HARDENING OF ASPHALT CEMENTS BY EXPOSURE TO ULTRAVIOLET AND SHORT WAVE LENGTH VISIBLE LIGHT

by
R. N. Traxler
Research Chemist
Texas Transportation Institute

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TEXAS TRANSPORTATION INSTITUTE
Texas A&M University
College Station, Texas 77843

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I. OBJECTIVES OF STUDY NO. 2-8-59-9, RESEARCH AREA 8

The objectives of the study are:

(1) Investigate the asphalt cements used by the Texas Highway Department.

(2) Establish specifications to assure the use of superior asphalts by the Department, and

(3) Determine how the durability of asphalt cements in service can be improved.

This report falls under item (1) above.

II. HISTORY

The hardening of asphalts by short wave length solar radiation has been under investigation for more than half a century. Rosinger(1) in 1914 studied the effect of sunlight on thin films of asphalt which had been deposited by evaporation from benzene, chloroform and other solutions. He found that after exposure to light the asphalts became partially insoluble in the solvents used in preparation of the thin films. Much later, Zapata(2) studied the effect of actinic light obtained from an arc lamp on asphalt films from 0.025 to 0.050 inches thick. Many other studies were made in the 1930-40 period in which the effects of actinic light from arc lamps were studied in conjunction with the action of air, ambient temperature, freezing and water spray (rain) on rather thick films of asphalt.

In 1958 Dickinson, Nicholas and Traube[3] showed that light in the wave length range of 3000 to 5000 Angstroms accelerated the reaction of oxygen with asphalts. Visible light includes wave lengths from approximately 3800 to 7700 Angstroms, thus, the Dickinson, et. al. experiments included the longer wave lengths of ultraviolet radiation.

Blokker and van Hoorn[4] found that the rate of oxidation of asphalt is higher in the presence than in the absence of light, and the reactions are different. These investigators believed that oxidation in the light is promoted mainly by the ultraviolet radiation and the effect is restricted to a depth of about 4 microns. The author of this report and his associates, in unpublished work, found that the short visible waves were more destructive to asphalts than the ultraviolet radiation alone.

It was shown by Sparlin[5] that ultraviolet energy is capable of producing measurable increases in the viscosity of asphalt films sealed from the atmosphere (air).

Photo-oxidation and Photochemical reactions have been investigated by Traxler[6] under Study 2-8-59-9 using asphalts sold to the Texas Highway Department. The procedures used were quite simple and the results obtained were informative enough to inspire the experiments discussed below.

III. CONCLUSIONS

It is concluded that:

(1) Irradiation of grades AC-10 and AC-20 of asphalts 6, 3 and 11 are hardened to different degrees by irradiation with light possessing wave lengths ranging from 3200 to 4200 Angstroms.

(2) Since such energy does not normally penetrate very far into a film of asphalt it was necessary to use films of 10 to 20 microns in thickness to obtain sufficient hardening to give definitive viscosity values.

(3) Asphalt 6 hardens much more under the conditions established for this investigation than do asphalts 3 and 11, which are affected to about the same degree.

(4) The degree of hardening by irradiation is different from the effect of heat, air and time on the three asphalts in the absence of short wave length light. Under the latter environmental conditions asphalt 6 hardens the least, the asphalts 3 and 11 to about the same extent.

(5) The amounts of nickel and zinc in the asphalts varied to a measurable degree. Asphalt 6, which hardened the most when exposed to ultraviolet light contained the largest amount of both metals. Asphalt 11 had the least amount of nickel and showed the least Relative Hardening. Asphalt 3 was intermediate in both nickel content and susceptibility to hardening.

IV. RECOMMENDATIONS

No recommendations are made.

V. FUTURE WORK

No future work is planned, but when an opportunity arises this study on the action of actinic (chemically active light) on road and roof building asphalts should be reactivated.

VI. EXPERIMENTAL WORK

1. Asphalts Investigated

Asphalt Cements of 10 and 20 grades from 1967 production of suppliers number 3, 6 and 11 were used in the experiments discussed below. Viscosity data for the six asphalts are shown in Table 1, facing.

