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# LOSS OF DURABILITY IN BITUMINOUS PAVEMENT SURFACES - IMPORTANCE OF CHEMICALLY ACTIVE SOLAR RADIATION

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## PREFACE

This is the third report issued under Research Study 2-8-69-127, which is being conducted at the Texas Transportation Institute in the cooperative research program with the Texas Highway Department and the Federal Highway Administration. The first two reports are:

1. "Performance Requirements of High Quality Flexible Pavements," by Douglas Bynum, Jr., and R. N. Traxler, Research Report 127-1, Texas Transportation Institute, August, 1969.

2. "A Thermoviscoelastic Characterization of An Asphaltic Concrete," by Douglas Bynum, Jr., Research Report 127-2, Texas Transportation Institute, August, 1970.

## DISCLAIMER

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Federal Highway Administration.

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## ABSTRACT

Data concerning the hardening of asphalts used in the surface courses of pavements indicated that laboratory tests, currently used by asphalt technologists, do not accurately predict the hardening which occurs in a pavement during service. It became evident that some prime factor involved in the hardening of the road surface had been neglected. Extensive experimental work pointed out that this important factor was the chemical hardening of asphalts by short wavelength solar radiation. During this study a new test was developed which utilizes time, heat, air, and measured concentrations of chemically active (actinic) radiation. Hardening Indices obtained by this new test correlated well with the Hardening Indices obtained on asphalts extracted from pavement surface courses at several Texas locations.

A great variation in degree of hardening was shown by application of the new test to 65 asphalts from a wide variety of crude oil sources, including 16 not used by the Texas Highway Department. Also, it was discovered that 80% of the asphalts subjected to the laboratory test showed good correlation between the degree of hardening and the vanadium content (ppm) of each material. Content of vanadium atoms in each asphalt was measured by Neutron Activation Analysis.

It also became apparent that the activity of the vanadium atoms vary with the way they are combined in the organic molecules present in the asphalt. A portion of the vanadium atoms present in some asphalts are rendered chemically inactive by being bound (sequestered) within large molecules. In other asphalts a large part of the vanadium atoms appear to be constituents of compounds that permit them to stimulate chemical reactions in the asphalt by transforming radiant energy into chemical energy. This conversion to

chemical energy results in chemical reactions responsible for hardening of the asphalts. Such reactions can be retarded by using additives that either inhibit the radiant energy or make the vanadium atoms unreactive. Work has started on this important aspect of the problem of hardening of asphalt by solar energy.

Finally, further work on the new laboratory test is under way to develop a suitable diagnostic control test for selecting asphalts to be used in the surface courses of high class bituminous pavements.

## SUMMARY

Hardening Indices of asphalts recovered from surface courses of bituminous pavements, at a number of locations in Texas, did not correlate well with Hardening Indices obtained by the usual laboratory test values for the original asphalt used at each site.

An extensive laboratory investigation indicated that the neglected factor in the hardening of surface courses is the chemical hardening of asphalt by short wavelength (actinic) solar radiation. Incidentally organic materials other than asphalt, such as rubbers, polymers, paints, etc. are hardened by actinic radiation.

Also, it has been established from both field and laboratory investigations that asphalts manufactured from different petroleum sources vary greatly in their resistance to hardening by the short wavelength solar radiation. The cause for this variation of hardening was sought by analyzing a number of asphalts for the amounts of trace metals present. Thermal Neutron Activation Analysis was used to determine the quantity of each element in each asphalt analyzed. From these tests it became evident that vanadium was more involved than any other element in the chemical hardening of asphalts. The degree of hardening appeared to depend on (a) the amount of vanadium present, and (b) the way the element is located in the complex organic compounds in each asphalt. For example, a small number of vanadium atoms in a very active state can greatly stimulate the change of radiant energy into chemical energy. On the other hand a large amount of vanadium atoms with a high percentage of them bound (sequestered or chelated) in large complex molecules do not strongly stimulate the conversion of radiant into chemical energy and, thus, do not result in serious hardening of the

asphalt.

Five correlations established from this research are presented below.

1. Hardening Indices ($X_1$) developed, in 14 different asphalts, after two years service in pavements versus Hardening Indices ($X_3$) developed by subjecting the 14 original asphalts to an old laboratory test not utilizing actinic solar radiation.

Linear regression equation: $X_1 = 5.39 + 4.23X_3$

Correlation Coefficient = 0.52

Standard Deviation = 8.4 ($X_1$ ranged from 7.3 to 40.0)

2. Hardening Indices ($X_1$) developed, in 14 different asphalts, after two years service in pavements versus Hardening Indices ($X_2$) developed by subjecting the original asphalts used in the pavement to a new laboratory test utilizing time, heat, air and short wavelength solar (actinic) radiation.

Linear regression equation : $X_1 = 10.21 + 0.272X_2$

Correlation Coefficient = 0.87

Standard Deviation = 4.9

3. Hardening Indices ($X_1$) developed, in 14 different asphalts, after two years in pavements versus parts per million of vanadium ($X_4$) in the asphalt.

Non-linear regression equation: $X_1 = 13.17 + 20.95\ (1-e^{-.0002900X_4^2})$

Correlation coefficient = 0.82

Standard Deviation = 5.6

4. Hardening Indices ($X_2$) obtained by the new actinic test, on the 14 original asphalts, used in the field tests versus parts per million of vanadium ($X_4$) in the asphalts.

Non-linear regression equation: $X_2 = 7.03 + 78.54\ (1-e^{-.0003500X_4^2})$

Correlation Coefficient = 0.95

Standard Deviation = 9.5 ($X_2$ ranged from 5.5 to 89.0)

5. Hardening Indices ($X_2$) obtained by the new actinic test, on 52 different asphalts, (including the 14 used in field tests) versus parts per million of vanadium ($X_4$) in the asphalts.

Non-linear regression equation: $X_2 = 14.11 + 84.49\ (1-e^{-.0002500X_4^2})$

Correlation Coefficient = 0.88

Standard Deviation = 15.3 ($X_2$ ranged from 5.5 to 126.0)

The data established for (a) hardening during two years of service in a pavement surface, (b) hardening by subjecting the original asphalt to a new laboratory test utilizing the combined effects of time, heat, air and short wavelength solar radiation, and (c) by analyzing the asphalt for vanadium content, show good correlations. The commonly used dark oven test utilizing only time, heat and air gives poor correlations with other tests. This research has led to a fuller understanding of asphalt hardening in the surface courses of bituminous pavements.

Now that one of the prime causes for hardening of asphalts in pavements surfaces has been established, remedies for this economically important problem must be developed. Small amounts of ultraviolet inhibitors have been used successfully with a few asphalts possessing extreme sensitivity to actinic radiation. This approach will be extended to other kinds of asphalt. Also, additives known as metal deactivators will be investigated in an effort to substantially upgrade asphalts for use under the severe environmental conditions encountered at a pavement surface.

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# I. INTRODUCTION

## A. Purpose

The purpose of this phase of the study was to investigate performance of asphalts in terms of chemical aging (hardening). This report is in fulfillment of part of the overall objectives of the study, namely:

1. Determine the performance requirements of an asphaltic material needed to serve as the cohesive-adhesive waterproof binder for a first-class, long-life flexible pavement surface course.

2. Develop improved control tests for use in a specification for asphaltic material that will meet the performance requirements in objective one.

This report comprises a summary of research work accomplished under Phase 3, "Laboratory Investigation".

## B. Need for the Research

For several decades the need for a definitive test for determining the rate at which an asphalt can be expected to harden under service conditions has become increasingly obvious. This necessity for predicting hardening rate, as well as isolating and determining the prime cause or causes for differences in hardening of asphalts used in construction of high grade, high cost pavement surface courses was responsible for a series of researches conducted cooperatively by The Texas Highway Department and The Texas Transportation Institute, during the past twelve years.

C. Implementation Statement

Based on the results described in this report it is recommended that a specific research study be set up to pursue further the causes of hardening of asphalt cements under highway service conditions with the objective of determining warrants and appropriate control tests for writing a specification for improving the quality of asphalts used in pavement surface courses.

D. Background

Maintenance of the surface courses of high class bituminous pavements has presented technical and economic problems for many years. Causes of failure during service are numerous and sometimes complex. The basic problem facing the design engineer and the bituminous chemist is to isolate the more important elements of this problem and then try to eliminate or reduce the destructive forces. Following is a brief, chronological review of some of the steps taken toward a solution of this problem.

1. Technically sound methods for measuring the hardness of asphalts at normal atmospheric temperatures were first developed and applied. Viscosities measured in megapoises at 77°F were found suitable for evaluating changes in hardness of an asphalt encountered in service or by any suitable laboratory (accelerated hardening) test. These studies, which covered a period of 15 or more years, culminated in wide application of viscosity data to highway problems.

2. In 1963, field tests were started by THD-TTI at a number of widely separated locations in Texas. The sites selected were a part of the THD annual maintenance program and careful control of all operational procedures were maintained by THD and TTI. Extensive tests were made concerning hardening of the asphalts during preparation of the

hot-mix, transport to site, and laying of the surface course. Changes in properties of the asphalts were determined at established times during three years of service. A large amount of physical, rheological and chemical data were obtained on the original asphalts, on samples of asphalts carefully recovered from the aggregate-asphalt mixture and on the paving mixtures at different periods of time. Characteristics of the aggregate used were determined by a qualified mineralogist.

3. Serious consideration of the mass of data, thus made available, led to the conclusion that the fundamental cause or causes of the excessive hardening with time of certain asphalt cements in surface courses had not been pinpointed. After a careful review of the various environmental factors affecting the surface of a pavement, it became clear that the hardening of asphalts by short wavelength solar chemically active (actinic) radiation had not been measured quantitatively.

4. This conclusion was responsible for the development of a laboratory test which numerically measured the combined effects of time, heat, air and solar radiant energy on an asphalt. After extensive experimental work a test was developed which included the following parameters.

a. Film thickness of the asphalt test sample - 10 microns

b. Temperature of the asphalt during the test - 95°F

c. Air - slowly moving over the asphalt surface

d. Light intensity - 1000 microwatts (10,000 ergs/$cm^2$) measured at a wavelength of 3600 Angstroms

e. Time exposed to radiation - 18 hours

5. Viscosity of an asphalt after hardening, by the laboratory test described above, is determined in a sliding plate viscometer at 77°F and calculated at $5 \times 10^{-2}$ $sec^{-1}$ rate of shear. This value is divided

by the viscosity of the original asphalt determined at the same temperature and calculated at the same rate of shear. The resulting quotient is called the Hardening Index* of the asphalt caused by the combination of factors mentioned above.

(Note: An older test, which has been used on asphalt, operates in the same fashion except that the parameters are:

a. Film thickness of the asphalt test sample - 15 microns.
b. Temperature of the asphalt during the test - 225°F.
c. Air - slowly moving over the asphalt surface.

This test which does not include the effect of the actinic radiation is not very discriminatory among most of the samples investigated.)

6. The question then arose as to why the radiant energy has such a pronounced but variable effect on hardening of the asphalts investigated. Considerable experimental work indicated that the vanadium content of an asphalt (in parts per million) correlated reasonably well with the Hardening Index obtained by the new actinic light test described above. The vanadium content is rapidly and accurately determined by thermal neutron activation analysis. Sixty-five different asphalts have been investigated and the data obtained are presented in the body of this report.

* See page 46 for a list of the symbols used to represent different types of Hardening Index.

## II. 1963 FIELD TESTS

Test sites in widely separated areas were selected by the Texas Highway Department in connection with their annual surface course maintenance program. At each site a 1-1/4 to 1-1/2 inch thick surface course was laid in compliance with THD standard specifications.

Before the paving machine arrived at the selected section of a road, heavy aluminum foil was tacked to the base course by roofing nails. This was done to facilitate removal of 2 foot x 2 foot slabs of the surface course and to prevent contamination by primer applied to the base.

Pertinent information obtained at each site included District number, County, highway designation, project number, stations, producer, date pavement surfacing was laid, and temperature of the freshly prepared mixture.

Aggregate samples were taken from each aggregate bin at each experimental site. A mineralogical description of the contents of each bin is given in literature reference (1).

At each field site the following samples were collected.

(1) Original asphalt as it entered the hot-mix plant,

(2) Hot asphalt-aggregate mixture as it entered the truck,

(3) Asphalt-aggregate mixture when it was placed in the paving machine,

(4) 2 foot x 2 foot samples of the surface course taken 1 day, 2 weeks, 4 months, 1 year, 2 years and 3 years after the pavement was laid and compacted.

All samples of pavement were removed from between the wheel path of the outer lane.

(Note: Difficulties were encountered in testing a few samples after 3 years in service because of contamination (softening) of the asphalt by motor oil dripped on the surface by passing cars. This trouble was identified by separating such oil from the recovered asphalt. In most cases it is impossible to detect visually the spillage of oil at a particular point in a pavement and consequently it is often difficult to avoid obtaining a contaminated sample. This happened at three of the selected sites in the series of field tests.)

A. Extraction and Recovery of Asphalt Cements

About 25 pounds of asphalt-aggregate mixture or surface course removed from each road were placed in large Colorado type apparatus for extraction of the asphaltic binder. A mixture of 6 parts benzene and 1 part ethyl alcohol was used to dissolve the asphalt from the bituminous mixtures. Alcohol was added to the benzene to assure essentially complete removal of all asphaltic components from the various aggregate surfaces.

The benzene-alcohol solution of asphalt was centrifuged to remove any fine mineral that may have passed through the filter paper in the extraction apparatus. The essentially mineral-free solution of asphalt was first distilled by the standard Abson procedure until a large portion of the benzene-alcohol was removed and the concentrated solution then transferred to a thin film evaporator and the remaining solvent removed at 125°F and 15 mm of mercury pressure. The thin film evaporator

is illustrated in literature references (2) and (3). About 1.5 pounds of asphalt was recovered from each sample delivered from the field.

B. Tests on Surface Courses Removed from the Pavements

Hveem Stability and Cohesiometer values on each hot mix were supplied by the THD District in which the experiment was conducted. Densities were determined on each slab after delivery to TTI. Measurements were also made using the Air Permeometer to ascertain porosity of the pavement to air. Complete data on density, stability, cohesion and permeability to air are shown in literature references (2) and (3). It should be noted that a somewhat similar investigation was conducted cooperatively by the California Highway Department and the Shell Development Company starting in 1954 (4).

C. Flow (Rheological) Data on Original and Extracted Asphalts

Viscosities at 77°, 95°, 140° and 275°F and ASTM penetration at 77°F, 100 grams, 5 secs were determined on each original and the recovered asphalts listed on page 5. Measurement of viscosities at 77° and 95°F were made in the thin film (sliding plate) Hallikainen viscometer and values were calculated at $5 \times 10^{-2}$ $sec^{-1}$ rate of shear. Kinematic viscosities at 140° and 275°F were determined in Cannon-Manning vacuum capillary tube viscometers.

