USE OF ADDITIVES TO RETARD HARDENING OF ASPHALTS BY ACTINIC SOLAR RADIATION

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PREFACE

This is the first report issued under Research Study 2-9-72-175, "Hardening of Asphalt," which deals with the retardation of the hardening of asphalts by the use of Ultraviolet Inhibitors.

DISCLAIMER

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ABSTRACT

In order to establish a base for the reader's understanding of the overall project, this abstract must, of necessity, mention research done prior to the current investigation.

Hardening of asphalts used in the surface courses of bituminous pavements has been studied by Texas Transportation Institute during the past nine years. This subject is of economic importance because the deterioration (hardening) of the asphaltic binder in the surface course has often resulted in excessive maintenance costs.

The factors involved are quite complex and it has become evident that the laboratory tests used in the past are not adequate to determine whether a particular asphalt used in a pavement surface will possess good durability under service conditions.

The effect of chemically active (actinic) solar radiation on organic materials has been recognized for many years by the rubber, polymer, and paint industries. But, no informative test has been developed to evaluate and quantify the effect of solar radiation on asphalts.

Lord Kelvin said, "When you can measure what you are talking about and can express it in numbers, you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind".

Using this philosophical approach, a test was developed which characterizes the hardening of an asphalt under controlled conditions of film thickness, air supply, heat (temperature), and chemically active solar radiation.

The original asphalt and the same material after exposure to the hardening agents applied in the laboratory test are measured for viscosity (in megapoises) in a sliding plate, thin film viscometer at 77° F and 5 x 10^{-2} sec^{-1} rate of shear.

The hardening conditions of the test are bounded by the following limitations: A 10-micron film of the asphalt is exposed in air to 1,000 microwatts/cm^2 of 3,660 Angstrom radiation at 95 $\pm$ 2° F for 18 hours. The viscosity of the hardened asphalt is divided by the viscosity of the original material to obtain a Hardening Index, HI(X_2). The Index obtained for more than 60 different asphalts varied from 5.5 to 277 fold. Three asphalts, tested under the conditions given above, were too hard to be measured.

The results obtained led to immediate speculation concerning the chemical reactions responsible for the wide range of hardening shown by the different asphalts exposed to the light test. The chemical reactions involved are thought to be mainly of the photochemical or photooxidation type or possibly a combination of the two.

It is known that small quantities of various metals are capable of stimulating such reactions. For this reason, analyses for several "trace" metals were made on a number of different asphalts. An apparent relation was found to exist between the HI(X_2) of the asphalts tested and their content of vanadium in parts per million by weight. This discovery led to the determination of vanadium content in the 60 odd samples that have been tested for susceptibility to hardening. A study of the relation existing between the parts per million of vanadium present and the hardening index of an asphalt indicated that a significant correlation exists between these two parameters.

Based on the experience with other organic materials (rubber, polymers, etc.) the data obtained on asphalts pointed to the possibility that certain additives should be useful for inhibiting hardening of the asphaltic binder used in the surface course of a bituminous pavement. Four additive materials, used in small amounts, were found to reduce the hardening determined by the test discussed above. These were:

1. Dow Corning Silicone 200.
2. Goodyear Pliopave, L170.
3. Zinc Diethyl Dithiocarbamate (ZDC).
4. UOP-256.

Use of the first three additives was limited to two or three representative asphalts. The fourth additive was used to the extent of one to 1.5 percent by weight in 39 different bitumens which, without UOP-256, had HI(X_2) values above 20. Reduction in Hardening Index, HI(X_2), by use of this additive ranged from 25 to 90 percent.

KEY WORDS

Actinic Light
Air
Hardening
Hardening Index
Heat
Pliopave 170
Silicone 200
Time
Ultra-violet inhibitor
UOP-256
Vanadium
Zinc Diethyl Dithiocarbamate (ZDC)
Viscosity

SUMMARY

An extensive investigation, described in previous reports, indicated that short wavelengths of solar radiation have severe deteriorating effects on certain asphalts. It is well known in the rubber, polymer, paint and other industries that hardening is caused by chemically active (actinic) solar energy. This radiant energy is converted into chemical energy which results in the formation of larger organic entities in these materials. Also, it is known that certain metals present in small amounts can stimulate this conversion of radiant to chemical energy.

First, a test was developed to measure the extent of hardening suffered by a particular asphalt sample of fixed film thickness exposed in air to the effects of time, heat and actinic light. Further investigations indicated that the vanadium content of a particular asphalt in general correlated reasonably well with the magnitude of hardening which occurred during the test.

The study discussed in this report deals with the use of additive materials that inhibit or retard the hardening process discussed above. Such additives are known variously as ultra violet inhibitors or metal deactivators. Several additives used were found to possess a considerable range of effectiveness.

A well known proprietary additive (UOP-256) was used with 39 different asphalts having Hardening Indices, $HI(X_2)$, above 20. This means that exposure of the original asphalt to the laboratory test resulted in more than a 20 fold increase in viscosity at 77° F. The presence of one percent UOP-256 by weight resulted in an average reduction of 60 percent in the Hardening Indices.