2. Radiation Equipment

Five Sylvania Black Light 15-watt Lamps (F15T8-B1) each 18 inches long were mounted as a block to irradiate an area 18 x 18 inches. This block of lights was supported in an adjustable cabinet open on all sides with a loose aluminum coated cloth curtain which could be raised or lowered. The curtain was used to protect the operator against excessive radiation. The lamps could be located at a maximum of 14.5 inches from the bottom of the cabinet or at any lesser desired distance from the source of radiation.

Wave lengths emitted by these lamps ranged from 3200 to 4200 Angstroms with a maximum intensity of 3600 Angstroms. Center of the cabinet floor was marked off with a square 10 x 10 inches. Samples were always placed in this area in order for them to receive uniform and maximum radiation at each distance from the bank of lamps.

A Blak-Ray Ultraviolet Intensity Meter with a 3660 Angstrom Sensor was used to determine the intensity of radiation over the area of the samples at the various distances from the lamps. The meter reports radiation intensity in microwatts per square centimeter (mw/cm^2).

3. Controlled Variables

Considerable preliminary experimental work was necessary to establish practical limitations for certain of the variables inherent in the study.

Ambient Temperature: This was established at 95-100°F (35-37.8°C) because it was undesirable to operate at a higher temperature and inject excessive thermal energy into the picture. Maintenance of a lower temperature would have required a rather expensive control system.

Time of Exposure to Radiation: This variable was fixed at 18 hours. Shorter times of exposure were tried but did not cause sufficient change in the asphalt properties of the irradiated films. Even longer times were considered but were abandoned because of excessive time used and the problem with an occasional lamp losing its intensity during a run. The selection of 18 hours appeared to be a good compromise.

Asphalt Film Thickness: Films used were varied from 10 to 2700 microns. Films thicker than 30 microns, after exposure for 18 hours to the maximum intensity available, did not show notable changes in hardness. Since it would require many hours exposure of thick films, in our equipment, to satisfactorily discriminate between the asphalts used by THD, testing of films greater than 30 microns was abandoned.

Intensity of Radiation: The films were exposed at various distances from the source of radiation. Of course, distance from the lamps regulates the intensity of radiation at the asphalt surface, namely 700, 775 and 1000 microwatts (7,000, 7750 and 10,000 ergs) per square centimeter for the tests conducted.

Formation of Films: The thick films were formed in shallow glass dishes. Hot asphalt was poured into the dish and the weight of the asphalt determined. From this value and the density of the asphalt and the area of the asphalt surface the thickness of the film was calculated. Films approximately 10 to 30 microns thick were prepared on 4 cm x 4 cm glass plates. These were the kind of plates prescribed by ASTM for the laboratory hardening tests for asphalts (7).

4. Viscosities of Original and Irradiated Asphalt Films

The Hallikainen, sliding plate, thin film viscometer was used to determine the viscosities, at 77°F (25°C) and 5×10^{-2} sec^{-1} rate of shear, of the asphalts before and after irradiation. This apparatus requires about 0.05 gram of asphalt for one run which yields data at four different shearing stresses. The procedure for operating this viscometer is given by Traxler (8).

In order to compare hardening of the asphalts used, without confusion caused by differences in the viscosities of the original bitumens, we resorted to the quotient obtained by dividing the viscosity of the irradiated (hardened) asphalt by that of the original asphalt at the same temperature and the rate of shear. This quotient has been called hardening index, aging index or relative viscosity. Since viscosity was used as the basic unit, the term relative viscosity (R.V.) is used in the discussion that follows.

5. Investigation of Thick Films

Table 2, facing, gives data on the 6 asphalts studied using films 400 to 2700 microns thick. The relative viscosities for a particular kind and grade of asphalt always decrease with increased thickness of the film. This is what would be expected. However, the differences shown by the samples of varying thickness are quite small. It should be pointed out that the viscosities given in the table for the irradiated asphalts, and thus the calculated Relative Viscosity, are the average of two runs under the same operating conditions.

It is obvious that irradiation of such thick films with 1000 microwatts/cm^2 for 18 hours results in comparatively small increases in viscosity of the asphalts.

6. Investigation of Thin Films

a-Grade AC-10 asphalts

Attention was next turned to the irradiation of films 10 to 30 microns thick where the effects of the short wave length radiation on the six asphalts are pronounced. Tabulations of the data are given in Table A-1 of the Appendix. In Figures I and II, pages 12 and 13, arithmetic plots are shown of Relative Hardening of 10 and 20 micron films of the AC-10 grade asphalts versus Intensity of Radiation in microwatts/cm^2.