Hardening Index (HI), for each recovered asphalt was calculated by dividing the viscosity of the recovered asphalt at 77°F by the viscosity of the original asphalt at the same temperature. The resulting quotient indicates how many fold the asphalt had increased in hardness because

Data Obtained During Field Tests Conducted Cooperatively by THD-TTI

| Site[1] | Asphalt No. | Mix Temp. °F | Hveem Stability | Hveem Cohesion | Aggregate | Condition surface after 2 years service | ADT | Permeability[2] | Hardening Index After 2 years service ($X_1$) | Hardening Index After Lab. test[3] ($X_3$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 5 | 300 | 34 | -- | Hard Dolomite | Good | 2000 | -- | 22.0 | 2.55 |
| 3 | 8 | 300 | 50 | 389 | Limestone | Excellent | 1820 | 41.0 | 7.3 | 2.70 |
| 4 | 11 | 270 | 31 | 63 | Gravel and Clay | Good | 1700 | 0.53 | 12.8 | 2.70 |
| 10 | 11 | 270 | 38 | 158 | Iron Ore | Good | 1350 | 61.5 | 20.5 | 2.70 |
| 14 | 6 | 325 | 58 | -- | Porous Limestone | Good | 6970 | 1380 | 12.7 | 2.80 |
| 7 | 15 | 275 | 42 | 134 | Hard Non-Porous | Some Cracks | 1200 | 272 | 23.0 | 3.20 |
| 11 | 6 | 265 | 36 | 126 | Gravel & New Reef Shell | Very Poor | 4580 | 36 | 27.0 | 3.20 |
| 12 | 2 | 275 | 51 | 159 | New Reef Oyster Shell | Fair | 3305 | 132 | 29.0 | 3.20 |
| 17 | 3 | 305 | -- | -- | Gravel | Excellent | 9240 | -- | 18.8 | 3.80 |
| 1 | 3 | 320 | 32 | 156 | Siliceous Gravel | Good | 5040 | 103 | 9.3 | 4.20 |
| 9 | 3 | 325 | 32 | 287 | Iron Ore Slag & Sand | Very Good | 3140 | 164 | 11.3 | 4.70 |
| 8 | 7 | 325 | 50 | 214 | Limestone | Poor | 3590 | 473 | 33.0 | 5.10 |
| 6 | 7 | 250 | 36 | 90 | Gravel | Fair | 3700 | 65.0 | 40.0 | 6.35 |

[1] To make possible identification of differences or similarities in properties of asphalts delivered by individual manufacturers to different paving sites.
[2] Permeability of slab to air (ml/in/min) after two weeks service.
[3] Laboratory test of 15 micron film, 2 hours at 225°F in dark oven.

of the treatment or length of service it had encountered. Complete data are given in references (2) and (3).

A laboratory hardening test, which measures the combined hardening effect of time, heat and air, was made on each original asphalt. A 15-micron film of the asphalt was placed on 4 cm x 4 cm glass plates and exposed in a dark oven at 225°F for two hours. A razor blade was used to remove the cool, hardened asphalt from the glass plates. The asphalt was then placed in the form of 25 to 30-microns between the 3 cm x 2 cm glass plates used in the sliding plate (Hallikainen) viscometer. Viscosities were measured at 77°F and calculated at $5 \times 10^{-2}$ $sec^{-1}$ rate of shear. Viscosity of each hardened asphalt was divided by the original viscosity at 77°F. The resulting quotient called the Hardening Index, $HI(X_3)$, is a measure of the susceptibility of the particular asphalt to hardening by time, heat and air.

D. Comments on Data Obtained from the 1963 Field Tests

Information obtained from the field tests discussed below are condensed in Table 1 to show the relationship between durability of the surface courses as evaluated by visual inspection and the data available on the asphalts and asphalt-aggregate mixtures.

1. Within the 250 - 325°F range of temperatures at which the asphalt and graded stone were mixed, temperature does not appear to be an important factor in the durability of the pavement surface. This situation may be explained by the careful control of temperature at each hot mix plant.

2. Values for stability and cohesion of the freshly prepared asphalt-aggregate mixtures do not show any meaningful correlation with the durability of the pavements or the hardness of the recovered asphalts.

3. An effort was made to determine whether chemical reactions between the asphalt and certain types of aggregate could be responsible for part of the asphalt hardening during service in the road. For example, it was reasoned that new reef oyster shell with its known content of aragonite (a chemically active kind of calcium carbonate) might be responsible for the excessive hardening of the asphalt used at Site No. 11. Polarographic measurements on some of the aggregates involved in the Field Tests gave no helpful information. Also, samples of eight aggregates used in the Field Tests were pulverized and the 200-270 mesh material was mixed with equal volumes of two representative asphalts (No. 6 and 11) used in the field tests. The fine aggregate presented a high surface area to the asphalt. The blends were heated at 113°F (45°C) for 2 and 6 months in closed cans to prevent access of air, moisture or light. After this treatment the asphalt was extracted from the stone, carefully recovered and viscosities determined at 77°F and calculated at $5 \times 10^{-2}$ $sec^{-1}$ rate of shear. Insignificant increases in hardening of the asphalts were obtained by these protracted tests.

4. Slabs taken from the test sites were measured for permeability to air (connected voids). The air Permeometer developed by the California Research Corporation and sold by Soil Test, Inc. was used for these tests. Values were obtained on slabs from each site after 1 day, 2 weeks, 4 months, 1 year, 2 years and 3 years in service. Complete data are given in (1). A few slabs had developed cracks during shipment although the containers

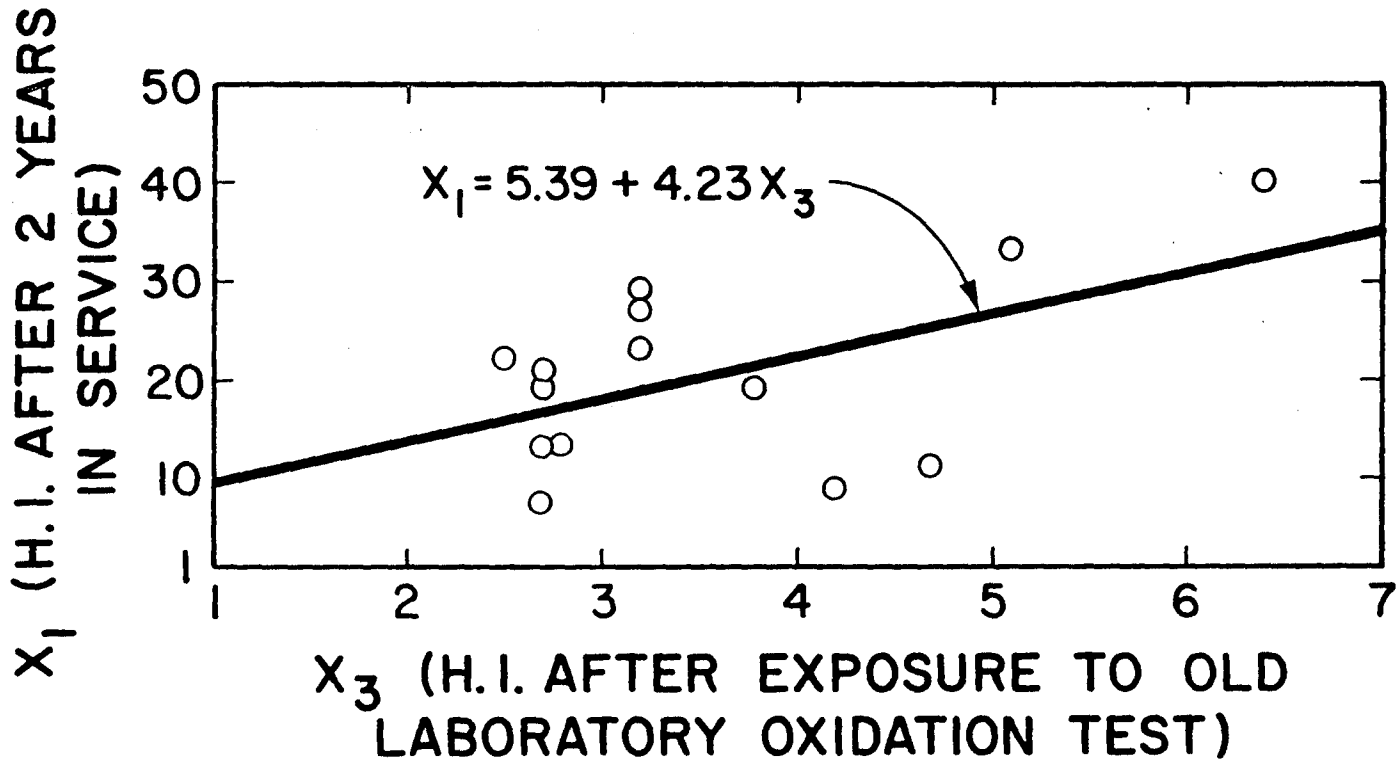


FIGURE 1 - Hardening Index, $X_3$, versus Hardening Index, $X_1$, on 14 asphalts.

were designed to protect the slabs during shipment. Included in Table 1, page 8, are the air permeability data on slabs after 2 weeks in service. A poor correlation exists between durability by visual inspection and porosity of the pavement surface. For example, the slab from Site 11, which failed after 2 years in service, showed low permeability after 2 weeks (36 ml/in/min). Site 14 was in excellent condition after 3 years service, but after 2 weeks service showed a permeability of 1380 ml/in/min.

5. Average Daily Traffic count also did not correlate well with durability of the surface course as estimated by visual inspection.

6. Only a fair correlation was obtained between Hardening Index, ($X_1$), for each asphalt extracted after two years in service and the Hardening Index, ($X_3$), obtained on each original asphalt by the dark oven laboratory test described on page 9. The data shown in the final two columns of Table I, page 8, are plotted in Figure 1, facing. Linear regression analysis was used to obtain the curve representing the data plotted in that figure. The correlation coefficient was r = 0.52.

7. But, an interesting relationship was obtained between Hardening Index, ($X_1$), for the asphalt recovered after two years in the pavement surface and the subjective evaluation of each pavement by THD personnel presented in column 7 (Condition of Surface after 2 years service) of Table I, page 8.

The following data are copied from Table I for ready reference.

| Site No. | Hardening Index ($X_1$) | Subjective Rating of Pavement Surface |
|---|---|---|
| 6 | 40.0 | Fair |
| 8 | 33.0 | Poor |
| 12 | 29.0 | Fair |
| 11 | 27.0 | Very Poor |
| 7 | 23.0 | Some Cracks |
| Mean | 32.0 HI | |

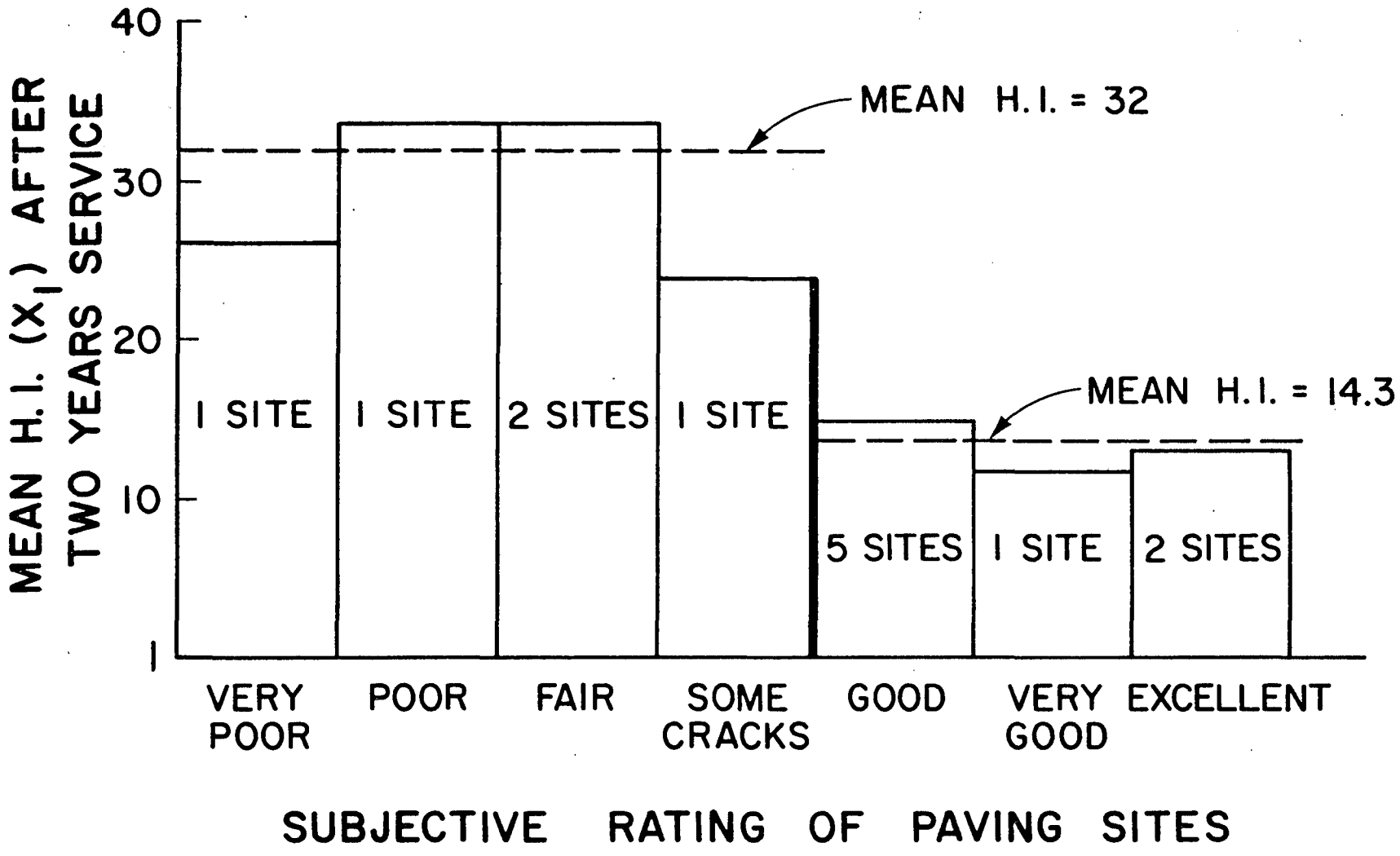


FIGURE 2 - Subjective Rating of Pavement Sites versus Mean Hardening Index, $X_1$, after two years service on 13 asphalts.

| Site No. | Hardening Index ($X_1$) | Subjective Rating of Pavement Surface |
|---|---|---|
| 13 | 22.0 | Good |
| 10 | 20.5 | Good |
| 17 | 18.8 | Excellent |
| 4 | 12.8 | Good |
| 14 | 12.7 | Good |
| 9 | 11.3 | Very Good |
| 1 | 9.3 | Good |
| 3 | 7.3 | Excellent |
| Mean | 14.3 | |

Figure 2, facing, shows graphically the relationship between the values presented above. Further confirmation of this correlation is shown in Figure 5, page 38, under Section IV of this report.

8. Regression analyses were made to evaluate the accuracy of the Hardening Indices obtained on each of 10 different asphalts recovered after 4 months, and 1, 2 and 3 years service in the pavements.

The model used in obtaining the linear regression was

$$\log_e \log_e X = \log_e A_o + A_1 \log_e T$$

which can be rearranged to the form $X = e^{A_o T^{A_1}}$. Table II, following, contains site and asphalt code numbers, Hardening Index (X) at 120, 365, 730 and 1095 days (T), correlation coefficient (R) and constants ($A_o$) and ($A_1$) used in the model shown above. The correlation coefficients, R, for 8 of the 10 asphalts are excellent ranging from 0.94 to 0.99+. However, the analyses for Site 1 gave an R value of 0.71 which indicates the presence of errors in the basic data on the asphalts recovered from this site. Site 4 showed an R value of 0.86. Plots of the determined data and points taken from the equation are shown in Figures A-1 through A-10 of the Appendix.

