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NATIONAL BUREAU OF STANDARDS REPORT

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COMPARISON OF XENON AND CARBON ARCS AS RADIATION SOURCES FOR LABORATORY WEATHERING OF ASPHALTS

by

Keith G. Martin, Paul G. Campbell and James R. Wright

~~Not for publication or for reference.~~

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U.S. DEPARTMENT OF COMMERCE

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Organic Building Materials Section
Building Research Division
Institute of Applied Technology

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COMPARISON OF XENON AND CARBON ARCS AS RADIATION SOURCES FOR LABORATORY WEATHERING OF ASPHALTS

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1. INTRODUCTION

Laboratory weathering of coating-grade asphalts by an accelerated weathering cycle was first described by Strieter in 1930 [1][2/]. The equipment consisted of an enclosed carbon arc radiation source, a rotating cylinder to hold test specimens, vertical water jets to simulate rain, and lawn sprinklers for vigorous spraying. The heat produced by the carbon arc maintained a temperature of approximately 60°C (140°F) at the surface of the panels. A refrigerator, as a separate unit, was used to obtain sudden temperature changes. Asphalt specimens, 25-mils thick, were made on aluminum panels and specimen failure was determined by visual inspection. Data were presented on several asphalts exposed to the accelerated weathering cycle and to outdoor weather. The results were sufficiently similar so that Strieter recommended the method as a tentative standard of test.

In 1933, Strieter's work was published by ASTM as a "Recommended Practice for Accelerated Weathering Test of Bituminous Materials" [2] and, although the test has undergone some modification, it is widely used at the present time [3]. The principal modifications have been the use of more cycles [4], a uniform method of sample preparation [5], the use of a single probe spark-generating instrument for detecting crack failures [6, 7], and a multi-probe detector [8].

Numerous papers have been written over the past 35 years in which the carbon-arc accelerated weathering test was evaluated *per se* or the test was used as a research and development tool [9]. However, in none of of these papers has the test been shown to correlate with actual weathering beyond the status shown by Strieter in 1930. Also, it has not been shown conclusively that this test can be used to predict asphalt durability. A number of reasons have been advanced showing why it would be

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2/ Numbers in brackets refer to the list of references at the end of this report.

difficult to obtain a correlation between asphalts exposed to the accelerated cycle and to outdoor weathering. Those reasons include: the rigid aluminum panel backing [10], the regularity of the test method [11], variations in asphalt-aluminum adhesion [12], variations in radiation intensity [13], and differences in the spectra of solar and carbon arc radiant energy.

Within the past 5 years, a more realistic radiant energy source became available for the laboratory weathering of organic materials. This source was the xenon arc which has a radiation spectrum remarkably similar to solar energy in the ultraviolet and visible regions [14]. While this machine has found extensive use in the plastics, textiles, and photographic industries, the first published use in asphalt degradation has been reported only recently by Martin [15] and by Wright and Campbell [16]. In both of these references, films 25-μ thick were used without water spray or thermal shock.

It was the objective of the present work to: (a) make a direct comparison of the carbon-arc weatherometer and the xenon-arc weatherometer as devices for the laboratory weathering of coating-grade asphalts using the ASTM Daily A cycle and the spark-generating apparatus to detect failure, (b) to measure, by infrared analysis, the photooxidation rates of the same asphalts upon exposure to both radiation sources, and (c) to determine the role of thermal shock in asphalt degradation.

2. EXPERIMENTAL

2.1 Materials

Ten commercial coating-grade roofing asphalts (Nos. 2, 3, 6, 8, 9, 11, 16, 18, 19, and 22) were used in this study. Asphalts 2 and 22 were of Venezuelan origin, asphalts 6 and 8 were of Southeastern USA origin, asphalts 3, 9, and 18 were of California Coastal origin, and asphalts 11, 16, and 19 were of Mid-Continent USA origin. The physical properties of these asphalts are given in Table I.

2.2 Apparatus

The xenon-arc radiant energy source was an Atlas Weather-Ometer, Model 60-WR, equipped with a constant wattage transformer to operate a 6000-watt high pressure water cooled lamp. The water jacket assembly contained an outer cylinder of pyrex glass which filtered out all wavelengths below approximately 275 mμ. A specimen rack, 37-3/4 in. diameter, was employed and this rack is rotated at one revolution per minute. For

experiments requiring a water spray, the machine was modified with a specimen spray unit employing four No. 50 nozzles capable of delivering 4.4 to 5.2 pints per minute. The nozzles were 3 inches from the plane of the specimen surface. The asphalt panels exposed to the water spray were mounted normal to the xenon-arc source. For experiments requiring constant temperature and humidity with no water spray, the automatic temperature-humidity controlling devices of the machine were utilized.

The carbon-arc radiant-energy source was an Atlas Weather-Ometer, Model SMC, with a single enclosed carbon arc. The spray unit was the same as that used in the xenon-arc weatherometer. A standard specimen rack, 30 in. in diameter, was employed. In all experiments using either 25 μ or 625 μ (25 mils) asphalt films, the asphalt specimens were mounted on the drum in the area of greatest radiant energy flux (see Appendix).

2.3 Exposure of Asphalt Films

The asphalt films of approximately 625-μ thickness (25 mils) were prepared by the hydraulic-press method described in Standard Method for Preparation of Test Panels for Accelerated and Outdoor Weathering of Bituminous Coating (D 1669-62) [17]. Triplicate samples of each asphalt were exposed in the weatherometers at a black panel temperature of 60°C and the test conditions followed Daily Cycle A in the Recommended Practice for Accelerated Weathering Test of Bituminous Materials (D 529-62) [3]. The test conditions used in this cycle were as follows: 51 min. of light only (black panel temperature 60 ±2°C), followed by 9 min. light and spray (spray water temperature 7 ±2°C at the nozzle). The cycle consisted of 22 periods at these conditions, daily. The cracks in the weathered asphalt film were determined by the spark-generating method described in Tentative Method of test for Failure End Point in Accelerated and Outdoor Weathering in Bituminous Materials (D 1670-62T) [18]. The clear plastic grid, used in these experiments was that described by Kleinschmidt and Greenfeld [19] and it consisted of 60 equal rectangles in an area approximately 2 in. wide and 5 in. long.

The method used to measure the photooxidation of 25-μ thick films of asphalt was based on changes in the infrared spectra at 1700 cm^{-1} due to exposure to xenon-arc radiant energy. Detailed procedures for the preparation, irradiation, and infrared analysis of these films have been reported previously [12]. Briefly, the method used in the present work is as follows: the asphalt films are prepared by pressing vacuum-dried, solid samples of asphalt between sheets of dry unlacquered cellophane in a hydraulic press with platens heated to

121°C. The films obtained are measured for thickness with a dial thickness gage, suitable exposure areas are mapped, and the films are separated from the cellophane by soaking in distilled water. The films are then mounted on aluminum holders, 3/8 in. by 1/4 in. by 2 in., with an opening 5/16 in. by 13/16 in., and allowed to dry overnight at room temperature. The infrared spectrum of each film is recorded, and the films are exposed to xenon-arc radiation at chamber conditions of 49°C and 40% R.H.

At the desired time, the exposed samples are removed from the exposure chamber and rescanned in the infrared spectrophotometer. The change in absorbance, ΔA, in the carbonyl band (1700 cm^{-1}) is calculated and used as a measure of the oxidation that has taken place during a given exposure period. The photooxidation rate is obtained by exposing a sufficient number of samples of a given asphalt for varying durations of time.

2.4 Temperature Cycle Measurement

Each of the weatherometers was equipped with a black panel thermometer unit. This unit acts as a standard specimen to enable correlation of temperatures between weatherometers, and the temperature so indicated is the maximum temperature of the artificial weathering cycle. This panel temperature is not that of the asphalt coatings, although the variation may not be great. Also, the unit does not permit a continuous record of temperature.

In order to obtain a continuous measure of the temperature of an asphalt coating during a weatherometer cycle, a thermocouple junction of copper and constantin wires was gently embedded into the surface of a 625-μ specimen of asphalt coating on an aluminum panel. The thermocouple was previously calibrated against ice and boiling water. Connections from the asphalt coating on the weatherometer drum to a millivolt recorder, of response time one second, were made through the hollow shaft upon which the drum was mounted. Twisting of the insulated connecting wires occurred in the hollow shaft with each revolution, but did not prevent the recording of two complete hourly cycles.

2.5 Chemical Dosimetry

The relative incident radiant flux in each weatherometer was measured with the chemical actinometer, potassium ferrioxalate-phenanthroline [20]. When exposed to radiant energy of less than 510 mμ wavelength, solutions of the ferrioxalate reduce to the ferrous state which forms a very stable compound with the phenanthroline and has a strong absorption band at 510 mμ. The amount of ferrous iron formed is determined by spectrophotometry. Details of the procedure and discussion of the applicability of the method to asphalt irradiation have been given previously [13, 15].

In brief, three milliliter lots of 0.15 molar potassium ferrioxalate solution were placed in a light-tight holder, equipped with a manual shutter to allow the solution to be exposed for a timed duration to the radiation to be measured. Two-minute exposures were made with the shutter normal to and at a distance of 27 in. from each arc. The carbon arc was operated at the 5A voltage setting (approximately 1.8 KW power consumption) and the xenon arc was operated at various power settings between 5.5 and 6.0 KW according to the age of the arc. One set of 4 exposures was made with the carbon arc and 11 sets of 4 exposures were made with the xenon arc. This latter program was designed as a check on the decay of intensity of the xenon arc, exposures being made at the beginning and end of each period at a particular power setting (approximately 500 hr. or 23 days of 22 hr. cycling). The exposed solutions were transferred to volumetric flasks and reacted with aliquots of 0.1 percent solution of o-phenanthroline at pH 3.5 (sodium acetate-sulfuric acid buffer). The reactions were carried out in a dark room and, after standing 45 minutes, the absorbance of the solutions determined at 510 mμ with a spectrophotometer, Beckman Model DU. These results were then calculated in terms of millimoles per liter of ferric iron reduced by use of a calibration curve previously established for known amounts of ferrous iron.

3. RESULTS AND DISCUSSION

3.1 Daily A Cycle Exposures - Carbon-Arc Weatherometer

The artificial weathering of the asphalts used in this study were previously reported by Greenfeld and Wright [21]. The carbon-arc weatherometer was used and the number of days (22 hours) for both a "Wet" and a "Dry" inspection of the ratings for cracks was reported. Failure was defined at the 50 percent level of cracking according to a 60-square grid count. Four of the asphalts were selected for repeat testing and these results together with those previously reported are given in Table II. The repeat testing involved inspection of the coatings at the middle of an hourly cycle and gave results in good agreement with those previously inspected 20 minutes after the end of the spray period.