Figure I indicates that 10-micron films of Asphalts 3 and 11 show similar degrees of hardening by ultraviolet radiation. Asphalt 6 is affected to a greater extent and for the range of intensity studied the arithmetic plot is curved instead of essentially straight as for Asphalts 3 and 11.

The same information is given in Figure II for the three AC-10 grades of asphalt tested in the form of 20-micron films. In this plot of Relative Hardening versus Intensity of Radiation, the lines for Asphalt 3 and 11 superimpose. Again Asphalt 6 shows the greatest hardening but the plot is a straight line and not a curve as appears in Figure I, concerned with the 10-micron films.

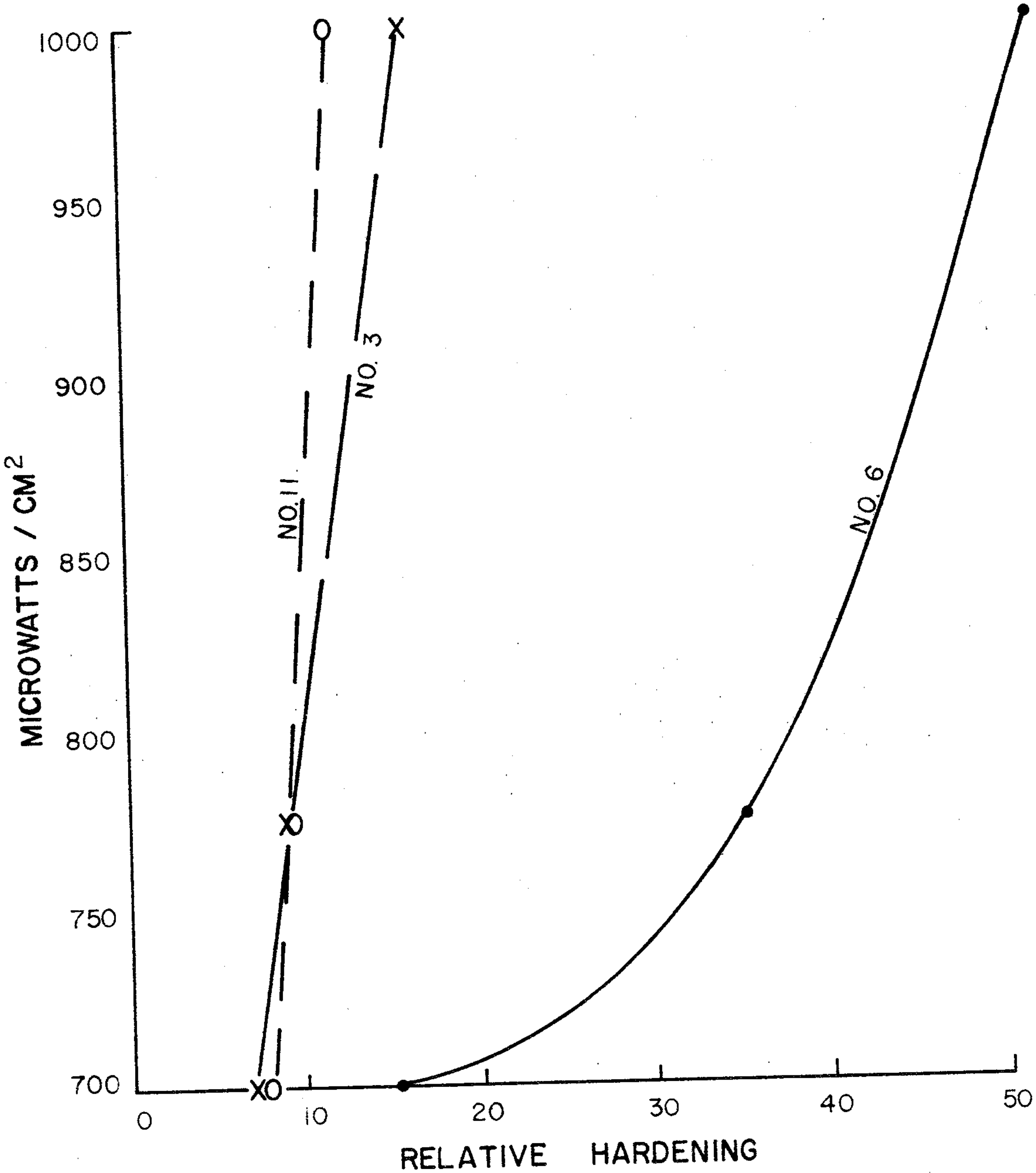

FIGURE I

AC–10 GRADE ASPHALTS
IRRADIATED 18 HOURS
10 MICRON FILMS
X—ASPHALT NO. 3
•—ASPHALT NO. 6
O—ASPHALT NO. 11

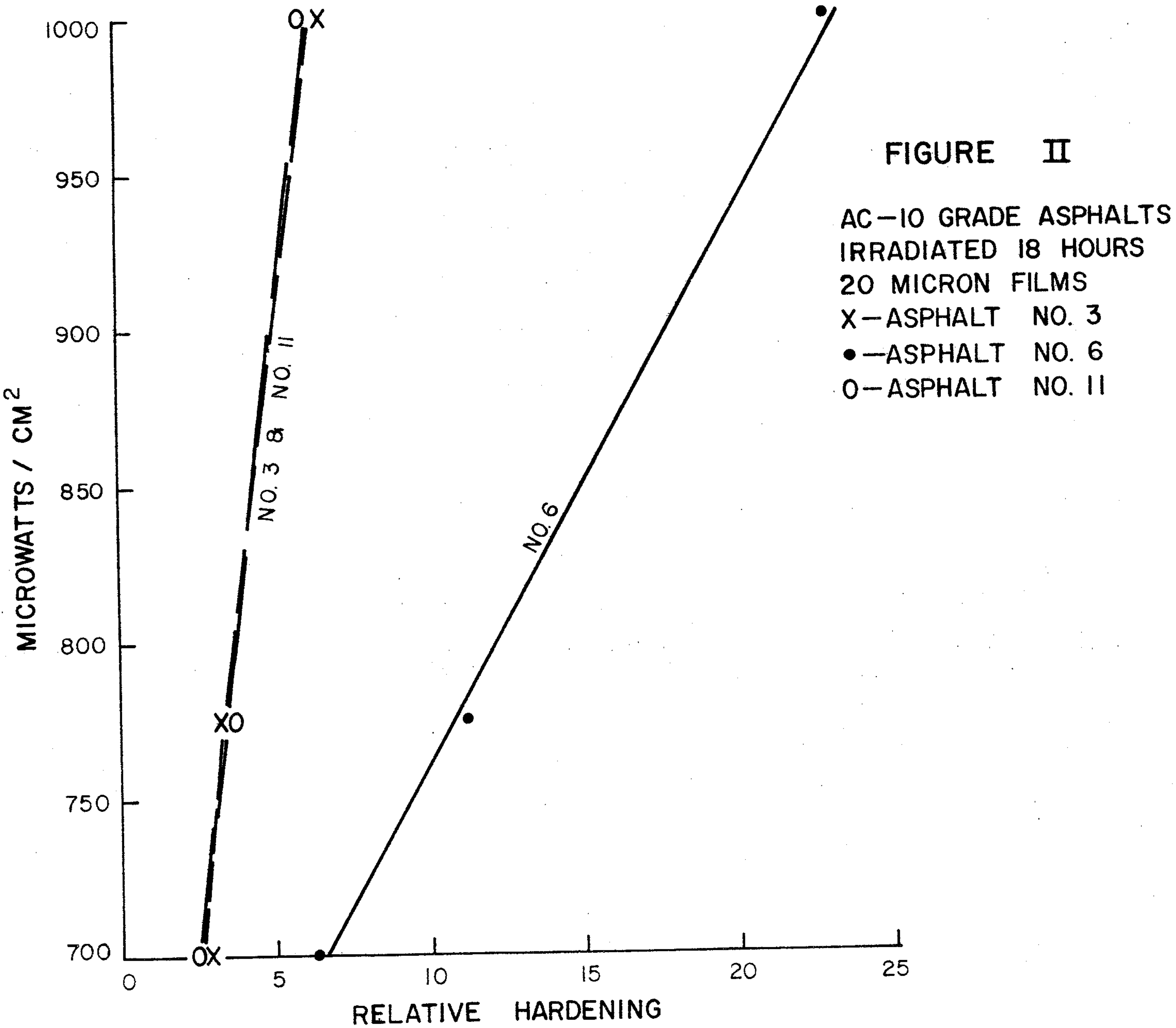
FIGURE II
AC-10 GRADE ASPHALTS
IRRADIATED 18 HOURS
20 MICRON FILMS
X-ASPHALT NO. 3
●-ASPHALT NO. 6
O-ASPHALT NO. 11
MICROWATTS / CM2
RELATIVE HARDENING
1000
950
900
850
800
750
700
0
5
10
15
20
25
NO. 3 & NO. 11
NO. 6