Table II

Correlation Between Hardening Index (X) and Days of Service in Pavement (T)

| Site | Asphalt No. | Hardening Index (X) Age - Days (T) 120 | 365 | 730 | 1095 | Results of Linear Regression: Correlation Coefficient (R) | Constants in Model, $X = \exp.(A_o T^{A_1})$ $A_o$ | $A_1$ |
|---|---|---|---|---|---|---|---|---|
| 10 | 11 | 8.3 | 13.8 | 20.5 | 27.4 | 0.99+ | 0.8047 | 0.2014 |
| 4 | 11 | 9.7 | 10.7 | 12.8 | 22.0 | 0.86 | 1.2231 | 0.1213 |
| 9 | 3 | 7.4 | 10.2 | 11.3 | 14.4 | 0.99 | 1.1170 | 0.1220 |
| 14 | 6 | 5.0 | 10.6 | 12.7 | 20.0 | 0.98 | 0.4561 | 0.2681 |
| 1 | 3 | 8.9 | 9.1 | 9.3 | 13.5 | 0.71 | 1.5850 | 0.614 |
| 13 | 5 | 5.8 | 9.9 | 22.0 | 23.0 | 0.98 | 0.4551 | 0.2808 |
| 7 | 15 | 13.2 | 14.5 | 21.5 | 23.0 | 0.94 | 1.6082 | 0.0946 |
| 8 | 7 | 14.3 | 17.5 | 33.0 | 35.0 | 0.95 | 1.3137 | 0.1425 |
| 6 | 7 | 21.5 | 25.0 | 40.0 | 41.5 | 0.95 | 1.9110 | 0.0956 |
| 12 | 2 | 5.7 | 15.3 | 29.0 | 32.5 | 0.98 | 0.3795 | 0.3253 |

## E. Discussion of Results

It is evident from the discussion given in the preceding pages that the field study, although informative, did not reveal the prime cause or causes for the large differences in durability encountered in the pavement surfaces investigated.

However, it had been recognized for several decades that chemically active solar radiation had definite but variable adverse effects on organic materials such as paint, textile dyes, etc. including asphalt. In addition, preliminary investigation had been reported (5) from TTI laboratories concerning the effects of time, heat, air (oxygen) and sunlight on a few different asphalts. Stimulated by these exploratory studies, controlled amounts of chemically active solar radiation, heat, air and time have been applied to 65 different road building asphalts. From the data obtained a test procedure was developed which will be described in Section III following.

# III. HARDENING OF ASPHALTS CAUSED BY EXPOSURE TO TIME, HEAT, AIR AND CHEMICALLY ACTIVE (ACTINIC) SOLAR RADIATION

## A. History

The deteriorating effects of chemically active solar radiation on asphalts have been recognized for many years. Toch (6) in 1908 found that blue light from the solar spectrum decomposed various kinds of bitumen. Exposure to the green wavelengths had moderate to slight action and the long red wavelengths had no noticeable deteriorating effect. Six years later Rosinger (7) studied the effect of sunlight on thin films of asphalt which had been deposited by evaporation from benzene, chloroform and other solvents. He found that after exposure to light the asphalt became partially insoluble in the solvents used in preparation of the thin films.

Streiter's work (8, 9) in 1933 and 1936 on the development of accelerated testing of roofing asphalts must not be ignored. He subjected panels coated with the hard asphalts to a repetitive cycle which included alternate exposure to actinic light from a carbon arc, wetting and chilling. His data showed that the products from accelerated weathering are similar to those resulting from outdoor exposure. Weetman (10) and Zapata (11) made extensive additions to the subject of accelerated weathering. A prodigious amount of work culminated in the development of the Weatherometer, which is described by the American Society for Testing and Materials (12).

In 1958, Dubrisay (13) suggested that the hardening of asphalts exposed to the atmosphere is essentially an oxypolymerization stimulated by heat and solar radiation extending from the short ultraviolet wavelengths through the yellow. About the same time, Sparlin (14) showed

that ultraviolet radiation is capable of producing measurable increases in the viscosity of asphalt films sealed from the atmosphere (air).

In 1958, Dickinson, Nicholas and Traube (15) determined that light in the wavelength range of 3000 to 5000 Angstroms accelerated the reaction of oxygen with asphalts. Visible light includes wavelengths from approximately 3800 to 7700 Angstroms; thus, the experiments conducted by Dickinson, et. al. included the longer wavelengths of ultraviolet radiation.

Blokker and van Hoorn (16) 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. This concept of the limited effectiveness of radiant energy has not been verified. In fact, Simpson, Griffin and Miles on pages 60 and 61 of reference (4) found that cores of pavement surfaces after 30 to 35 months in service showed progressively less hardening from the top down. This was determined by cutting the cores into 1/4 inch thick slices by a diamond saw, and measuring the viscosities of the asphalts recovered from the thin discs. Also, it is known from other situations that short wavelength radiant energy applied to a heterogeneous material may be transmitted to a considerable distance (more than 4 microns) during exposure to the radiation.

Photo-oxidation and photochemical reactions have been investigated by Traxler (5) using asphalts supplied by the Texas Highway Department. The procedures used were simple and the results obtained were informative enough to inspire the more extensive experiments discussed below.

B. Development of a New Test for Asphalt Durability

Experience gained in recent years, and reviewed above, points to the need for a reasonably rapid, convenient and informative laboratory test that can be applied to road building asphalts. The test should incorporate the effects of time, air, moderate ambient temperature, and actinic radiation, such as the ultraviolet and at least some of the short visible solar radiation. Results should be expressed in numerical values that can be used to classify the asphalt cements in reference to their serviceability.

In the development of a satisfactory test it was necessary to consider the asphalt film thickness to be used, concentration of the actinic radiation (power per $cm^2$), a standard time of exposure and a reasonably constant temperature of the asphalt film. The establishment of the most discriminatory and convenient combination of the four variables turned out to be involved and time consuming. Brief discussions are presented below.

1. Film Thickness

Thickness of the asphalt film was varied from 10 to 2700 microns and it was found that thin films were essential for a reasonably rapid test. Ten microns were selected as the most useful film thickness to be used in the exploratory work discussed in this report.

2. Source and Intensity of Radiant Energy

Five Sylvania Black Light 15-watt Lamps (F15T8-B1) each 18 inches long were mounted as a block to irradiate an area of 18" x 18". 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. Wavelengths emitted by these lamps ranged from 3200 to 4200 Angstroms with a maximum intensity at 3600 Angstroms. The center of the cabinet floor was marked off with a square 10 inches x 10 inches. Samples were always placed in this area in order for them to receive uniform and maximum radiation from the bank of lamps.

A Black-Ray Ultraviolet Intensity Meter with a 3660 Angstrom Sensor was used to determine the intensity of radiation over the area covered by the samples. The meter reports radiation intensity in microwatts per square centimeter ($mw/cm^2$).

The films were exposed at various distances from the source of radiation to give 500, 750 and 1000 microwatts (5,000, 7,500 and 10,000 ergs per second) per square centimeter of exposed sample. One thousand $mw/cm^2$ was found to be the most satisfactory concentration of radiation and was used in obtaining the data presented in the following pages. Asphalt films were located three inches from the lamps to obtain this quantity of radiant energy.

3. Exposure Time

Exposure time varied from 3 to 18 hours. Continuous exposure during a normal work day (8 hours) was not sufficiently severe for many of the asphalts investigated. Thus, 18 hours was established as an adequate time of exposure for most of the asphalts studied and a convenient time for a one-shift laboratory. A test started at 3 p.m. was terminated the next day at 9 a.m.

Table III

Hardening Indices of Asphalts After Two Years Service in Pavements Compared with Those Determined by the New Laboratory Test

| Pavement Site No. | Asphalt Producer Code No. | Hardening Index After: 2 Years In Service ($X_1$) | Hardening Index After: Subjection to Ultraviolet Radiation ($X_2$) |
|---|---|---|---|
| 3 | 8 | 7.5 | 5.5 |
| 10 | 11 | 20.5 | 7.0 |
| 4 | 11 | 12.8 | 8.5 |
| 17 | 3 | 18.8 | 13.5 |
| 9 | 3 | 11.3 | 16.5 |
| 14 | 6 | 12.7 | 17.0 |
| 1 | 3 | 9.3 | 17.5 |
| 2 | 18 | 19.8 | 30.0 |
| 13 | 5 | 22.0 | 33.0 |
| 7 | 15 | 23.0 | 42.0 |
| 8 | 7 | 33.0 | 66.0 |
| 11 | 6 | 27.0 | 75.0 |
| 6 | 7 | 40.0 | 85.0 |
| 12 | 2 | 29.0 | 89.0 |

4. Temperature of Sample

With the bank of lights operating in the cabinet, which was located in an air conditioned room held at 75 ± 2°F, the temperature of the glass plates coated with the film of asphalt was maintained at 95 ± 5°F.

5. Details of the New Test

Ten-micron thick films of asphalt are applied to 4 cm x 4 cm glass plates by the technique given in ASTM Book of Standards (17) and the asphalt film is exposed to 1000 mw/cm$^2$ of 3660 Angstrom actinic radiation at 95°F for 18 hours. The glass plates are taken from the cabinet and allowed to cool. A razor blade is used to remove the hardened asphalt from the 4 cm x 4 cm plates prior to placing on the 3 cm x 2 cm glass plates used in the thin film, sliding plate viscometer. Viscosities of the original and hardened asphalt are determined at 77°F and calculated at 5 x $10^{-2}$ sec$^{-1}$ rate of shear. The Hardening Index ($X_2$) of an asphalt is its viscosity at 77°F after exposure to heat, air and ultraviolet radiation divided by its original viscosity at the same temperature.

C. Data Obtained by the Actinic Light Test on Asphalts Used in 1963 Field Tests

Table III, facing, gives Hardening Index data on the asphalts used in the 1963 Field Tests. Figure 3, following, is a plot of Hardening Indices ($X_2$) after subjection of the original asphalts to the new hardening test described above versus Hardening Indices, ($X_1$), of the same asphalts after 2 years service in pavement surfaces at various locations in Texas.

Table IV, page 24, gives the linear equations representing the data shown in Figure 1, page 11, and Figure 3, page 23.

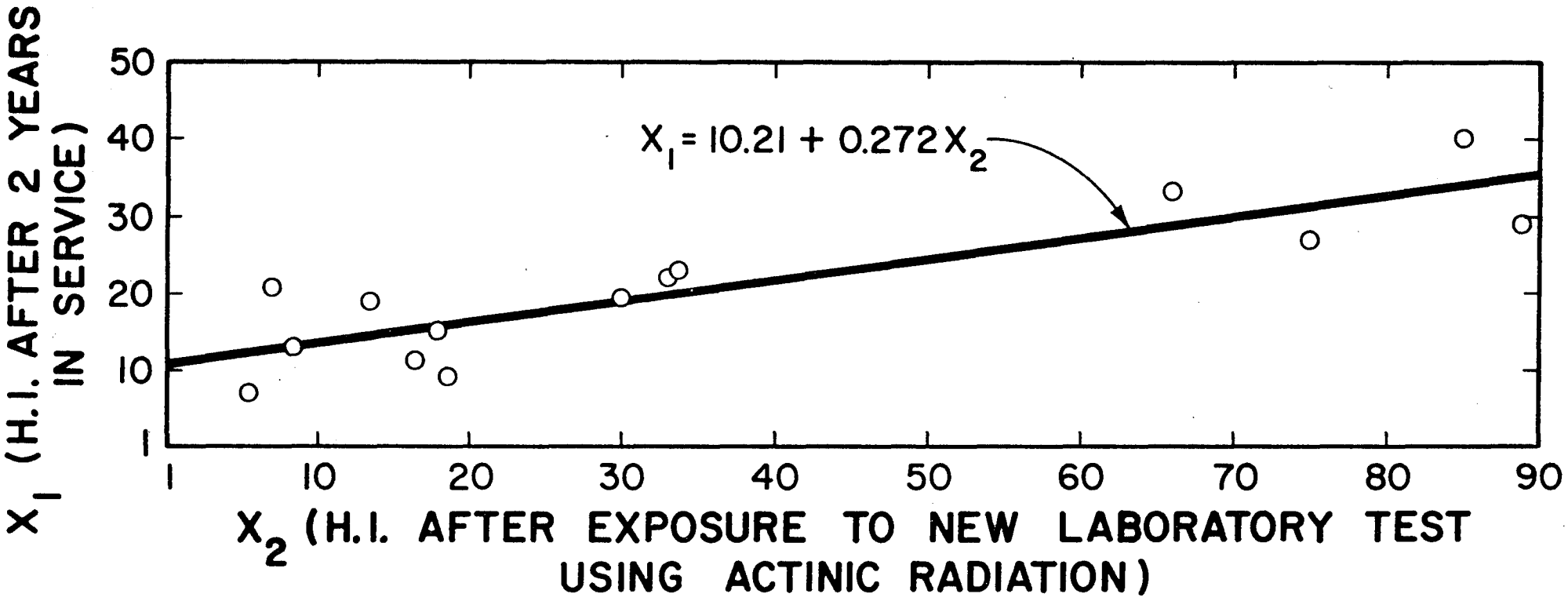


FIGURE 3 - Hardening Index, $X_2$, versus Hardening Index, $X_1$, on 14 asphalts.

Table IV

Comparison of Old and New Laboratory Tests in Respect to Hardening of the Asphalts after Two Years in Service

| Laboratory Procedure | Regression Equation | Correlation Coefficient | Standard Deviation |
|---|---|---|---|
| Old (Dark) | $X_1 = 5.39 + 4.23X_3$ | 0.52 | 8.4 (Equation 1) |
| New (Light) | $X_1 = 10.21 + 0.272X_2$ | 0.87 | 4.9 (Equation 2) |

It is evident from these two equations that the new test, which includes the effect of short wavelength solar radiation together with air and heat, exhibits a better statistical correlation with the hardening which occurs in service than does the older test which is conducted in the dark.

D. Results Obtained by Eliminating Active Solar Radiation from the New Accelerated Hardening Test

Tests were made on a few representative asphalts by subjecting 10-micron films to air in a dark oven at 95°F for 18 hours. This would, in essence, expose the asphalts to the same environment as in the new test, but with the elimination of the actinic light. Data on five asphalts are shown in Table V, following. The results emphasize the importance of chemically active solar radiation on the hardening of asphalts in the surface course of a pavement.

Table V

Hardening Indices Obtained With and Without Application of Actinic Light

| halt Code No., Grade and Year Produced | H. I. obtained by exposing 10 micron films of asphalt to air at 95°F for 18 hours. | |
|---|---|---|
| | In a dark oven | In the presence of 1000 mw/cm$^2$ of 3600 Angstrom Radiant Energy |
| 2, Site 12 85-100 pen, 1963 | 1.6 | 89.0 |
| 6, Site 11 85-100 pen, 1963 | 1.1 | 75.0 |
| 6, AC-10, 1967 | 1.6 | 51.0 |
| 3, AC-10, 1967 | 1.8 | 16.5 |
| 11, AC-20, 1967 | 1.6 | 10.0 |

E. Resume of Section III

This portion of the study indicates that for asphalts to be used in the construction of pavement surfaces the new laboratory test, which incorporates the effect of solar radiation, correlates better ($R = 0.87$) with hardening in service than does the old laboratory test ( $r = 0.52$). First class pavement surfaces possessing long service life, will require high quality asphalts resistant to the hardening effect of solar radiation. Structures not subjected to radiation will not necessarily require the same high quality asphalt as is needed for surfacing a pavement.