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I. INTRODUCTION

A. Purpose

The purpose of this study was to investigate the use of chemical additives to retard the hardening of asphalts by heat, air (oxygen), and especially by actinic solar radiation.

B. Need for the Research

In preceding studies of the causes for hardening of asphalts used in the surface courses of bituminous pavements, it was found that the susceptibility of asphalt cements to deterioration by chemically active solar radiation varies greatly. Thus, the need became evident for a way to reduce the hardening which, in many asphalts, is responsible for excessive maintenance costs in asphalt surface courses.

C. Implementation Statement

Based on the results described in this report, it is recommended that laboratory and field studies be set up to establish the economic return to be expected by adding small amounts of an effective antihardening chemical to asphalts used in the surface courses of bituminous pavements.

D. Background

1. Experienced asphalt technologists for some time have recognized that excessive hardening of asphalt used in the surface course of a bituminous pavement is an important factor contributing to pavement distress. Research conducted during the past ten years has established

that hardening of pavement surfaces is caused by the combined action of time, heat, air (oxygen), and the chemically active (actinic) components of solar radiation. These environmental factors cause undesirable changes in many economically important organic products such as rubber, polymers, paints, textiles, etc. Asphalt must be included in this list. Cross-linking of the molecules in organic materials by radiant energy has been discussed by Adler.[(1)] The hardening (deterioration) of asphalts by exposure to sunlight may be caused to a considerable extent by the type of reactions discussed in his paper.

2. There is a voluminous patent and journal literature concerning the addition of many materials to asphalts in an effort to improve their serviceability. Unfortunately, most of these early efforts were based on a "pick and try" procedure. But, during the past decade, more scientific approaches have been established, which led to a better understanding of the basic causes for hardening and the establishement of potentially sound methods for decreasing the large maintenance costs brought about by hardening (deterioration) of asphalt in service. Beitchman [(2)] discussed in detail the action of antioxidants on asphalt durability. Combinations of eight asphalts with twelve antioxidants were examined by Martin [(3)] for susceptibility to oxidative hardening. The same author [(4)] added 34 different antioxidants to a partially airblown Kuwait asphalt. He found that antioxidants of the free radical trap type were generally effective in stabilizing this asphalt against photo-oxidation. Januski [(5)] added a large number of chemical additives to Near Eastern asphalts and evaluated the resulting decrease in oxidative hardening.

3. In 1963 a cooperative investigation between the Texas Highway Department and the Texas Transportation Institute was established, in which 13 paving sites in widely separated areas of Texas were involved.[6] Extensive data were obtained on the original asphalts used at each site and samples of hot-mix were obtained as each mixture entered the truck and as each entered the paver. Samples of the road surface were taken after one day, two weeks, four months, one year, two years, and, in most cases, after three years of service. These samples were subjected to standard tests. Also, the asphalt was carefully extracted and recovered from the paving mixtures and then tested extensively.

A field Hardening Index, $HI(X_1)$, was obtained for each asphalt at each of the established intervals during two years in service. $HI(X_1)$ was determined by dividing the viscosity of each recovered asphalt by the viscosity of the original asphalt before becoming a part of the pavement. All viscosities were determined in poises at 77° F using the thin film sliding plate type viscometer.

Subjective evaluations of each pavement were made at intervals of time by skilled personnel. Much effort was expended in trying to isolate the cause or causes for the poor serviceability of some of the pavement surfaces and the excellent service life of others.

4. A laboratory test for evaluating hardening of asphalts by the combined action of time, heat, and air has been used for several years. In this procedure, a 15-micron film of asphalt is placed on 4 cm x 4 cm glass plates and exposed for two hours in a dark oven at 225° F. Viscosity of the hardened asphalt is determined and the value obtained is divided by the viscosity of the original asphalt at the same temperature. The resulting

quotient is designated as Hardening Index, HI(X_3). This index indicates how many fold the asphalt is hardened by the test conditions.

A linear regression equation established between HI(X_1) and HI(X_3) gave a correlation coefficient of 0.52.

5. The experimental results mentioned above indicate that some other important environmental factor, in addition to time, heat, and air (oxygen), has a pronounced effect on the hardening of the asphalt in the surface of a bituminous pavement.

It is well-known that the short wave length components of solar radiation have a powerful deteriorating effect on most organic materials. A new laboratory test was developed [7] in which a 10-micron film of asphalt was formed on 4 cm x 4 cm glass plates and then exposed in air to 1,000 microwatts per cm^2 of 3,660 Angstrom wave length radiation for 18 hours at 95 $\pm$ 2° F. As in the test mentioned above, the hardened asphalt was measured for viscosity in poises at 77° F and the value obtained was divided by the viscosity of the original asphalt. The resulting quotient is designated as Hardening Index, HI(X_2), which includes the effect of the short wave length (actinic) solar radiation on the asphalt. Linear regression analyses yielded a correlation coefficient of 0.87, which is considerably better than the value of 0.52 obtained from the old laboratory test, HI(X_3), which does not include the hardening (deteriorating) effect of actinic sunlight.

