SUMMARY REPORT 175-1(S)

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

SUMMARY REPORT
of
Research Report Number 175-1
Study 2-9-72-175

Cooperative Research Program of the
Texas Transportation Institute and the Texas Highway Department
In cooperation with the
U. S. Department of Transportation, Federal Highway Administration

March, 1972

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

Use of Additives to Retard Hardening of Asphalts by Actinic Solar Radiation

by

Ralph N. Traxler

In order to establish a basis for the reader's understanding of the overall project, this summary report 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 decade. 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 concentration of chemically active solar radiation. The original asphalt and the same material after exposure to the hardening agents applied in the laboratory test was measured for viscosity (in megapoises) in a sliding plate, thin film viscometer at 77°F and 5×10^{-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 ± 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 also 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. A reasonable relationship 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 Piopave, L170.
3. Zinc Diethyl Dithiocarbamate (ZDC).
4. UOP-256.

Twenty-five to 50 parts per million of Dow Corning 200 Silicone added to two different asphalts resulted in 22 to 45 percent decrease in hardening for one of the asphalts and none for the other.

Three percent by weight of Goodyear Pliopave added to two different asphalts resulted in 22 and 57 percent reduction in hardening.

One to three percent Zinc Diethyl Dithiocarbamate (ZDC) added to two grades of three different asphalt caused from 13 to 57 percent decrease in hardening.

One percent by weight of UOP-256 added to 39 different asphalts resulted in reduction of hardening ranging from about 15 to 90 percent. Table I gives data on 9 of the 39 asphalts tested. The reduction in Hardening Index for the group of 39 asphalts amounted to about 60 percent.

TABLE 1

EFFECT OF ADDING ONE PERCENT BY WEIGHT OF UOP-256 TO 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
21	THD	AC-20 (1970)	3.40	71.0	21.0	1.90	11.0	5.8	72.5	36.0
11	THD	AC-10 (1970)	0.96	31.0	32.0	0.50	7.5	15.0	53.0	11.0
Dept. Hwys. Calif. R4255 Valley Crude		60-70 pen (1970)	2.14	84.0	39.0	1.4	19.4	13.8	65.0	28.5
1	THD	AC-20 (1969)	2.70	140	52.0	3.50	64.0	18.3	65.0	74.0
Imperial Oil "C" Saskatchewan		94.5 pen (1970)	0.90	58	64.5	0.66	13.0	19.7	69.0	38.2
6	THD Site 11	85-100 pen (1963)	0.80	60	75.5	0.52	18.0	35.0	53.0	60.5
2	THD Site 12	85-100 pen (1963)	0.86	76.5	89.0	0.80	30.6	38.0	51.0	208.0
9	THD	AC-20 (1970)	1.56	174	111	1.44	24.0	16.7	85.0	148.0
Mexican No. 1		85 pen (1970)	1.30	360	277	1.08	46.0	42.5	85.0	300.0

Effect of UOP-256 on Asphalts Used in Texas Highway Department Maintenance Program for 1963

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 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. Seven sites received ratings from Excellent to Good after two years in service. 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 II. 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 earlier in this summary report. The $HI(X_2)$ values resulting from this test showed a range of 5.5 to 85.0 (65 average). See Column 6, Table II. Use of 1% UOP-256 in the six asphalts with unsatisfactory subjective ratings resulted in a range of $HI(X_2)$ values from 6.7 to 41.8 (average 27). See Column 7 of Table II.

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.

Future Work

Further work should include:

1. A search for additives that may be more effective and/or less expensive than those discussed in this report.

2. Small scale field tests using one percent UOP-256 in several different asphalts to determine how such blends will react under atmospheric and traffic conditions.

TABLE II

SUBJECTIVE RATINGS OF PAVEMENT SURFACES AND HI(X_1) OF ASPHALTS EXTRACTED AFTER 2 YEARS IN SERVICE COMPARED WITH HI(X_2) WITH AND WITHOUT ADDITION OF UOP-256 HARDNESS INHIBITOR

Asphalt No.	THD Site No.	Percent Decrease in Pen @ 77° After 2 Years in 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.

3. Use 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.

The published version of this report may be obtained by addressing your request as follows:

R. L. Lewis, Chairman
Research & Development Committee
Texas Highway Department—File D-8
11th and Brazos
Austin, Texas 78701
(Phone 512-475-2971)