3.2 Daily A Cycle Exposures - Xenon-Arc Weatherometer

The results obtained from the exposure of the asphalt coatings to the A cycle in the xenon-arc weatherometer are given in Table III. The data are presented as the number of squares of the exposed asphalt surface, out of 60 possible, having cracks. Periods of exposure duration are

given in terms of 22 hours of Daily A cycling. (Twenty-two hourly cycles comprise one day's exposure in the carbon-arc weatherometer). Generally, regular increases of the incidence of cracking with increased exposure duration were noted, and the occasional decreases in the cracking were attributed to variation in operation of the spark probe and to the grid method of counting cracks. Some of the data in Table III are plotted in Figure 1 to indicate the patterns of rate of crack formation.

It is apparent that the level of crack formation selected as the failure condition will influence the relative rating of the asphalts. For instance, in Figure 1 the decreasing order of durability of the asphalts in the xenon-arc weatherometer is 11, 19, 16, 22, 2, 9, 18, 3, 6, and 8 at the 50 percent level of cracking, but 19, 16, 11, 2, 22, 9, 3, 18, 6, and 8 at the 25 percent level of cracking. It is interesting to note that the changes of order take place within groups of common source of asphalts only; there is no cross over of asphalts of different sources. As shown in Figure 1, the 50 percent level of cracking represents a generally well-defined condition in that most of the asphalts show a rapid crack growth at this level of exposure. However, Figure 1 also illustrates that this definition of failure is an arbitrary one.

3.3 Comparison of Carbon- and Xenon-Arc Weatherometers

Table IV gives the results for each of the carbon-arc and xenon-arc weatherometer durabilities of the asphalts. The carbon-arc results are those reported for wet inspection (table II) of the asphalt coatings at the 50 percent level of cracking. Also, it may be observed in Table IV that the overall correlation of durabilities of asphalts from the same source exposed in the two weatherometers is poor. Within each of the four sources the trend of durabilities of the asphalts examined is the reverse for the carbon arc compared to the xenon-arc machine. This is attributed to the arbitrary nature of the failure point, and the method of detection of the incidence of cracking. Concerning the latter aspect, some of the panels were subjected to both the single probe detection method of Hunter, et al. [7] and the multi-probe method of Jones [8]. The results are shown in Table V and indicate a significant improvement in the crack detection ability of the multi-probe unit.

In particular, it was noticed on occasions that the single probe detector missed cracks near the edge of the specimen. When insulating tape was placed over the edge of the asphalt coating to prevent the single probe from sparking to the aluminum panel adjacent to the test specimen, most of these cracks were detected as indicated in Table VI.

When the asphalts of similar source are considered in groups, the overall correlation of the weatherometer results shown in Figure 2 is good, except for asphalts 6 and 8. These two Southeastern USA asphalts failed earlier in the xenon-arc weatherometer than predicted from the carbon-arc weatherometer results. Similarly, anomalous behavior of these asphalts was observed previously in photooxidation rate experiments [12]. Repeat testing of asphalts 6, 8, and 9 were therefore made in the xenon-arc weatherometer and the results are given in Table VII. Asphalts 6 and 9 behaved very similarly to the earlier tests, but asphalt 8 showed very poor reproducibility. At the 33 days exposure duration of the repeat tests, it was observed that very large cracks had formed in the asphalt 8 coating. After this stage, the rate of development of new cracks was much slower than observed in the previous tests. Figure 3, the photograph of panels of asphalt 8, illustrates the differences in the type of film crack failure found in the initial and repeat tests.

Concerning the general correlation between the two weatherometers as shown in Figure 2, it is of interest to note that the xenon-arc weatherometer takes 1.2 times more exposure time than the carbon-arc weatherometer to fail the asphalts. In actual time involved, the advantage of the essentially continuous operation of the xenon-arc compared to week-end and daily shutdowns of the carbon-arc weatherometer more than offsets the slower artificial weathering of the former machine. This factor becomes particularly significant when it is realized that the xenon source has a spectral energy distribution very similar to that of solar energy while that of the carbon arc is unrealistically intense in the ultraviolet region and lacks intensity throughout the visible and infrared regions (see figure 4).

3.4 Daily A Cycle - Temperature Measurements

The results of the measurements of asphalt-coating temperature during weatherometer cycling are illustrated in Figures 5 and 6 for the carbon-arc and xenon-arc machines, respectively. It is believed that these are the first continuous records of the temperature cycle in weatherometers to which asphalt panels are subjected. Both machines gave similar temperature cycles, the only minor difference was that the coatings spent a longer time in the spray of the carbon-arc machine (7 to 8 seconds) than in that of the xenon-arc machine (5 to 6 seconds) and, consequently, the former coatings reached a lower temperature after nine contacts with the water spray. The minimum temperatures reached were 8.9°C (48°F) and 12.8°C (55°F). Maximum asphalt temperatures in both machines were 3 to 4°C (5 to 7°F) higher than the 60°C (140°F) indicated by the black panel dial thermometers and both machines took 20 to 25 minutes to regain maximum temperature after the spray period.

It is of importance to note that the initial thermal shock (i.e. rate of temperature decrease for a given duration), due to the first contact of the cold water spray with the heated asphalt coating, is different for each position in the weatherometer drum. This difference is slight for most of the panels. However, the thermal shock may be greatly different for that panel first contacted when the water spray comes on and the remaining panels, if the first panel is not sprayed for the full contact time.[3/] The two extremes are illustrated in Figure 5. In case A, the coating with the embedded thermocouple made contact with the cold water spray about 10 seconds after the spray switched on and little temperature drop occurred between spray-on and the first direct contact of spray with coating. In case B, however, the spray switched on to immediately contact the coating for approximately 4 seconds and caused a considerable drop in the temperature before the first complete contact of spray with coating. While the rate of temperature drop is about the same for all panels on first spray contact, the total drop varies greatly with spray-contact time. For the carbon arc, the extreme case, of partial spray-contact time, would not be serious because the machine is serviced daily and sample rotation is interrupted. In the xenon-arc weatherometer this effect would be significant because the machine is serviced on a weekly basis. Figure 6 illustrates a case in the xenon-arc weatherometer where the period between switching-on of the spray and first complete contact with the coating was approximately 50 seconds without any partial initial contact.

It is apparent, when the extreme case is included, that the variability of thermal shock is so great between specimens in any one machine, that any variability between machines is overshadowed, particularly in the xenon-arc weatherometer. Furthermore, the major thermal shock experienced by the asphalt coatings in the weatherometers is much more severe than that occurring in practice. The order of maximum thermal shock in the weatherometers is 39°C in 4 to 6 seconds whereas from actual measurements, Cullen [22] has reported a figure of 44°C in 2 hours for asphalt coatings on model built-up roofs. Measurements of surface temperatures of asphalt coatings on actual roofs in Australia indicate maximum short-term decreases of about 8°C in the first minute [23].

3/ The exact same shock treatment could be obtained only if all samples were sprayed simultaneously.

3.5 Thermal Fatigue

Since the temperature cycle experienced by the asphalt coatings in the Daily A Cycle is variable and is much more severe than that encountered in actual practice, a test series was set up to determine what effect the temperature cycling alone had upon the asphalts. Asphalts 3, 6, 8, 9, 16, and 18 were exposed to temperature cycling without irradiation in a carbon-arc weatherometer in which the arc was surrounded with a blackened metal cylinder. The temperature cycle duplicated that found in the Daily A Cycle.

The samples were exposed to eighty 22-hour cycles (51 minutes of heating, 9 minutes of heating and cold water spray). At the end of this exposure period, none of the asphalts had any cracks as could be detected by the spark generating apparatus. The only noticeable effect was that of some surface dulling. Thus, thermal shock alone, without ultraviolet and visible radiant energy, was not effective in cracking the 625-μ asphalt films.

3.6 Radiant Energy Intensity

Table VIII gives the results of the incident radiation fluxes as determined by chemical dosimetry for the carbon and xenon arcs and also includes data previously obtained for solar radiation [15]. The results are expressed in terms of millimoles per liter of ferric iron reduced during the 2-minute exposure period and corrected values have been included to account for the drum radii of the carbon-arc (15 in.) and xenon-arc weatherometers (19 in.) in which the asphalt coatings were exposed.4/ It is apparent that the specimens in the carbon-arc weatherometer receive on average about five times more radiant energy of wavelength less than 510 mμ than the specimens in the xenon-arc weatherometer. Radiation intensity in the latter machine closely resembles that of solar radiant energy measured at noon on a clear July day in Washington, D. C.

4/ Maximum and minimum values were obtained for the xenon arc over a 2000-hour burning time. Conversely, all measurements on the carbon arc at the 5A position were made within an elapsed time of 10 minutes.

More detailed results concerning the decay of intensity of radiant energy from the xenon arc are illustrated in Figure 7. Each point represents the average of four determinations and has been corrected for drum radius. Despite a pre-burning of 100 hr., the lamps give a marked peak in their intensity when initially installed. Power step-ups at approximately 500-hr. intervals cause much smaller increases in the intensity and do not completely compensate for the decay of the lamp with age. However, the overall decay is relatively small compared, for example, to the fluctuations of solar radiation intensity at noon on cloudless days, which are also indicated in Figure 7. It should be noted that a power step-up was omitted at the 78-day exposure point; the result recorded represents two sets of readings taken before and after the weekly cleaning of filters and replacement of cooling water. This maintenance did not alter the intensity of the lamp as recorded by the dosimeter.

Figure 8 illustrates the initial decay of intensity of a new lamp (100 hr. pre-aged), each point being the average of duplicates. It is apparent that the decay is initially rapid and that the peak of radiant energy output would influence only one day of artificial weathering.

4. PHOTOOXIDATION RATES

Photooxidation rates, produced by carbon-arc irradiation, were determined previously by Wright and Campbell [12] for all of the asphalts used in the present study except asphalts 18 and 11. Martin [15] measured the photooxidation rates of asphalts 8, 11, 18, and 22 upon exposure to carbon-, xenon-, and solar radiant energy. In the present study, this work was extended to include photooxidation rate determinations, as produced by xenon-arc exposure, on all asphalts exposed to the Daily A cycle. Exposures for the rate determinations were made with the thin films (25 microns) exposed for varying durations at 49°C and relative humidity of 40 percent. The extent of oxidation was measured by infrared spectroscopy.

The oxidation values obtained on the six asphalts not previously evaluated in [12] and [15] are presented in Table IX. The results are expressed as ΔA values at 1700 cm^{-1} (carbonyl absorbance at various exposure durations to the xenon arc.