In addition to the original 13 asphalts used in the 1963-66 experiments, an additional **51** asphalts made from different petroleum sources by various manufacturers were subjected to the new test. The Hardening Indices, HI(X_2), for this larger group of asphalts varied from 5.5 to 277[8].

6. These results naturally raised the question as to why the hardening of asphalts varied so much when subjected to the same combined effects of time, heat, air and actinic solar radiation.

Since certain metals in small quantities are known to stimulate numerous chemical reactions, e.g. magnesium in chlorophyll, it was decided to determine if the metal contents of a particular asphalt had any relationship to its susceptibility to hardening as measured by the new laboratory test. A number of asphalts were tested for cobalt, magnesium, nickel, and vanadium. The results obtained indicated that vanadium appeared to stimulate the hardening caused by time, heat, air and actinic solar radiation.[7][8]

A non-linear regression analysis for Hardening Index, HI(X_2), and parts per million by weight of vanadium for the different asphalts gave a correlation coefficient of 0.88. These studies led to the conclusion that vanadium content of an asphalt is, to a great extent, responsible for stimulating the photo-chemical reactions which result in hardening of asphalts exposed to actinic solar radiation.

II. USE OF ADDITIVE MATERIALS TO RETARD HARDENING OF ASPHALTS CAUSED BY SOLAR RADIATION

It was mentioned in the Introduction that considerable success has been achieved in the development of additives capable of retarding deterioration (hardening) caused in organic materials by photo-chemical and photooxidation reactions. Consequently, an investigation was started to determine how helpful small (economically acceptable) amounts of certain materials could be in retarding the excessive hardening of the asphalt often encountered in the surface course of a bituminous pavement.

A. Materials Used as Additives

Although numerous different chemicals have been used in asphalts to improve their properties, few have shown real promise in helping to solve the serious problem caused by the action of solar radiation. The materials discussed below, used in the investigation, fall into the following categories:

> An additive that has shown improvement of the properties affecting handling and laying of hot mix pavements.
>
> A material that was first used to improve some of the physical and rheological properties of asphalt paving cements.
>
> A chemical additive that has been quite thoroughly investigated by others for its ability to reduce hardening of a few different asphalts exposed to various environmental conditions.
>
> A proprietary ultraviolet inhibitor effective in protecting rubbers, polymers, etc. from hardening by chemically active solar radiation.

TABLE I

BLENDS OF ASPHALTS NO. 6 AND NO. 11 WITH 25 AND 50 PPM BY WEIGHT OF DOW CORNING 200 SILICONE

Asphalt Number	Grade and Year	DC-200 ppm	Original Vis. Megapoises at 77° F	Vis. Megapoises at 77° After Hardening 1/	HI(X_2) 2/	Decrease in HI %	Vanadium ppm 3/
6	AC-20(1969)	0	1.82	88.0	48.5	--	45.0
6	AC-20(1969)	25 ppm	1.60	60.0	37.5	22.5	45.0
6	AC-20(1969)	50 ppm	1.24	33.0	26.5	45.5	45.0
11	AC-20(1969)	0	2.56	17.0	6.5	--	9.5
11	AC-20(1969)	25 ppm	1.80	11.2	6.2	No change	9.5
11	AC-20(1969)	50 ppm	2.00	14.0	7.0	No change	9.5

1/ Ten-micron films of asphalt on 4 cms x 4 cms glass plates are exposed to 1,000 microwatts/cm^2 of 3,660 Angstrom wave length solar radiation in air at 95 ± 2° F for 18 hours.

2/ HI(X_2) were obtained by dividing the viscosity at 77° F of the hardened asphalt by the viscosity of the original asphalt at the same temperature.

3/ Determined by Thermal Neutron Activation Analysis.

1. Dow Corning 200 Silicone Added to Two Different Asphalts

This compound has been used in the extent of 1 to 2 ppm by weight to improve the handling and laying of hot-mix asphalt pavements[9]. Later, the investigation was extended to include the effect of the additive, in various amounts, on reduction of hardening by actinic radiation. It was necessary to use more than the small amounts mentioned above to noticeably reduce photo-chemical hardening. Table I, facing, shows the effect of 25 and 50 ppm on the reduction of hardening of two typical paving asphalts. Asphalt No. 6 was considerably improved. The additive had no significant effect on Asphalt No. 11.