b-Grade AC-20 Asphalts

Plots of Relative Hardening (R.V.) vs Intensity of Irradiation (microwatts/cm^2) for the AC-20 grades are shown in Figures III and IV, pages 15 and 16. Data are given in Table A-2 of the Appendix.

Again the 10-micron films of Asphalt 6 give a curved line (Fig. III) whereas the data for 20-micron films plot to a straight line (Fig. IV). Both 10- and 20-micron films of AC-20 grade Asphalt 6 became harder (are more affected by radiation) than similar ones for Asphalts 3 and 11.

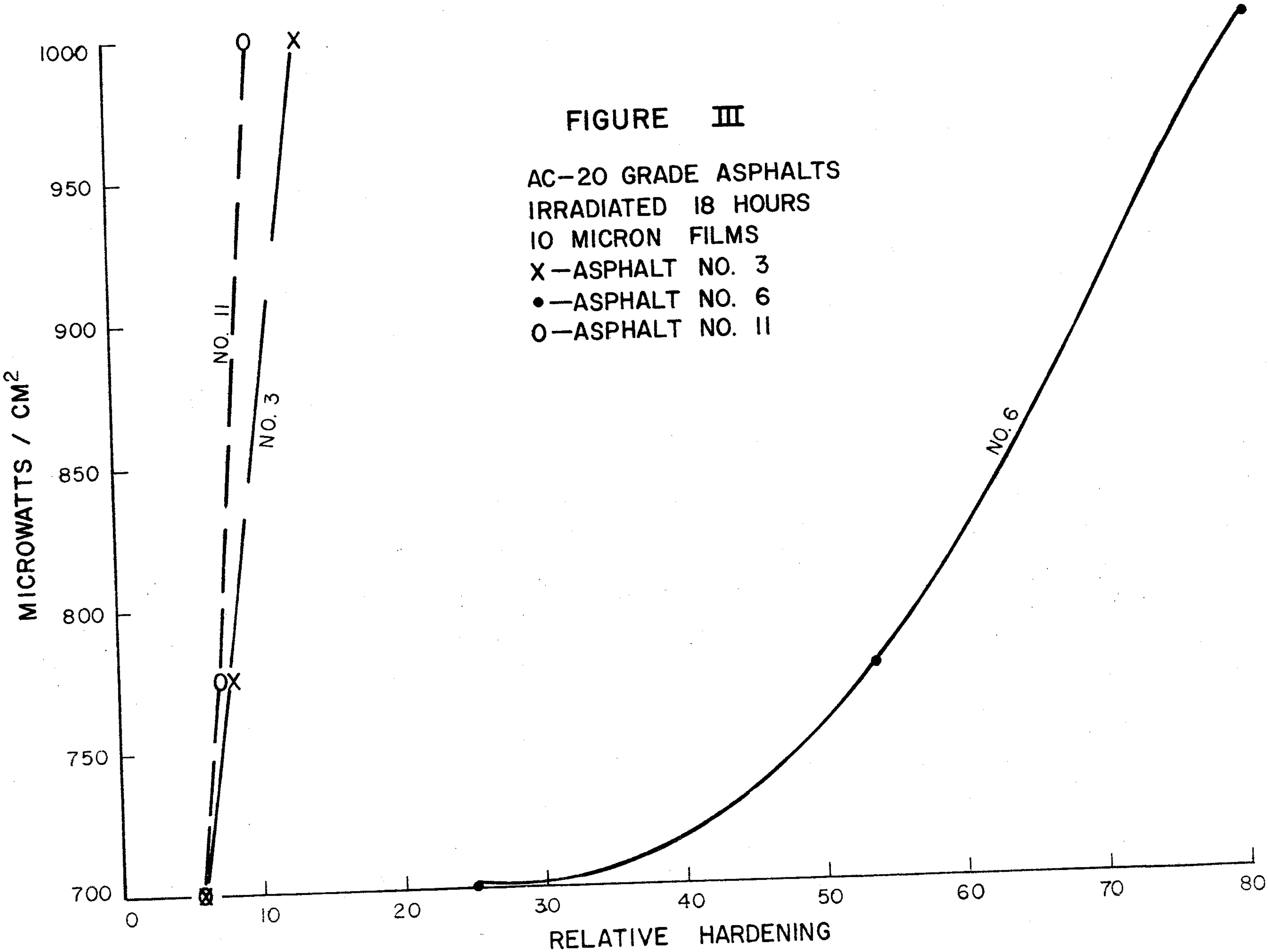
FIGURE III
AC-20 GRADE ASPHALTS
IRRADIATED 18 HOURS
10 MICRON FILMS
X—ASPHALT NO. 3
●—ASPHALT NO. 6
O—ASPHALT NO. 11
MICROWATTS / CM2
RELATIVE HARDENING
NO. 11
NO. 3
NO. 6
1000
950
900
850
800
750
700
0
10
20
30
40
50
60
70
80