In Figure 9, curves are plotted for the photooxidation rates of asphalts 9, 2, 6, and 19. These asphalts are from four different crude sources. As with carbon-arc exposure, the overall oxidation rates varied as a function of crude source, but the order based on increasing stability was California, Venezuela, Southeastern USA, and Midcontinent USA. The change in radiant energy source, i.e., from carbon arc to xenon arc, reversed the relative positions of the Venezuela and Southeastern USA asphalts. Martin [15] showed a similar reversal in order using other asphalt samples from the same four sources.

Although the overall oxidation rates were different for each asphalt, the rate curves were similar in general appearance, but unlike those obtained from carbon-arc exposures. Rather than an induction period, the xenon-arc irradiation induced definite breaks in the steady rates of oxidation for all four asphalts. Martin [15] characterized the photooxidation in the xenon source by initial and secondary oxidation rates, and by exposure time to cause failure of the asphalt film due to cracking. The curves in Figure 9 may be characterized in a similar manner. Also, it may be noted that with only one of the four asphalts, No. 6, does the straight-line initial oxidation rate pass through the origin, even though the origin is a valid point on each curve. The reason for this anomaly is not readily apparent.

In Table X the initial and secondary oxidation rates are shown, as ΔA/hour, for the four asphalts. Also, the times required to reach the inflection point, and to develop film failure due to cracking, are shown. It may be observed, except for the California asphalt No. 9, that the steady oxidation rates of the asphalts are of similar values. Greater stability in the Midcontinent USA asphalt is shown by a longer time to reach the inflection point and a correspondingly greater time to film failure.

For comparative purposes, the steady oxidation rate values and failure times are given in Table X for exposures of the same four asphalts to the carbon arc. The pronounced differences in the response of these asphalts to the two radiant energy sources may be observed in Figure 10a and 10b. This effect was previously observed by Martin [15] and by Wright and Campbell [16] when various asphalts were exposed to solar, xenon-, and carbon-arc irradiance in air [15] and in an ozone-enriched oxygen atmosphere [16].

5. CONCLUSIONS

From the results of this investigation, in which the xenon- and carbon-arc weatherometers were compared as radiant energy sources for the laboratory weathering of coating-grade asphalts, it was observed that:

1. The xenon-arc source requires an average of 1.2 times greater exposure duration than the carbon arc to fail 625-μ (25-mil) asphalt films by the Daily A Cycle, but a shorter total elapsed time period is needed since the former source operates on a near continuous basis.

2. The order of durability of asphalts from a single geographical source was reversed for the carbon arc compared to the xenon-arc machine. However, when asphalts of similar source were considered in groups, the overall correlation was good. The order of increasing durability for asphalts from four sources when exposed to the xenon arc were: Southeastern USA, California, Venezuela, and Midcontinent USA. The order for carbon-arc exposure was: California, Southeastern USA, Venezuela, and Midcontinent USA.

3. Asphalt durability to Daily A Cycle exposure was influenced greatly by the test method. An arbitrary 50 percent failure level gave an order of durability different from that at the 25 percent failure level for the ten asphalts studied. The number of cracks detected in the asphalt films by the spark generating apparatus increased as much as 14 percent when the aluminum panel edges were insulated and by as much as 25 percent when a multiprobe detector was used in place of the single probe type. The width of the cracks formed, presumably a function of asphalt-aluminum panel adhesion, affected final durability results.

4. Continuous measurement of asphalt coating temperatures in the Daily A Cycle revealed that the initial thermal shock due to cold water spray, while similar in both machines, was slightly different for each position on the sample drum, and greatly different for the first panel contacted when the spray came on if that panel received less than the full spray period. The major thermal shock in the weatherometer was much greater than that observed in actual practice. Thermal shock alone, without ultraviolet and visible radiant energy, was not effective in cracking the 625-μ asphalt films.

5. The incident radiant energy flux, as measured by chemical dosimetry, was an average five times greater for specimens exposed to the carbon arc than for those exposed to the xenon arc which, in turn, was of similar intensity to noontime solar irradiance on a clear summer day. The decay of irradiance intensity for the xenon source, over a 2000-hour burning period, was gradual and of small proportion after the first few hours of lamp use. Much greater variation was observed with solar radiation on a clear, summer day.

6. Photooxidation rates of 25-μ asphalt films, as measured by infrared spectroscopy, produced the same increasing order of stability for the xenon and solar sources, namely, California, Venezuela, Southeastern USA, and Midcontinent USA and, also, rate curves of the same general appearance with an initial oxidation rate, an inflection point, and a secondary oxidation rate. The carbon-arc source reversed the relative order of the Venezuela and Southeastern USA asphalts and produced rate curves unlike those from the other sources. The curves from carbon-arc irradiance showed an induction period followed by a single steady oxidation rate to failure of the asphalt film. The five-fold higher intensity of the carbon arc over the xenon-arc did not proportionately reduce film failure time. With most asphalts, exposure durations needed to cause failure from xenon irradiance were approximately twice those required by the carbon arc.

7. The radiant energy source appears to be the rate controlling factor in the photooxidation and cracking of asphalt films of 25-μ thickness, the xenon source producing results much like those from solar irradiance and the carbon arc giving different results. The effect of radiant energy source on the durability of 625-μ films exposed to the Daily A Cycle, evaluated by the spark probe method, is not readily apparent because final results are influenced greatly by other factors involved in the test method. Even so, the xenon source with its "solar" spectral energy distribution should provide laboratory weathering results more closely related to natural weathering than could be expected from the more intense but less realistic carbon-arc source.

6. ACKNOWLEDGMENT

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8. APPENDIX

8.1 Irradiance Distribution in Specimen Drums

To measure the irradiance distribution in the xenon-arc weatherometer relative to drum height, the difference in carbonyl absorbance (ΔA at 1700 cm^{-1}) of exposed 25-μ films of a Midcontinent USA asphalt, at different drum positions, was used as a (monitoring) dosimeter. The specimen drum in the xenon-arc weatherometer is 19-1/2 in. in height and is 19 in. in radius. The xenon arc is centrally located with regards to drum height. Two specimen holders (9 x 3 in.) cover the height of the drum from approximately 1/2 in. to 9-1/2 in. and 10 in. to 19 in., respectively. Eight films were distributed equidistant on the specimen holders and were exposed to xenon-arc radiation for 405 hours at a black panel temperature of 60°C. Four films were exposed at each of the eight positions relative to the drum height. The irradiance distribution is shown in Figure 11 and is based on the changes in absorbance (ΔA at 1700 cm^{-1}) of the asphalt films versus drum height.

The same procedure was used to measure the irradiance distribution in the carbon-arc weatherometer. The specimen drum is 17-1/2 in. in height and is 15 in. in radius. A specimen holder covers the height of the drum from 1 in. to 13.5 in. Six asphalt films were mounted equidistant on a specimen holder. Four films were exposed at each of the six positions relative to the drum height. The films were exposed to carbon-arc radiation for 14 hours at a black panel temperature of 60°C. The changes in absorbance (ΔA at 1700 cm^{-1}) of the asphalt films versus drum height are also shown in Figure 11.

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TABLE I

PHYSICAL PROPERTIES OF ASPHALTS

Asphalt No.	Source	Softening Point[a] °C	Penetration at 25°C, 1/10 mm	Flash Point,[b] COC, °C	Specific Gravity at 25°C
2	Tia Juana-Lago Colon	104	16	310	1.017
3	California coastal (catalyzed)	105	18	252	1.032
6	Talco	110	17	288	1.040
8	Talco	105	15	299	1.036
9	California coastal (fluxed)	110	20	238	1.026
11	Kansas, Lyons	94	21	307	1.000
16	Illinois-Kansas-Oklahoma	117	15	343	1.008
18	Los Angeles blend	99	18	241	1.022
19	Kansas	106	16	327	1.005
22	Laqunillas	107	14	277	1.030

a Ring and Ball Method.

b Cleveland Open Cup Method.

TABLE II

CARBON-ARC WEATHEROMETER RESULTS

Asphalt No.	DURABILITY Daily A Cycles (22 hrs.) to Failure[a] From Reference 21		Present Work
	b	c	d
6	46	41	-
8	53	46	41, 47, 54
3	53	44	-
9	32	32	-
18	45	40	36, 37
2	69	65	-
22	60	63	63, 64
11	104	94	92, 95
16	102.	93	-
19	95	90	-

a 50% failure level (30 out of 60 possible squares with cracks).

b Machine turned off 48 min. after end of spray; values are average of four specimens.

c Machine turned off 20 min. after end of spray; values are average of four specimens.

d Machine turned off 30 min. after end of spray; each value is that of a single asphalt specimen.

TABLE III. XENON-ARC WEATHEROMETER RESULTS

EXPOSURE - DAILY A CYCLES (22 HRS.)

Asphalt No.		20.5	23	25	26.5	30	32.5	37	40	43.5	47	49	50.5	53	57.5	64	73.5	76	78	81	88	93	100.5	103.5	112	116	122	125.5	130
		Number of Squares with Cracks[a]																											
6	a.		1		12	<u>35</u>	50																						
	b.		3		18	<u>40</u>	55																						
	c.		2		7	18	<u>45</u>																						
8	a.	0		25	25	<u>32</u>	41																						
	b.	8		<u>46</u>	42	53	58																						
	c.	2		25	19	<u>39</u>	43																						
3	a.						3	20	<u>46</u>	33																			
	b.						4	15	<u>49</u>	38																			
	c.						8	26	<u>55</u>	40																			
9	a.				7	7	12	14	14	15	21	<u>35</u>	41																
	b.				0	0	4	6	8	10	23	<u>37</u>	45																
	c.				9	13	22	27	<u>34</u>	35	54	54	56																
18	a.					2	14	17	21	23	<u>53</u>	57																	
	b.					2	11	12	18	20	<u>52</u>	57																	
	c.					0	14	18	28	<u>37</u>	54	46																	
2	a.							5		7	12	12	13	15	15	15	<u>43</u>	39											
	b.							2		3	13	14	15	17	17	19	<u>32</u>	38											
	c.							0		0	14	15	15	18	19	19	28	29	<u>48</u>										
22	a.												2		22	23	25	24	<u>40</u>	36									
	b.												0		3	3	3	3	<u>35</u>	38									
	c.												2		8	8	8	11	<u>40</u>	33									
11	a.																0			7	9	10		21	29	<u>31</u>	36	42	52
	b.																0			1	1	1		11	18	<u>19</u>	26	<u>32</u>	45
	c.																0			0	0	0		7	13	13	25	<u>40</u>	47
16	a.																0			10	10	10	13	<u>33</u>					
	b.																0			17	20	24	28	<u>38</u>					
	c.																0			12	15	17	29	<u>38</u>					
19	a.																0			6	7	7	7	<u>36</u>					
																	0			10	10	17	19	<u>37</u>					
																	0			10	12	17	20	<u>43</u>					

[a] 50% failure level used (30 out of 60 possible squares with cracks). Underlined value for each entry represents failure.

