

Interrelationship Between Performance-Related Properties of Asphalt Cement and Their Correlation with Molecular Size Distribution

S. W. BISHARA, R. L. McREYNOLDS, AND E. R. LEWIS

Rheological parameters, Corbett analysis, colloidal instability, and molecular size distribution (MSD) were applied to investigate relationships between several physicochemical parameters. Emphasis is on the correlation between MSD and viscosity at 60°C, viscosity at 135°C, viscosity ratio at 60°C (after and before thin film oven test), penetration at 25°C, viscosity-temperature susceptibility (VTS), penetration-viscosity number (PVN) at 60°C and 135°C, colloidal instability (I_c), and asphaltene content. The MSD was obtained using a semipreparative column and a gravimetric finish. The 20 virgin asphalts studied cover a wide viscosity range and were supplied over 7 years by 14 refineries. Virgin asphalts were laboratory-aged; field cores for seven were extracted. For virgin asphalts, viscosity at 60°C correlates strongly with each of viscosity at 135°C and penetration at 25°C. The MSD showed a strong correlation with viscosity at 135°C, PVN at 135°C, VTS, I_c , and asphaltene content, and a weak correlation with viscosity ratio. The direction (sign) of association demonstrates that a high PVN and a low VTS (i.e., low temperature susceptibility), a low viscosity ratio (i.e., high resistance to aging), a low I_c , and a low asphaltene content are all favored by high large molecular size (LMS), low medium molecular size (MMS), and low small molecular size percentages. Asphalts with high LMS/MMS ratios demonstrated common parameters.

The current methods used routinely to specify and characterize asphalts can no longer monitor asphalt chemical composition. It is possible to have asphalts with the same viscosity grading and similar physical test results but with very different performance in a pavement (1, p. 17; 2, p. 277; 3).

Evidence indicates that chemical or compositional factors have a major impact on performance of asphalt. The use of high-performance gel permeation chromatography (HPGPC) to study other physicochemical parameters such as molecular size distribution (MSD) has been recommended (3-9). The technique allows differentiation among asphalts of the same grade but different composition.

Garrick and Wood (5), working on asphalts of varying chemical composition (e.g., resins, oils, asphaltenes) but derived from the same crude and refinery process, have found that temperature susceptibility is relatively insensitive to chemical composition. They conclude that asphalts of different chemical composition can have similar rheological properties. They report a high correlation between MSD and viscosity at 60°C, MSD and viscosity at 135°C, and MSD and

penetration, but they wonder whether the relationships can be applied to asphalts from different sources. Other investigators (4,10) have also reported the possibility of asphalt cements with the same specifications but substantially different chemical compositions.

Price and Burati (3) present a quantitative HPGPC method to predict laboratory results of asphalt cement. They used samples collected monthly over a 7-month period from four suppliers; the asphalts were from different crude oil sources but belonged to the same viscosity grade, AC-20. It is not clear what type of detector was used to develop the HPGPC profiles.

The majority of investigations have used analytical, ultra-styragel columns (300 mm × 7.8 mm) in conjunction with either ultraviolet (UV) or refractive index (RI) detection to generate MSD profiles. Tetrahydrofuran (THF) seems to be the mobile phase (and solvent) of choice, even though toluene has been used (8). Recently, a semipreparative, phenogel column (300 mm × 22.5 mm)—as part of an HPGPC system—was used to fractionate asphalt cement samples into five fractions that were collected and weighed to give an exact measure of the amount of asphalt material eluting from a column over a given period of time (10,11).

In this study, 20 virgin asphalt samples (asphalt material that has not been used for paving and does not contain recycled asphalt), covering a wide viscosity range of 500 to 2,200 poises and collected over 7 years from 14 different refineries and crude sources, were analyzed for their MSD using a gravimetric finish. The virgin asphalts were laboratory-aged by a 16-hr thinfilm oven test (TFOT) and the residue treated similarly for MSD. Cores from field projects were obtained for 7 out of the 20 asphalts, and, after extraction following ASTM D1856-79, the asphalts were analyzed for MSD. The physical properties of the virgin, laboratory-aged, and field-aged asphalts were measured by the materials testing unit of the Kansas Department of Transportation.

