COMPOSITIONAL CONSIDERATIONS OF ASPHALT
FOR DURABILITY IMPROVEMENT

Rowan J. Peters, Arizona Department of Transportation

An investigation was performed to determine whether a laboratory procedure could be established that could provide a means to distinguish the durability (aging) qualities of asphalts when both their chemical and physical characteristics are considered. The investigation was also aimed at developing the means for predicting the effects on viscosity or an aging index of the interblending of various sources of asphalt. The investigation compared the effects on viscosity and aging indexes among asphalts, asphalt blends, and asphalt-additive blends. The research indicated that (a) asphalts can be blended to achieve practically any desired viscosity or aging index or combination of both, (b) Gilsonite in small quantities can be added to asphalt to achieve a desired viscosity without a subsequent loss of durability, (c) the chemical reactivity ratio can predict which base stock asphalts will age the fastest, and (d) the second acidaffin fraction appears to be the most important fraction for the improvement of durability (aging) and is available in commercial products or in selected asphalts for blending.

•IN ARIZONA, two problem areas, asphalt-aggregate adhesion and asphalt durability, have needed investigation. The Arizona Department of Transportation has expended considerable construction and maintenance funds on additive treatments to overcome potential adhesion problems and on asphalt rejuvenating agents to restore asphalt durability to roadway surfaces.

The problems are influenced by many factors such as asphalt characteristics, aggregate properties, mix design, environment, construction practices, and traffic loadings.

An investigation was initiated to consider the possibility of optimizing the composition of asphalt by blending known asphalt supplies.

The methods of evaluation are discussed, and the control method under consideration, i.e., that of possibly improving the durability of asphalt by compositional blending, is explored.

This study of asphalt durability was limited to the laboratory. Field evaluations of durability that do not rely on visual comparison or measurement systems independent of pavement sample recovery methods are subject to inherent weaknesses. To study asphalt aging in the field through use of recovered pavement sections or cores requires that the asphalt be totally recovered because selective absorption of asphalts with various aggregates has a surprisingly strong effect. The lighter volatile fractions that remain in the aggregate by selective absorption greatly influence subsequent testing. A very small quantity of these lighter fractions will considerably affect viscosity, penetration, and resulting chemical fractions.

Work conducted at Pennsylvania State University (1) indicated that the study of pavement durability is difficult because its effects are overshadowed by design considerations and actual air voids, aggregate types, and average daily traffic volumes. Also, in evaluation of asphalt performance, the pavements being compared must be sampled at the same time of year.

Work by Vallerga and Halstead (2) indicated similar problems in correlating pavement distress with original or present asphalt properties, and they recommend that experiments to establish causes of pavement distress be better controlled and have as few variables as possible.

The differences between laboratory and field evaluations must be considered in the

development of any field experiment. The differences exist because of the intrinsic nature of research, i.e., the environment is beyond control. Construction variables exist within and between test and control areas. The ability to establish two identical areas for study of one variable is indeed questionable. The problems in sample recovery have already been discussed.

The state of the art of predicting or measuring the durability of asphalt cements has not developed to the point where there are realistic and meaningful tests and specifications that relate to any form of field performance. The California Division of Highways developed a procedure in 1959 that applies heat and air aging to a rolling thin film of asphalt. The rolling thin film oven (RTFO) test was intended to predict the effects of hot-mix aging of asphalts. The original intent was to correlate the aging effects with actual asphalt plant aging. Subsequent work showed little correlation between the RTFO results and field aging; the RTFO test has been modified and is currently used only as a means to grade asphalt cements by viscosity.

The rolling microfilm circulating (RMFC) laboratory procedure reported by Schmidt (3) was designed around the modified RTFO. It was designed to relate laboratory and field predictions for durability, but a considerable amount of correlation work is needed before the procedure can be considered as a testing and specification tool.

Therefore, based on the problems of establishing uniform field experiments and because there are no laboratory-field correlated testing procedures, this durability study was limited to a laboratory evaluation based on ASTM procedure D 2872. Although this study was intended to be a relative comparison of the differences among asphalts, asphalt blends, and asphalt-additive blends and not an absolute quantity subject to field correlations, we feel a noteworthy observation and review can be made.