It is logical that bituminous pavement surfaces under sunny skies, and thus exposed to intensive solar radiation for long periods of time, will undergo more hardening of the asphalt than will occur in localities where the concentration of active radiation impinging on the pavement surface is reduced by passage through clouds and smog.

It should be recognized that apparatus known as Solar Simulators are now available in which any material can be exposed to solar radiation over a range of intensities varying from one to 200 suns. Such simulators would be helpful for testing the effect of the entire solar spectrum on the hardening of asphalts.

Finally, an important question now arises. What causes one asphalt in a pavement surface to harden more severely during service, or after exposure to the new laboratory test conditions, than does an asphalt made from a different kind of petroleum? A basic reason for differences in the durability or quality of such road building asphalts is presented in Section IV following.

# IV. EFFECT OF VANADIUM CONTENTS OF ASPHALTS ON THEIR SUSCEPTIBILITY TO HARDENING BY CHEMICALLY ACTIVE (ACTINIC) SOLAR RADIATION

## A. Prior Knowledge

An extensive literature exists concerning the occurrence of trace elements in petroleums and asphaltic materials. Possibly the most interesting investigations are those concerning the role played by vanadium. This element occurs in porphyrins and other moderately high molecular weight materials which may be related to the genesis of petroleum.

At this point a short review about the discovery of trace metals in asphalts is pertinent to the discussion that follows. Speilman, in his book, "Solid Bitumens," published in 1909, mentioned that petroleum frequently contained vanadium and nickel and stated these metals usually are not present in coal, or, if so, in limited amounts. Richardson (18) in 1910 identified vanadium in the bitumen known as grahamite. Hackford (19) found aluminum, calcium, gold, iron, lead, magnesium, nickel, silicon, tin, titanium and vanadium in highly asphaltic Mexican petroleum.

Ball, Haines and Helm (20) supplied data on metal contents of Wilmington (California) petroleum which is an asphaltic oil. Iron, nickel and vanadium ran about 36 parts per million in this oil, whereas the concentration of cobalt, copper, magnesium, sodium, tin, titanium and zinc amounted to about 0.2 ppm.

Erdman and Harju (21) supplied data for the retention of vanadium, nickel and copper by asphaltenes in benzene solution. They also pointed out that strong centrifuging or similar drastic physical treatment of petroleum, aimed at removal of suspended mineral matter and water, causes

a severe drop in most heavy metal contents of the supernatant oil. Vanadium and nickel were notable exceptions. The authors stated "These two metals therefore must be of particular importance in the geochemistry of petroleum". This statement probably is more applicable to asphaltic than to non-asphaltic crude oils.

Recently, Colombo (22) used neutron activation analysis to determine the amounts of the following metals in petroleum:

| | |
|---|---|
| Antimony | Iron |
| Chromium | Manganese |
| Cobalt | Molybdenum |
| Copper | Nickel |
| Gold | Vanadium |
| | Zinc |

Correlations based on nickel - vanadium ratios have been used in attempts to establish the origin of petroleum (23, 24).

It may be added that, vanadium has been pinpointed as a source of trouble in heating oils because of deterioration of furnace linings and the corrosion of boiler tubes. The presence of this metal and nickel in stocks subjected to catalytic cracking often result in poisoning of the catalyst.

## B. Testing for Metals in Asphalts

Sixty-five different asphalts were analyzed for vanadium by Thermal Neutron Activation Analysis and a number of the samples were tested for other trace metals. At first, it was thought the combined amounts of vanadium and nickel correlated well with the Hardening Indices obtained after two years service in the surface course of a pavement and by the new laboratory test utilizing actinic light. But, as the analytical procedure for nickel was improved and more varieties

of asphalt were tested it was concluded that vanadium content was the important factor in stimulating the hardening of asphalt by actinic light in the presence of heat and air.

Thus, Section IV is concerned only with the effects of vanadium. Of course, the importance of other metals may appear as more information is obtained.

## C. Determination of Various Elements by Neutron Activation Analysis

### 1. Basic Principles of the Method

Neutron activation analysis is a highly sensitive trace analytical method which is useful in the accurate measurement of a large number of chemical elements. This method is based upon the activation or irradiation of a sample with neutrons from a nuclear reactor to induce radioactivity. The irradiated sample is then observed with a special instrument to determine the energy and amount of radioactivity which is being emitted by the sample as it undergoes radioactive decay. The energy of the emitted radiation identifies the chemical element, and the amount of radiation is proportional to the concentration of the element in the sample. Over 70 elements can be determined with neutron activation analysis, some with sensitivities down to less than a billionth of a gram. Certain elements, such as vanadium, aluminum, oxygen and chlorine, can be measured very rapidly, while others, such as cobalt, antimony, chromium and iron, require several weeks between irradiation and measurement of the radioactivity to allow for decay of undesired short lived radioactivity from other elements in the sample.

Neutron activation analysis is ideally suited for the measurement of vanadium in petroleum products. The method is fast and non-destructive so that the sample may be intact for additional measurements if desired. When naturally occuring vanadium is exposed to thermal neutrons from a nuclear reactor, the radioisotope vanadium-52 is produced. Vanadium-52 decays with a short half-life (3.77 minutes) and emits a gamma ray of 1.43 MeV energy, which can be easily measured with a gamma ray spectrometer. The intensity of the vanadium-52 activity is proportional to the amount of vanadium present in the sample. More detailed information can be found in the work of Wainerdi and DuBeau (25) and Devoe (26).

2. Facilities and Equipment

The major facilities and equipment requirements for carrying out neutron activation analysis for vanadium are:

a. nuclear reactor for production of neutrons

b. fast sample transfer system to transport samples to and from the irradiation position in the reactor

c. gamma ray spectrometer for measuring the radioactivity emitted by the activated sample, and

d. computer for reducing raw data to parts-per-million of vanadium.

The facilities of the Activation Analysis Research Laboratory and the Nuclear Science Center at Texas A&M University were used for the analyses of asphalt samples in this project. Data reduction was carried out on the Data Processing Center's IBM 360/65.

3. Description of Procedures

a. Vanadium - Weighed asphalt samples of approximately 1 gram each were placed in small polyethylene vials for analysis. Standards containing known quantities of vanadium were prepared. Each standard and

sample was then irradiated for 1 minute in a thermal neutron flux of approximately 5 x $10^{11}$ n/$cm^2$/sec followed by a 1 minute delay and then a 1 minute count of the radioactivity. A pneumatic sample transfer system was used to send each sample and standard to the reactor core and return it to the counting laboratory after the irradiation. The gamma radiation emitted by the activated samples and standards was detected and recorded by a 3" x 3" sodium iodide scintillation detector coupled to a 400-channel pulse height analyzer with a punched paper tape data readout. After each 1 minute count of gamma radiation, the data were displayed on a cathode ray tube scope in the form of a gamma ray spectrum for visual inspection and then read out on punched paper tape for computer evaluation. Approximately 5 minutes were required to process one asphalt sample through the activation and counting phase of the analysis. Computer processing of the raw data was then carried out within one to two days; however, if rapid turn-around time is required, it is feasible to perform the calculations in the laboratory immediately after completion of the irradiation and counting, with only a slight degradation of computation precision.

Vanadium contents of 17 different asphalts were determined by a commercial analytical laboratory using emission spectroscopy for comparison with results obtained by neutron activation analysis at Texas A&M University. Results from emission spectroscopy ranged from 5 to 300 ppm in comparison with 10.5 to 208 ppm from NAA. There was sufficient disagreement in the two sets of data to indicate a need for further evaluation of the analytical methods employed, therefore, an in-depth study of neutron activation for vanadium determination in asphalts was carried out by the Activation Analysis Research Laboratory at Texas A&M University in direct support of this project.

A careful evaluation of gamma ray spectra showed that the vanadium activity was unambiguous and interference free. Since the neutron activation method is non-destructive, validity of the analytical results was further tested by repeating vanadium measurements on duplicate samples and a range of comparison standards containing known amounts of vanadium. Results of these tests confirmed the reliability of neutron activation for the determination of vanadium.

b. Nickel - Stable nickel, when irradiated with thermal neutrons in the nuclear reactor, activates to form radioactive nickel-65 which has a half-life of 2.56 hours. The procedure for determining nickel concentration in asphalt samples is slightly more complicated than for either vanadium or the other metals determined in this study because of the necessity to chemically remove the nickel from the sample after irradiation and prior to counting (27). The purpose of this chemical separation is to eliminate the sodium activity which would overshadow the nickel activity during the sample counting process.

Samples to be analyzed for nickel are irradiated for a period of 2 hours. After a delay of 1 hour to allow for cooling of the shorter lived radioactivities, the samples are returned to the Activation Analysis Research Laboratory where chemical separation of the nickel is carried out. The radioactive nickel from each sample is then counted on a gamma ray spectrometer for 20 minutes and the data punched onto paper tape for data processing. The computer then calculates the nickel concentrations. This procedure requires approximately 6 hours (in addition to irradiation time) to analyze a batch of 6 samples.

c. Other Elements - The determination of other trace elements including molybdenum, antimony, chromium, cobalt and zinc was carried out by first irradiating batches of up to 50 asphalt samples and standards simultaneously for 8 hours in the Nuclear Science Center reactor. After a delay of approximately 1 to 2 weeks, the gamma radiation from each sample and standard was measured with a high resolution gamma ray spectrometer for a period of 1 to 2 hours in order to determine the intensity of the radiation emanating from each of the elements of interest. The data from this instrument were then processed with a special computer program to calculate the concentrations of each element being sought.

4. Economic Considerations

The facilities and equipment required to carry out neutron activation analysis are expensive. Likewise, the analysis of small batches of samples for many different elements by neutron activation is time consuming and expensive. If, however, the analytical requirement can be narrowed to the measurement of only one element in large batches of similar samples, the analysis cost can be reduced substantially and can be carried out in

Table VI

Correlation of Vanadium with Hardening Indices
of Asphalts After Two Years Service in Pavements

| ement ite . (1) | Asphalr Producer Code No. | Hardening Index ($X_1$) (2) After Two Years Service | Parts Per Million of Vanadium ($X_4$) (3) |
|---|---|---|---|
| 3 | 8 | 7.5 | 18.5 |
| 10 | 11 | 20.5 | 10.5 |
| 4 | 11 | 12.8 | 10.5 |
| 17 | 3 | 18.8 | 16.0 |
| 9 | 3 | 11.3 | 23.5 |
| 14 | 6 | 12.7 | 25.0 |
| 1 | 3 | 9.3 | 24.0 |
| 2 | 18 | 19.8 | 23.0 |
| 13 | 5 | 22.0 | 11.0 |
| 7 | 15 | 23.0 | 37.0 |
| 8 | 7 | 33.0 | 87.0 |
| 11 | 6 | 27.0 | 60.5 |
| 6 | 7 | 40.0 | 97.0 |
| 12 | 2 | 29.0 | 208.0 |

To make possible identification of similarities or differences in properties of asphalts delivered by individual manufacturers to different paving sites.

Viscosity of the hardened asphalt at 77°F divided by that of the original asphalt at the same temperature.

Determined by thermal neutron activation analysis.

facilities which are designed to provide this type of analytical service. As a point of reference, a commercial activation analysis group currently advertises a rate of $20 per sample plus $100 per batch ($100 charge waived for batches greater than 20 samples) for measurements such as those described above for vanadium. The cost of performing these determinations at Texas A&M would depend upon two factors:

a. the number of samples per batch, and

b. the maximum allowable time between submission of sample and availability of analytical results.

D. Asphalts Tested and Data Obtained on Vanadium Content

1. Hardening of Asphalts after Two Years in Service versus Vanadium Content of the Asphalts

Hardening Indices of 14 different asphalts after two years service in pavements, and vanadium contents of the original asphalts in parts per million, are given in Table VI, facing. These data are also shown graphically in Figure 4, following, where $X_1$ (the Hardening Index of an asphalt after two years of service in a pavement) is plotted against $X_4$ (the vanadium content of the original asphalt in parts per million). The regression equation is shown as Equation 3, together with related data in Table IX, page 45.

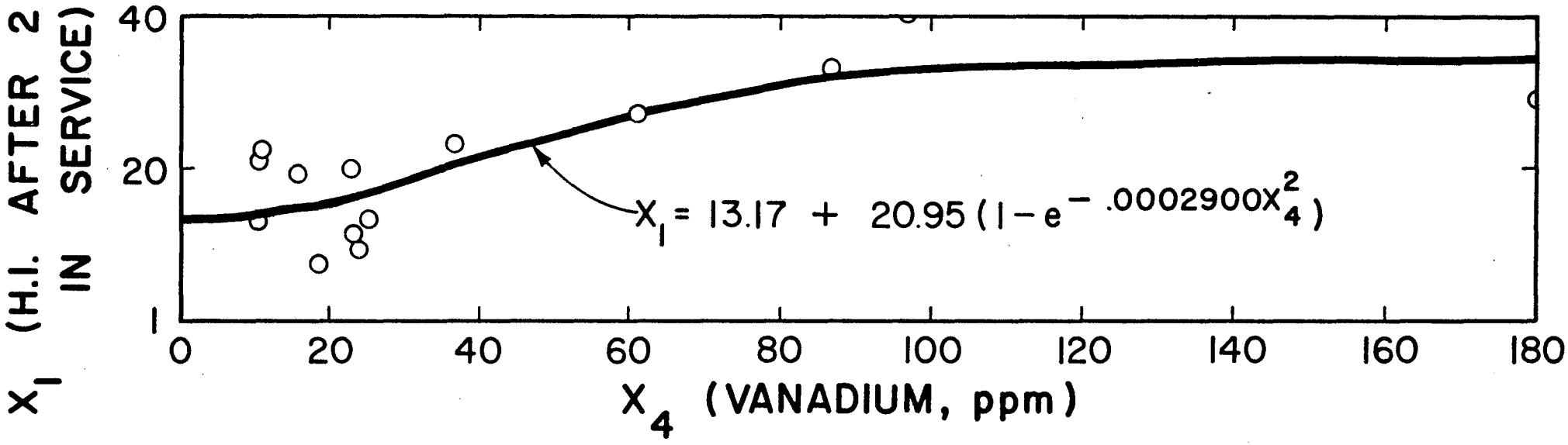


FIGURE 4 - Vanadium Content, $X_4$, versus Hardening Index, $X_1$, on 13 asphalts.

Table VII

Hardening Indices by the New Light Test ($X_2$) and Vanadium Content ($X_4$) of the 14 Original Asphalts Used in the Field Tests

| ent (1) | Asphalt Producer Code No. | Hardening Index After Subjecting To New Actinic Light Test, ($X_2$) | Parts per million of Vanadium, ($X_4$) |
|---|---|---|---|
| | 8 | 5.5 | 18.5 |
| | 11 | 7.0 | 10.5 |
| | 11 | 8.5 | 10.5 |
| | 3 | 13.5 | 16.0 |
| | 3 | 16.5 | 23.5 |
| | 6 | 17.0 | 25.0 |
| | 3 | 17.5 | 24.0 |
| | 18 | 16.0 | 23.0 |
| | 5 | 33.0 | 11.0 |
| | 15 | 42.0 | 37.0 |
| | 7 | 66.0 | 87.0 |
| | 6 | 75.0 | 60.5 |
| | 7 | 85.0 | 97.0 |
| | 2 | 89.0* | 208.0* |

analysis but not shown on graph.

