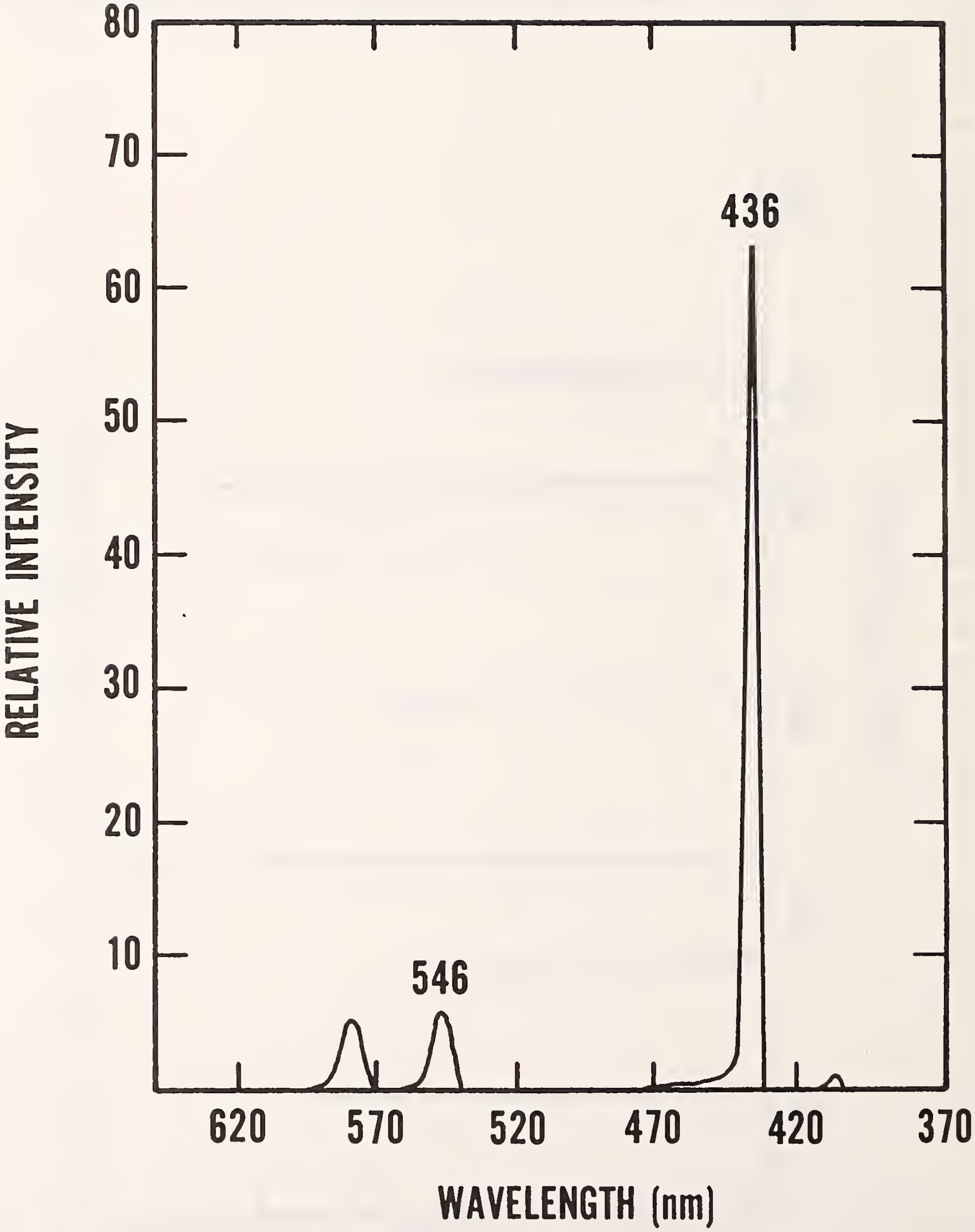

Figure 4. Spectral distribution of the 436 nm (blue) light band (from flood lamp with special filter).

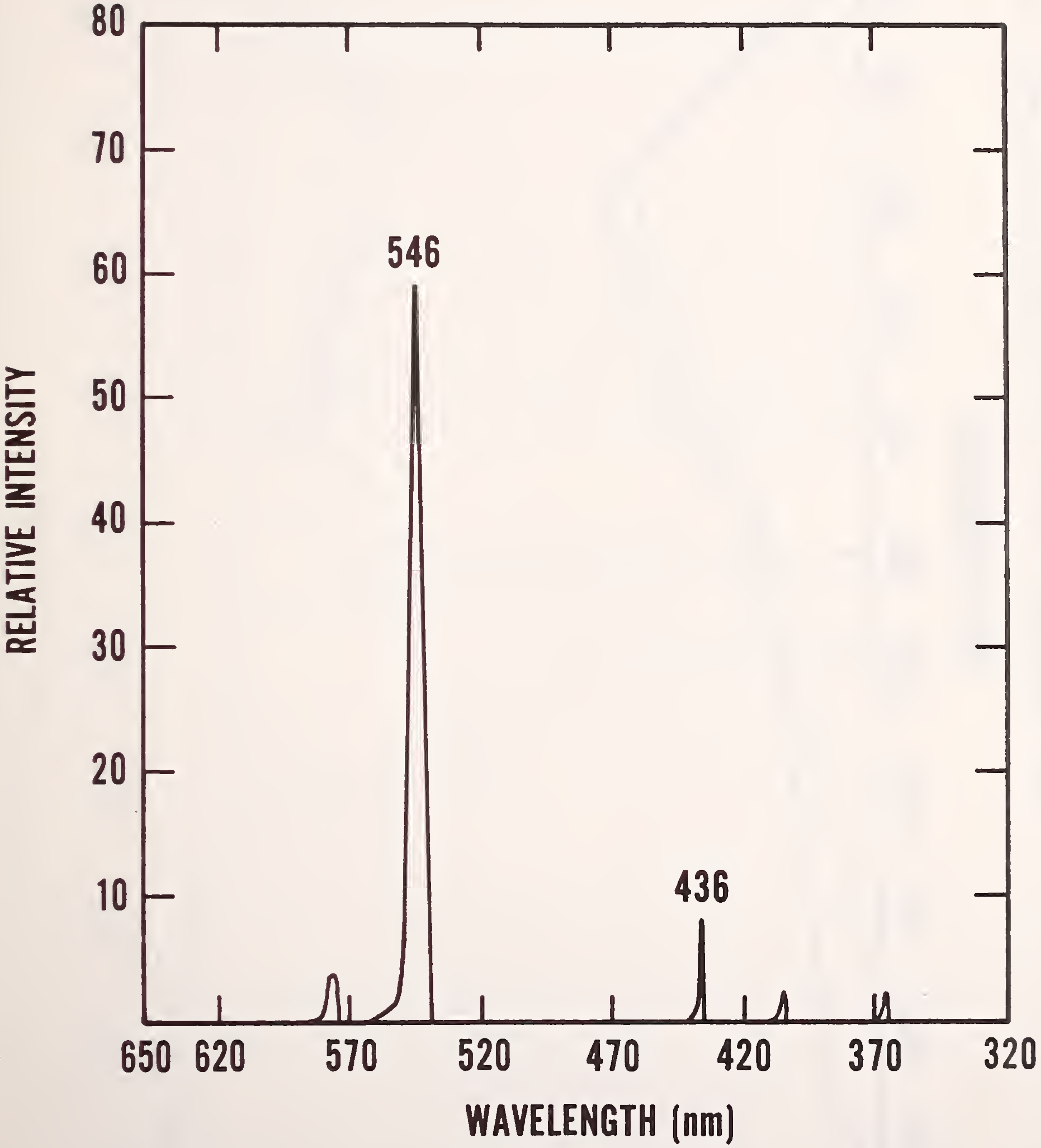

Figure 5. Spectral distribution of the 546 nm (green) light band (from flood lamp with special filter).