DEVELOPMENT OF A QUICKER ROSTLER PROCEDURE

Before asphalts and asphalt blends were tested for durability in the rolling thin film oven (ASTM D 2872), a chemical method of asphalt fraction analysis devised by Rostler and Sternberg (4) and modified for operational simplicity was established. Previous asphalt analyses resulted in problems with the standard Rostler procedure because the normal analysis required 50 hours and because less than a complete chemical analysis was found to be adequate.

The 50-hour procedure is necessary for complete chemical separation. The asphalt is separated into six fractions, five of which are based on chemical reactivity and one on solubility (5, 6, 7). If the asphaltene (A) fraction and the chemical reactivity ratio (CRR) are of primary interest, then the A fraction is precipitated with normal pentane and the remainder is treated with 98 percent sulfuric acid. Since this leaves the second acidaffin (A_2) and paraffin (P) fractions, one can then determine the CRR by the difference.

By using the modified procedure (Figure 1), a complete analysis can be performed in 8 hours or less. Because fuming sulfuric acid is not needed in the modified procedure, the analysis is safer and can be performed by laboratory personnel with a minimum of training. As with the standard analysis, the normal practice of six simultaneous analyses was continued. A comparison of the standard and modified procedures is given in Table 1.

ASPHALT BLENDING PROGRAM

Blends were produced by mixing a base stock asphalt with either base stock asphalt from a different source or an asphalt additive or both. Regional location descriptions of the base stock asphalts used are given in Table 2.

The table also indicates the Rostler separation for each base stock and additive. It was assumed that Rostler separations did not change significantly from sample to sample taken from the base stock (sealed can of asphalt). It was also assumed that, when one base stock was blended with another base stock or additive or both, no reaction occurred.

Figure 1. Modified Rostler-Sternberg analysis.
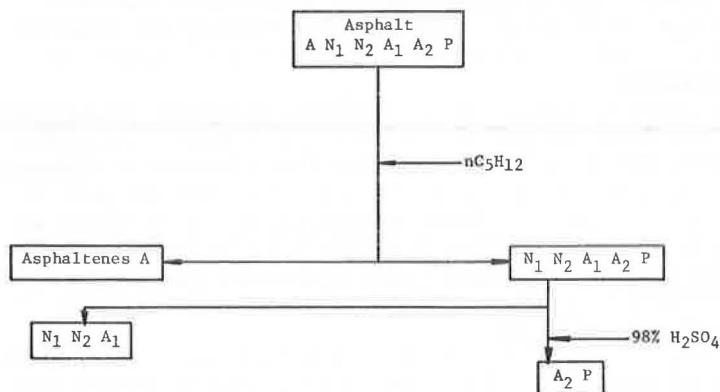
A	–	Asphaltenes	Insoluble in normal Pentane–Tech.
N_1	–	1st Nitrogen Bases	Precipitated by 98% Sulfuric Acid
N_2	–	2nd Nitrogen Bases	Precipitated by 98% Sulfuric Acid
A_1	–	1st Acidaffins	Precipitated by 98% Sulfuric Acid
A_2	–	2nd Acidaffins	Unreacted by 98% Sulfuric Acid
P	–	Paraffins	Unreacted by 98% Sulfuric Acid

Table 1. Comparison of results of standard Rostler and modified procedures.

Asphalt	Asphaltenes (percent)		Chemical Reactivity Ratio	
	Standard	Modified	Standard	Modified
85/100	19.7	19.6	1.18	1.27
60/70	19.9	19.6	1.80	1.81
85/100, unaged	21.9	21.9	2.07	2.00
85/100, 75 min[a]	23.7	23.6	2.22	2.19
85/100, 300 min[a]	29.0	29.0	1.90	1.86
60/70, unaged	25.9	25.4	1.75	1.74
60/70, 75 min[a]	27.2	27.0	1.78	1.68
60/70, 300 min[a]	35.1	35.1	1.56	1.49

[a]Time in rolling thin film oven at 325 F (163 C).

Table 2. Rostler fractions for asphalt base stocks and additives.