2. Hardening Indices Obtained by Subjecting the Original Fourteen Asphalts Used in the 1963 Field Tests to the New Actinic Light Test versus Vanadium Contents of the Asphalts

Table VII, facing, presents vanadium contents and the Hardening Indices after subjecting the original fourteen asphalts used in the field tests to the new Actinic Light Test. These data are plotted in Figure 5, following. The regression equation is shown as Equation 4 together with related data in Table IX, page 45.

The solid circles in Figure 5 represent the five asphalts from the field tests that received very poor to fair ratings in the subjective evaluation of the sites obtained during the 1963 field studies. All five show Hardening Indices, ($X_2$), above 30 by the laboratory test using actinic light. The other asphalts used in the pavements rate good to excellent and have Hardening Indices, ($X_2$), ranging from 5.5 to 17.5, when subjected to the actinic light test.

The petroleum used in the manufacture of an asphalt is responsible for its hydrocarbon composition and its oxygen, nitrogen, sulfur and metal contents such as vanadium. The sensitivity of an asphalt to heat, air, and chemically active solar radiation are largely responsible for its hardening during service. Thus, a change of petroleum source can result in a small or large change in durability of an asphalt used in the construction of a pavement surface. At this point it must be emphasized that all vanadium compounds in an asphalt do not necessarily stimulate hardening by actinic solar radiation. Phrased another way, the amount of the element vanadium present in an asphalt is not necessarily in a condition to convert solar energy to chemical energy thereby causing hardening of the bitumen. This situation is being studied and conclusions drawn will be presented in a future report.

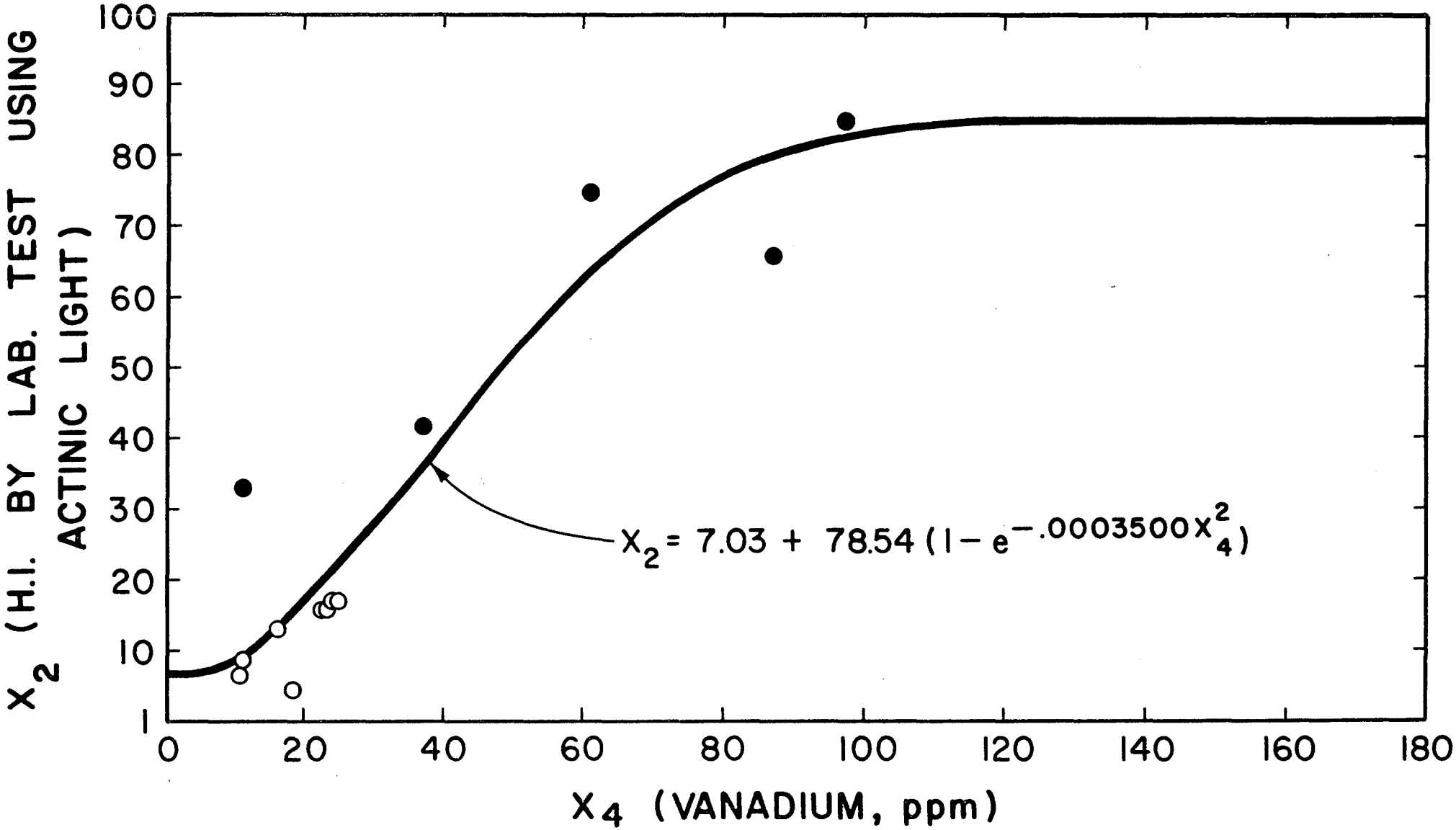


FIGURE 5 - Vanadium Content, $X_4$, versus Hardening Index, $X_2$, on 13 asphalts.

3. Hardening Indices of 65 Original Asphalts by the New Actinic Light Test and Their Vanadium Contents

Table VIII, pages 41, 42 and 43, includes data on the 65 asphalts considered in this report. Pavement sites are given for the 14 asphalts studied in the field and sources of all 65 asphalts are identified. Also, the grades (in terms of penetration or viscosity) are supplied together with the year the asphalt was delivered to TTI. Hardening Index, ($X_2$), and Vanadium content, $X_4$, are shown for each asphalt.

a. Among the other data, shown in Table VIII, three asphalts are marked by a single asterisk. These asphalts gave relatively low H. I. values (19, 58.5 and 75) associated with relatively high vanadium contents (112, 146.5 and 161 ppm). This situation indicates that a substantial percentage of the vanadium atoms present in each of the three asphalts did not take part in the hardening caused by radiant energy. The most logical explanation of this behavior is that many of the vanadium atoms in these three asphalts were rendered ineffective by the complex compounds within which the vanadium atoms were bound.

b. Three other asphalts are designated on Table VIII by double asterisks. These materials gave relatively high H. I. values (81, 85 and 110) associated with reasonably low vanadium contents (36.5, 37 and 32.9 ppm). Such data indicate that a high percentage of the vanadium in the asphalts reacted strongly to the actinic energy applied to the material. It can be postulated that a small amount of the vanadium atoms present exists in a chelated (inactive) form. Thus, the strong tendency of these three asphalts to hardening by actinic radiation could be retarded by ultra violet inhibitions or by chelating agents. Some preliminary experiments have shown this explanation to be reasonable.

c. The last three asphalts listed in Table VIII, indicated by three asterisks, were extremely hard after subjection to the test utilizing actinic light. Hardening Indices ($X_2$) for these asphalts are marked "Too Hard". The data for the remaining 62 asphalts shown in Table VIII were subjected to non-linear regression analysis. The results are shown in Figure 6, page 44 and the equation used is given as Equation 5 on page 45.

Table VIII

Correlation of Hardening Indices ($X_2$) by the New Light Test with Vanadium Content ($X_4$)

65 Samples Listed in Order of Increasing H. I. Values

| Pavement Field Site No. | Code No. of Supplier | Asphalt Grade | Year Produced | Hardening Index, $X_2$ | Vanadium parts per million, $X_4$ |
|---|---|---|---|---|---|
| 3 | 8 | 85-100 pen | 1963 | 5.5 | 18.5 |
| -- | 11 | AC-20 | 1969 | 6.5 | 9.5 |
| 10 | 11 | 85-100 pen | 1963 | 7.0 | 10.5 |
| -- | 8 | AC-20 | 1970 | 7.0 | 7.3 |
| -- | 8 | AC-10 | 1970 | 7.5 | 11.5 |
| 4 | 11 | 85-100 pen | 1963 | 8.5 | 10.5 |
| -- | 11 | AC-20 | 1967 | 10.0 | 13.0 |
| -- | 15 | AC-20 | 1970 | 10.5 | 30.5 |
| -- | 11 | AC-10 | 1967 | 12.0 | 14.5 |
| -- | Imperial Oil Pembina | 83 pen | 1970 | 12.5 | 5.4 |
| -- | 11 | AC-20 | 1970 | 13.0 | 10.8 |
| -- | R4397 Calif. Arkansas | 60-70 pen | 1970 | 13.0 | 11.0 |
| 17 | 3 | 85-100 pen | 1964 | 13.5 | 16.0 |
| -- | 3 | AC-20 | 1967 | 14.0 | 23.5 |
| 2 | 18 | 85-100 pen | 1964 | 16.0 | 23.0 |
| -- | 3 | AC-10 | 1967 | 16.5 | 24.5 |
| 9 | 3 | 85-100 pen | 1963 | 16.5 | 23.5 |
| 14 | 6 | 85-100 pen | 1963 | 17.0 | 25.0 |
| 1 | 3 | 85-100 pen | 1963 | 17.5 | 24.0 |
| -- | 11 | AC-10 | 1969 | 18.5 | 12.5 |
| -- | R4483 Calif. Arkansas | 85-100 pen | 1970 | 18.5 | 10.5 |
| -- | 10 | AC-20 | 1970 | 19.0 | 112.0* |
| -- | 3 | AC-10 | 1970 | 20.0 | 18.1 |
| -- | 21 | AC-20 | 1970 | 21.0 | 36.0 |
| -- | 3 | AC-20 | 1970 | 22.5 | 18.7 |

| Pavement Field Site No. | Code No. of Supplier | Asphalt Grade | Year Produced | Hardening Index, $X_2$ | Vanadium parts per million, $X_4$ |
|---|---|---|---|---|---|
| -- | 21 | AC-10 | 1970 | 23.0 | 37.7 |
| -- | 11 | AC-10 | 1970 | 32.0 | 11.0 |
| 13 | 5 | 85-100 pen | 1963 | 33.0 | 11.0 |
| -- | R4398 Calif. Canadian | 60-70 pen | 1970 | 35.5 | 56.0 |
| -- | 11 | OA-65 Louisiana | 1970 | 38.0 | 17.0 |
| -- | R4255 Calif. Valley Crude | 60-70 pen | 1970 | 39.0 | 28.5 |
| -- | 6 | AC-10 | 1970 | 40.0 | 20.9 |
| 7 | 15 | 85-100 pen | 1963 | 42.0 | 37.0 |
| -- | 11 | OA-90 Louisiana | 1970 | 46.0 | 31.0 |
| -- | 12 | AC-10 | 1970 | 47.0 | 21.8 |
| -- | R4319 Calif. L. A. Basin | 85-100 pen | 1970 | 48.0 | 74.0 |
| -- | 6 | AC-20 | 1969 | 48.5 | 45.0 |
| -- | 6 | AC-10 | 1967 | 51.0 | 51.0 |
| -- | 1 | Sol. Ref. AC-20 | 1969 | 52.0 | 74.0 |
| -- | 6 | AC-20 (1935) | 1970 | 52.5 | 40.9 |
| -- | 6 | AC-20 (2096) | 1970 | 54.5 | 41.9 |
| -- | 19 | AC-10 | 1970 | 58.5 | 146.5* |
| -- | Imperial Oil "C" - Saskatchewan | 94.5 pen | 1970 | 64.5 | 38.2 |
| 8 | 7 | 85-100 pen | 1963 | 66.0 | 87.0 |
| -- | 1 | AC-10 | 1970 | 70.0 | 86.0 |
| -- | R4310 Calif. Calif. Valley | 85-100 pen | 1970 | 70.0 | 34.0 |
| -- | 21 | AC-10 | 1970 | 71.0 | 32.0 |
| 11 | 6 | 85-100 pen | 1963 | 75.0 | 60.5 |
| -- | 17 | AC-10 | 1970 | 75.5 | 161.0* |
| -- | 1 | AC-20 | 1970 | 80.0 | 89.6 |
| -- | 6 | AC-20 | 1967 | 81.0 | 36.5** |
| 6 | 7 | 85-100 pen | 1963 | 85.0 | 97.0 |

| Pavement Field Site No. | Code No. of Supplier | Asphalt Grade | Year Produced | Hardening Index, $X_2$ | Vanadium parts per million, $X_4$ |
|---|---|---|---|---|---|
| -- | 6 | AC-10 | 1969 | 85.0 | 37.0** |
| 12 | 2 | 85-100 pen | 1963 | 89.0 | 208.0 |
| -- | Kuwait | 87 pen | 1970 | 106.0 | 84.7 |
| -- | 6 | AC-10 | 1970 | 110.0 | 32.9** |
| -- | 9 | AC-20 | 1970 | 111.0 | 148.0 |
| -- | 19 | AC-20 | 1970 | 116.0 | 151.0 |
| -- | Imperial Oil "A" - Alberta | 94.5 pen | 1970 | 126.0 | 134.0 |
| -- | 1 | AC-10 | 1969 | 155.0 | 19.0 |
| -- | Mexican No. 2 | 95 pen | 1970 | 191.0 | 201.0 |
| -- | Mexican No. 1 | 85 pen | 1970 | 277.0 | 300.0 |
| -- | R4099 Calif. Special Crude | 74 pen | 1970 | Too Hard | 253.0*** |
| -- | R4277 Calif. Boscan, Vene. | 60-70 pen | 1970 | Too Hard | 1365.0*** |
| -- | R4316 Calif. Santa Maria | 85-100 pen | 1970 | Too Hard | 230.0*** |