TABLE II

BLENDS OF ASPHALTS NO. 6 AND NO. 11 WITH 3 PERCENT BY WEIGHT OF GOODYEAR PLIOPAVE L170

Asphalt Number	Grade and Year	Pliopave Wt. %	Original Vis. Megapoises at 77° F	Vis. Megapoises at 77° After Hardening 1/	HI(X_2) 2/	Decrease in HI %	Vanadium ppm 3/
6	AC-10(1969)	0	0.66	51.0	85.0	--	37.0
6	AC-10(1969)	3	1.12	41.0	36.5	57	37.0
11	AC-10(1969)	0	0.88	16.0	18.5	--	12.5
11	AC-10(1969)	3	1.56	22.5	14.5	22	12.5

1/ Ten-micron films of asphalt on 4 cms x 4 cms glass plates are exposed to 1,000 microwatts/cm^2 of 3,660 Angstrom wave length solar radiation in air at 95 ± 2° F for 18 hours.

2/ HI(X_2) were obtained by dividing the viscosity at 77° F of the hardened asphalt by the viscosity of the original asphalt at the same temperature.

3/ Determined by Thermal Neutron Activation Analysis.

2. Goodyear Pliopave Added to Two Different Asphalts

Initially, Pliopave in the amount of three percent by weight of the blend were added to two different road building asphalts to determine improvement of their physical and rheological properties. The study was later extended to learn whether the additive caused any definite decrease in hardening of each bitumen when exposed to time, heat, air and actinic solar radiation. Table II, facing, shows the data obtained. Addition of 3% Pliopave to Asphalt No. 6 resulted in a 57% decrease of Hardening Index, HI(X_2), when exposed to the light test. Asphalt No. 11, which in the original state was less sensitive to short wave length radiation, showed only 22% reduction in Hardening Index, HI(X_2), after addition of 3% Pliopave.

TABLE III

BLENDS OF ASPHALTS NO. 1, NO. 6, AND NO. 11 WITH ONE TO THREE PERCENT ZINC DIETHYL DITHIOCARBAMATE (ZDC)

Asphalt Number	Grade and Year	ZDC %	Original Vis. Megapoises at 77° F	Vis. Megapoises at 77° After Hardening 1/	HI(X_2) 2/	Decrease in HI %	Vanadium ppm 3/
1	AC-10(1969)	0	0.88	136	155	-	19.0
1	AC-10(1969)	2	0.86	76	89.0	42.5	19.0
1	AC-10(1969)	3	1.08	74	68.0	57.5	19.0
1	AC-20(1969)	0	2.7	140	52.0	-	74.0
1	AC-20(1969)	2	3.0	84	28.0	46	74.0
1	AC-20(1969)	3	3.4	80	24.5	56	74.0
6	AC-10(1969)	0	0.66	57	85.0	-	37.0
6	AC-10(1969)	1	0.80	42	53.0	37	37.0
6	AC-10(1969)	2	0.74	31	42.0	50	37.0
6	AC-20(1969)	0	1.82	88	48.5	-	45.0
6	AC-20(1969)	1	2.00	52	26.0	47	45.0
6	AC-20(1969)	2	2.18	66	30.3	37	45.0
11	AC-10(1969)	0	0.88	16	18.5	-	12.5
11	AC-10(1969)	2	1.5	17	11.3	39	12.5
11	AC-20(1969)	0	2.56	17	6.7	-	9.5
11	AC-20(1969)	2	2.0	11.6	5.8	13	9.5

*Could not be calculated.

1/ Ten-micron films of asphalt on 4 cms x 4 cms glass plates are exposed to 1,000 microwatts/cm^2 of 3,660 Angstrom wave length solar radiation in air at 95 $\pm$ 2° F for 18 hours.

2/ HI(X_2) were obtained by dividing the viscosity at 77° F of the hardened asphalt by the viscosity of the original asphalt at the same temperature.

3/ Determined by Thermal Neutron Activation Analysis.

3. Zinc Diethyl Dithiocarbamate (ZDC) Added to Two Grades of Three Different Asphalts

Other investigators (4)(5)(10)(11) have found ZDC to be reasonably effective for reducing hardening of both road building and roofing asphalts. In view of the extensive investigations made by these Australian scientists, this compound, in the form of a fine powder, was incorporated into AC-10 and AC-20 grades of Asphalts No. 1, 6, and 11 in amounts ranging from one to three percent by weight of the blend. Data are given in Table III, facing.

Asphalt No. 1, grade AC-10, in the original state was very susceptible to hardening by the light test. Reduction of HI(X_2) by two and three percent ZDC was 42.5 and 57.5 percent respectively. Use of the same amounts of additive in AC-20 grade, Asphalt No. 1 resulted in 46 and 56 percent decreases in HI(X_2).

Both grades of Asphalt No. 6 were somewhat less susceptible to hardening by actinic light than were the samples of Asphalt No. 1, but the decreases in HI(X_2) were similar.

Asphalts No. 11 (both grades) were not very seriously hardened by the actinic light test. But, using two percent by weight of ZDC reduced the HI(X_2) of the blends by 39 and 13 percent, respectively.

4. Effect of Adding One Percent of UOP-256 to Thirty-nine Different Asphalts

(a) Asphalts Used.