TABLE IV

COMPARISON OF CARBON-AND XENON-ARC WEATHEROMETER RESULTS

Asphalt No.	DURABILITY Daily A Cycles (22 hrs.) to Failure[a] Carbon Arc[b]	Xenon Arc[c]
6	41	31
8	46	28
3	44	40
9	32	46
18	40	46
2	65	75
22	63	78
11	94	122
16	93	104
19	90	104

[a] 50% Failure level (30 out of 60 possible squares with cracks).

[b] Machine turned off 20 min. after spray; values are average of 4 specimens.

[c] Machine turned off 30 min. after spray; values are average of 3 specimens.

TABLE V

COMPARISON OF CRACK RATINGS OF
ASPHALT FILM SURFACES USING SINGLE AND MULTI-PROBE TESTERS[a]

Asphalt No.	Spark Generating Apparatus Single Probe[b]	Multi-Probe[c]	Difference %
8	32	40	25
	44	51	15.9
11	53	53	0
18	54	60	11.1
	54	60	11.1
22	59	60	1.7
	54	58	7.4

[a] Ratings presented as number of squares out of a possible 60 with cracks due to carbon-arc exposure.

[b] See reference No. 7.

[c] See Reference No. 8.

TABLE VI

EFFECT OF TAPING ALUMINUM PANEL EDGE ON CRACK RATINGS OF ASPHALT FILMS[a]

Asphalt No.	Squares Cracked Edge Untaped	Edge Taped	Difference %
2	13	14	7.7
	15	17	13.3
	15	15	0
	17	17	0
	18	19	5.3
9	41	45	9.8
8	50	57	14
18	57	59	3.5
6	51	58	13.7

[a] Cracks detected by single probe tester. Ratings presented as number of squares out of a possible 60 with cracks.

TABLE VII

REPEAT XENON-ARC WEATHEROMETER EXPERIMENTS

Asphalt No.		Exposure - Daily A Cycles (22-Hrs.)											
		20.5	23	26.5	30.5	33	37.5	40.5	43	45	48	52	56.5
		Number of Squares with Cracks[a]											
6	a.	0	1	12	18	48							
	b.	0	3	7	19	33							
	c.	0	2	18	32	51							
8	a.	0		4		18	24	23	28	28	33	34	39
	b.	8		9		17	21	22	22	22	23	25	52
	c.	2		8		8	11	11	13	13	14	21	36
9	a.	0		5		7	16	23	27	35	43		
	b.	0		0		3	15	21	26	33	42		
	c.	0		3		3	8	19	23	26	42		

a 50% failure level used (30 out of 60 possible squares with cracks). Underlined value for each entry represents failure.

TABLE VIII

CHEMICAL DOSIMETRY: EFFECT OF RADIANT ENERGY FLUX ON FERRIOXALATE SOLUTIONS

Radiant Energy Source	Ferric Iron Reduced, Millimoles per Liter[a]	
	b	c
Carbon arc[d]	0.094	0.304
Xenon arc		
Maximum	0.036	0.073
Minimum	0.025	0.051
Solar		
Maximum	0.067	0.067
Minimum	0.038	0.038

a Based on exposure of 1.0 sq. cm. area of 0.15 M $KFe(C_2O_4)_2$ for 2.0 min at a distance of 27 in. from the source (carbon and xenon). Values are average of 4 determinations.

b Experimental value at exposure distance.

c Corrected to exposure distance of asphalt panels; 15 in. for carbon arc and 19 in. for xenon arc.

d 5A voltage adjustment switch setting.

TABLE IX

CHANGES IN CARBONYL ABSORBANCE AT 1700 cm.$^{-1}$
OF ASPHALTS EXPOSED TO XENON ARC[a]

Exposure Time Hr	Δ A at 1700 cm^{-1} Asphalt No.					
	3	9	2	6	19	16
4	0.089	0.076	0.026	0.010	0.017	0.015
8	0.139	0.109	0.035	0.030	0.025	0.018
12	0.179	0.149	0.051	0.041	0.038	0.025
16	0.249	0.184	0.052	0.054	0.045	0.030
20	0.343	0.248	0.077	0.066	0.055	0.054
24	0.426	0.295	0.096	0.086	0.065	0.051
28	0.432	0.298	0.112	0.117	0.073	0.068
32			0.115	0.136	0.083	0.090
36			0.150	0.148	0.106	0.097
40			0.180	0.169	0.117	0.115
44					0.129	0.130
48					0.165	0.154
52					0.185	0.177

a Irradiated in Atlas 60-WR Weather-Ometer at 49°C and 40% R.H. for time periods indicated. Each value reported is average of a 2 or more values.

TABLE X

OXIDATION - RATE DATA FOR CARBON - AND XENON -ARC RADIANT ENERGY SOURCES[a]

Asphalt No.	Xenon - Arc Exposures: Inflection Point Hrs.	Oxidation Rates Δ A/hr. x 10^{-2}		Film Failure Hrs.	Carbon-Arc Exposures: Oxidation Rate Δ A/hr. x 10^{-2}	Film Failure Hrs.
		Initial	Secondary			
9	16	0.90	1.40	28	2.44	8
2	20	0.31	0.50	40	1.13	18
6	20	0.34	0.52	40	1.21	16
19	32	0.21	0.51	52	1.01	24

[a] All exposures made at 49°C and 40% R.H.

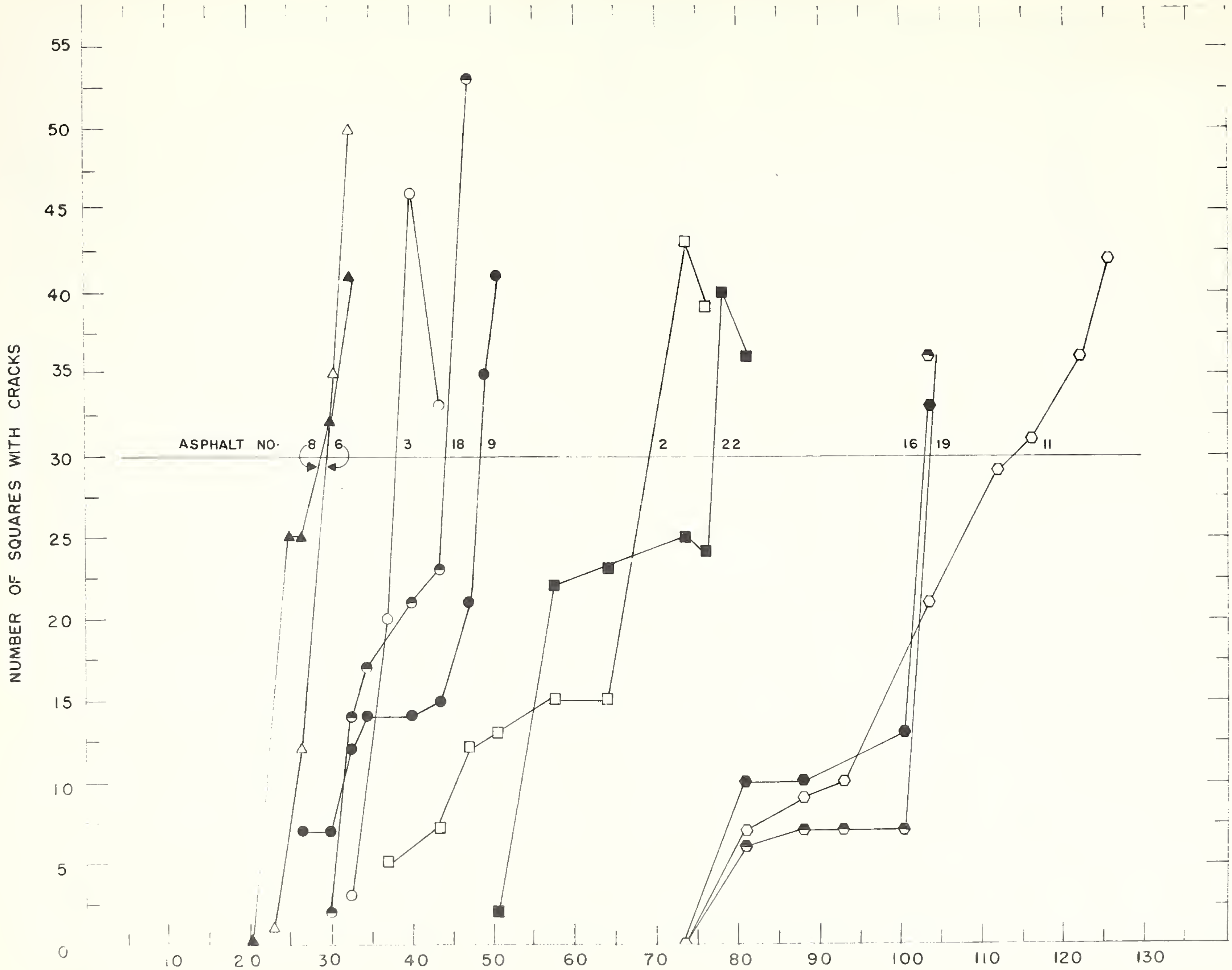

FIG. ... EXPOSURE IN THE XENON-ARC WEATHEROMETER ON THE RATE ... FILMS.