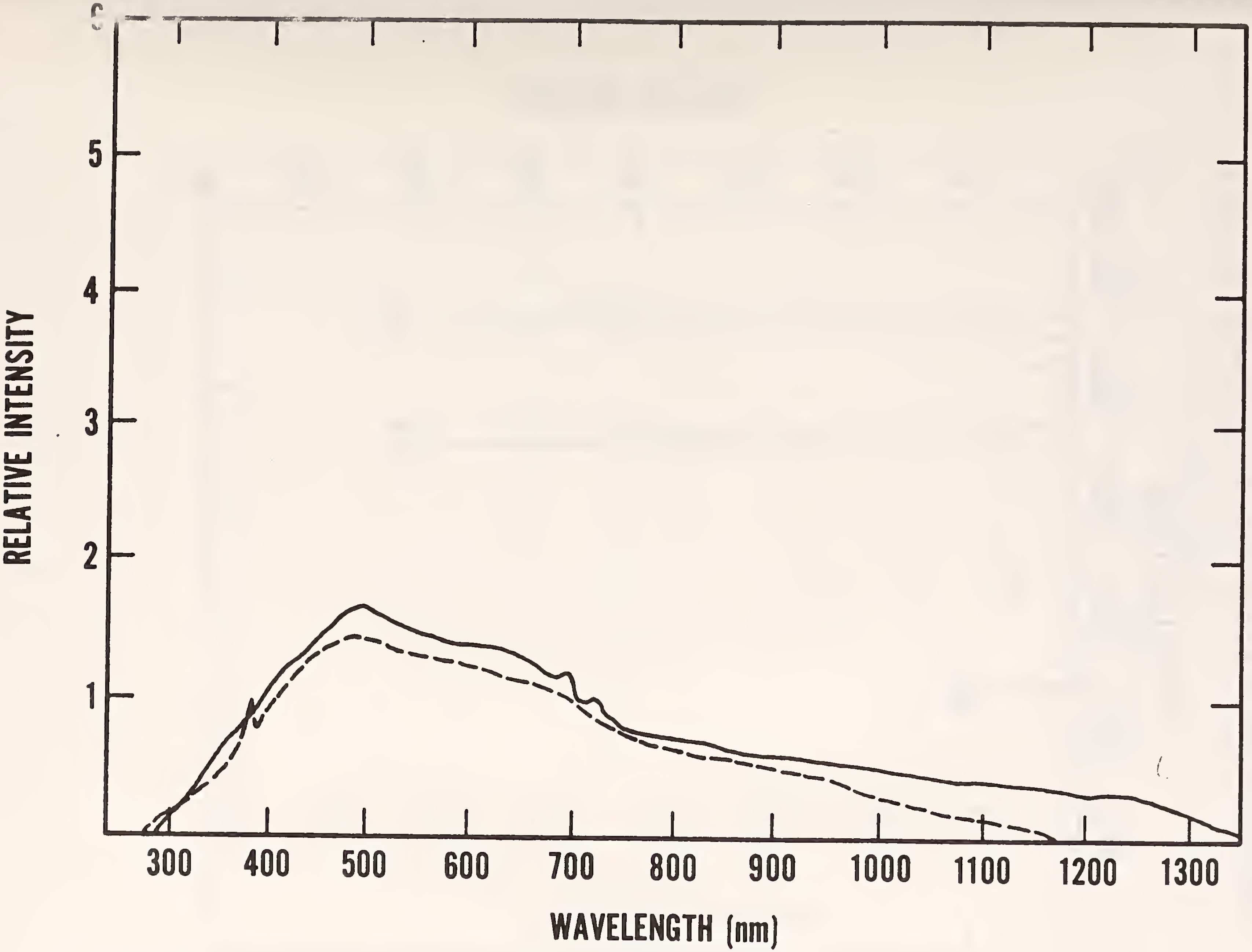

Figure 6. Spectral distribution of natural sunlight, noon June (——) and 6500 watt xenon lamp with IR filter (– – –).

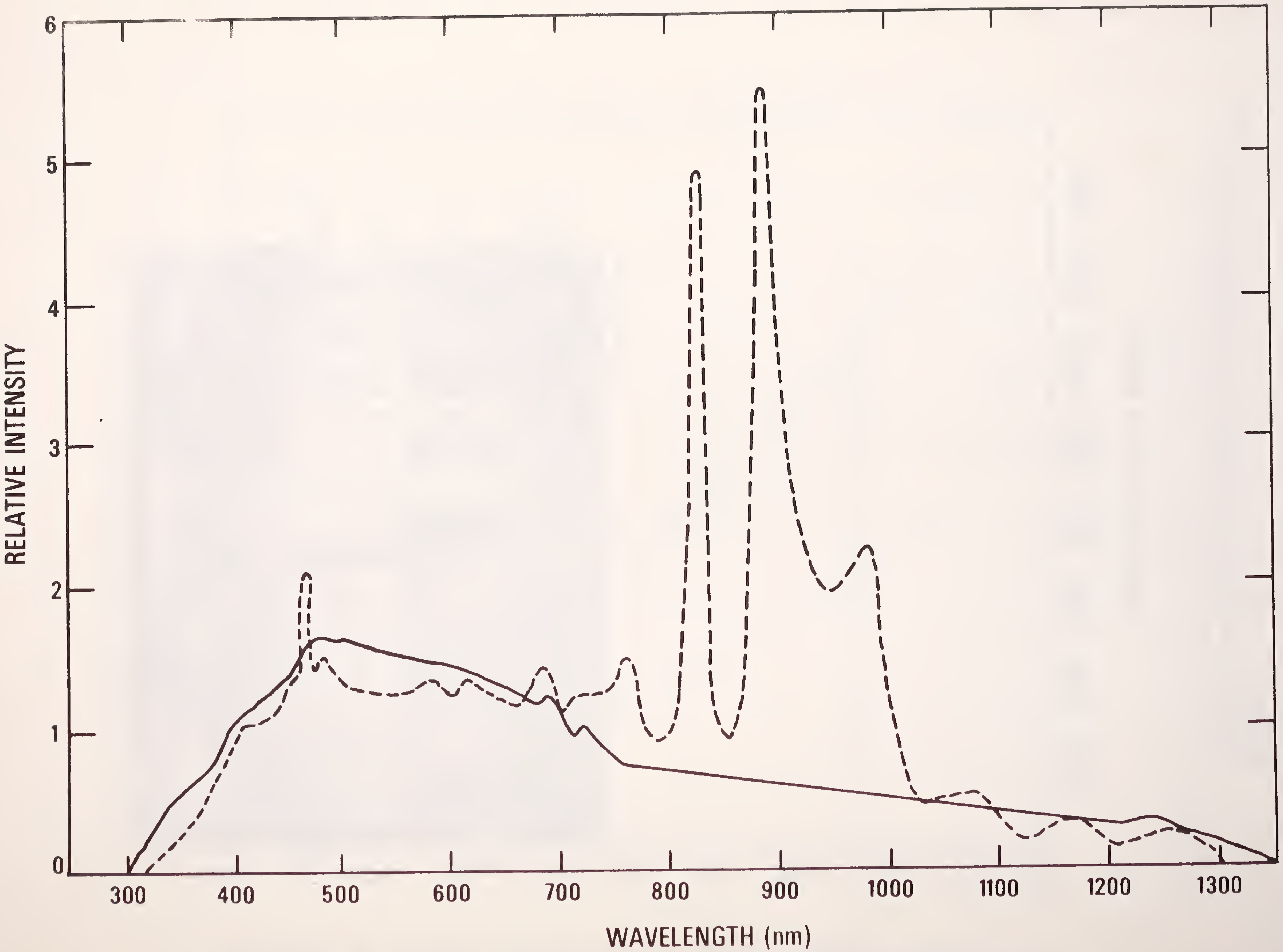

Figure 7. Spectral distribution of natural sunlight, noon June (——) and 6500 watt xenon lamp with borosilicate filter (–––).