Base Stock	A	N	A_1	A_2	P	CRR	Description
Los Angeles basin 40/50	19.0	37.1	8.0	24.4	11.5	1.26	From crudes that have gravities of approximately 23.5 deg American Petroleum Institute (API) and yield about 40 percent residuum.
Los Angeles basin 85/100	18.5	33.7	13.7	22.3	11.8	1.39	From crudes that have gravities of approximately 23.5 deg API and yield about 40 percent residuum.
Four Corners 85/100	3.7	24.9	23.4	36.9	11.2	1.00	From crudes that can have gravities of more than 30 deg API and usually are low in residuum yield (below 30 percent).
Gilsonite	75.2	20.6	1.0	2.3	0.9	6.75	Using Sparkling Black Grade. Asphaltenes probably have a molecular weight of 10,000 to 14,000 when extracted with normal pentane.
Emulsified petroleum resin	0.6	32.3	16.2	34.8	12.9	1.01	Derived from extraction refining of lube oils. Very high in the A_2 fraction.
Santa Maria	29.2	32.6	9.4	20.8	8.0	1.46	From crudes that have gravities of approximately 15.0 deg API and yield about 60 percent residuum.

That is, each base stock contributed to each Rostler fraction as a function of weight.

After a blend was made, approximately 50 g of material was separated for an unaged microviscosity and 35 g of material for aging in the RTFO, and 50 g was saved for future reference.

Microviscosities of unaged and aged blend material were measured on a Hallikainen sliding plate microviscometer at a constant temperature of 77 F (25 C), which is the proposed ASTM procedure. Glass plates were typically used with unaged blends, except for those blends with viscosities of about 50 megapoises (5 MPa·s). For the very viscous blends, steel plates were used. For blend material aged 300 min in the RTFO, steel plates again were used to measure the microviscosity. For all cases, a sample of blended material was tested with successively lighter weights, which imposed smaller shear rates. Usually at least four shear rates were imposed on a sample. Based on the shear rates and shear stresses, the microviscosity was determined for a constant shear rate of 0.05 sec^{-1}. For each blend, calculated Rostler values and unaged and aged microviscosities were determined.

Discussion of Results

The following rule was adopted to describe the way various blends were formed: Whatever constituent increased the viscosity of the base stock or base blend was considered the constituent being added to the base. For example, when 6-megapoise (0.6-MPa·s) Los Angeles basin 40/50 was blended with 1-megapoise (0.1-MPa·s) Four Corners 85/100 equally by weight, the resulting viscosity was 4 megapoises (0.4 MPa·s). This blend would be described as 50 percent Los Angeles basin 40/50 added to Four Corners 85/100, since this addition raised the final viscosity above that of the Four Corners 85/100.

All blend data included the concentration in percent of one constituent added to the base, microviscosity of the unaged blends in megapoises, the blend aged 300 min in RTFO microviscosity in megapoises, and the aging index. A listing of all blend data and subsequent tables and figures are available in the project final report (8).

After examination of the blend data, it appeared that the relationship of viscosity to concentration of "added to" constituent was a straight line on semilogarithmic paper; i.e., log Y = A + B (X), where X is the added to concentration and Y is viscosity (Figure 2). Also the theoretical aging index line, arrived at by dividing a value from the 300-min aged fitted straight line by the unaged straight line value at a constant added to concentration, became a measure of the convergence or divergence of the fitted straight lines found. The greater the divergence of the two lines was, the faster the material aged and vice versa. Figure 3 shows an example of a theoretical aging index line and the actual aging index values.

Review of the aging effects of the Four Corners crude (Figures 4 through 8) indicates that there must be a reason for the lower rates of aging for this crude source. From the listing of the Rostler fractions given in Table 2, the chemical nature of the Four Corners crude appears to be significantly different from that of the other crudes listed. The most noticeable differences are the low asphaltene content and comparatively high second acidaffin fraction. The Four Corners crude compares closest to that of the emulsified petroleum resin except for the nitrogen base (N) and A_1 fractions. However, the N and A_1 fraction contents of the emulsified petroleum resin are also similarly prevalent in the other crude sources. The factor common to both the emulsified petroleum resin and the Four Corners crude and the factor that is significantly different from all other crudes listed is the acidaffins and primarily the A_2. Since experience has indicated the rejuvenating effects of the emulsified petroleum resins and the apparent aging benefits of the Four Corners crude are borne out in the RTFO evaluation, it would appear that the one common factor affecting durability (aging) must then be the second acidaffins.