Thirty-nine of the asphalts discussed in Report No. 3 of Study 2-8-69-127, concerning the hardening of asphalts (8), were selected for investigation of the retardation of hardening by UOP-256. All of these asphalts without additive exhibited a Hardening Index, HI(X_2) above 20.

(b) Nature of UOP-256.

UOP-256 is a proprietary material made up of a combination of para-phenylene diamine antiozonates (and ultra-violet light inhibitors), which is marketed as a liquid having a viscosity of 2.2 stokes at 77°F. To ascertain its volatility at the maximum temperature encountered in blending with reasonably hard asphalts, a 3/8 inch layer of the additive was heated for 5 hours in a dark air oven at 325°F. Weight loss amounted to 5.5 percent.

(c) Blending and Testing Procedures.

In most cases 99 grams of an asphalt were weighed into a preweighed tin can followed by one gram of UOP-256 to give one percent of additive by weight of blend. When only a small sample of asphalt was available the blend was made by using 49.5 grams of asphalt and 0.5 gram of additive.

The covered can and contents were placed in a dark oven and heated to approximately 225°F. The blend was carefully and thoroughly stirred about every 15 or 20 minutes over a period of two hours in order to insure good dispersion of the additive throughout the asphalt.

The test procedure for determining Hardening Index, HI(X_2), is briefly described on page 4 of this report. Data on the 39 asphalts are presented in Table IV pages 14 through 17, following.

TABLE IV

EFFECT OF ADDING ONE PERCENT BY WEIGHT OF UOP-256 TO THIRTY-NINE DIFFERENT ASPHALTS

Identification of the Asphalt			Asphalt With No Additive			Asphalt + 1% UOP-256				
			Viscosity at 77° F, Megapoises			Viscosity at 77° F, Megapoises				
Number	Source	Grade (Year)	Original	After Light Test	$HI(X_2)$	Original	After Light Test	$HI(X_2)$	Percent Reduction in $HI(X_2)$	Vanadium ppm
3	THD	AC-10 (1970)	0.84	17.0	20.0	0.87	9.4	10.8	46.0	18.1
21	THD	AC-20 (1970)	3.40	71.0	21.0	1.90	11.0	5.8	72.5	36.0
3	THD	AC-20 (1970)	1.16	26.0	22.5	1.3	18.0	13.8	38.5	18.7
21	THD	AC-10 (1970)	1.80	42.0	23.0	1.15	8.0	7.0	70.0	32.0
11	THD	AC-10 (1970)	0.96	31.0	32.0	0.50	7.5	15.0	53.0	11.0
5	Site 13	85-100 pen (1963)	0.81	26.6	33.0	0.58	3.9	6.7	80.0	11.0
R4398	Calif. Canadian	60-70 pen (1970)	2.24	80.0	35.5	2.50	36.4	14.5	58.5	56.0
11	Louisiana	OA-65 (1970)	2.56	98.0	38.0	3.1	40.0	12.9	66.0	17.0
R4255	Calif. Valley Crude	60-70 pen (1970)	2.14	84.0	39.0	1.4	19.4	13.8	65.0	28.5
16	THD	AC-10 (1970)	1.64	88.0	40.0	1.76	18.4	10.4	74.0	20.9

TABLE IV (continued)

EFFECT OF ADDING ONE PERCENT BY WEIGHT OF UOP-256 TO THIRTY-NINE DIFFERENT ASPHALTS

Identification of the Asphalt			Asphalt With No Additive			Asphalt + 1% UOP-256				
			Viscosity at 77° F, Megapoises			Viscosity at 77° F, Megapoises				
Number	Source	Grade (Year)	Original	After Light Test	$HI(X_2)$	Original	After Light Test	$HI(X_2)$	Percent Reduction in $HI(X_2)$	Vanadium ppm
15	THD Site 7	85-100 pen (1963)	0.89	37.5	42.0	0.94	10.0	10.6	78.5	37.0
11	Louisiana	OA-90 (1970)	1.00	46.0	46.0	0.96	11.6	12.1	78.0	31.0
12	THD	AC-10 (1970)	1.02	52.0	47.0	0.98	13.0	13.3	72.0	21.8
R4319	Calif. L. A. Basin	85-100 pen (1970)	0.92	44.0	48.0	0.57	21.0	37.0	23.0	74.0
6	THD	AC-20 (1969)	1.82	88.0	48.5	2.56	54.0	21.0	58.5	45.0
6	THD	AC-10 (1967)	0.74	38.0	51.0	0.88	13.0	14.6	71.5	51.0
1	THD	AC-20 (1969)	2.70	140	52.0	3.50	64.0	18.3	65.0	74.0
6	THD (1835)	AC-20 (1970)	2.10	110	52.5	2.40	40.0	16.6	68.0	40.9
6	THD (2096)	AC-20 (1970)	2.06	110	54.5	2.15	40.0	18.5	65.0	41.9
19	THD	AC-10 (1970)	0.41	24.0	58.5	0.37	8.0	21.6	62.5	146.5*