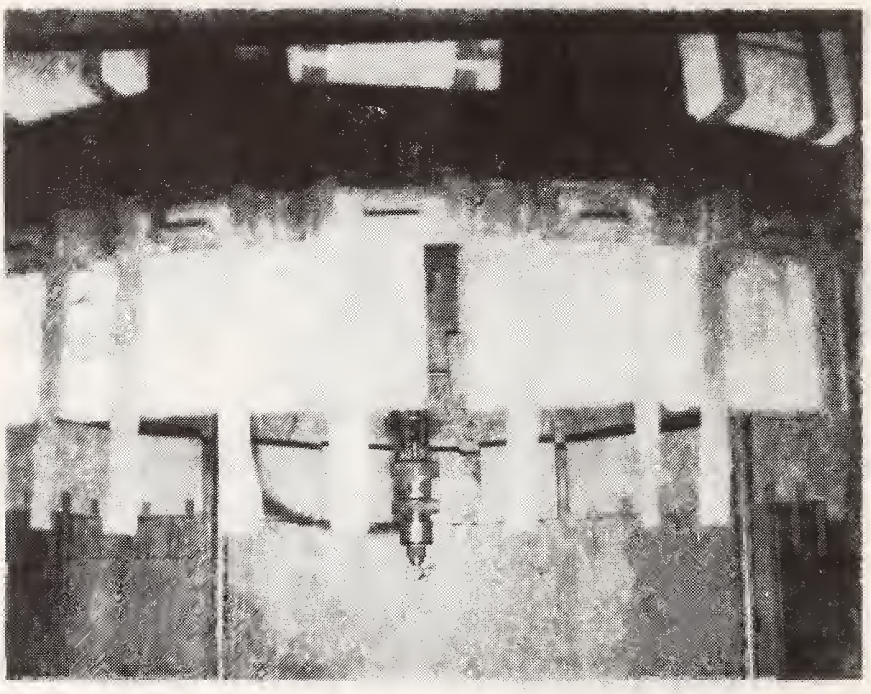

Figure 8. Inside view of the Xenon Arc Weatherometer.

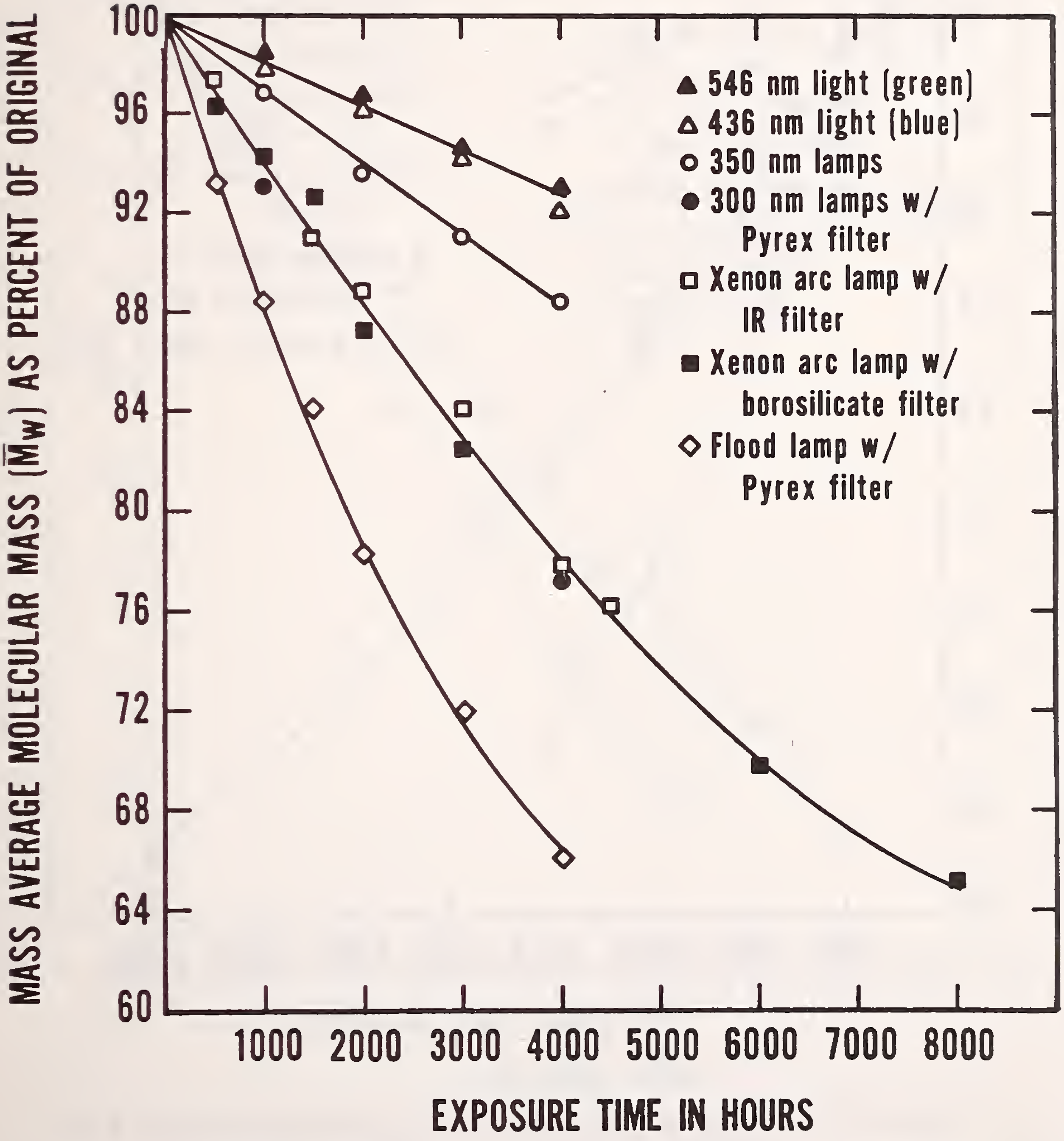

Figure 9. Percent degradation vs. exposure time for PMMA I exposed to different radiation sources in air.

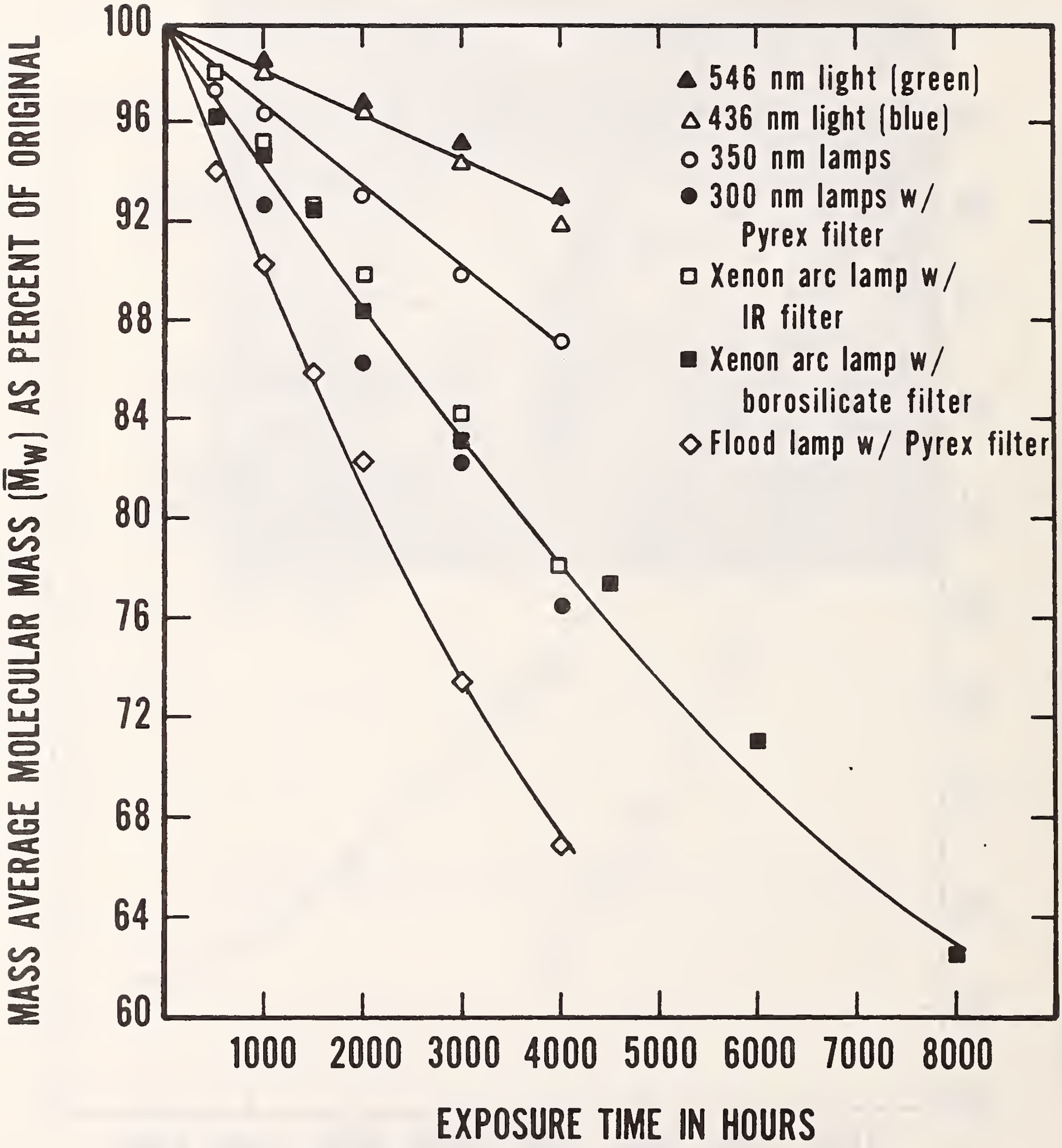

Figure 10. Percent degradation vs. exposure time for PMMA II exposed to different radiation sources in air.