Figure 2. Aging index versus percentage of L. A. basin by weight added to Four Corners.
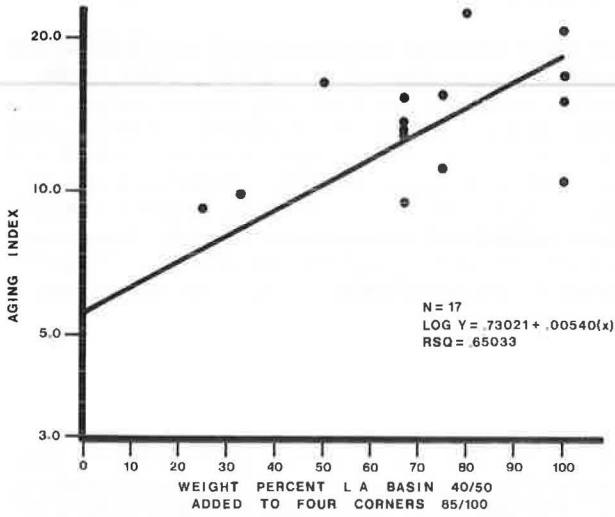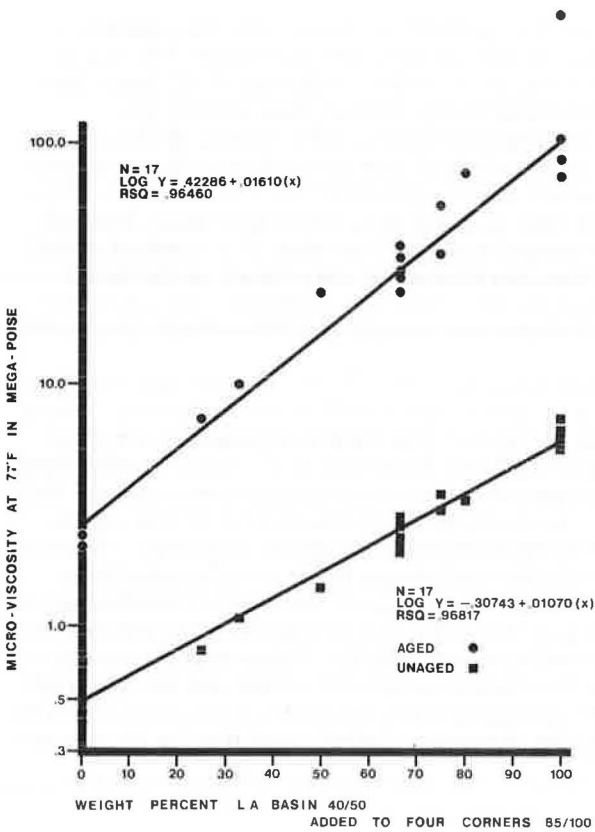

Figure 3. Microviscosity versus percentage of L. A. basin by weight added to Four Corners.

Extended Time Study

Additional information on aging was determined by subjecting selected asphalts to increasing times in the RTFO. The asphalts were removed from the RTFO at 75-, 180-, 240-, and 300-min intervals. Microviscosities were measured at 77 F (25 C), and modified Rostler tests were then performed (Table 3).

A plot of time in the RTFO versus the resulting microviscosity is shown in Figure 4. Also a plot of time in the RTFO versus aging index is shown in Figure 5. The slope of the lines formed from both Figures 4 and 5 is given in Table 4.

The viscosity and aging index increased with time in the RTFO (up to 300 min) as a function of $\log Y = A + B (X)$, where X is time in the oven and Y is viscosity. The function was a straight line on semilogarithmic paper. The CRR gave a good prediction of which asphalt would age the fastest.

The Los Angeles basin 85/100 and the Four Corners 85/100 were then aged in the RTFO at 1.25-, 5-, 16-, and 24-hour intervals. Figure 6 shows the curves for the two asphalts and the resultant aging index relationship of $\log Y = A + B (X)^{0.50}$. It appears that, in the 0 to 300-min range of aging, a straight line approximation is satisfactory and further confirms previous data analysis. An attempt to study the effects of extended aging times on a blend of two asphalts with similar unaged viscosities resulted in the findings shown in Figure 7. Apparently as greater quantities of the faster aging asphalt (pure A) are added to the slower aging asphalt (pure B), the aging index increases as does the viscosity of initial blends. A design viscosity and aging index apparently could be determined for any given series of asphalt blends if desired.

Effects of Gilsonite on Aging

Figure 8 shows the results of blending a slow aging asphalt (pure A) with Gilsonite. For this theoretical treatment, the unaged viscosity of Gilsonite was hypothesized to be 9,000 megapoises (900 MPa·s) inasmuch as a means for directly determining its unaged viscosity at 77 F (25 C) was not available. Subsequent extrapolation of data, however, indicated this value to be conservatively low. The aging index was apparently lowered, and the unaged viscosity was greatly increased. Because the viscosity of Gilsonite is so high, it seems reasonable to expect small additions of Gilsonite (less than 10 percent by weight) to have little detectable influence on aging index although the increase in viscosity will be quite large.