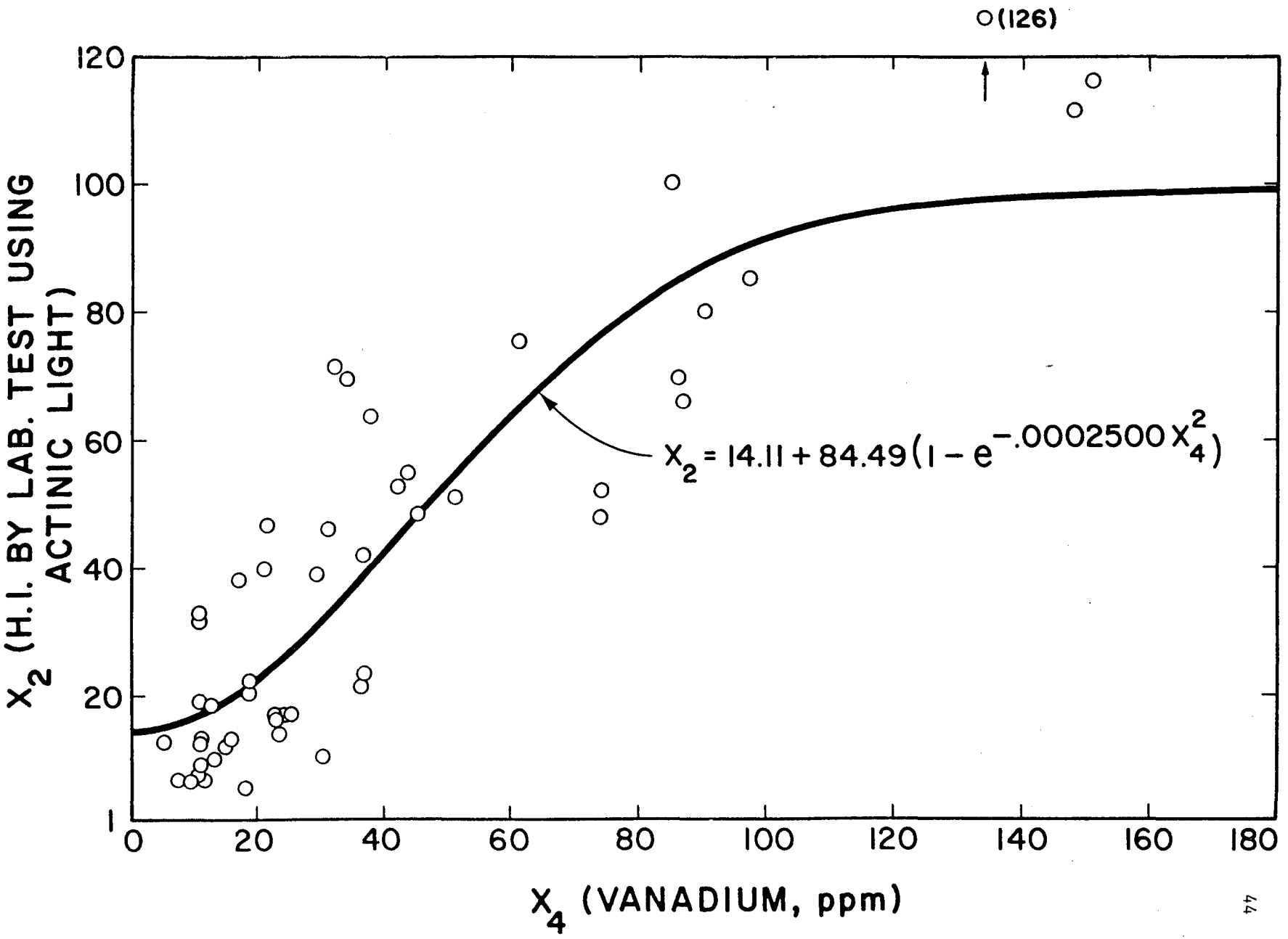


FIGURE 6 - Vanadium Content, $X_4$, versus Hardening Index, $X_2$, on 52 asphalts.

Table IX

Equations for Hardening as a

Function of Vanadium Content

1. Hardening Index after two years of service:

$X_1 = 13.17 + 20.95 \ (1 - e^{-.0002900X_4^2})$ Equation 3

Inflection point: $X_4 = 58.7$, $X_1 = 26.4$

Correlation coefficient = .82

Standard deviation = 5.6

Range of $X_1$ = 7.5 to 40.0

Number of asphalts tested = 14

2. Hardening Index obtained on the original asphalts used in 1963 Field Tests after exposure to new laboratory test:

$X_2 = 7.03 + 78.54 \ (1 - e^{-.0003500X_4^2})$ Equation 4

Inflection point: $X_4 = 53.5$, $X_2 = 56.7$

Correlation coefficient = .95

Standard deviation = 9.5

Range of $X_2$ = 5.5 to 89

Number of asphalts tested = 14

3. Hardening Index obtained on asphalts after exposure to New Laboratory Test.

$X_2 = 14.11 + 84.49 \ (1 - e^{-.0002500X_4^2})$ Equation 5

Inflection point: $X_4 = 44.7$, $X_2 = 47.4$

Correlation coefficient = .88

Standard deviation = 15.3

Range of $X_2$ = 5.5 to 126.0

Number of asphalts tested = 52

E. NOMENCLATURE

$X$ = Hardening Index at any time T (days)

$X_1$ = Hardening Index at the end of two years service in pavement

$X_2$ = Hardening Index after subjection to new laboratory test using actinic light

$X_3$ = Hardening Index after subjection to old laboratory test not using actinic light

$X_4$ = Parts per million of vanadium in the asphalt

F. Mathematical Model and Fitting Technique

The following mathematical model relating $X_1$ to $X_4$ was constructed after studying plots of the experimental data

$$X_1 = A_1 + A_2 \ (1 - e^{-A_3 X_4^2}) \qquad \text{Equation 6}$$

The model plots as an S-shaped curve and has the characteristics given below.

(a) When $X_4 = 0$: $X_1 = A_1$, and the slope of the curve, $dX_1/dX_4 = 0$. Thus, the model infers that the Hardening Index of any field sample, taken at the end of two years service in a pavement containing no vanadium would be the constant, $A_1$.

(b) When $X_4 = \infty$: $X_1 = A_1 + A_2$ and the slope of the curve, $dX_1/dX_4 = 0$. Thus, as the vanadium content, $X_4$, is increased without limit, the model infers that the Hardening Index of the asphalt in the Field Samples approaches the limit, $A_1 + A_2$.

(c) The point of inflection in the S-shaped curve occurs at the point $X_4 = 1/\sqrt{A_3}$, and $X_1 = A_1 + A_2 \ (1 - 1/e)$. Beyond the inflection point, the model infers that the effect of vanadium on Hardening Index steadily decreases.

The constants $A_1$, $A_2$ and $A_3$ in the model were determined from the $X_1$, $X_2$ data by means of a special non-linear, least squares regression technique developed by Moore and Milberger (28). The same model and technique, except that $X_2$ was substituted for $X_1$, were used in analyzing the $X_2$, $X_4$ data.

# V. CONCLUSION

The experimental work presented in this report leads to the following conclusions.

1. A satisfactory correlation does not exist between the hardening of an asphalt recovered from a pavement surface course and the results from a laboratory thin film test involving only the action of time, heat and air on the original.

2. It is also concluded that the rather unsatisfactory correlation mentioned above is caused by the omission from the old thin film laboratory test conducted in the dark of some prime factor responsible for the hardening of asphalts used in the surface courses of bituminous pavements. This was confirmed by the development of a new laboratory test which used short wavelength, chemically active (actinic), solar radiation in addition to time, heat, and air. The inclusion of this new factor in the laboratory test resulted in good correlation with hardening in the pavement during two years of service.

3. The hardening of 65 different asphalts measured by this new test also revealed that the hardening of asphalts from different sources varied greatly. Analysis for trace metal contents of the asphalts pointed to the presence of trace metals as being connected with the hardening caused by actinic energy. Testing each of the 65 asphalts for vanadium content led to the conclusion that much of the hardening by solar energy is stimulated by the chemically active vanadium content of each asphalt.

4. Finally it is concluded that the use of measured amounts of actinic solar radiant energy together with time, heat, and air is a promising diagnostic control test for the screening of asphalts used in the surface courses of bituminous pavements.

# VI. RECOMMENDATION

Based on the results described in this report, it is recommended that serious consideration be given to establishing a specific research study that would

1) involve the study of problems left unresolved in connection with the proposed laboratory test,

2) initiate a study of additives which, in small amounts, can retard the hardening of asphalt in the surface course of a pavement. Such additives are known as (a) ultraviolet light inhibitors or (b) metal deactivators,

3) pursue the causes of hardening of asphalt cement under highway service conditions with objectives of determining warrants and appropriate control tests for use in writing a proper specification.