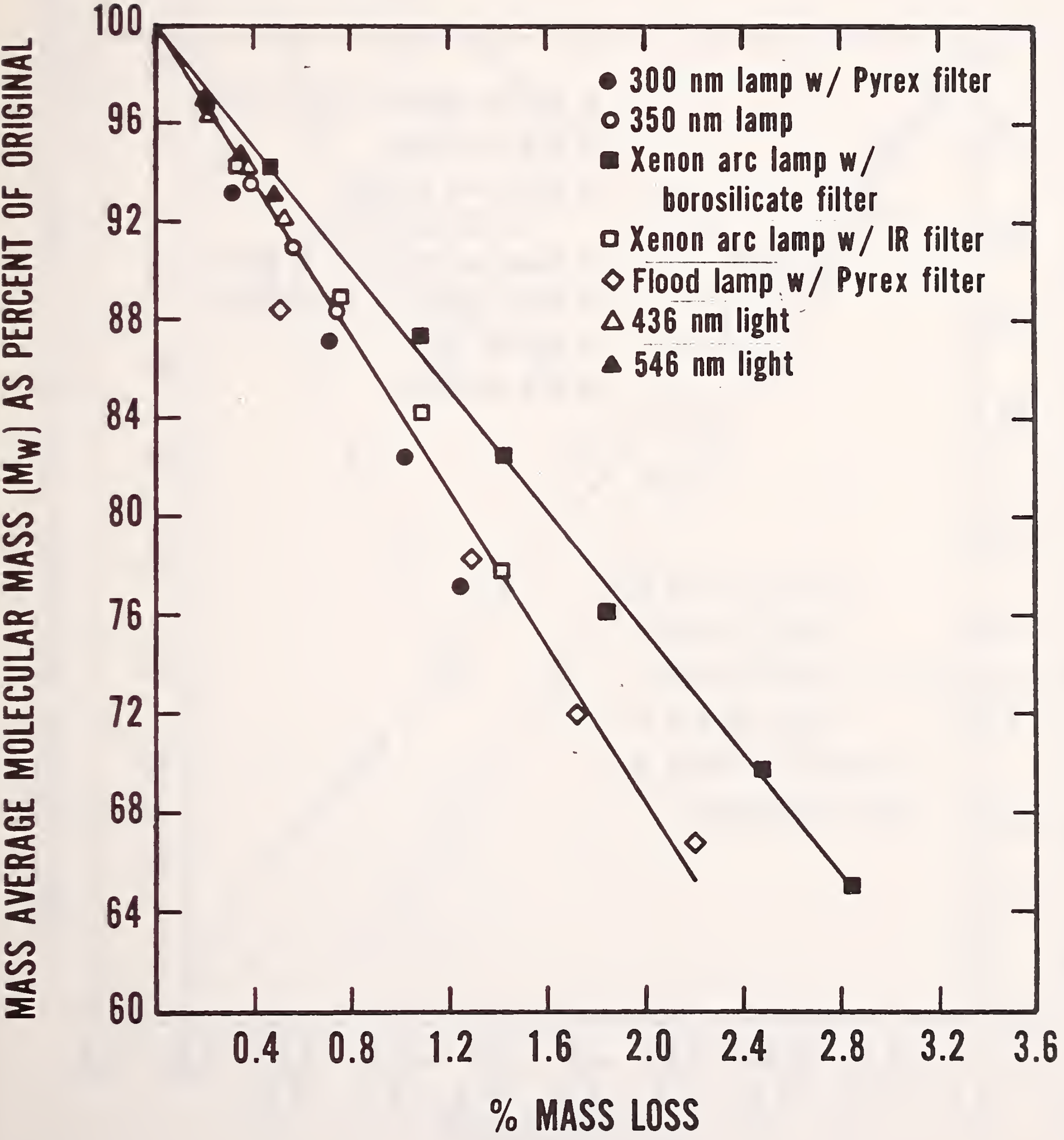

Figure 11. Percent degradation vs. percent mass loss for PMMA I exposed to different light sources in air.

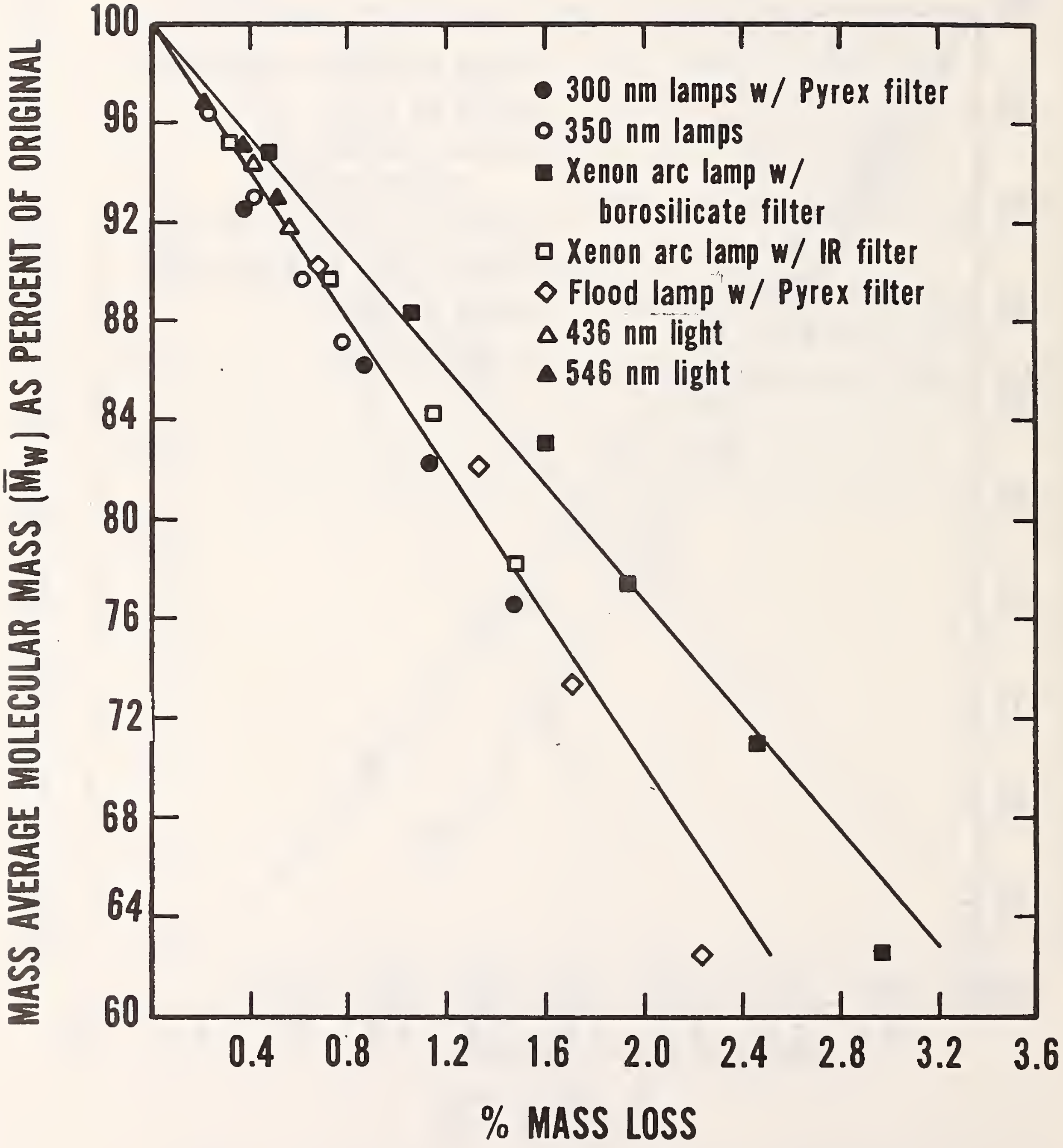

Figure 12. Percent degradation vs. percent mass loss for PMMA II exposed to different light sources in air.