TABLE IV (continued)

EFFECT OF ADDING ONE PERCENT BY WEIGHT OF UOP-256 TO THIRTY-NINE DIFFERENT ASPHALTS

Identification of the Asphalt: Number	Source	Grade (Year)	Asphalt With No Additive: Viscosity at 77° F, Megapoises: Original	After Light Test	$HI(X_2)$	Asphalt + 1% UOP-256: Viscosity at 77° F, Megapoises: Original	After Light Test	$HI(X_2)$	Percent Reduction in $HI(X_2)$	Vanadium ppm
Imperial Oil "C"	Saskatchewan	94.5 pen (1970)	0.90	58.0	64.5	0.66	13.0	19.7	69.0	38.2
7	THD Site 8	85-100 pen (1963)	0.80	53.0	66.0	0.71	29.0	41.8	38.0	87.0
1	THD	AC-10 (1970)	1.08	76.0	70.0	2.76	86.0	31.0	56.0	86.0
R4310	Calif. Valley	85-100 pen (1970)	0.68	48.0	70.0	0.52	17.0	32.7	53.0	34.0
6	THD Site 11	85-100 pen (1963)	0.80	60.0	75.0	0.52	18.0	35.0	53.0	60.5
17	THD	AC-10 (1970)	0.78	59.0	75.5	0.84	16.4	19.5	75.0	161.0
1	THD	AC-20 (1970)	3.20	256	80.0	4.00	96.0	24.0	70.0	89.6
6	THD	AC-20 (1967)	2.40	194	81.0	2.00	57.0	28.5	64.0	36.5
7	THD Site 6	85-100 pen (1963)	0.96	82.0	85.0	1.20	28.0	23.0	73.0	97.0
6	THD	AC-10 (1969)	0.66	57.0	85.0	0.84	20.0	24.0	72.0	37.0

TABLE IV (continued)

EFFECT OF ADDING ONE PERCENT BY WEIGHT OF UOP-256 TO THIRTY-NINE DIFFERENT ASPHALTS

Identification of the Asphalt			Asphalt With No Additive			Asphalt + 1% UOP-256			Percent Reduction in HI(X_2)	Vanadium ppm
			Viscosity at 77° F, Megapoises			Viscosity at 77° F, Megapoises				
Number	Source	Grade (Year)	Original	After Light Test	HI(X_2)	Original	After Light Test	HI(X_2)		
2	THD Site 12	85-100 pen (1963)	0.86	76.5	89.0	0.80	30.6	38.0	51.0	208
-	Kuwait	87 pen (1970)	1.04	110	106	0.96	38.0	39.5	62.5	84
6	THD	AC-10 (1970)	0.47	52.0	110	0.50	18.0	36.0	58.0	33
9	THD	AC-20 (1970)	1.56	174	111	1.44	24.0	16.7	85.0	148
19	THD	AC-20 (1970)	1.20	140	116	1.40	15.2	10.8	91.5	151
Imperial Oil "A"	Alberta	94.5 pen (1970)	0.88	108	126	0.58	42.0	72.0	43.0	134
1	THD	AC-10 (1969)	0.88	136	155	0.88	30.0	34.0	78.0	79
-	Mexican No. 2	95 pen (1970)	1.10	210	191	0.76	14.0	18.5	91.0	201
-	Mexican No. 1	85 pen (1970)	1.30	360	277	1.08	46.0	42.5	85.0	300

TABLE V

EFFECT OF ADDING ONE PERCENT UOP-256 ON THE VISCOSITIES OF THE ORIGINAL ASPHALTS

Asphalt No. or Name	Number of Samples	Average Viscosities, Megapoises at 77°F. Original	Blend
Group 1 - Blend Became Harder			
1	4	2.00	2.80
6	8	1.40	1.50
Group 2 - Blend Became Softer			
21	2	2.60	1.50
California	3	1.25	0.85
Imperial Oil	2	0.90	0.60
Mexico	2	1.20	0.90
7	2	0.80	0.70
Group 3 - No Change Occurred			
11	3	1.50	1.50
3	2	1.00	1.00

(d) Reduction of Hardening Indices, HI(X_2), by Use of the Additive.

The Hardening Indices, HI(X_2), of the 39 asphalts with no UOP-256 present varied from 20 to 277, with an average value of 73. After blending with one percent of the additive the HI(X_2) values ranged from 5.8 to 72 with an average value of 28. This means that a 60 percent decrease of HI(X_2) for the group of asphalts resulted from the use of one percent additive.

(e) Effect of Addition of One Percent UOP-256 on the Viscosities of the Original Asphalts.

When this additive was added to asphalts from various sources the viscosities of the original asphalts varied considerably depending on the source of the sample and the method of processing used.

In situations where two or more samples were available from a given source the average viscosity of the original and that of the corresponding blend were compared. Nine different sources comprising 24 of the 39 asphalts studied were found to fall into three groups shown in Table V, facing.