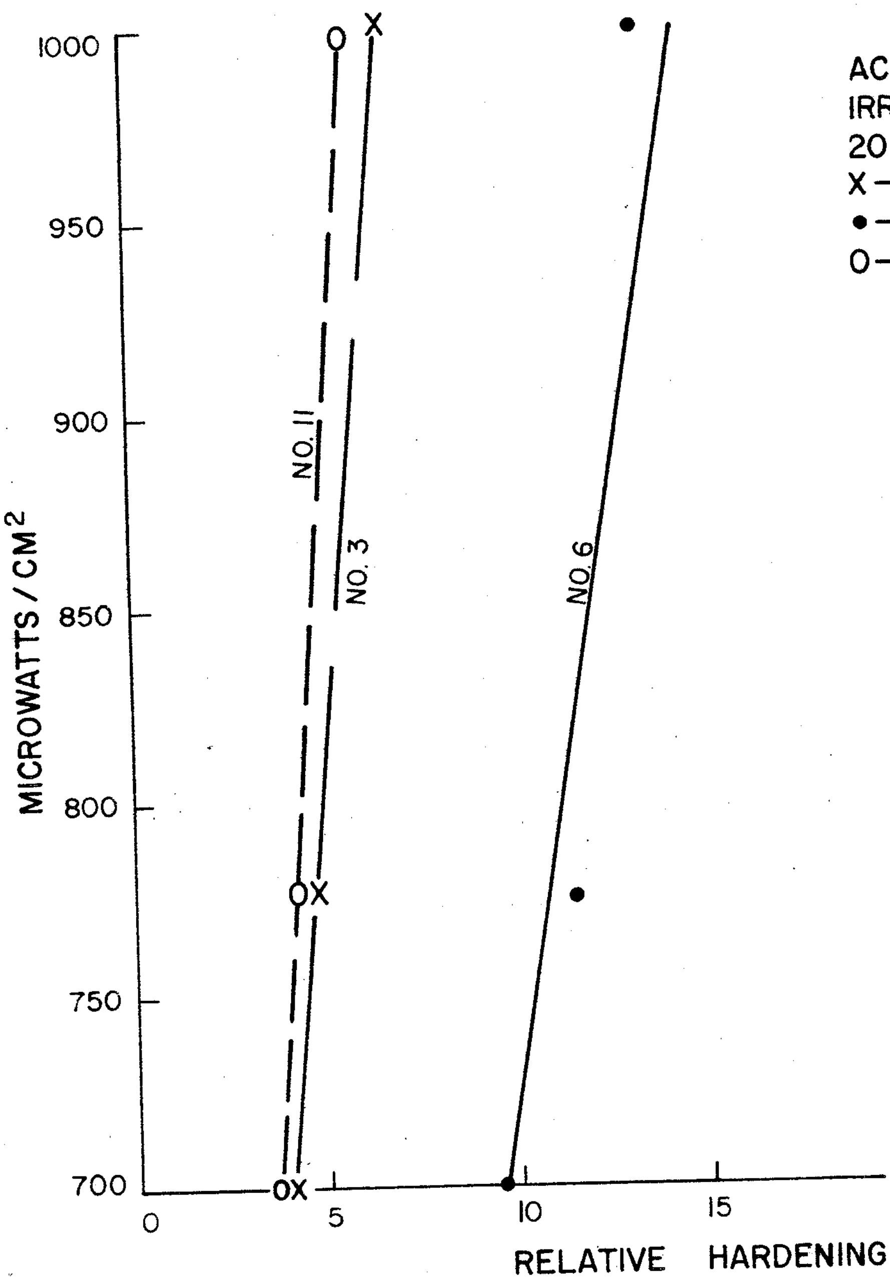

FIGURE IV
AC–20 GRADE ASPHALTS
IRRADIATED 18 HOURS
20 MICRON FILMS
X – ASPHALT NO. 3
● – ASPHALT NO. 6
O – ASPHALT NO. 11

7. Relationship Between Hardening by Ultraviolet Radiation and Trace Metal Content

Asphalt technologists have frequently discussed the possibility that trace metals present in asphalts could be responsible, to some extent, for accelerating changes in roads and roofs during service. However, no measurements have been made of trace metal content of asphalts used in environmental studies such as those described herein concerning the hardening effect of actinic light. To partially close this gap, Atomic Adsorption Spectroscopy was used to measure the nickel and zinc content of the six asphalts used in the investigation described above.

Table 3, facing, shows the Relative Hardening values, obtained by irradiating 10-micron films with 1000 microwatts/cm^2 for 18 hours, compared with parts per million of nickel and zinc in the six asphalts.

Both grades of Asphalt 6 show the greatest hardening by irradiation and also the highest content of nickel and zinc. Asphalt 11 (both AC-10 and AC-20 grades) shows the least nickel content but a slightly greater zinc content than for Asphalt 3. This latter asphalt contains the imtermediate amount of nickel and the hardening by irradiation is intermediate to Asphalts 6 and 11. The difference in zinc content of Asphalts 3 and 11 may fall within the limits of error for the determination.