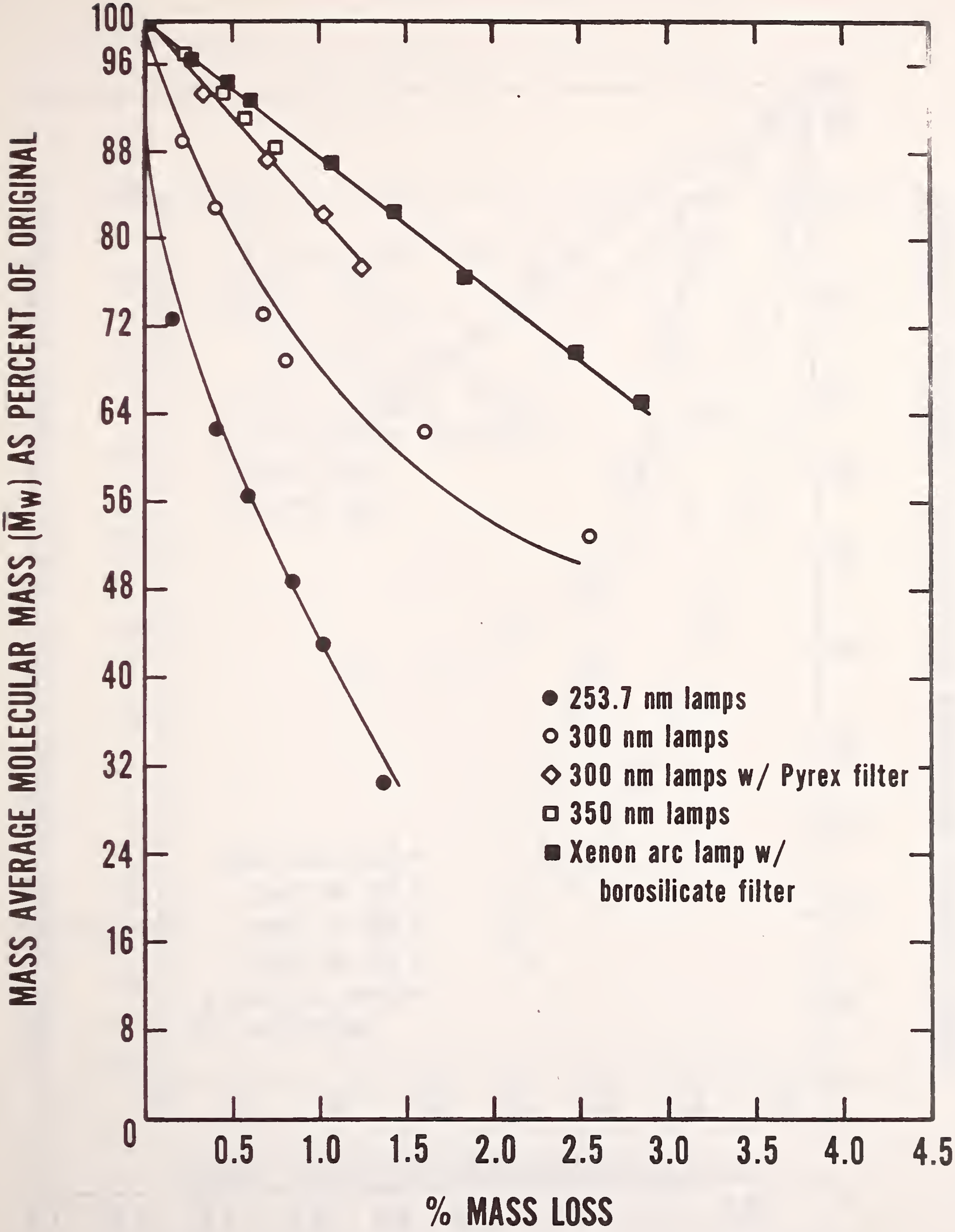

Figure 13. Percent degradation vs. percent mass loss for PMMA I exposed to different light sources in air.

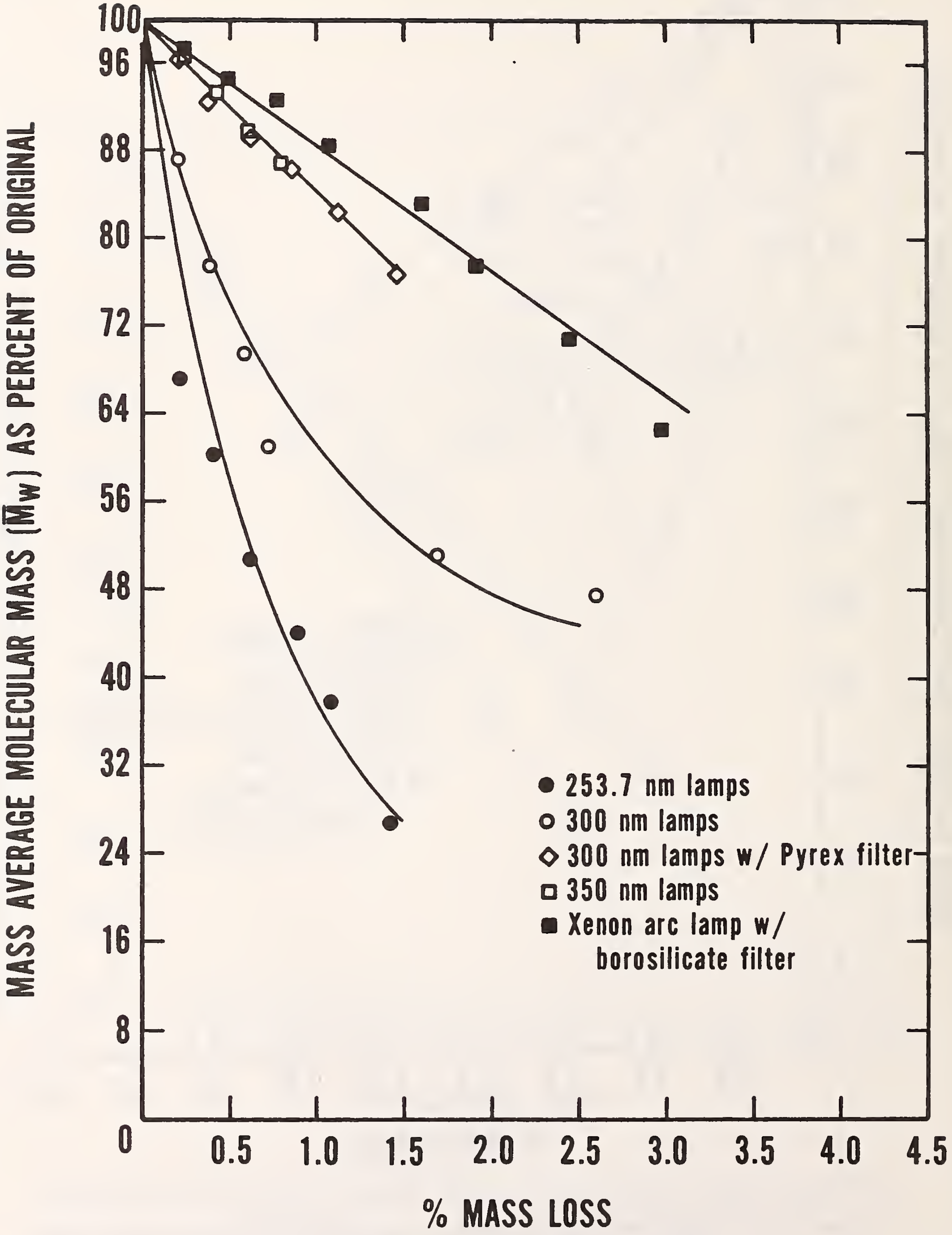

Figure 14. Percent degradation vs. percent mass loss for PMMA II exposed to different light sources in air.