The reactions of the asphalts to a fixed amount (1%) of the additive is a strong indication that the chemical compositions of the asphalts in each group are somewhat similar. However, in each group the asphalts therein may be quite different from those in the other two groups.

(f) Increase of Pavement Cost by Addition of One Percent UOP-256 to the Asphalt.

Currently the cost of materials and construction for one ton of pavement surface course is assumed to be $7.50.

Current cost of asphalt is $28.00 per ton. Assuming that one ton of asphalt-aggregate mixture contains 6% (120 pounds) of asphalt, cost of asphalt per tone of mixture is $0.014 x 120 or $1.68.

UOP-256 costs about $1.20 per pount. One percent of additive in 120 pounds of asphalt would increase the cost by $1.20 x 1.2 or $1.44.

Blending the one percent of UOP-256 into 100,000 tons of asphalt should cost about \$50,000 for storage and blending equipment amortized in one year and for the labor cost to handle the 100,000 tons of asphalt-additive blend. This amounts to a cost of \$0.50 per ton or \$0.00025 per pound of blend. Since there would be 120 pounds of blend in one ton of mixture the increased cost for blending asphalt and additive would be \$0.03 per ton of pavement mixture.

Consequently the cost of one ton of paving mixture containing 1% of additive in the 120 pounds of asphalt would amount to \$7.50 + \$1.44 + \$0.03 = \$8.97. This is a cost increase of \$1.47 (19.6%) per ton of high grade asphalt in the laid pavement surface.

An expenditure of this magnitude during construction should result in a considerable reduction in maintenance costs.

TABLE VI

EFFECT OF ADDING 1.5 PERCENT OF UOP-256
TO EIGHT DIFFERENT ASPHALTS

Asphalt No.	Source	Grade & Year	Hardening Index, HI(X) for Original Asphalt	Blend with UOP-256 1.0%	1.5%
6	THD Site 11	85 - 100 pen 1963	75.0	35.0	12.0
2	THD Site 12	85 - 100 pen 1963	89.0	38.0	14.5
R4310	Calif. Valley	85 - 100 pen 1970	70.0	33.0	17.0
6	THD	AC-20 1967	81.0	28.5	21.0
1	THD	AC-10 1969	155	34.0	23.0
7	THD Site 8	85 - 100 pen 1963	66.0	42.0	25.5
Imperial Oil "A"	Alberta	94.5 pen 1970	126	72.0	35.5
No. 1	Mexican	85 pen 1970	277	42.5	39.5

5. Effect of Adding 1.5 Percent of UOP-256 to Asphalts Subject to Excessive Hardening.

A review of the 64 asphalts subjected to the laboratory test utilizing time, heat, air and actinic solar radiation (8) indicates that 26 different asphalts tested (40% of the group) gave HI(X_2) values below 25 without the use of any additive. The addition of one percent of UOP-256 to each of the remaining 38 asphalts reduced the HI(X_2) of 20 samples to below 25. Thus, 46 (72 percent) of the original 64 asphalts studied can attain an HI(X_2) value below 25 either without additive or by use of only one percent UOP-256.

The remaining 18 asphalts from the group of 64 showed higher than 25 HI(X_2) after blending with one percent additive. Thus it was decided to add 1.5% UOP-256 to 8 of these asphalts possessing high susceptibility to hardening by heat, air and chemically active solar radiation. Data on these asphalts shown in Table VI, facing, indicate the use of 1.5% by weight of UOP-256 resulted in 5 samples attaining HI(X_2) values below 25. Thus, of the original 64 different asphalts used in this extensive investigation 54 (85% the group) possess HI(X_2) values below 25 without additive or by blending with a maximum of up to 1.5 percent of UOP-256.

The remaining 10 asphalts (15% of the 64 samples) would require 2 or more weight percent of the additive to reduce HI(X_2) values to less than 25. Use of such an amount of additive would result in costs that could not, in most cases, be justified in pavement surfaces. The 10 asphalts, however, could be used in situations where they would not be exposed to the deteriorating action of actinic solar radiation.

Table VII

Subjective Ratings of Pavement Surfaces and HI(X_1) of Asphalts Extracted after 2 years in Service Compared To HI(X_2) with and without Addition of UOP-256 Hardness Inhibitor

Asphalt No.	THD Site No.	Percent Decrease in Pen @ 77°F after 2 years Service	Subjective Rating of Pavement after 2 years in Service	Hardening Indices of Asphalts		HI(X_2) after Addition of UOP-256	
				HI(X_1)x	HI(X_2)xx	1%	1.5%
8	3	43	Excellent	7.3	5.5		
3	1	59	Good	9.3	17.5		
3	9	60	Very Good	11.3	16.5		
6	14	65	Good	12.7	17.0		
11	4	61	Good	12.8	8.5		
3	17	67	Excellent	18.5	13.5		
11	10	68	Good	20.5	7.0		
AVERAGE		60		13.2	12.1		
5	13	71	Good	22.0	33.0	6.7	
15	7	67	Some Cracks	23.0	42.0	10.6	
6	11	73	Very Poor	27.0	75.0	35.0	12.1
2	12	75	Fair	29.0	89.0	38.0	14.5
7	8	75	Poor	33.0	66.0	41.8	25.3
7	6	73	Fair	40.0	85.0	23.0	
AVERAGE		72		29.0	65.0	27.0	17.0

x: HI(X_1) of extracted asphalt after 2 years in Service.

xx: HI(X_2) after exposure of original asphalt to new laboratory light test utilizing time, heat, air and actinic light on 10 micron films.