Closing Comments

The physical or chemical properties that influence the rate of aging are probably different from asphalt to asphalt and also between environments. To understand these physical and chemical properties requires that the crude oil source and what processing the crude oil was exposed to (refining process) be known and that the various compounds in the asphalt (composition, size, molecular weight) be investigated thoroughly.

The relationship between durability and its importance to asphalt mixture design needs to be established. Asphalt blends that improve durability may be needed for specific uses, such as surface treatments, whereas the larger volume usage such as in deep lift construction may not need this total refinement. The development of specifications for these controls will require knowledge and use of chemical control in the future. Because of the growing safety interests for more open-graded mixtures for surface courses, asphalts need to be chemically designed for totally different environments than currently considered, i.e., dense graded, low void designs.

In an attempt to define the properties eventually needed, the Arizona Department of Transportation is conducting studies to determine the effects of natural environmental aging on various blends produced under this program. An experimental feature was also added to a construction project in 1972 wherein a blend was made and used as the binder for a seal coat. Discussions of these projects should be forthcoming.
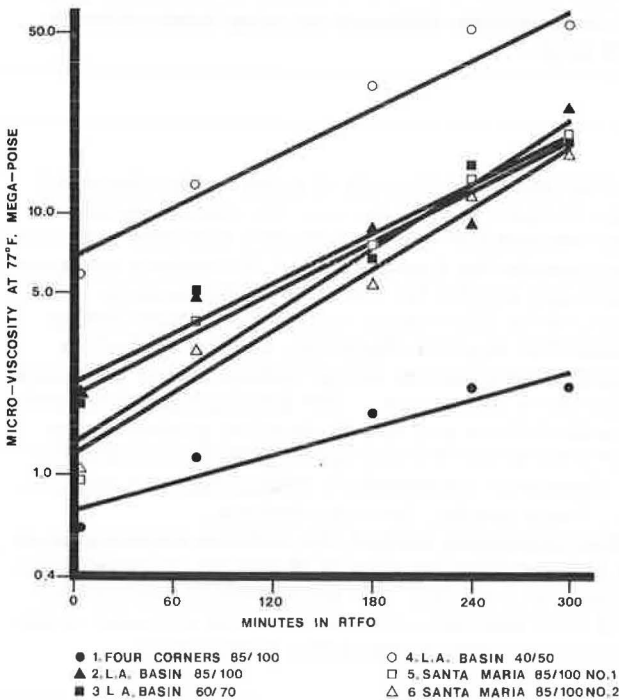
Table 3. Properties of asphalts aged in RTFO.

Type	Time in RTFO (min)	Viscosity at 77 F (megapoises)	A	N + A₁	A₂ + P	CRR	Aging Index[a]
Los Angeles basin 85/100	0	2.08	13.68	47.09	39.24	1.20	1.0
	75	4.43	18.75	44.16	37.08		2.1
	180	8.54	23.31	47.29	26.76		4.1
	240	9.59	25.96	49.00	27.69		4.6
	300	23.50	26.73	44.05	29.22		11.3
Los Angeles basin 40/50	0	5.83	25.13	47.95	26.91	1.78	1.0
	75	12.80	27.90	45.30	26.80		2.2
	180	31.50	32.47	42.20	25.33		5.4
	240	50.80	32.09	39.19	28.72		8.7
	300	52.60	37.10	38.02	24.87		9.0
Los Angeles basin 60/70	0	1.90	18.43	50.55	31.01	1.63	1.0
	75	4.18	21.72	50.14	28.14		2.2
	180	6.55	27.20	43.53	29.28		3.4
	240	14.70	28.89	41.08	30.03		7.7
	300	18.70	29.16	46.27	24.67		9.8
Four Corners 85/100	0	0.61	8.58	47.32	44.10	1.07	1.0
	75	1.10	10.76	45.96	43.28		1.3
	180	1.69	11.59	46.42	41.99		2.1
	240	2.20	12.53	46.17	41.29		3.6
	300	2.10	13.48	44.87	41.65		3.5
Santa Maria 85/100 (No. 1)	0	0.94	29.42	47.17	23.41	2.01	1.0
	75	3.78	31.55	44.03	24.42		4.0
	180	7.72	36.95	41.42	21.62		8.1
	240	13.10	39.95	39.23	20.83		13.9
	300	18.90	42.14	37.34	20.52		20.0
Santa Maria 85/100 (No. 2)	0	1.03	26.39	47.43	26.19	1.81	1.0
	75	2.90	29.14	45.17	25.69		2.8
	180	5.14	30.46	44.70	24.83		5.0
	240	11.90	33.01	41.74	25.25		11.6
	300	17.20	37.00	38.29	24.72		16.7