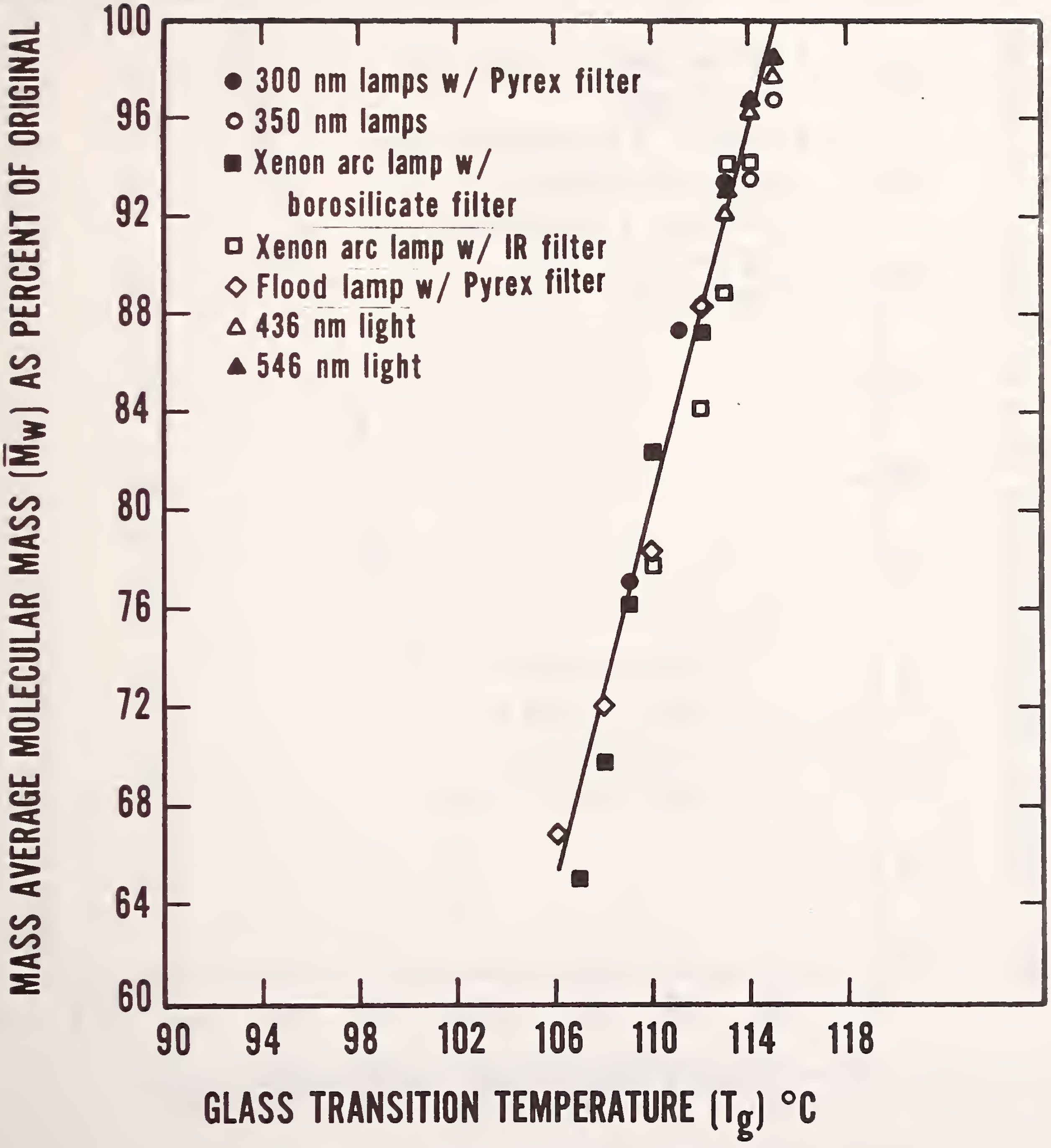

Figure 15. Percent degradation vs. Tg for PMMA I exposed to different light sources in air.

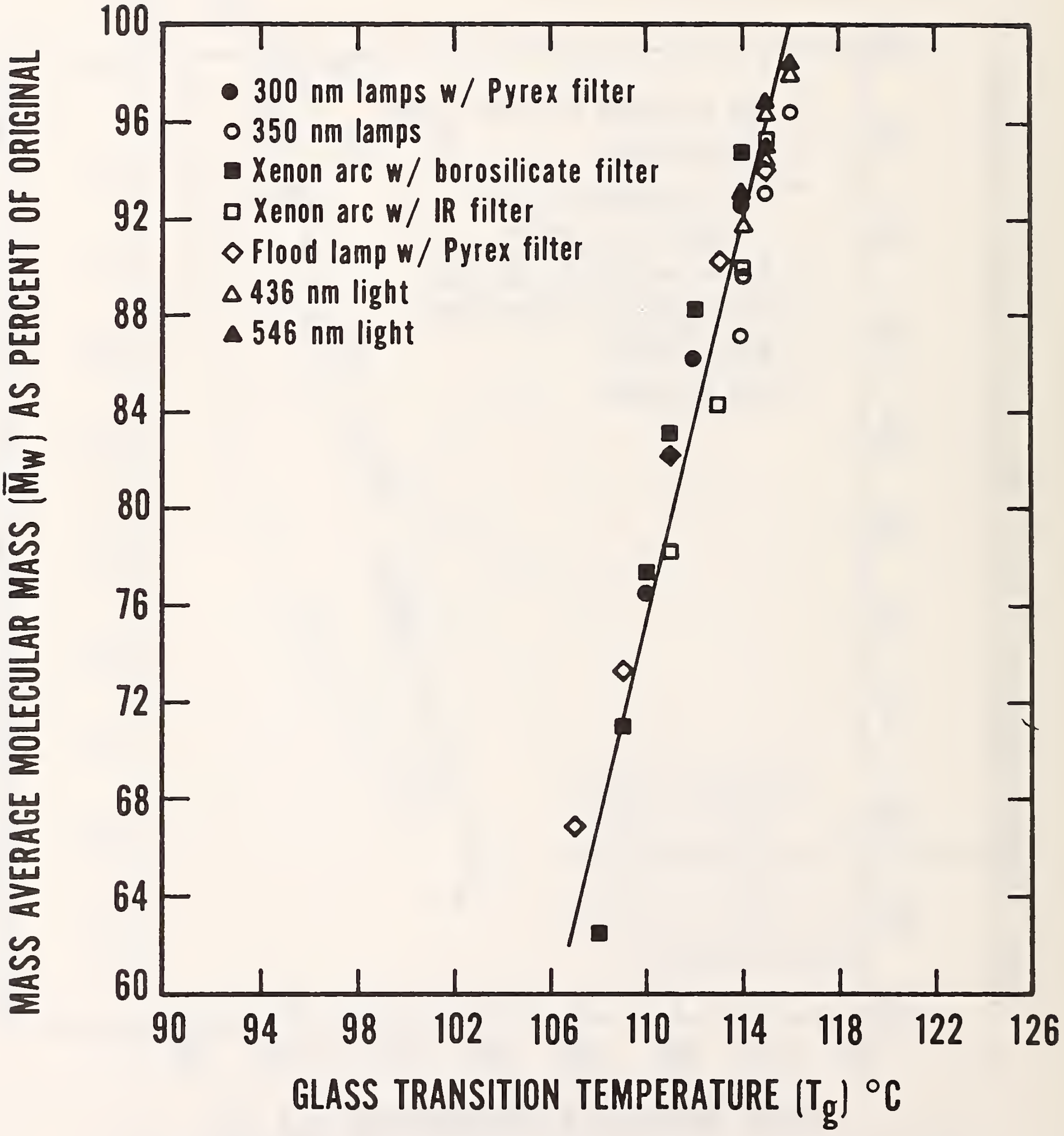

Figure 16. Percent degradation vs. Tg for PMMA II exposed to different light sources in air.