It is hoped that these experiments will be a stimulus to the exploration of other trace metals on the susceptibility of asphalts to hardening by ultraviolet and visible short wavelength sunlight (chemically active radiation).

VII. REFERENCES

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(4) Blokker, P. C. and van Hoorn, H., Fifth World Petroleum Congress, VI 417 (1959).

(5) Sparlin, R. F., Proc. Am. Soc. Testing and Materials 58 1316 (1958).

(6) Traxler, R. N., Texas Transportation Institute-Texas Highway Department Cooperative Research. Study 2-8-59-9, Progress Report No. 4 October 1962.

(7) A. S. T. M. Standards Part 11, Bituminous Materials, Soils, Skid Resistance, 863 (1968).

(8) Traxler, R. N. Book, Bituminous Materials Volume I Chapter 4, page 151 Arnold J. Hoiberg, Editor, Interscience Publishers (1964).

VIII. APPENDIX

TABLES

Table A-1

AC-10 Asphalts-Irradiation of 10-, 20- and 30-micron films at 700, 775 and 1000 micro watts/cm^2 for 18 hours

Supplier	Films Thickness, Micron	Relative Hardening		
		1000 uw/cm^2	775 uw/cm^2	700 uw/cm^2
6	10	52.0	35.3	15.1
3	10	16.3	9.0	6.8
11	10	12.2	9.2	7.9
6	20	23.0	12.2	7.8
3	20	8.2	5.6	5.0
11	20	8.6	7.0	6.0
6	30	7.1	4.9	3.6
3	30	4.3	4.0	2.9
11	30	6.1	3.3	2.1

Table A-2

AC-20 Asphalts-Irradiation of 10-, 20- and 30-micron films at 700, 775 and 1000 micro watts/cm^2 for 18 hours

Supplier	Film Thickness, Micron	Relative Hardening		
		1000 uw/cm^2	775 uw/cm^2	700 uw/cm^2
6	10	81.0	53.3	25.0
3	10	13.8	7.25	5.9
11	10	10.0	7.1	6.3
6	20	13.3	11.6	9.6
3	20	6.6	4.3	4.1
11	20	5.5	4.8	3.8
6	30	7.1	4.6	3.9
3	30	5.7	3.7	2.9
11	30	3.8	3.2	3.1