Note: 1 F = 1.8 C + 32; 1 megapoise = 0.1 MPa·s.

[a] $\dfrac{\text{Viscosity of aged asphalt}}{\text{Viscosity of unaged asphalt}}$

Figure 4. Microviscosity versus time in RTFO for various crude sources.

● 1. FOUR CORNERS 85/100   ○ 4. L.A. BASIN 40/50
▲ 2. L.A. BASIN 85/100   □ 5. SANTA MARIA 85/100 NO.1
■ 3 L.A. BASIN 60/70   △ 6 SANTA MARIA 85/100 NO.2

Figure 5. Aging index versus time in RTFO for various crude sources.

- 1. FOUR CORNERS 85/100 ●
- 2. LA BASIN 85/100 ▲
- 3. LA BASIN 60/70 ■
- 4. LA BASIN 40/50 ○
- 5. SANTA MARIA 85/100 NO. 1 □
- 6. SANTA MARIA 85/100 NO. 2 △
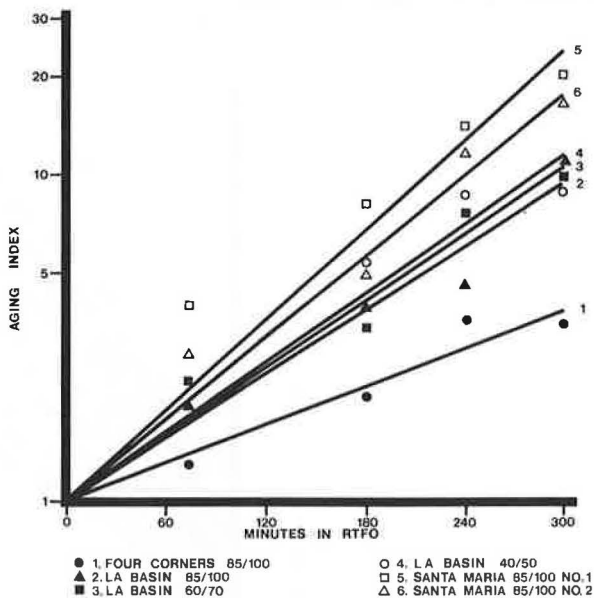
Table 4. Rate of aging of various asphalts.

Type	Viscosity/Time[a]	Aging Index/Time[b]	CRR
Four Corners 85/100	0.00423	0.00464	1.07
Los Angeles basin 85/100	0.00731	0.00733	1.20
Los Angeles basin 60/70	0.00758	0.00756	1.63
Los Angeles basin 40/50	0.00723	0.00769	1.78
Santa Maria 85/100 (No. 1)	0.00917	0.00919	1.81
Santa Maria 85/100 (No. 2)	0.00954	0.00953	2.01

[a]From Figure 3. [b]From Figure 4.

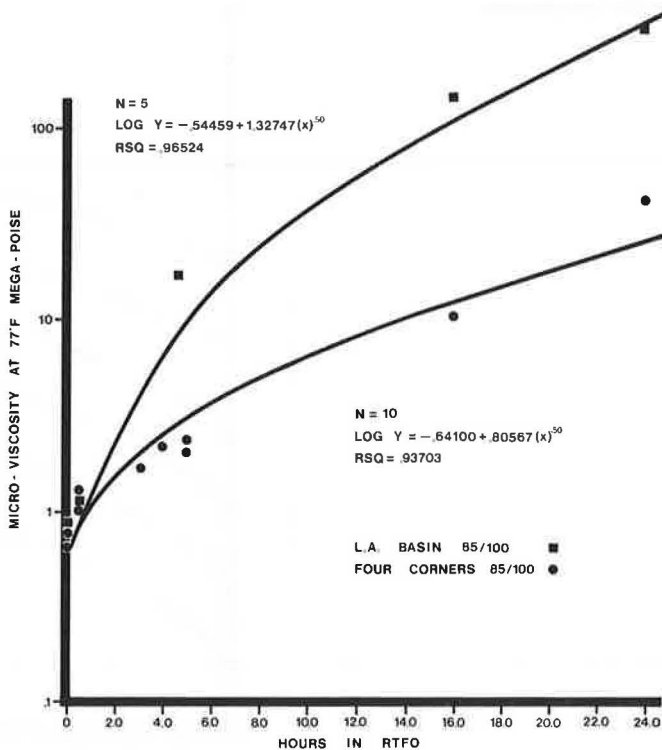**Figure 6. Microviscosity versus time in RTFO for slow and fast aging asphalts.**