EXPERIMENTAL METHODS

Apparatus

A Waters HPGPC system was used. This consisted of a solvent delivery system, a U6K injector, a Digital Equipment

Corporation computer, a printer, and a Waters system interface module. A Phenomenex, 5 μm , 500 \AA phenogel semi-preparative column (300 mm \times 22.5 mm) with THF as solvent was used.

Procedure

An asphalt sample was weighed accurately (to within 0.01 mg) in the range of 2.0 to 2.5 g. About 25 mL of THF was added before sonifying for 15 min at room temperature. The sample was then transferred quantitatively to a 50-mL volumetric flask, and the flask was filled to volume with THF. The solution was then filtered through a 0.2 μm membrane.

An exact aliquot (100–200 μL) chosen to contain 6 to 7 mg of the asphalt material was then injected. A mobile phase, composed of 95 percent THF and 5 percent pyridine at a flow rate of 6.0 mL/min, was used. The phenogel column was maintained at ambient temperature. The eluting material was collected in a series of five small, glass, accurately weighed (to within 0.01 mg) petri dishes at 4.5 to 7.5, 7.5 to 8.5, 8.5 to 9.5, 9.5 to 11, and 11 to 14 min from injection. The petri dishes were then set aside to allow the solvent to evaporate.

Under exactly the same conditions, the injection was repeated using an aliquot equal to that used before. Fractions were collected in corresponding petri dishes from the previous injection. This repeated injection was done to have fraction weights compatible with the balance available at the time of study. The petri dishes were set aside until dry, then heated in an oven at 160°C for 90 min. The dishes were then cooled in a desiccator until constant weight was attained. For more details, see Bishara and McReynolds (11).

DISCUSSION OF RESULTS

Rheological Parameters

Asphalts with high temperature susceptibility may contribute to rutting at high temperatures and cracking at low temperatures. Temperature susceptibility can be evaluated by penetration ratio, penetration index, penetration-viscosity number (PVN) based on viscosity at 60°C or at 135°C, and viscosity-temperature susceptibility (VTS). However, it has recently been reported (12) that penetration of some asphalts can be significantly affected by routine handling, for example storage and reheating. It is therefore believed that PVN and VTS would provide a better measure of temperature susceptibility. A high PVN and a low VTS indicate minimum susceptibility.

The rheological properties of 20 virgin asphalts are given in Table 1. The VTS was calculated using the formula reported by Glover et al. (6). Resistance to aging may be expressed by viscosity ratio (viscosity at 60°C after and before TFOT).

Asphalt performance is thought to be primarily related to temperature susceptibility and resistance to aging; the two characteristics are indirectly specified in ASTM D3381 and AASHTO M226. Figures 1 and 2 plot the two characteristics expressed as PVN (at 135°C, Figure 1, and at 60°C, Figure 2) versus viscosity ratio. The best-performing asphalts are those with low temperature susceptibility (high PVN) and high

resistance to aging (low viscosity ratio). Therefore, points at the upper left corner of Figures 1 and 2 represent asphalts with desirable properties (9). It is shown that the majority (about 75 percent) of the 20 asphalts fall in the upper left corners of the two figures.

Table 1 reveals that PVN at 135°C, changes over a relatively wide range (–0.07 to –1.18) compared with that (–1.05 to –1.30) reported by Garrick and Wood (5), who used asphalts from the same source and refinery. Corbett and Schweyer (13) report a perfectly linear relationship between \log_{10} of absolute viscosity and \log_{10} of kinematic viscosity and between \log_{10} of absolute viscosity and \log_{10} of penetration for asphalt cements of varying consistency level but the same source. Garrick and Wood (5) report similar observations. Plotting \log_{10} of absolute viscosity versus \log_{10} of kinematic viscosity for the 20 asphalts used in this study (and obtained from different crude sources and refineries) revealed a correlation coefficient (r) of 0.67 (Figure 3). Because r is not resistant (14) (i.e., one entry can greatly change the value of r), the correlation coefficient was recalculated after excluding data corresponding to two asphalt cements obtained from one refinery (Diamond Shamrock). The value of r for the remaining 18 samples amounted to 0.87. Excluding the two points corresponding to Shamrock asphalts may be justified as follows: In 1988, Glover et al. (6) compared asphalts from six suppliers and reported that five of the six HPGPC profiles were quite similar; the profile of Shamrock asphalt demonstrated that it is composed, on average, of larger molecular size material. This was found to be also true for the two asphalts studied, and it will be discussed later under HPGPC analysis. Glover et al. further noted that Shamrock asphalt is different in other characteristics as well, which makes it a unique and interesting asphalt for further study. The present work confirms this observation.