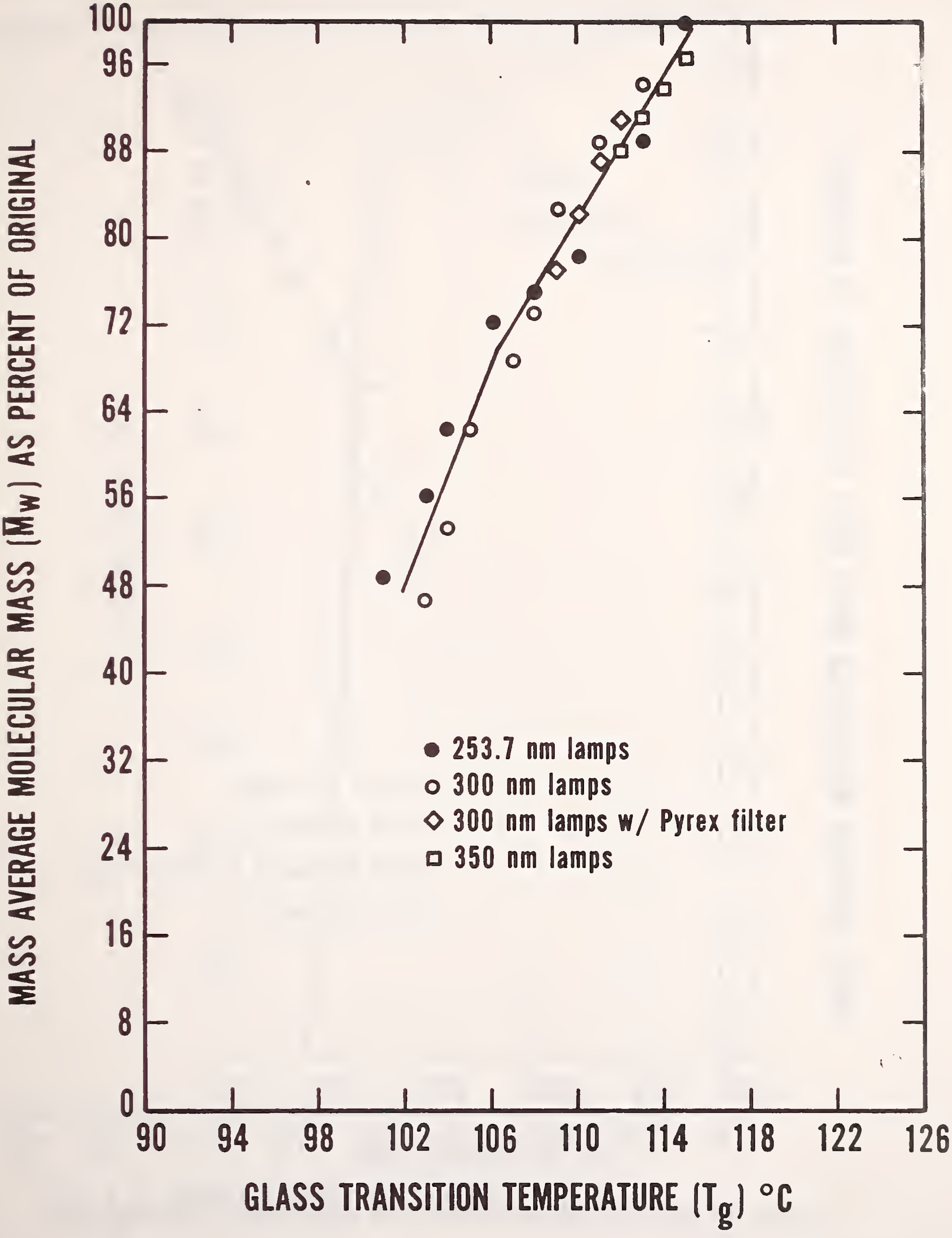

Figure 17. Percent degradation vs. Tg for PMMA I exposed to different light sources in air.

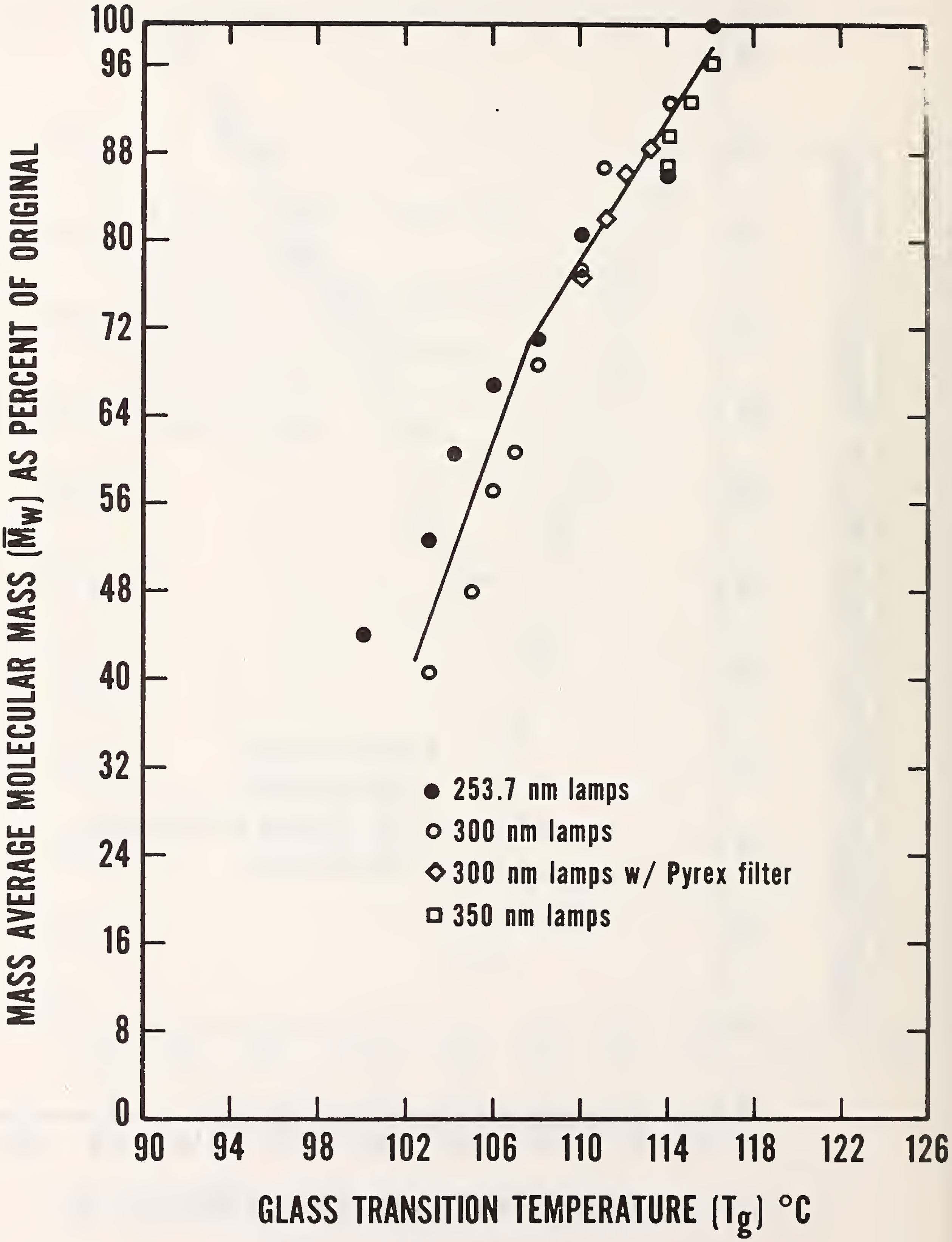

Figure 18. Percent degradation vs. Tg °C for PMMA II exposed to different light sources in air.