$N = 5$
$LOG\ Y = -.54459 + 1.32747\,(x)^{.50}$
$RSQ = .96524$

$N = 10$
$LOG\ Y = -.64100 + .80567\,(x)^{.50}$
$RSQ = .93703$

L.A. BASIN 85/100 ■
FOUR CORNERS 85/100 ●

Figure 7. Effect of aging on blend of two asphalts.

A.I.= 20.0
100%
A.I.= 16.7
90%
80%
A.I.= 14.9
A.I.= 12.9
70%
A.I.= 11.2
60%
A.I.= 9.8
50%
A.I.= 8.4
40%
A.I.= 7.·
30%
A.I.= 6.4
20%
A.I.= 5.7
10%
A.I.= 5.0
0%

PURE A

PURE B

A = FAST AGING ASPHALT
B = SLOW AGING ASPHALT

MICRO - VISCOSITY AT 77°F MEGA - POISE

HOURS IN °RTFO
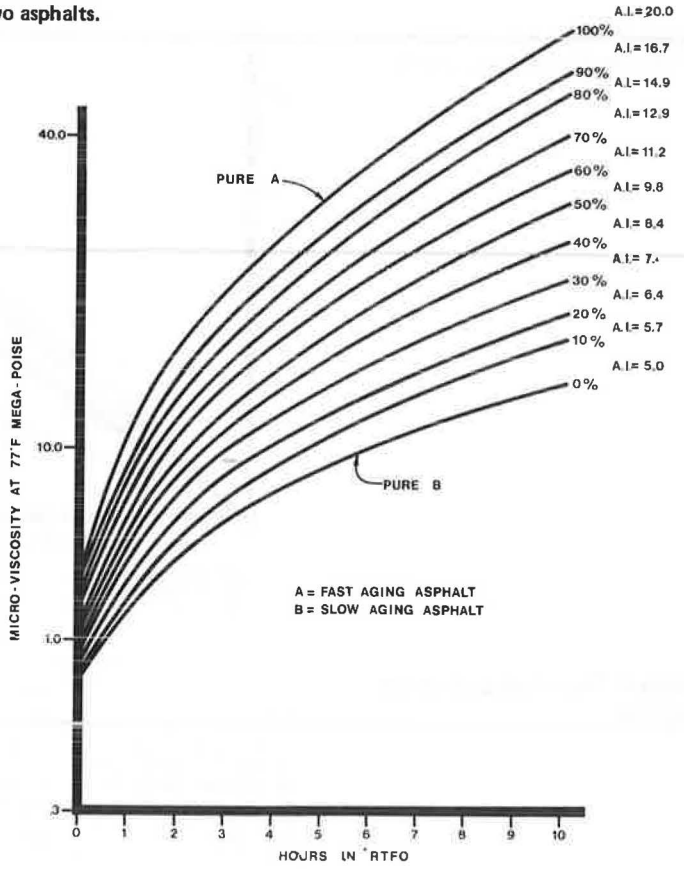
Figure 8. Effect of Gilsonite added to a slow aging asphalt.