A plot of \log_{10} absolute viscosity versus \log_{10} penetration at 25°C for the 20 asphalts under investigation (Figure 4) has a correlation coefficient of –0.81. Contrary to Figure 3, excluding the two Shamrock asphalts produced a small and adverse effect on r , causing it to drop to –0.79, that is, farther from the perfect correlation of –1.0 (14). It is therefore evident that the absolute viscosity-penetration plot could not detect the two unique asphalts that were shown to be different from the rest by the absolute viscosity-kinematic viscosity plot (as well as HPGPC analysis discussed later). The distinctly higher proportion of large molecular size components of the 2 unique asphalts, as opposed to the other 18, may have caused kinematic viscosity to be relatively higher than would be expected, thus forcing the two data points away from the linear relationship (Figure 3). The predominance of large molecular size components, however, does not appear to have a parallel effect on absolute viscosity or penetration. It may be that prior existence of a high percentage of large molecules, being predominantly polar, enhances the tendency toward formation of even larger viscosity-building molecules that contribute positively to the viscosity value when measured at high temperature (135°C).

Data in Table 1 reveal that the two Shamrock asphalts (88-2570 and 88-2787) are characterized by the lowest VTS and the highest PVN at 135°C (i.e., low temperature susceptibility), as well as a low viscosity ratio (i.e., high resistance to aging). Because their absolute viscosities and penetration at

TABLE 1 PHYSICAL PROPERTIES OF 20 VIRGIN ASPHALTS

* Sample	Pen 25°C, mm	Vis. 60°C, poises	Vis. 60°C (after TFOT) poises	Vis. Ratio	Vis. 135°C, cst	VTS	** PVN 60°C	*** PVN 135°C
82-1214	93	1678	3966	2.36	416	3.454	-0.33	-0.25
1332	79	1141	3056	2.68	271	3.659	-0.99	-1.06
1522	85	1727	5051	2.93	398	3.500	-0.45	-0.42
2746	87	1204	2765	2.29	305	3.579	-0.79	-0.81
83-3203	65	2149	6335	2.95	395	3.591	-0.64	-0.71
3284	99	1464	3530	2.41	369	3.500	-0.37	-0.36
85-1230	85	1311	3253	2.48	359	3.454	-0.74	-0.57
3695	94	1408	3693	2.62	352	3.522	-0.50	-0.49
3890	94	858	1822	2.12	248	3.614	-1.03	-1.02
4116	96	1368	3844	2.81	321	3.591	-0.50	-0.60
86-3063	93	1353	3960	2.93	360	3.489	-0.56	-0.47
3113	96	1265	5127	4.05	326	3.545	-0.58	-0.58
87-2040	94	881	2361	2.68	223	3.727	-1.00	-1.18
88-2381	85	1275	1435	1.12	307	3.591	-0.77	-0.78
2192	162	501	1248	2.49	233	3.432	-0.74	-0.51
2483	119	979	3214	3.28	301	3.492	-0.51	-0.46
2570	130	707	1386	1.96	360	3.204	-0.72	-0.07
2787	93	1123	2483	2.21	450	3.216	-0.76	-0.13
3680	105	1090	2295	2.10	343	3.432	-0.60	-0.40
3719	103	994	2589	2.60	283	3.557	-0.73	-0.72

*The first two digits refer to the year sample was received.

$$**PVN, 60^{\circ}C = \frac{-1.5(6.489 - 1.59 \log_{10} Pen_{25^{\circ}C} - \log_{10} \eta_{60^{\circ}C})}{1.05 - 0.2234 \log_{10} Pen_{25^{\circ}C}} \quad \text{Ref. (21)}$$

$$***PVN, 135^{\circ}C = \frac{-1.5(4.258 - 0.79674 \log_{10} Pen_{25^{\circ}C} - \log_{10} \eta_{135^{\circ}C})}{0.795 - 0.1858 \log_{10} Pen_{25^{\circ}C}} \quad \text{Ref. (5)}$$