## VII. LITERATURE REFERENCES


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# VIII APPENDIX

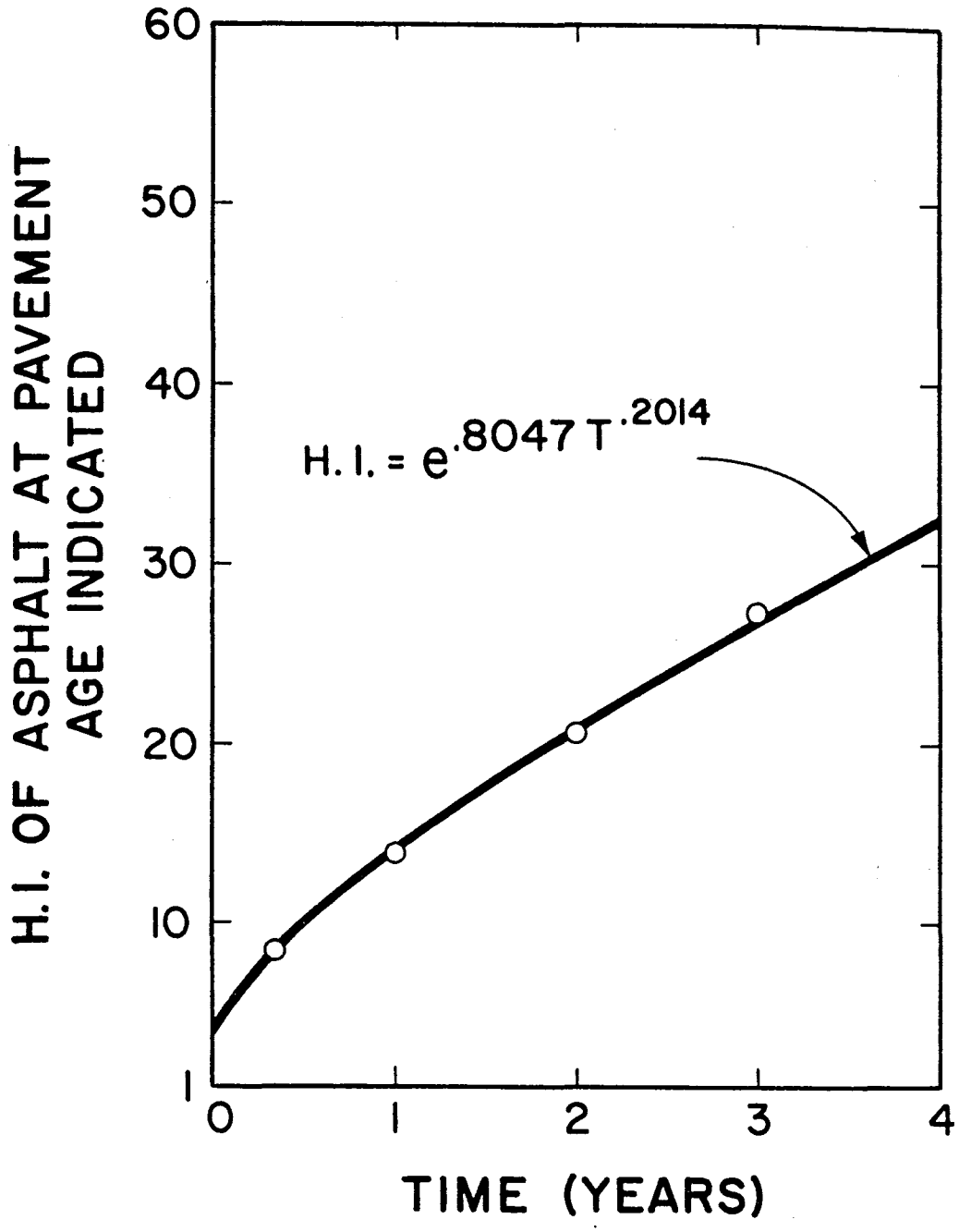



FIGURE A-1, SITE 10 ASPHALT 11

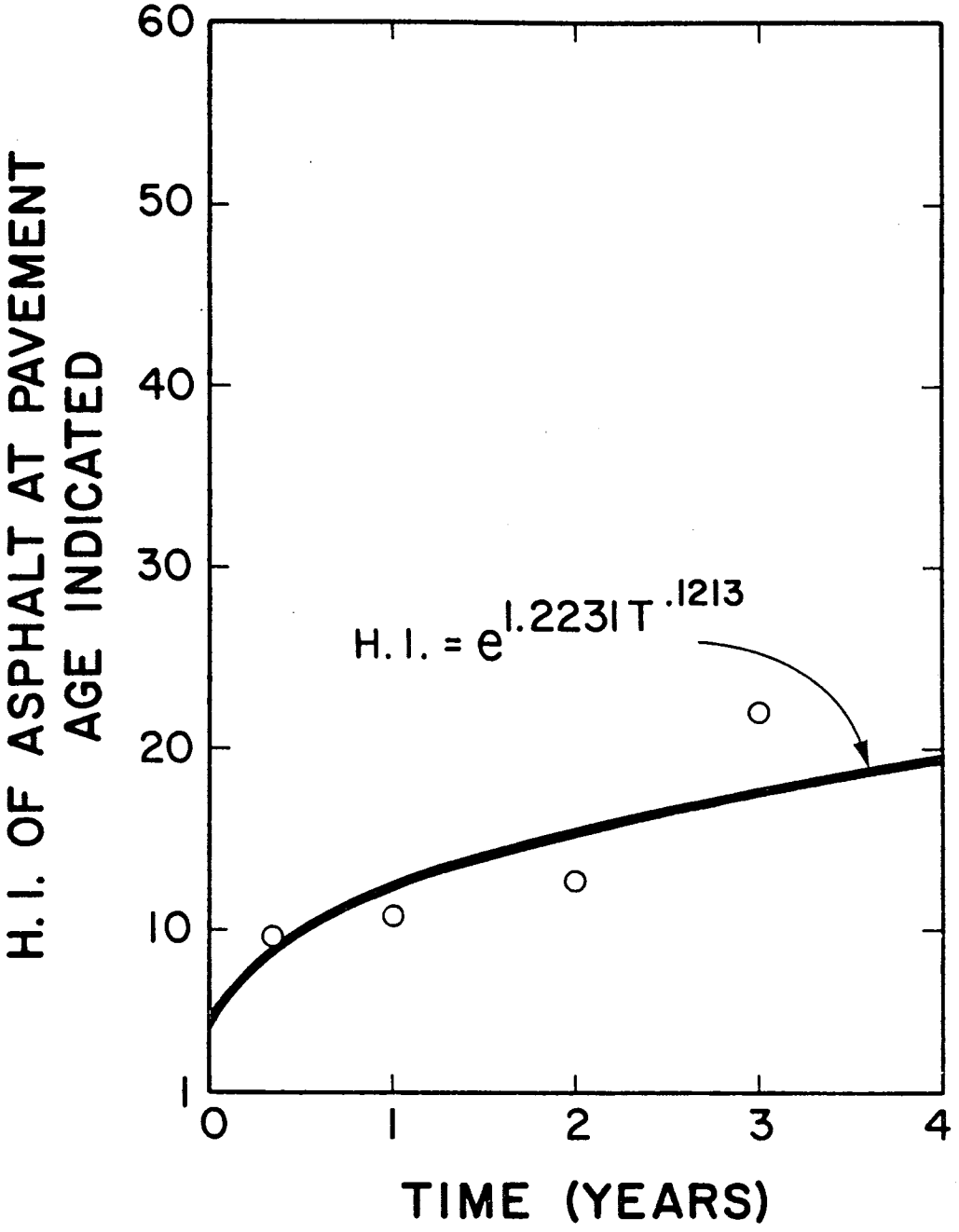



FIGURE A-2, SITE 4 ASPHALT II

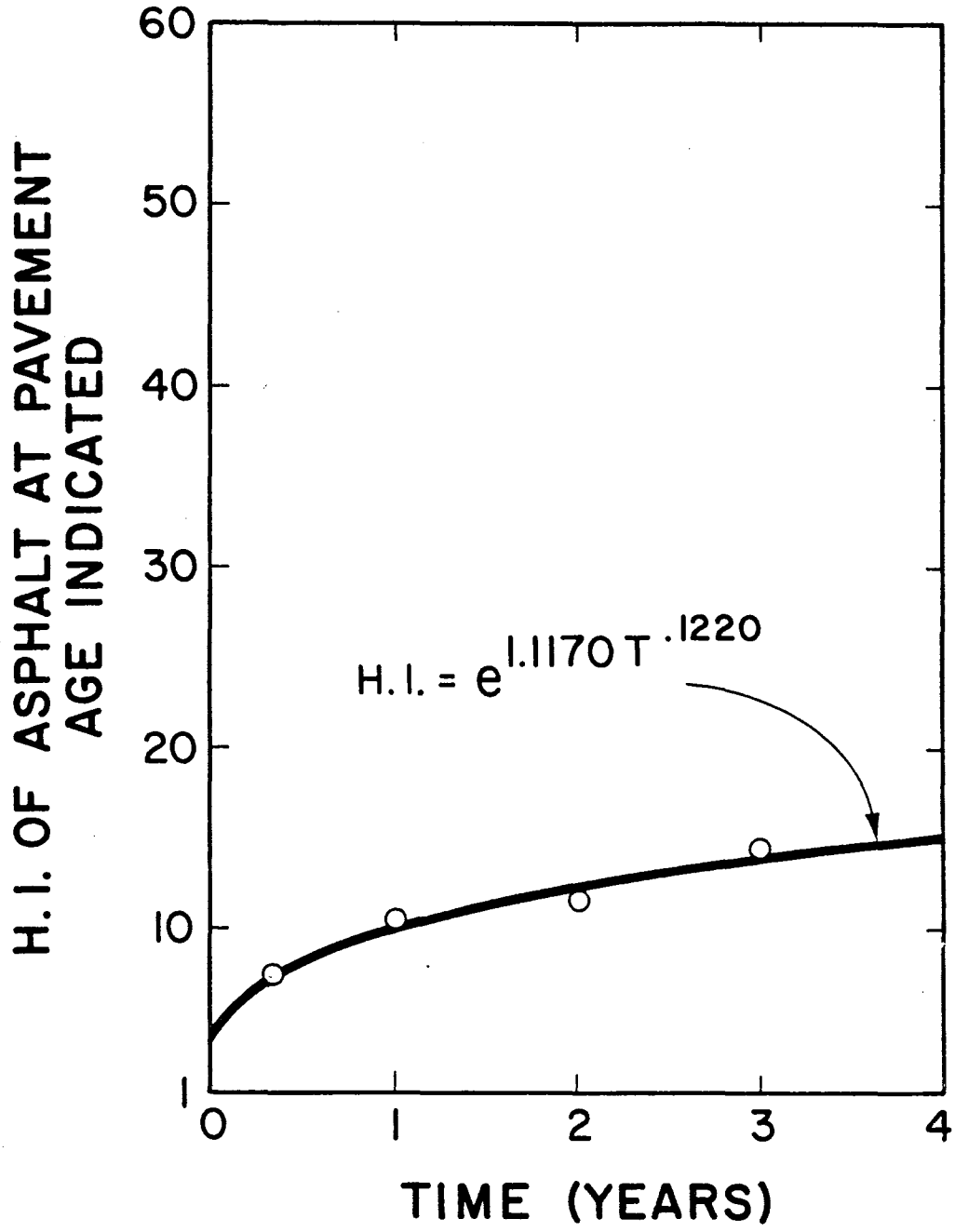



FIGURE A-3, SITE 9 ASPHALT 3

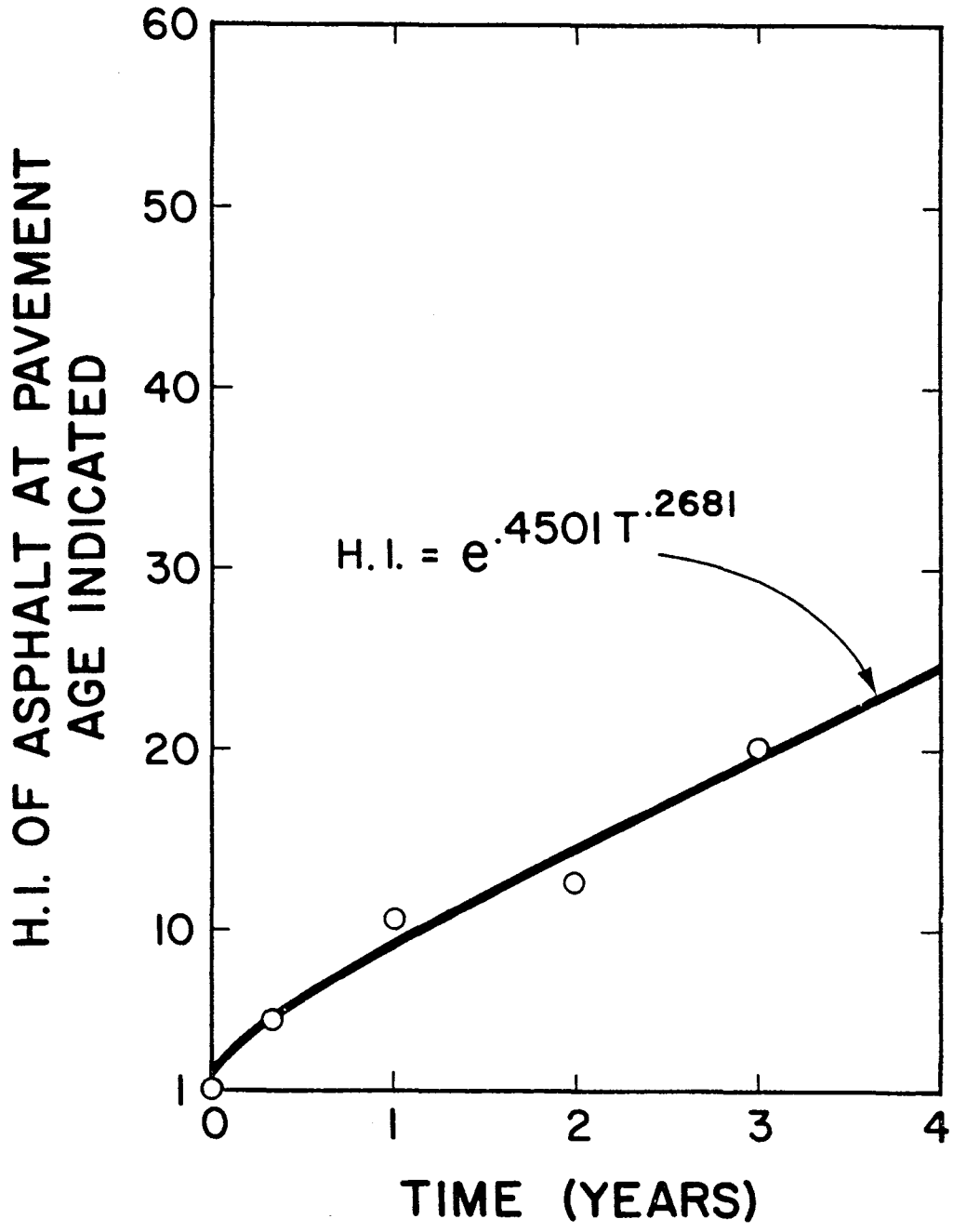



FIGURE A-4, SITE 14 ASPHALT 6

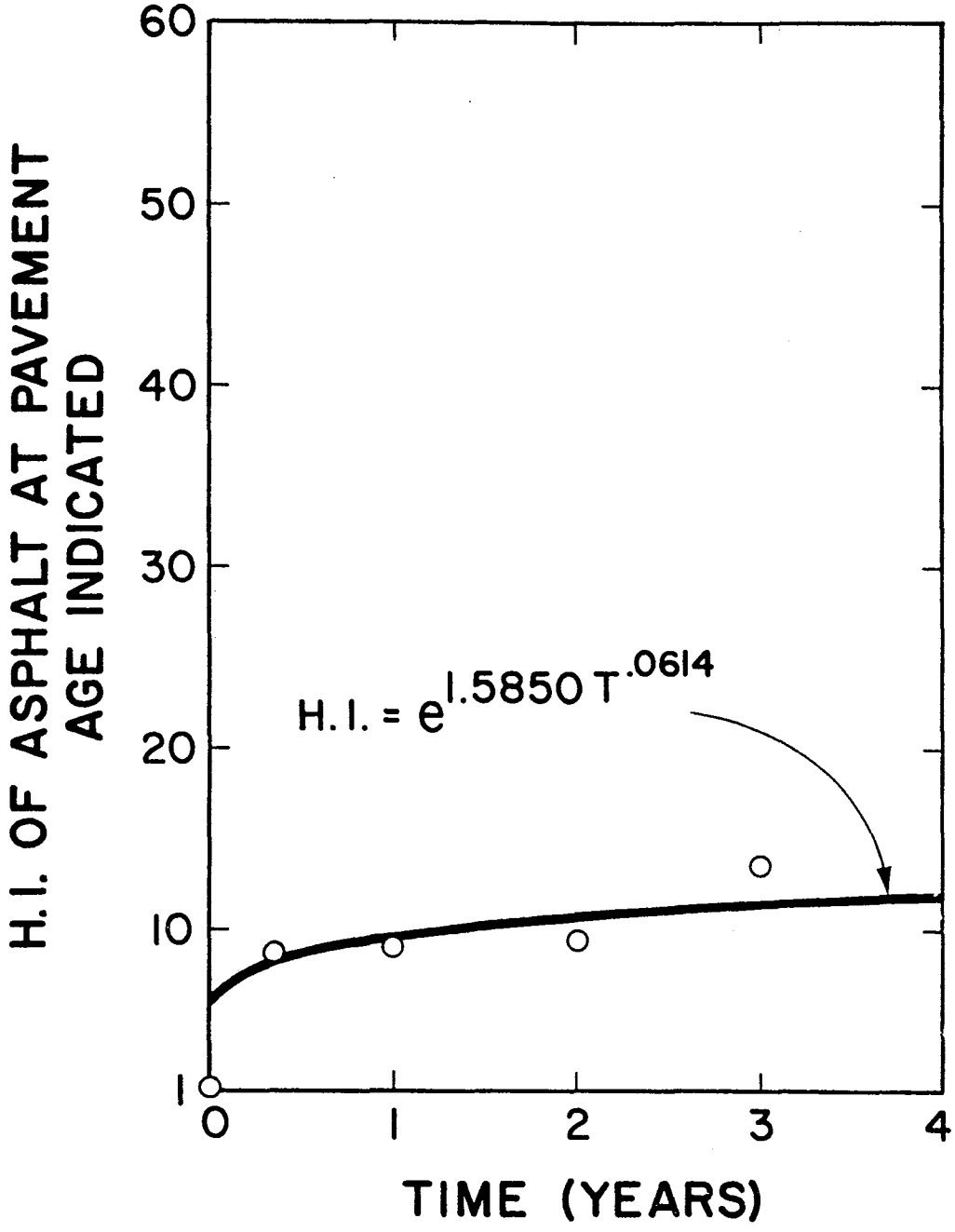