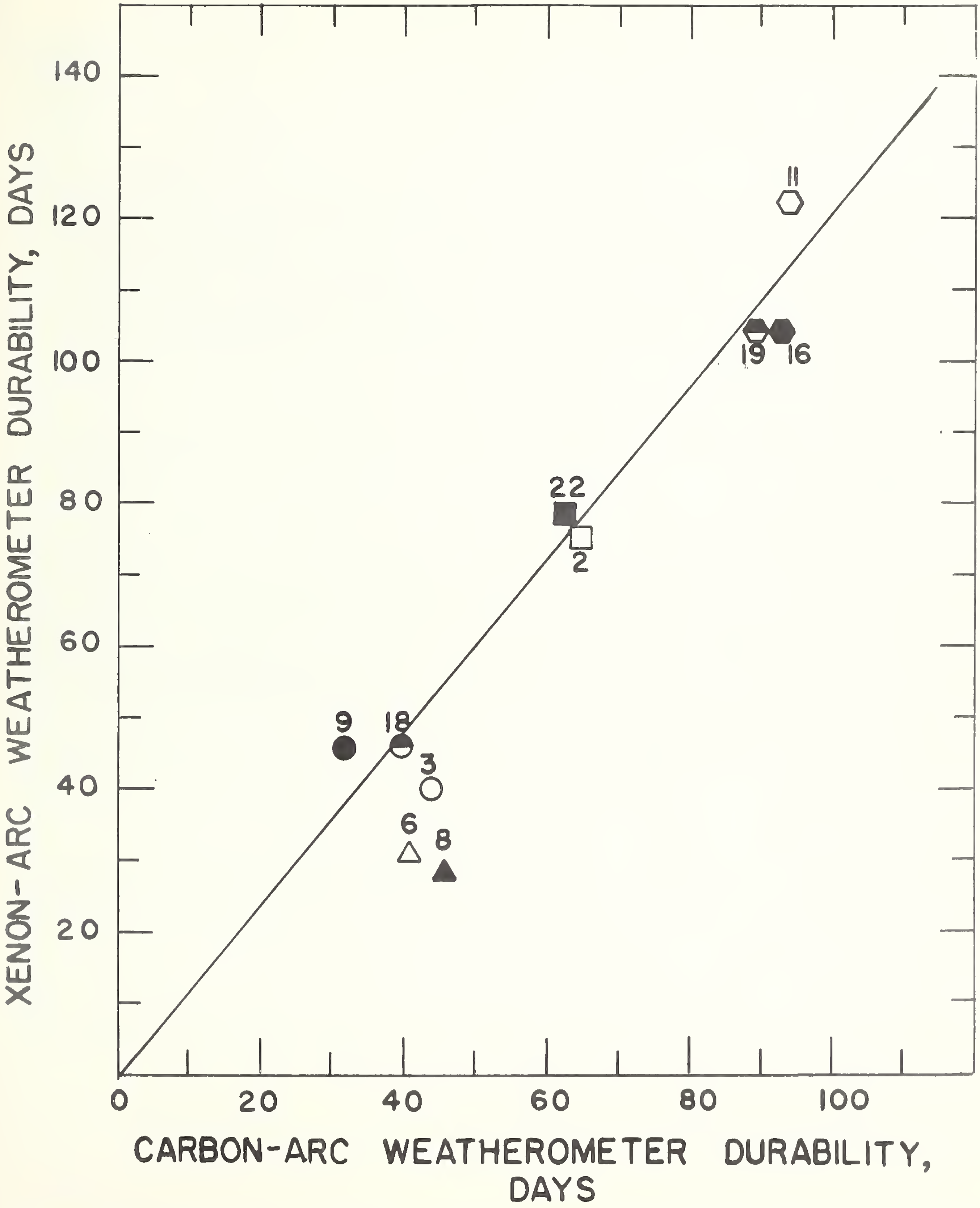

FIGURE 2. CORRELATION OF ASPHALT DURABILITIES FROM XENON- AND CARBON-ARC EXPOSURES (DAILY A CYCLE) OF 625μ FILMS.

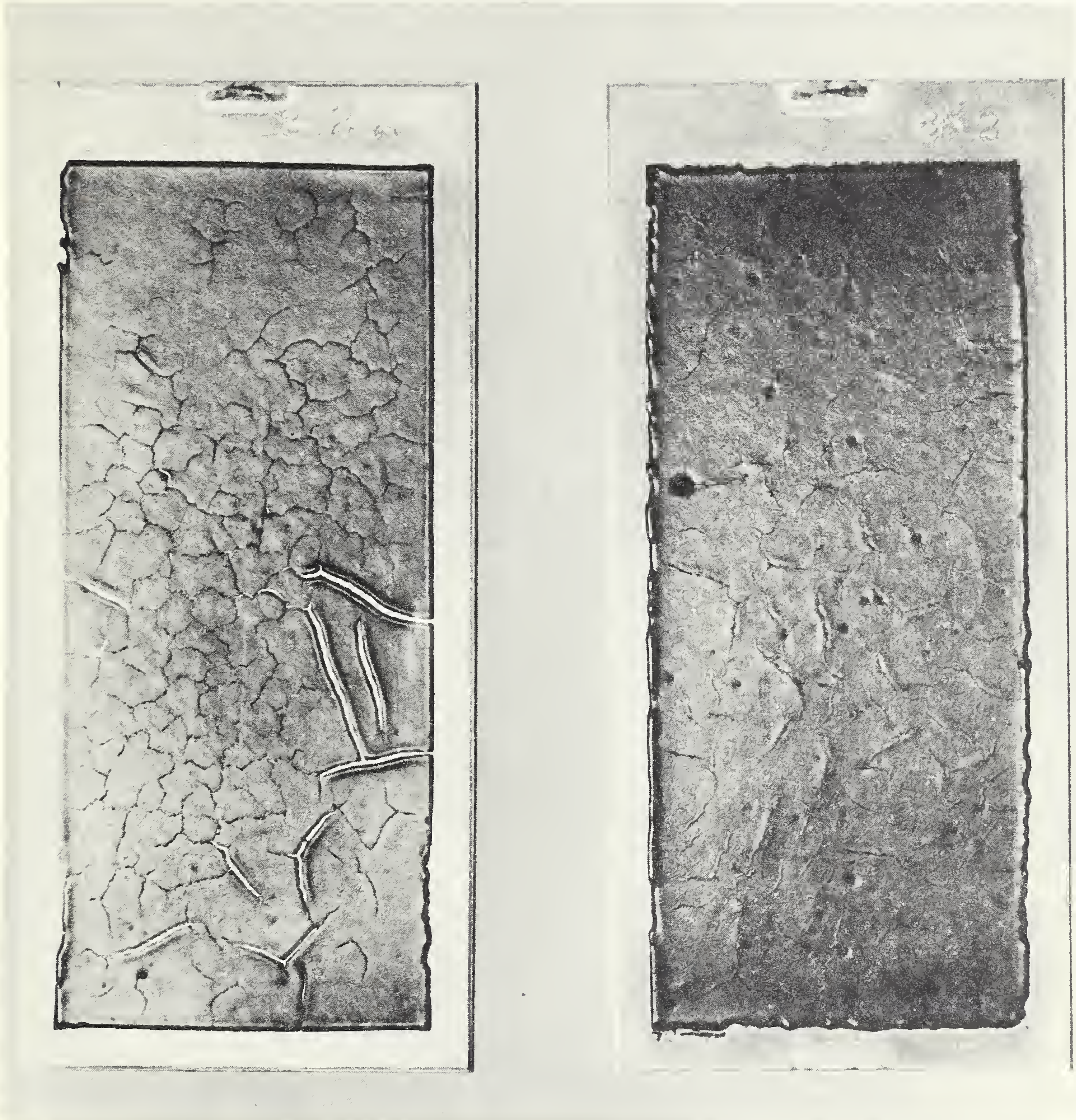

FIGURE 3. FILMS OF ASPHALT NO. 8 AFTER EXPOSURE TO THE DAILY A CYCLE IN THE XENON-ARC WEATHEROMETER.

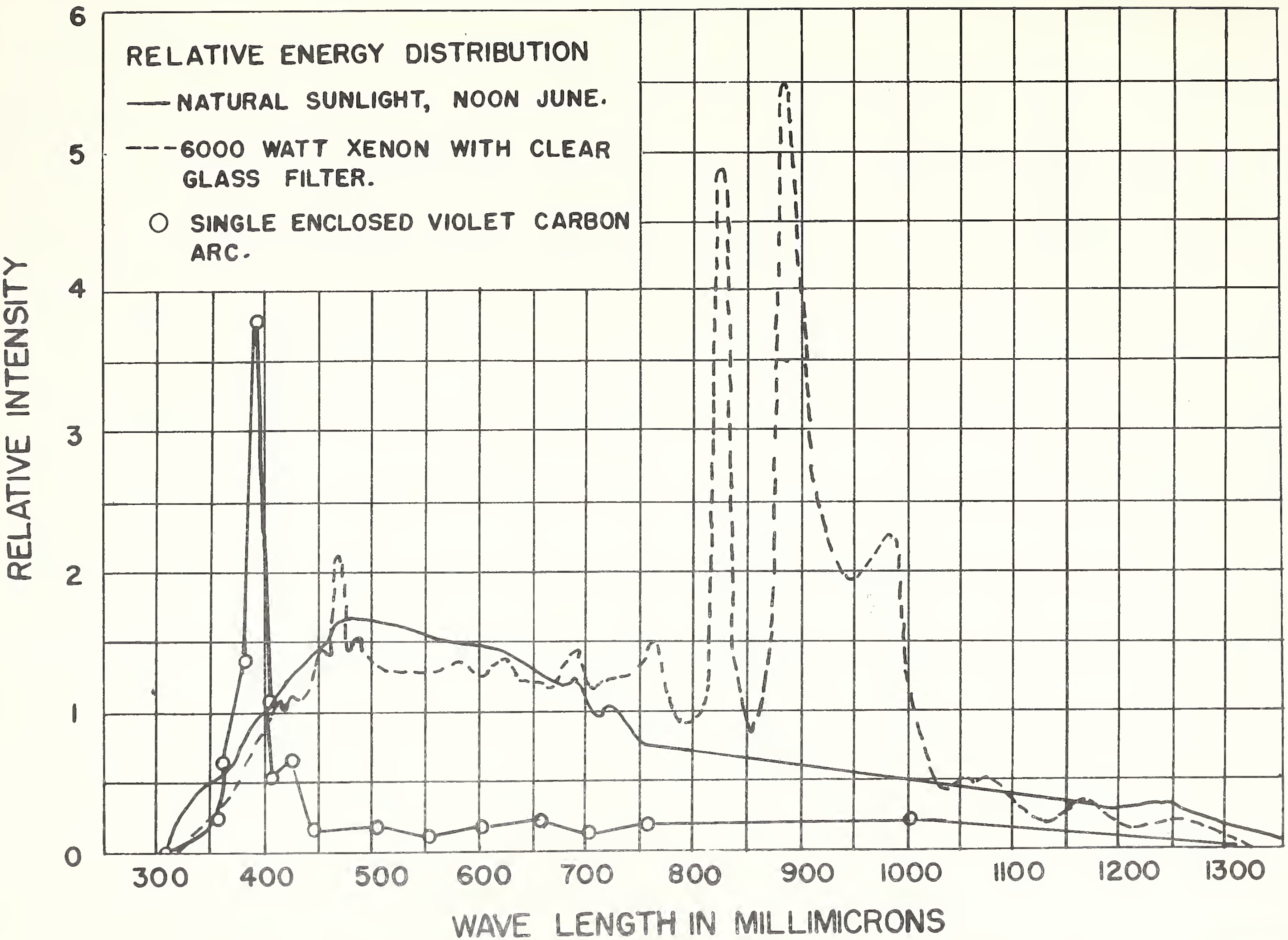

FIGURE 4. SPECTRAL DISTRIBUTION OF SOLAR, XENON-ARC, AND CARBON-ARC RADIANT ENERGY.