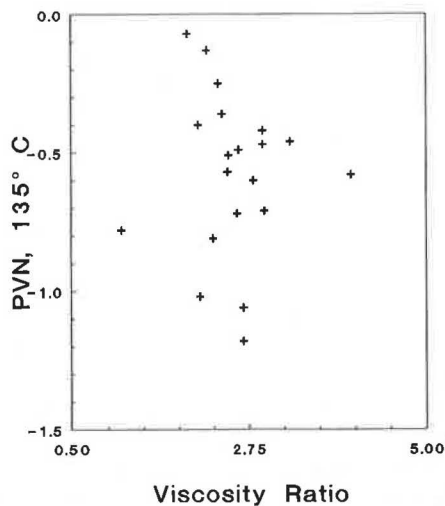


FIGURE 1 PVN at 135°C versus viscosity ratio.

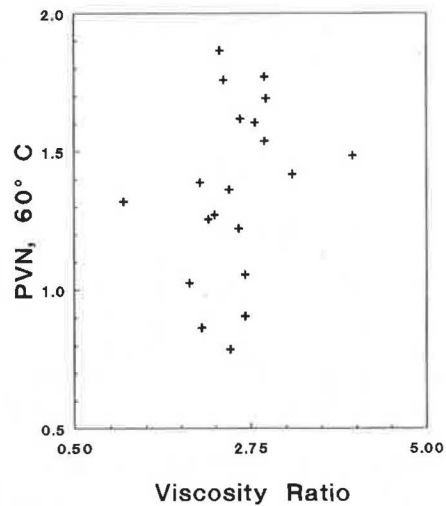


FIGURE 2 PVN at 60°C versus viscosity ratio.

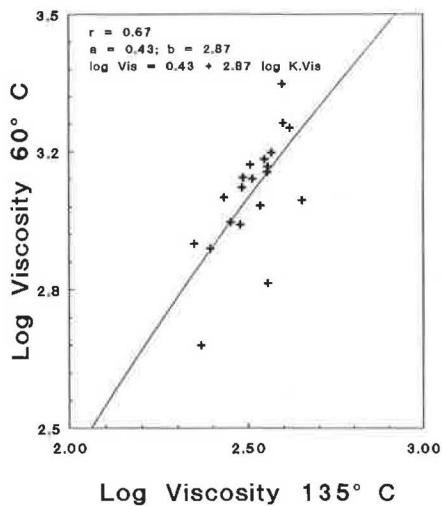


FIGURE 3 Absolute viscosity versus kinematic viscosity.

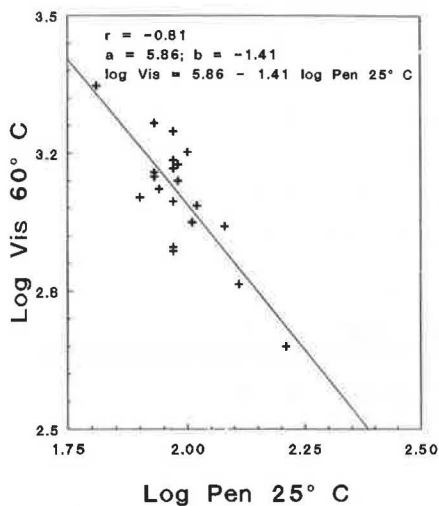


FIGURE 4 Absolute viscosity versus penetration at 25°C.

25°C are more or less concordant with those of the rest, their PVNs at 60°C are well within the range of variation of the whole set.

Effect of Aging on Rheological Properties

Table 2 presents the physical properties of the 20 asphalts after a 16-hr TFOT. Comparing Tables 1 and 2 reveals that laboratory aging causes penetration to decrease and causes absolute viscosity, kinematic viscosity, VTS, PVN at 60°C, and PVN at 135°C to increase. The only exception was one of the two Shamrock asphalts (88-2787), whose PVN at 135°C decreased; the other Shamrock sample showed practically no change.