FIGURE A-5, SITE I ASPHALT 3

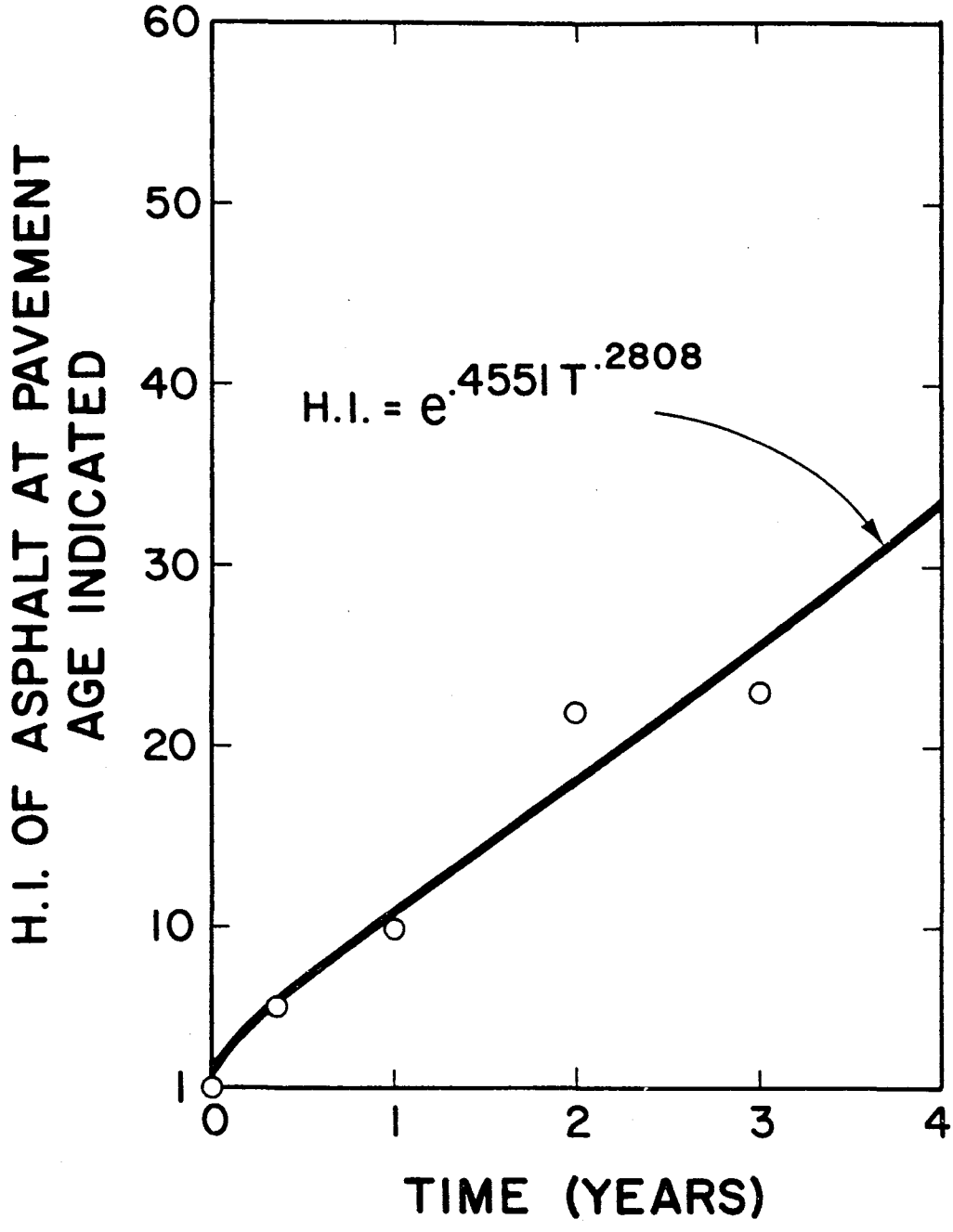



FIGURE A-6, SITE 13 ASPHALT 5

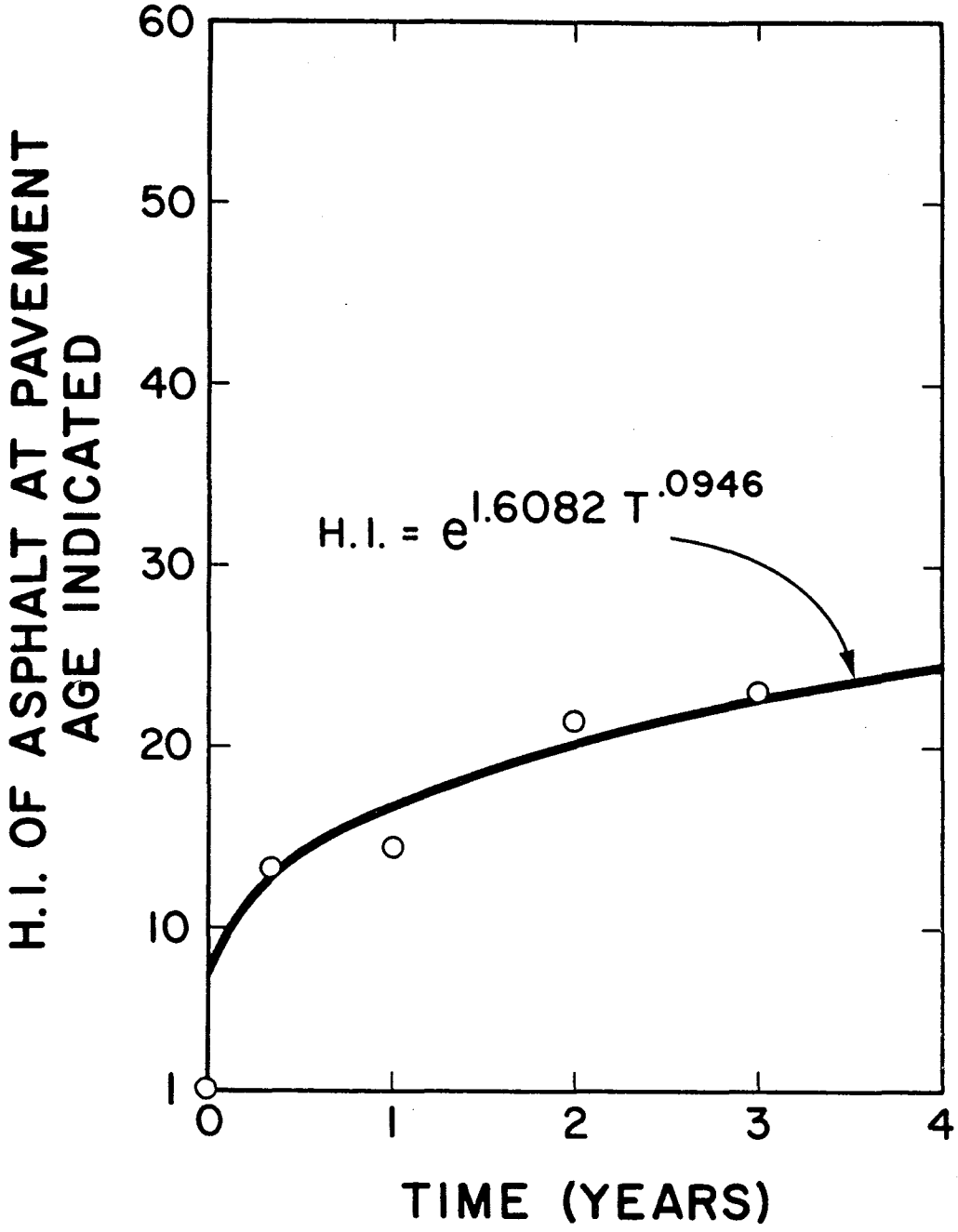



FIGURE A-7, SITE 7 ASPHALT 15

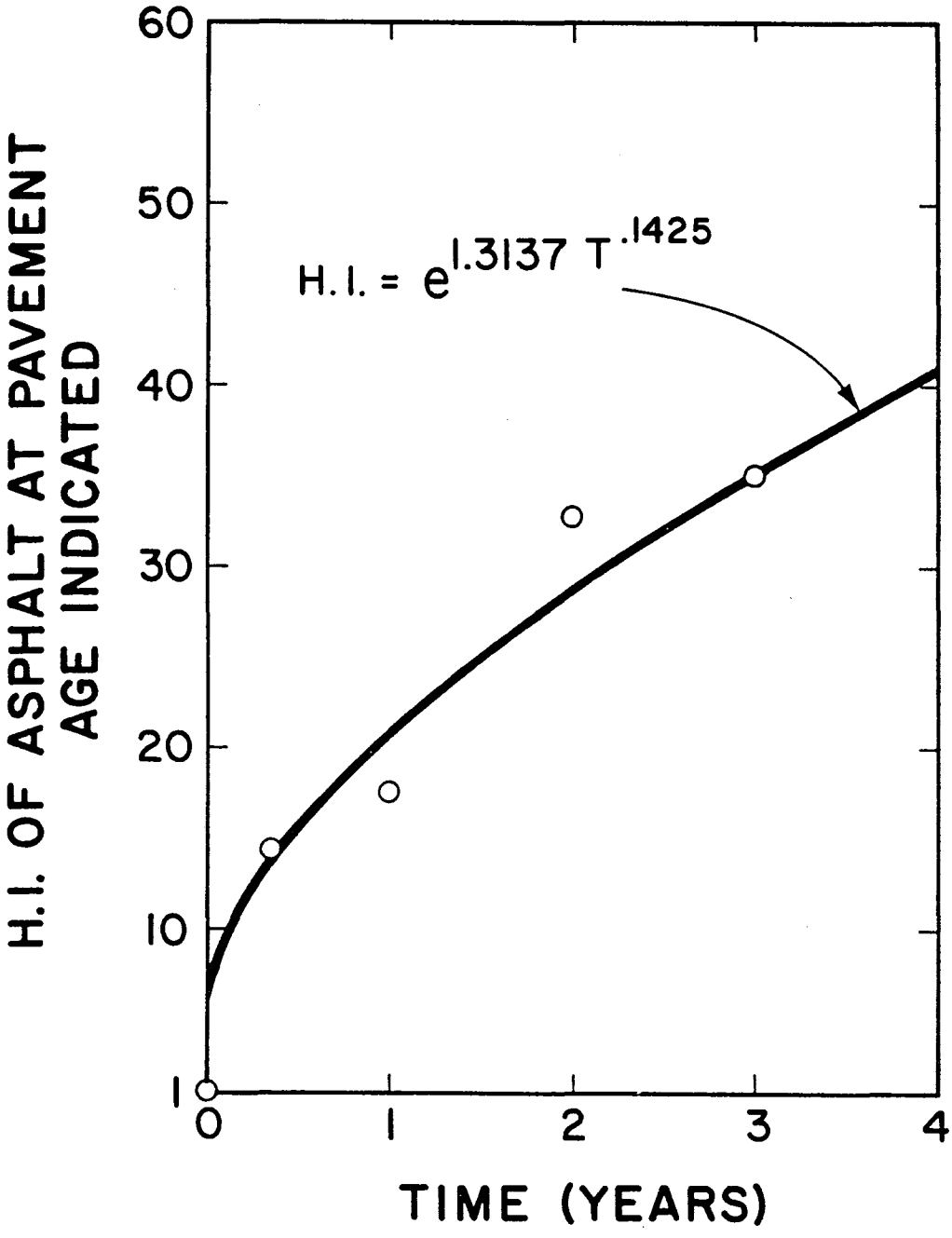
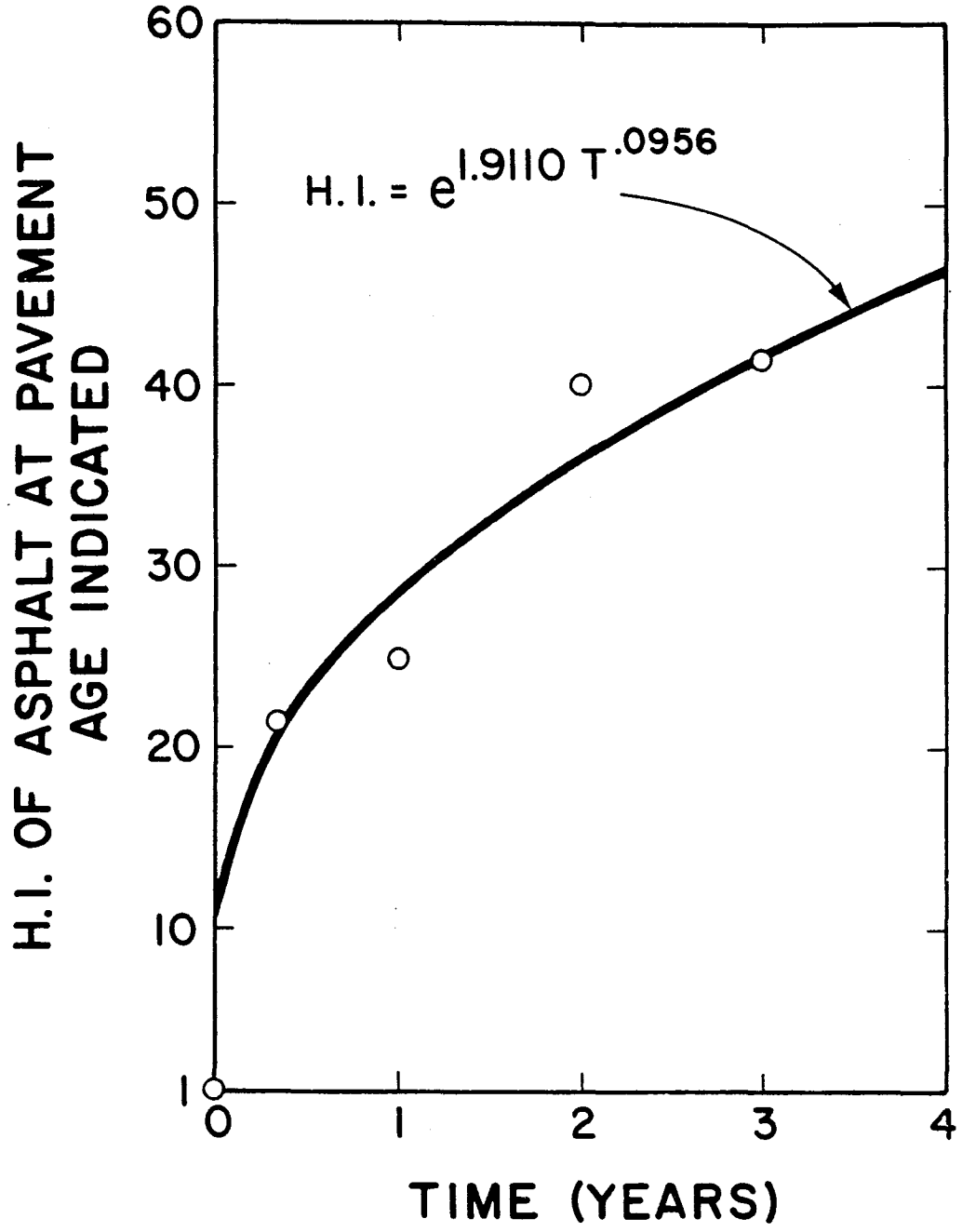



FIGURE A-8, SITE 8 ASPHALT 7

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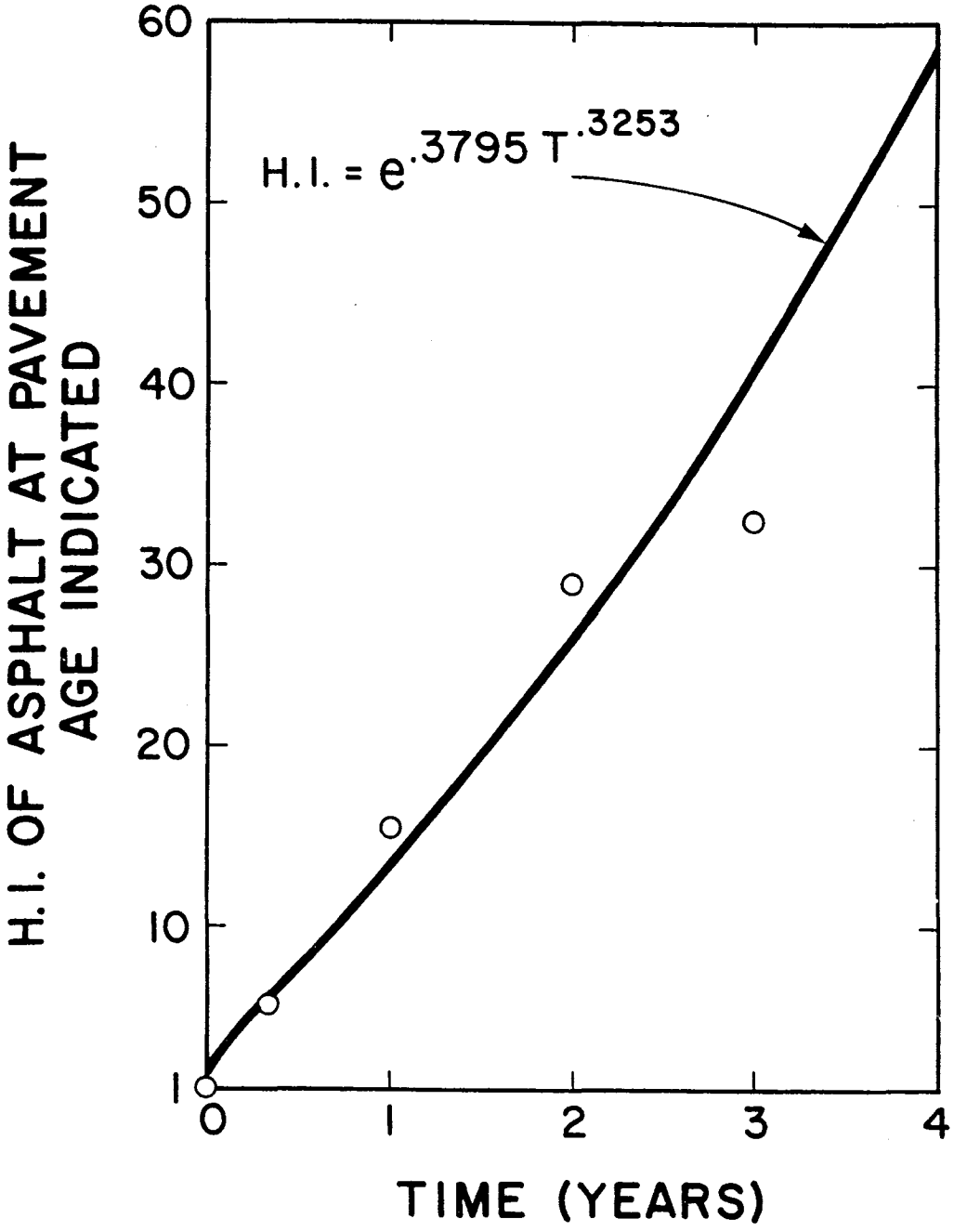


FIGURE A-10, SITE 12 ASPHALT 2