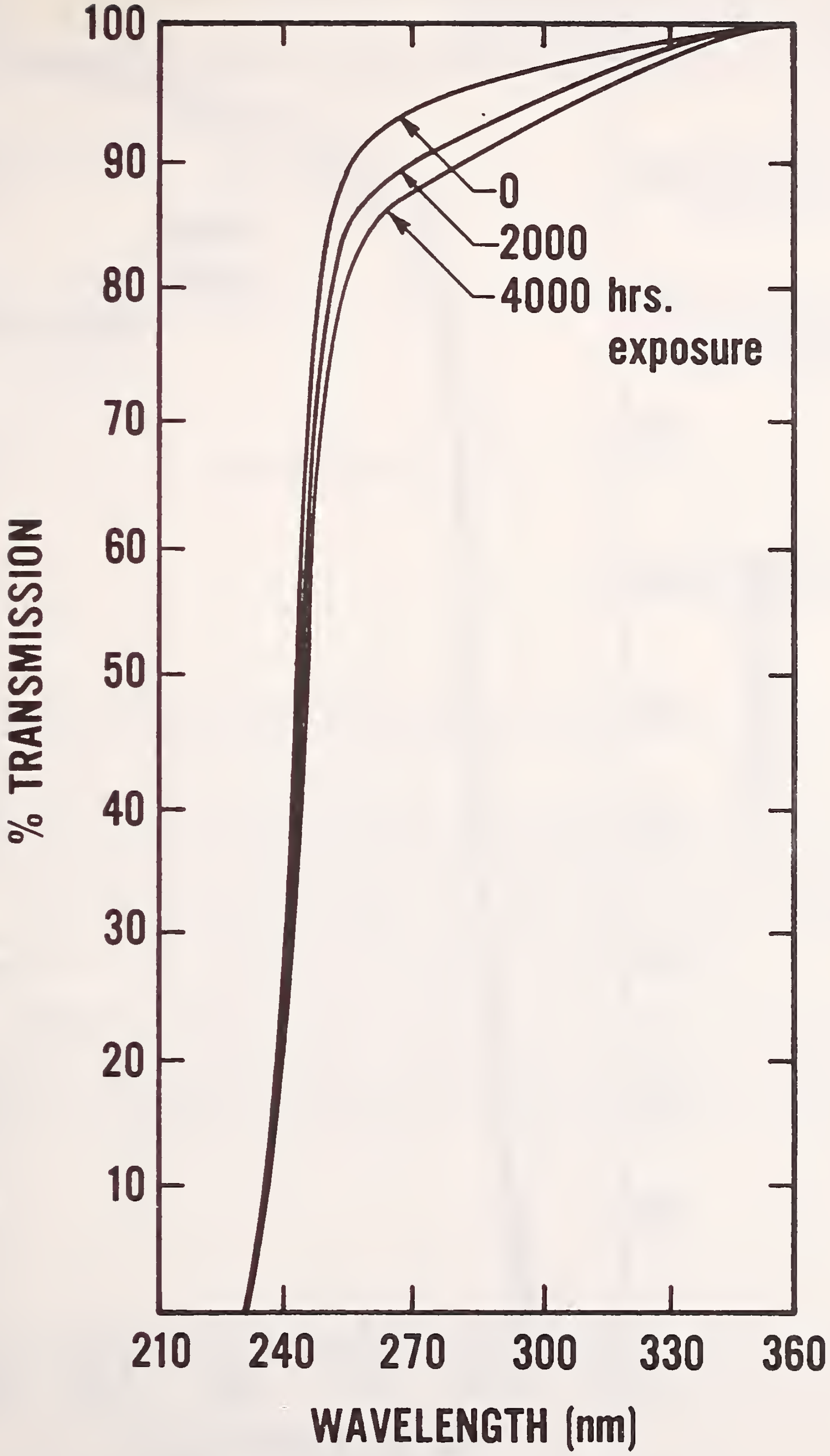

Figure 19. Changes in the ultraviolet spectrum of PMMA II during irradiation with flood lamp (H33-FY400, with Pyrex filter) in air.

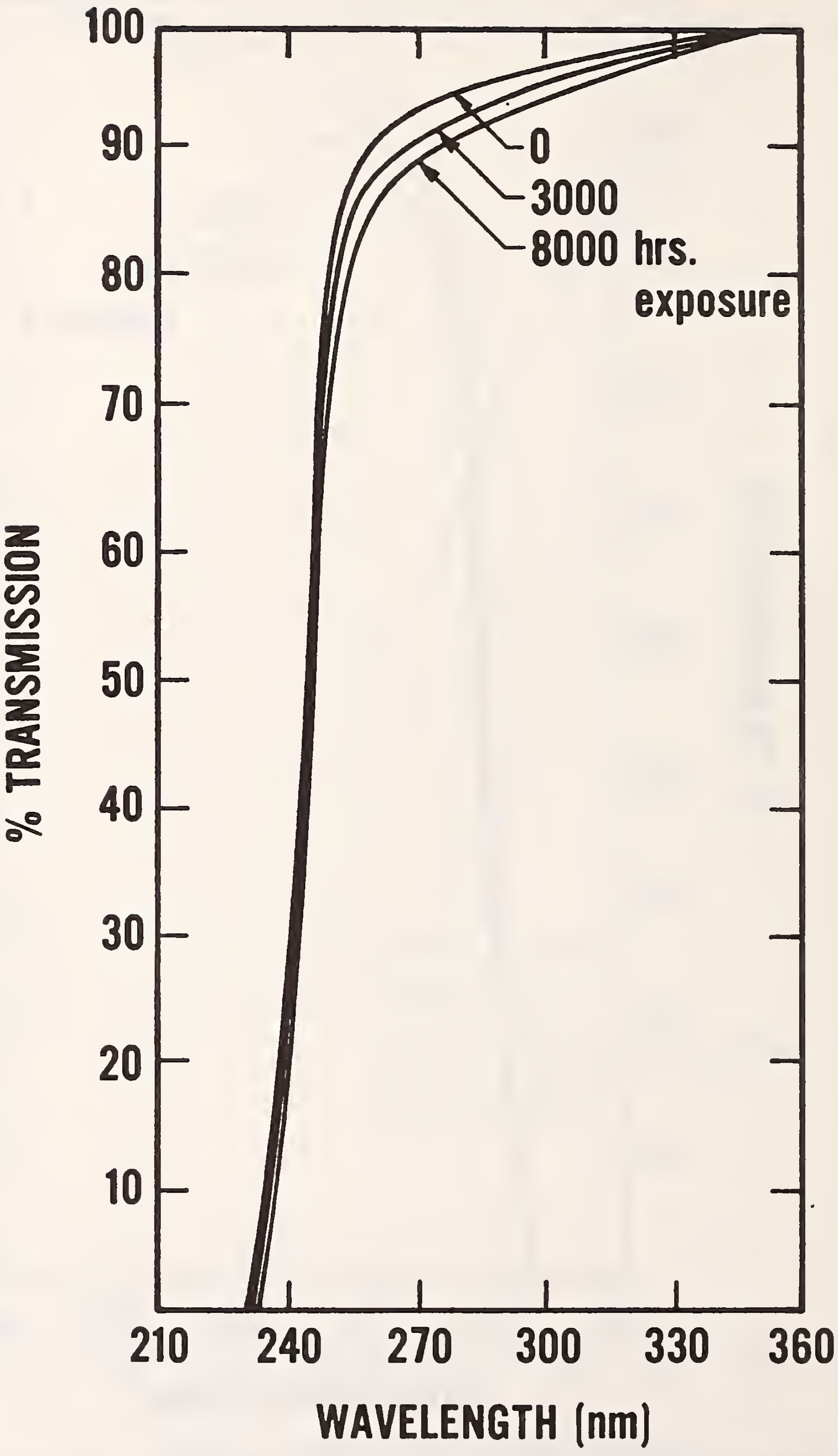

Figure 20. Changes in the ultraviolet spectrum of PMMA II during irradiation with xenon lamp (borosilicate filters) in air.

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15. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

When poly (methyl methacrylate), PMMA, is exposed to sunlight, it gradually degrades and, after long-term exposures, may be unable to perform its intended functions. While the photodegradation of PMMA has been studied extensively using radiation sources below 300 nm, natural sunlight at the earth's surface does not extend below 292 nm. This study was performed in order to examine the effect of the radiation from the upper part of the ultraviolet, UV, and the visible regions on PMMA and to identify the mechanism(s) of degradation induced by the radiation.

Thin films of PMMA were irradiated in air with upper UV, upper UV-visible, upper UV-visible-near infrared and 436 and 546 nm radiation. Exposure to either the upper UV or visible radiation caused degradation of the polymer. The data show that both random scission and unzipping of the polymer chain are operative in the degradation. Unzipping becomes increasingly important with incident radiation of increasing wavelength.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Degradation; IR; photodegradation; poly (methyl methacrylate); UV; visible.

18. AVAILABILITY ☒ Unlimited

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