Cores from seven field projects were treated according to ASTM D1856-79. The physical properties of extracted asphalts are given in Table 3. Generally, penetration decreased, whereas absolute viscosity, kinematic viscosity, VTS, PVN at

TABLE 2 PHYSICAL PROPERTIES OF VIRGIN ASPHALTS AFTER 16-hr TFOT

Sample	Pen 25°C, mm	Vis. 60°C, poises	Vis. 135°C, cst	VTS	PVN 60°C	PVN 135°C
82-1214	41	19456	1190	3.568	0.79	0.31
1332	22	11656	704	3.773	-0.58	-0.94
1522	30	56352	1270	3.875	1.27	0.66
2746	20	20456	910	3.773	-0.22	-0.71
83-3203	24	39750	1269	3.761	0.62	-0.15
3284	30	25203	1256	3.614	0.54	0.05
85-1230	23	12747	930	3.602	-0.44	-0.58
3695	30	22308	1035	3.716	0.43	-0.19
3890	24	11395	641	3.841	-0.48	-0.98
4116	27	35449	1180	3.773	0.69	-0.13
86-3063	38	47083	1230	3.841	1.50	0.27
3113	24	93751	1442	3.943	1.37	0.00
87-2040	30	17172	696	3.920	0.20	-0.68
88-2381	22	16711	889	3.727	-0.26	-0.66
2192	50	20657	798	3.875	1.18	-0.01
2483	30	70334	1593	3.784	1.47	0.35
2570	42	8251	879	3.489	0.02	-0.06
2787	35	10632	827	3.625	-0.02	-0.33
3680	40	12425	1024	3.523	0.33	0.08
3719	30	17600	914	3.727	0.22	-0.34

TABLE 3 PHYSICAL PROPERTIES OF ASPHALTS EXTRACTED FROM FIELD CORES

Sample*	Pen 25°C, mm	Vis. 60°C, poises	Vis. 135°C, cst	VTS	PVN 60°C	PVN 135°C
82-1332	34	3581	422	3.739	-1.06	-1.21
82-1522	37	21342	1029	3.704	0.72	0.01
85-4116	26	17518	979	3.670	0.01	-0.39
86-3063	44	8114	644	3.716	0.07	-0.43
87-2040	59	3018	441	3.636	-0.44	-1.04
88-2483	46	6719	613	3.682	-0.04	-0.07
88-3680	93	2416	432	3.568	0.06	-0.19

*The first two digits refer to the year sample was received.

60°C, and PVN at 135°C increased. Only one field sample (82-1332) had a lower PVN at 135°C as compared with that of corresponding virgin asphalt.

Data in Tables 2 and 3 confirm previous findings (4,9) that characteristics of asphalt after laboratory aging (short term, high temperature) may not necessarily reflect aging characteristics of asphalt in pavement (long term, low temperature). Exposing asphalt to a high temperature (as with a 16-hr TFOT) destroys steric hardening (15).

HPGPC Analysis

Evidence is growing about the potentialities of HPGPC as a tool to provide insight into a unique physicochemical parameter of asphalt—the MSD. HPGPC can distinguish between asphalts that belong to the same viscosity grade (3,6) and that have identical rheological properties (absolute viscosity, kinematic viscosity, and penetration) and temperature susceptibility (expressed by PVN). Garrick and Wood (5) report two AC-10 samples with a difference of less than 2 percent between their absolute viscosities, kinematic viscosities, PVN, and a difference of about 5 percent between their penetrations at 25°C. Comparison between MSD parameters revealed detectable differences between the two otherwise similar asphalts. In the present work, two samples provided from the same supplier yielded the results in Table 4. Rheological properties are not much different, but fraction percentages exhibit detectable differences, especially for the two major parts—large molecular size (LMS) and medium molecular size (MMS)—as well as the LMS/MMS ratio.

An advantage of using gravimetry to determine fraction proportion is the nonexistence of sources of error associated with UV and RI detectors. RI detectors are neither highly reproducible (16) nor sensitive, and RI varies with molecular weight. UV detectors suffer from undetectability of saturated oils as well as continuous variation of the molar absorptivity “constant” throughout the duration of analysis (10,11,16). Gravimetric analyses are known to be highly accurate and reproducible. The cutoff points were selected so that each of the five fractions contained approximately the same proportion of asphalt material. As mentioned before (11), the sample elutes over the period of 5 to 14 min after injection. Therefore, where appropriate, reference will be made to LMS, MMS, and small molecular size (SMS) to designate $F_1 + F_2$ (5.0 to 8.5 min), $F_3 + F_4$ (8.5 to 11.0 min), and F_5 (11.0 to 14.0 min), respectively. Table 5 shows the MSD of the 20 virgin asphalts. For the following correlations, the MSD data ($F_1, \%$, $F_2, \%$,