10,000 +   (GILSONITE)

A.I. = 2.3   50%
GILSONITE

A.I. = 2.6   40%
GILSONITE

A.I. = 3.2   30%
GILSONITE

A.I. = 3.7   20%
GILSONITE

A.I. = 4.3   10%
GILSONITE

A.I. = 5.0   0%

PURE A

MICRO - VISCOSITY AT 77° MEGAPOISE

HOURS IN RTFO
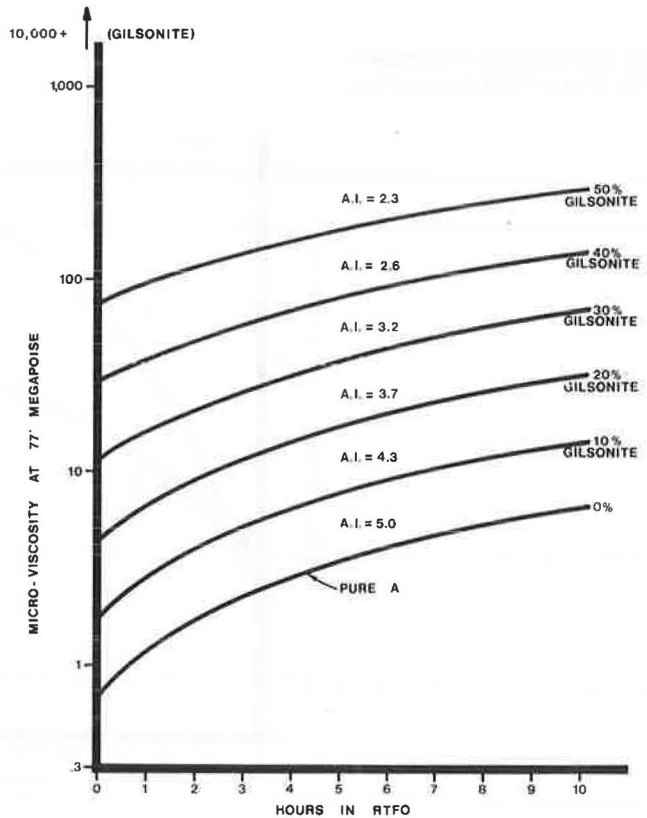
CONCLUSIONS

1. Asphalt ages in the RTFO for times longer than 5 hours by the function, $\log Y = A + B (X)^{0.50}$, where Y is viscosity and X is time in hours.

2. Asphalt ages in the RTFO for times less than 5 hours by the function, $\log Y = A + B (X)$, where Y is viscosity and X is time in hours.

3. The chemical reactivity ratio can predict which base stock asphalts will age the fastest.

4. Asphalts can be blended together to achieve practically any desirable viscosity or aging index or combination of both. The function describing the blending process is $\log Y = A + B (X)$, where Y is either viscosity or aging index and X is the concentration of the added to constituent.

5. If the difference between the unaged viscosity of two asphalts is smaller than the difference between the aged viscosities (5 hours in the RTFO or more) of the same asphalts, the aging index will increase with increasing viscosity of any blends of the two asphalts. Likewise, if the original difference in viscosity is greater than the aged difference in viscosity, the aging index will decrease with increasing viscosity of any blends of the two asphalts.

6. Gilsonite can be added to asphalt to achieve desired viscosity level without a subsequent loss in aging properties.

7. The second acidaffin fraction is the most important fraction for the improvement of durability (aging) and is available in commercial products and in selected asphalts for blending.

ACKNOWLEDGMENTS

REFERENCES

1. W. H. Gotolski et al. A Study of Physical Factors Affecting the Durability of Asphalt Pavements. Pennsylvania State Univ., Research Rept. IR-9, Sept. 1968.
2. B. Vallerga and W. Halstead. Effects of Field Aging on Fundamental Properties of Paving Asphalts. Highway Research Record 361, 1971.
3. R. J. Schmidt. Laboratory Measurement of the Durability of Paving Asphalts. Presented at ASTM meeting, Los Angeles, June 1972.
4. F. S. Rostler and H. W. Sternberg. Compounding Rubber With Petroleum Products. Industrial and Engineering Chemistry, Vol. 41, March 1949, pp. 598-608.
5. F. S. Rostler and R. M. White. Chemical Nature of Oil Extenders for Synthetic Rubbers. Industrial and Engineering Chemistry, Vol. 46, March 1954, pp. 610-620.
6. F. S. Rostler and R. M. White. Composition and Changes in Composition of Highway Asphalts, 85/100 Grade. Proc., AAPT, Vol. 31, 1962.
7. R. M. White, W. R. Mitten, and J. B. Skog. Fractional Components of Asphalts Compatibility and Interchangeability of Fractions Produced From Different Asphalts. Proc., AAPT, Vol. 39, 1970, pp. 492-531.
8. R. J. Peters. Asphalt Cement Durability and Aggregate Interaction. Research Division, Arizona Department of Transportation, Rept. 4.