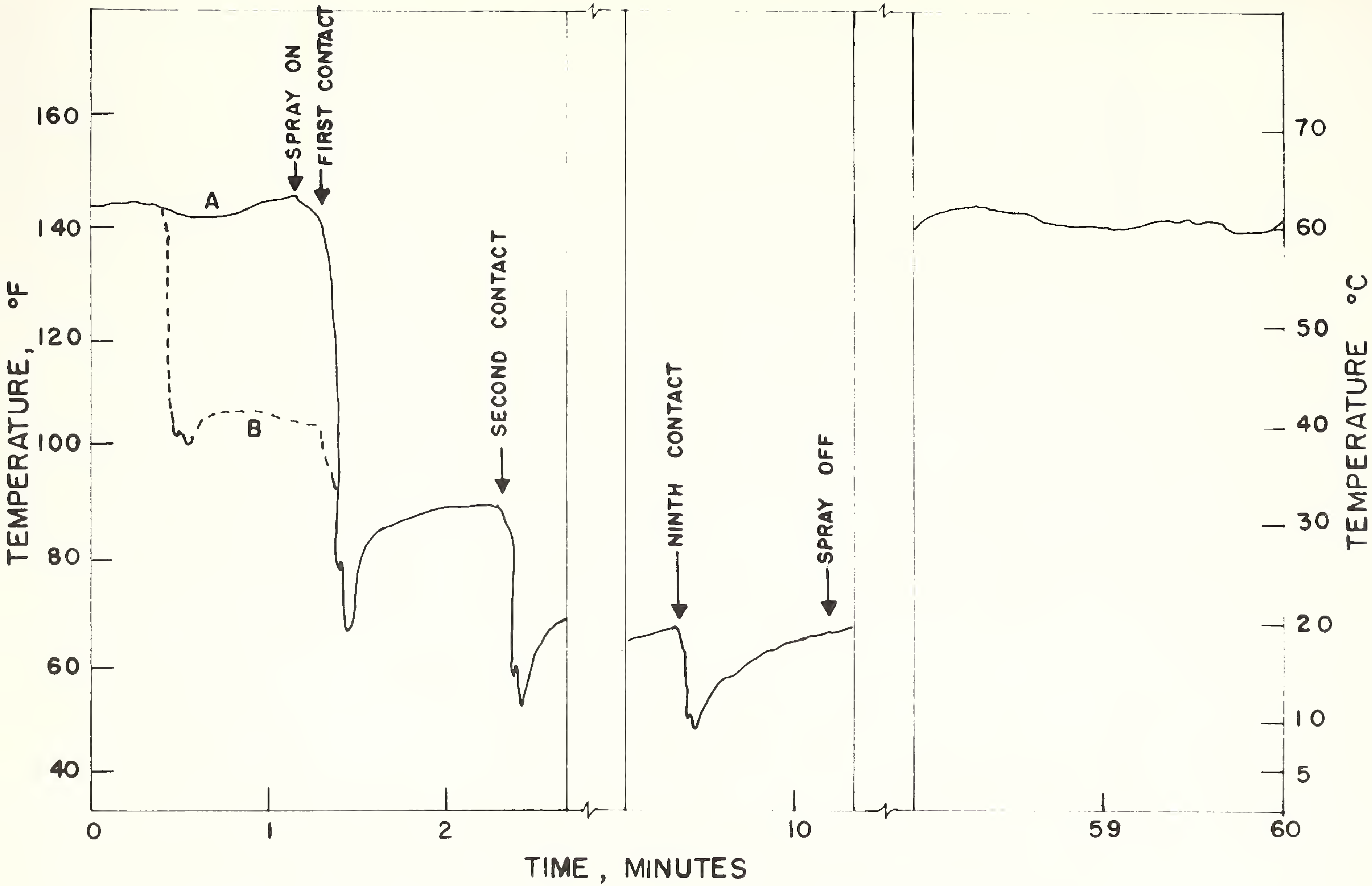

FIGURE 5. ASPHALT TEMPERATURE IN THE DAILY A CYCLE IN THE CARBON-ARC WEATHEROMETER. IN CURVE A, WATER SPRAY CAME ON 10 SEC. BEFORE CONTACT WITH PANEL SURFACE. IN CURVE B, SPRAY ON AND PANEL-SURFACE CONTACT WERE SIMULTANEOUS.

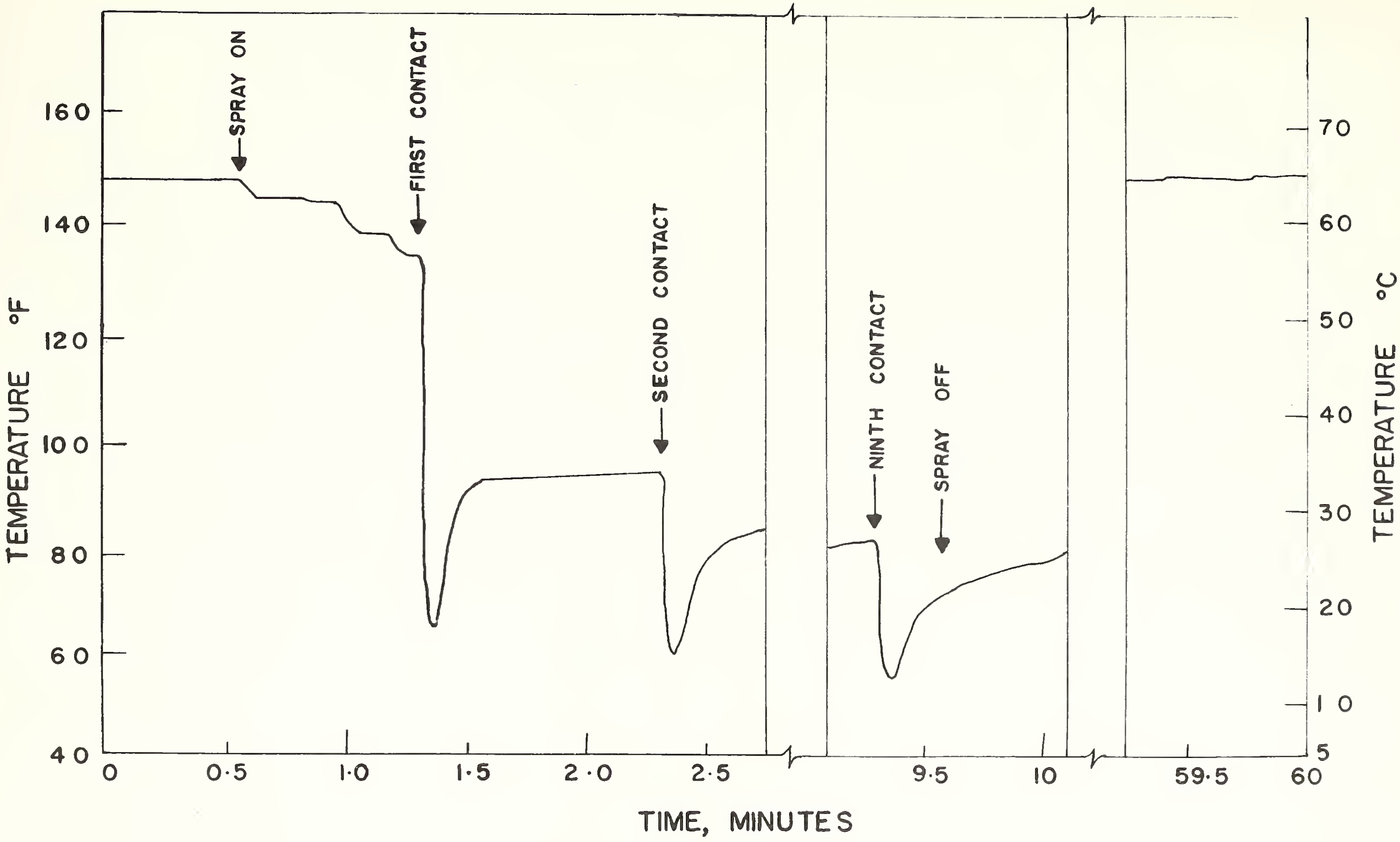

FIGURE 6. ASPHALT TEMPERATURE IN THE DAILY A CYCLE IN THE XENON-ARC WEATHEROMETER.

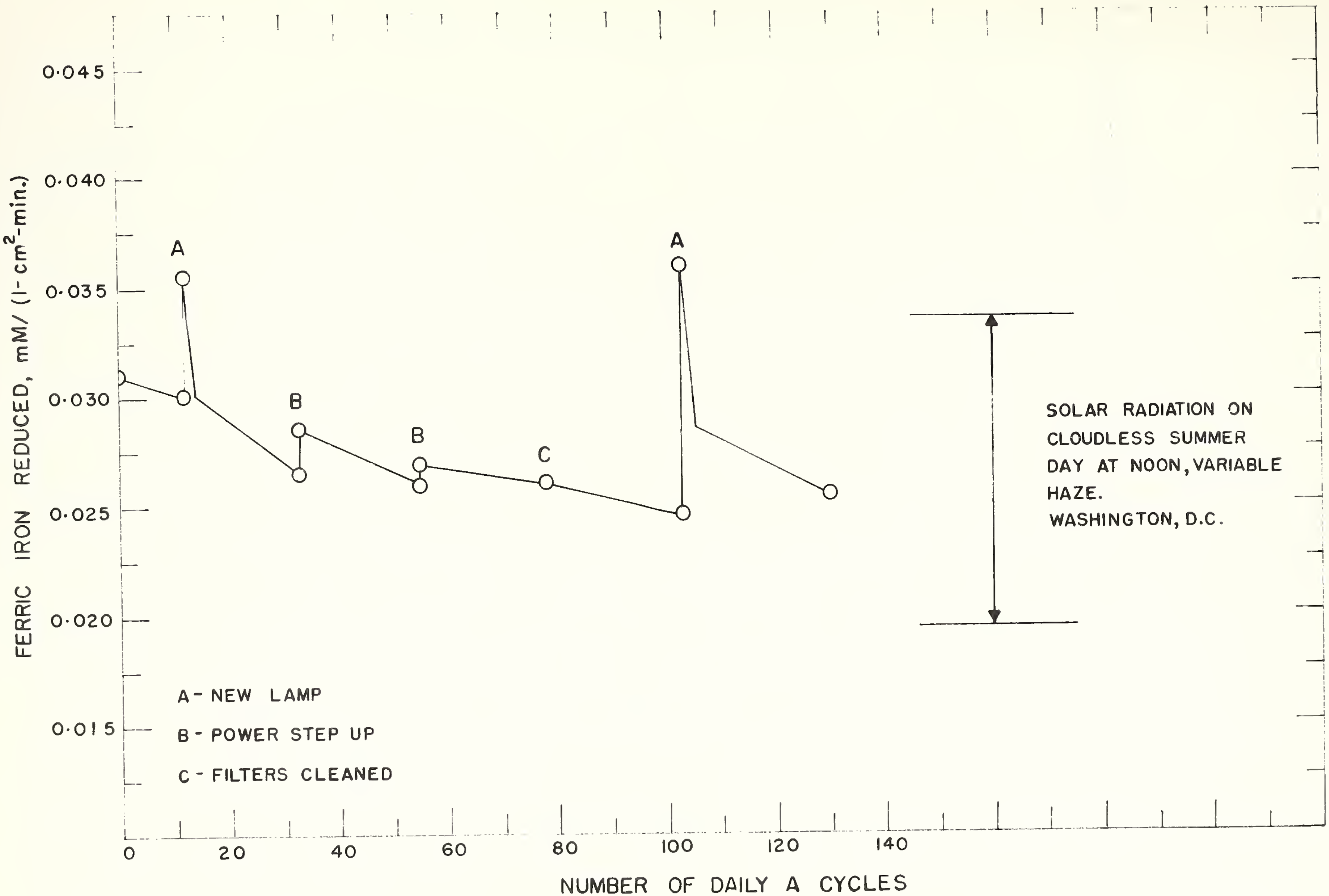

FIGURE 7. DECAY OF INTENSITY OF XENON ARC DURING WEATHEROMETER EXPOSURES.