III. EFFECT OF UOP-256 ON ASPHALTS USED IN TEXAS HIGHWAY DEPARTMENT MAINTENANCE PROGRAM FOR 1963

An extensive discussion of a cooperative research program conducted by the Texas Highway Department and Texas Transportation Institute during the period 1963-66 is presented in literature references (6) and (8). The purpose of the investigation was to determine the cause or causes of deterioration of certain bituminous pavement surfaces, during two years in service, while other pavements using different asphalts were in good to excellent condition after service for the same length of time. The reports, mentioned above, gave clues that eventually led to the research described in this report.

The thirteen pavement sites used in the 1963-66 program were each given a subjective rating at intervals by Texas Highway Department Engineers possessing broad experience. These ratings after two years service are shown in column 4 of Table VII, facing. Seven sites received rating from Excellent to Good. The other six sites were assigned rating from Good to Very Poor.

Asphalts extracted and recovered from the pavement surfaces were tested for the degree of hardening which had occurred during two years of service. The resulting Hardening Indices, $HI(X_1)$, of the recovered asphalt are shown in column 5 of Table VII. It should be noted that the values ranged from 7.3 to 40.0. The seven taken from the best pavement surfaces gave $HI(X_1)$ values from 7.3 to 20.5. $HI(X_1)$ values for the remaining six asphalts associated with the Good to Very Poor pavement conditions after two years service, ranged from 22 to 40. These results indicate that the evaluation of a pavement surface by expert visual rating agrees quite well with the degree of hardening suffered by the asphalt exposed to the action of heat, air and solar radiation during service in the pavement surface.

The original asphalts used in the 13 different sites were next tested by the new actinic light test described on page 4 of this report. The HI(X_2) values resulting from this test are presented in column 6 of Table VII. The seven asphalts used in pavement sites rated Excellent to Good after two years service gave HI(X_2) values ranging from 5.5 to 17.5 (average 12.1). The group of six asphalts used in pavement surfaces rated Good to Very Poor had HI(X_2) values ranging from 33 to 85 (average 65).

One percent of UOP-256 was blended with each of the six original asphalts used in the pavement surfaces that showed undesirable hardening after two years in service. HI(X_2) data obtained are shown in column 7 of Table VII. Hardening was considerably reduced resulting in a range of HI(X_2) values from 6.7 to 41.8 (average 27).

Since three of the six asphalts blended with one percent UOP-256 still gave HI(X_2) values above 25, blends were made using 1.5 percent by weight UOP-256 prior to subjection to the actinic light test. A range of HI(X_2) values from 12.1 to 25.3 (average 17) were obtained. Asphalt No. 7 used at pavement Site 8 gave an HI(X_2) value slightly above 25. Use of any larger quantities of this additive probably would not be economically feasible.

IV. Conclusions

1. A study of 64 different road building asphalts indicates that

   (a) Twenty-six samples gave $HI(X_2)$ values below 25 without the use of any additive.

   (b) Twenty-three other samples mixed with 1.0 weight percent of UOP-256 gave $HI(X_2)$ values below 25.

   (c) Five additional samples blended with 1.5 weight percent of UOP-256 gave $HI(X_2)$ values below 25.

Thus, 54 of the original 64 asphalts originally were, or could be brought to, an $HI(X_2)$ value below 25.

2. The remaining 10 asphalts would require 2 percent or more of the additive to attain values less than 25 $HI(X_2)$. Use of such amounts of additive, in some cases, would not be economically feasible for up-grading bituminous pavement surfaces.

V. Recommendations

Based on the results described in this report, it is recommended that:

1. A search be made for additives that may be more effective and/or less expensive than those discussed in this report.
2. Small scale field tests be conducted using one percent UOP-256 in several different asphalts to determine how such blends will react under atmospheric and traffic conditions.
3. Asphalts possessing HI(X_2) value above 25, even after use of 1.5 percent UOP-256, should not be put to use in surface courses. Such materials could, however, be applied to other highway needs.
4. Some of the now available separation and analytical techniques be applied to selected samples from the different asphalts studied in this and former reports. Gross separation of each asphalt selected for study could be accomplished by gel permeation chromatography. Each sample thus obtained could be further fractionated and analyzed for chemical composition by high resolution mass spectrometry. Such a procedure should offer assistance in solution of the problems raised by the results shown in this report.

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