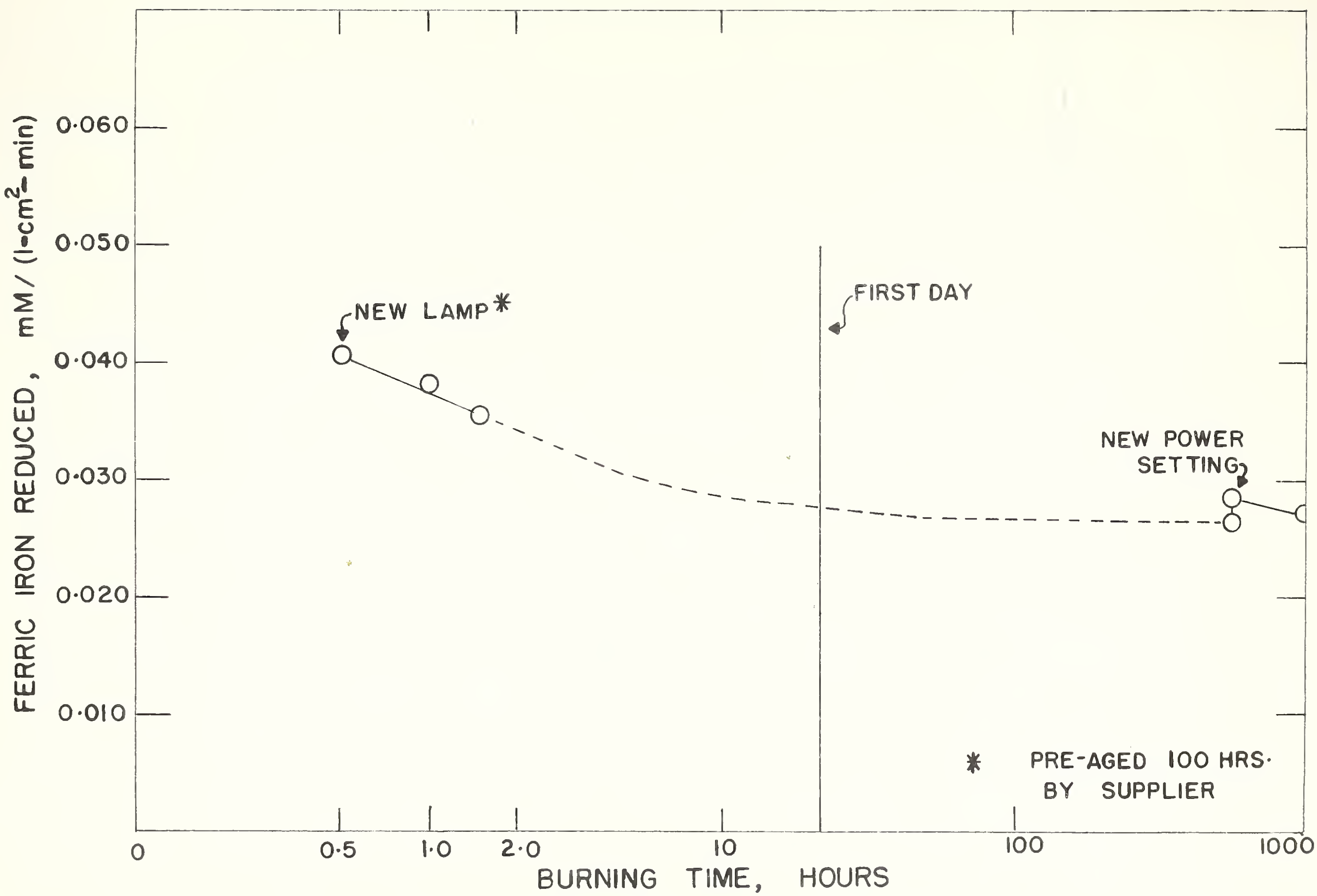

FIGURE 8. INITIAL DECAY OF INTENSITY OF THE XENON ARC.

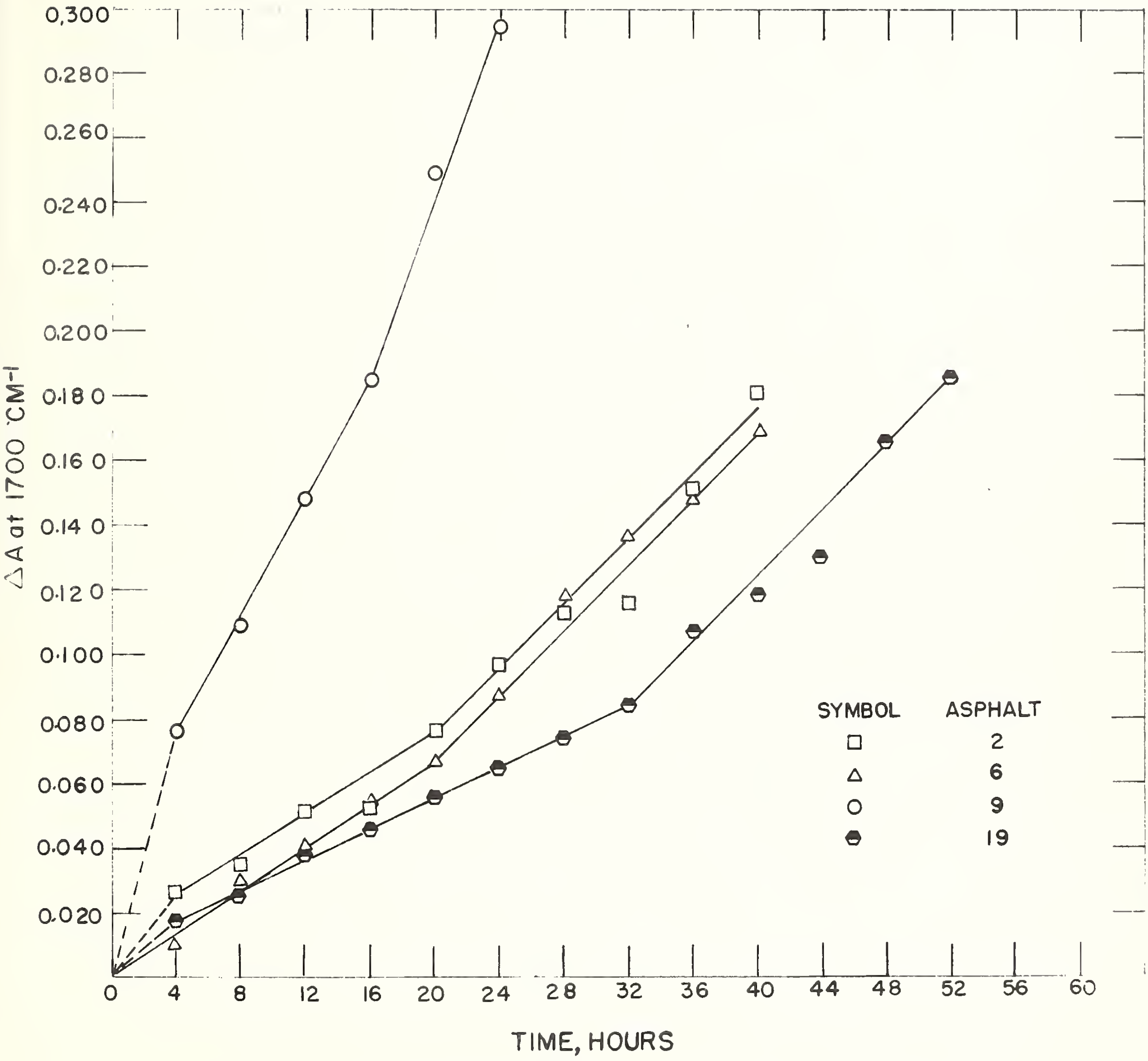

FIGURE 9. EFFECT OF XENON-ARC EXPOSURE (49°C, 40% R.H.) ON THE CHANGE IN ABSORBANCE AT 1700 cm^{-1} OF FOUR COATING-GRADE ASPHALTS.

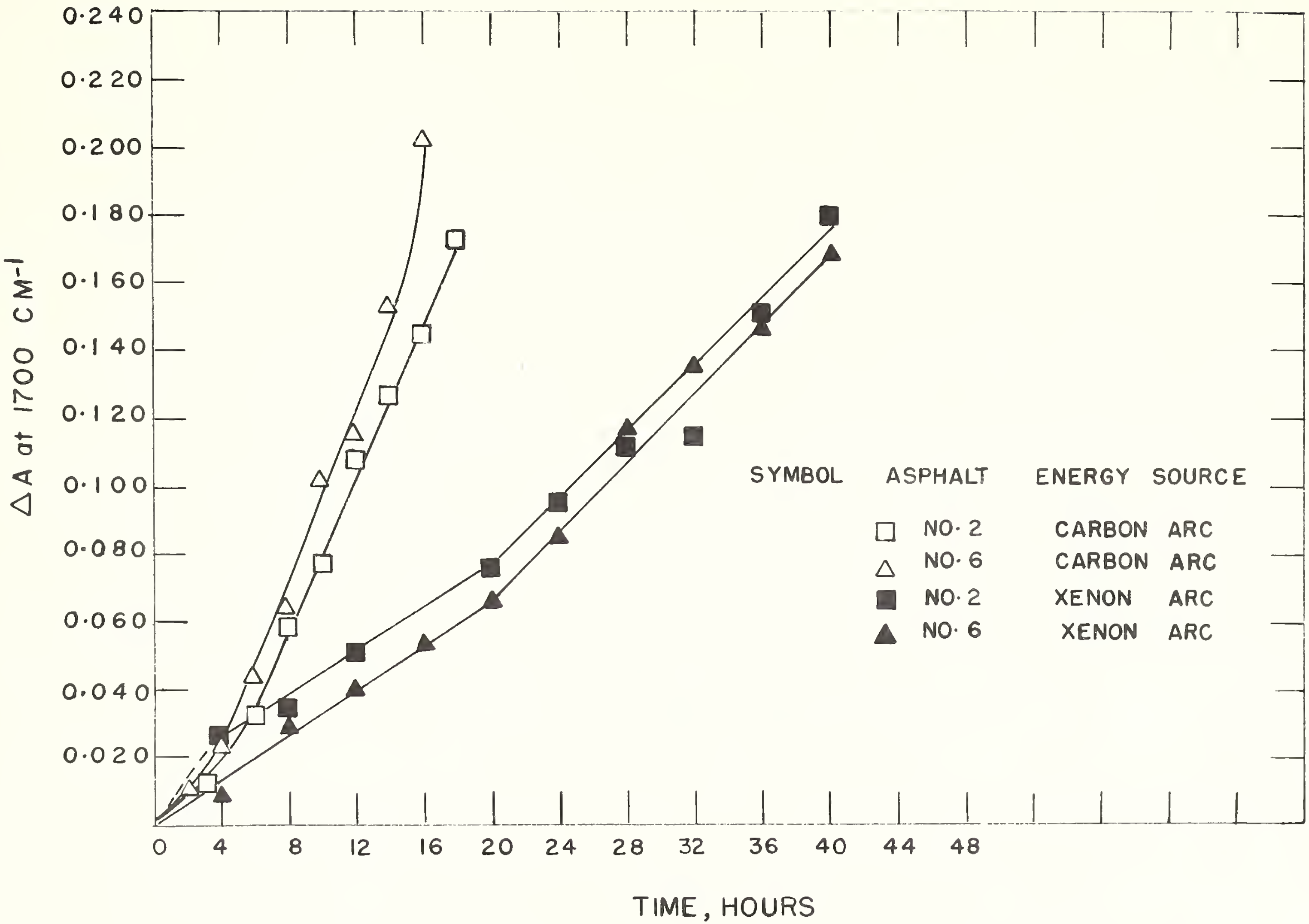

FIGURE 10a. RELATIVE EFFECTS OF CARBON- AND XENON-ARC EXPOSURES (49°C, 40% R.H.) ON THE CHANGE IN ABSORBANCE OF VENEZUELA ASPHALT (□ , ■) AND SOUTHEASTERN USA ASPHALT (△ , ▲).

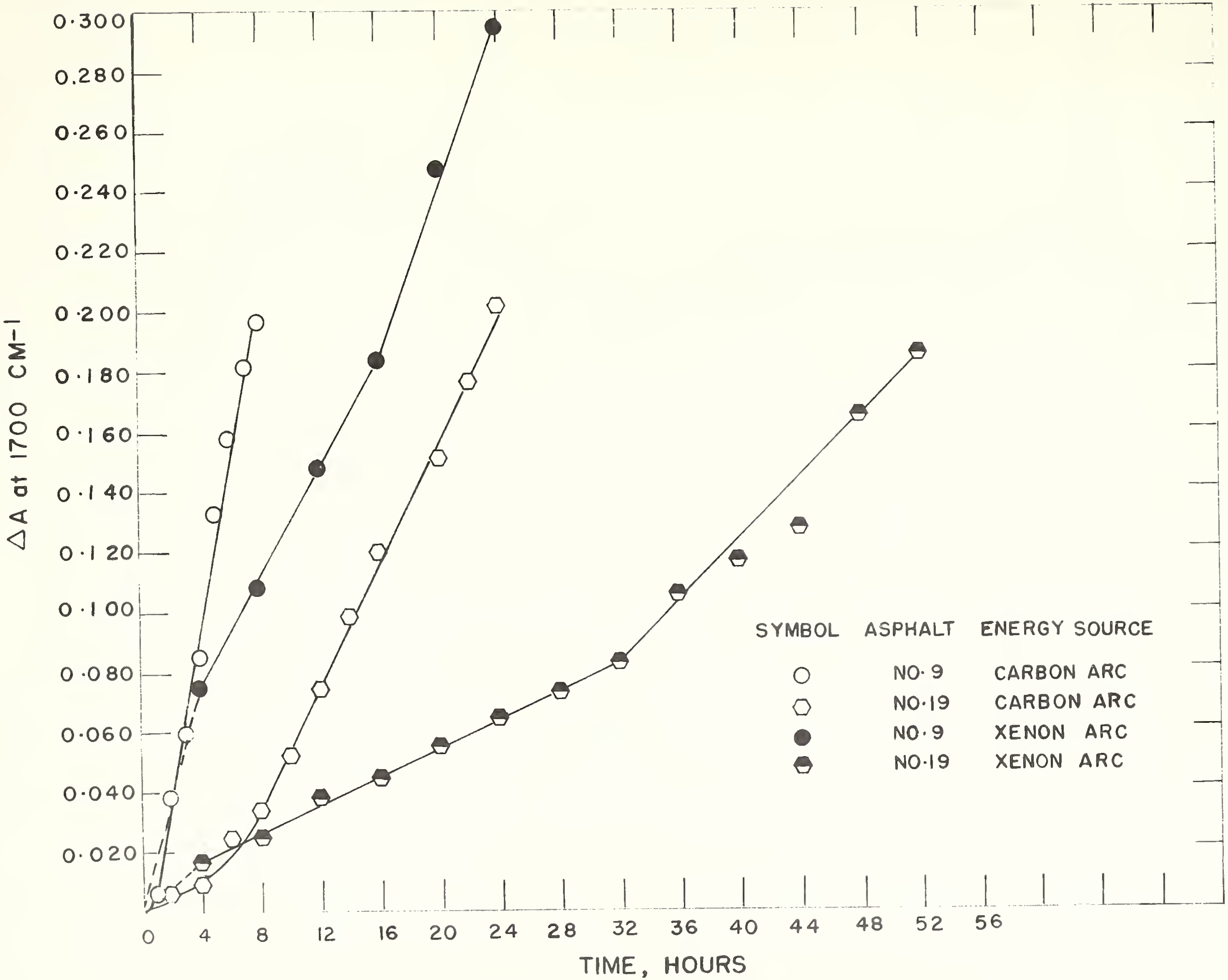

FIGURE 10b. RELATIVE EFFECTS OF CARBON- AND XENON-ARC EXPOSURES (49°C, 40% R.H.) ON THE CHANGE IN ABSORBANCE OF CALIFORNIA (○ , ●) AND MIDCONTINENT USA ASPHALT (⬡ , ⬢).

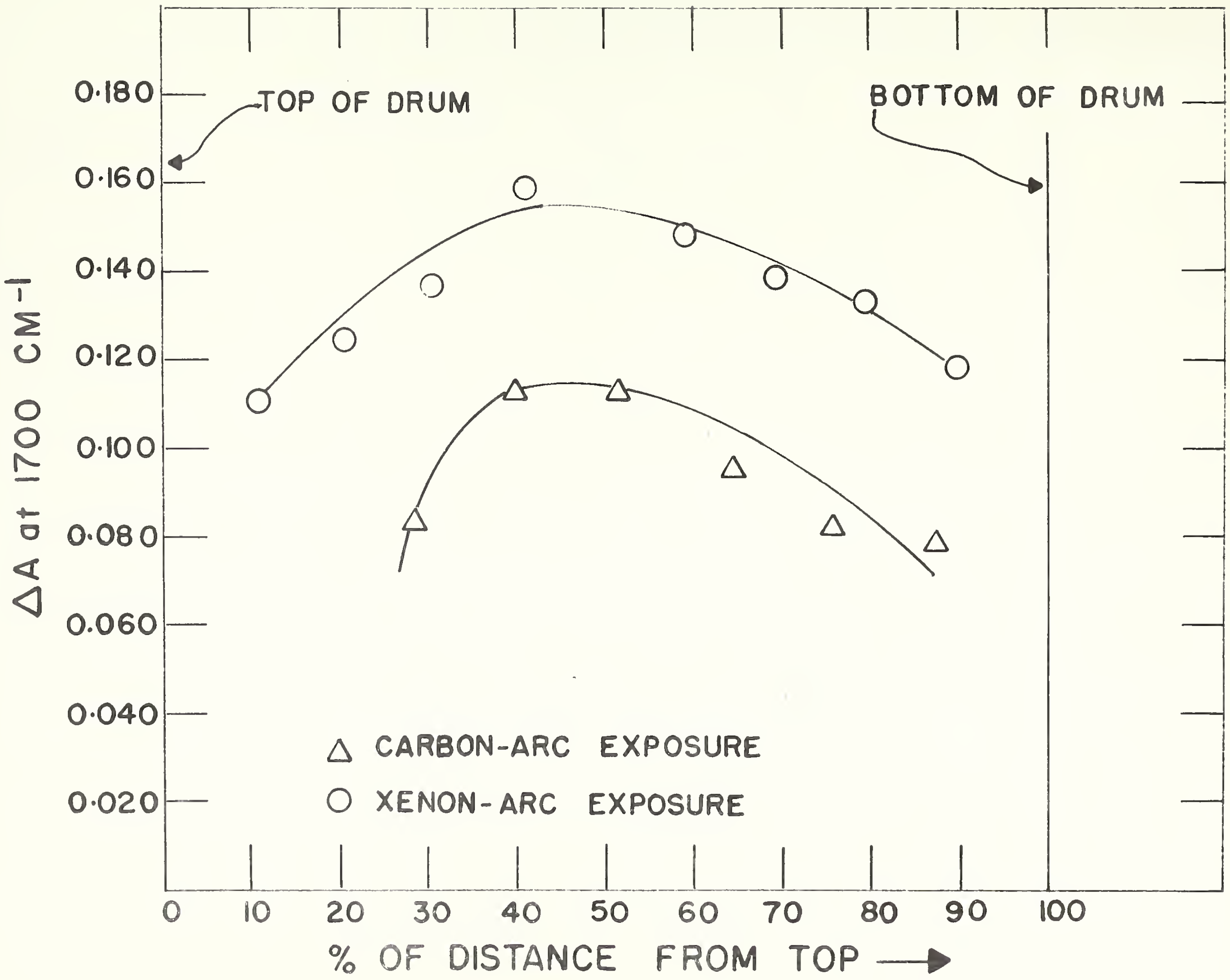

FIGURE 11. EFFECT OF DRUM HEIGHT ON THE IRRADIANCE DISTRIBUTION IN THE CARBON-ARC AND XENON-ARC WEATHEROMETERS.

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