TABLE 4 COMPARISON OF TWO SAMPLES PROVIDED BY SAME REFINERY

Pen. 25°C	99	94
Vis. 60°C, poises	1464	1408
Vis. 135°C, cst	369	352
Tests on TFOT Residue		
Loss on heat, %	0.09	0.22
Pen. 25°C	63	64
Vis. 60°C, poises	3530	3693
Duct. 25°C	100+	100+
VIS	3.500	3.522
HPGPC Analysis*		
$F_1, \%$	18.3	15.4
$F_2, \%$	22.9	22.5
} LMS		} 41.2
$F_3, \%$	35.6	38.3
$F_4, \%$	16.2	16.0
} MMS		} 51.8
$F_5, \%$ -SMS	7.1	7.8
LMS/MMS	0.795	0.698

* F_1 denotes the largest molecular size components, F_5 the smallest.

TABLE 5 GPC DATA FOR 20 VIRGIN ASPHALTS USING GRAVIMETRIC FINISH

Sample	$F_1, \%$	$F_2, \%$	$F_3, \%$	$F_4, \%$	$F_5, \%$
82-1214	14.1	27.3	40.7	12.9	4.9
82-1332	11.0	22.9	42.3	18.3	5.5
82-1522	16.2	26.7	39.4	11.7	6.0
82-2746	14.5	28.1	36.5	12.9	4.9
83-3203	13.7	22.6	38.6	15.7	9.4
83-3284	18.3	22.9	35.6	16.2	7.1
85-1230	17.1	28.9	34.6	13.7	5.6
85-3695	15.4	22.5	38.3	16.0	7.8
85-3890	7.8	25.3	45.5	18.0	3.4
85-4116	15.9	23.6	37.1	18.6	4.8
86-3063	16.4	27.4	42.0	11.2	3.0
86-3113	13.8	25.0	40.7	13.7	6.8
87-2040	12.3	24.2	41.6	15.7	6.2
88-2381	12.6	25.5	36.3	14.6	11.0
88-2192	15.2	25.4	43.4	10.5	5.4
88-2483	14.3	24.8	39.2	15.4	6.4
88-2570	23.4	36.1	25.7	9.6	5.3
88-2787	26.3	35.3	25.1	8.2	5.2
88-3680	12.4	34.1	37.4	10.4	5.7
88-3719	12.6	21.2	39.5	17.8	8.9

. . .) are considered the independent variables, and the physical property investigated as the dependent variable.

Correlation Between MSD Data and PVN

No correlation exists between PVN at 60°C and the percentage of any of the separate fractions (F_1, F_2, \dots); for the composite LMS fraction, r amounted to only -0.01 .

On the other hand, PVN at 135°C correlates with each of the five fractions. The correlation is stronger if the collective fractions LMS and MMS are used (Table 6). Because good performance is to be expected from asphalts with low temperature susceptibility (high PVN), and because PVN is associated positively with LMS percentage, it follows that a high LMS proportion is desirable. This agrees with Enustun et al. (9), who recommend that the LMS percentage and its amount of change after a TFOT be included in the Iowa trial specification. The negative association of MMS and PVN at 135°C suggests a low MMS content for better performance; the same applies for SMS content. However, the fact that the SMS percentage for any of the 20 asphalts never exceeded 11 percent limits the significance of this fraction.

The MSDs of seven asphalts extracted from field cores are given in Table 7. A correlation exists between fraction percentage and PVN at 135°C (Table 8). The correlation has the same direction (sign) but differs in strength from that calculated for virgin asphalts (Table 6).

TABLE 6 CORRELATION COEFFICIENT (r) FOR MSD DATA AND SOME PHYSICAL PROPERTIES FOR 20 VIRGIN ASPHALTS

Fraction	PVN 135°C	Kine- matic Visc- osity, 135°C	Visc- osity ratio	Abs. Vis. 60°C	VTS	pen. 25°C
F ₁	0.59	0.64	-0.09	-0.02	-0.84	0.21
LMS*	0.76**	0.59	-0.26	-0.16	-0.91	0.24
F ₂	0.65	0.43	-0.36	-0.26	-0.80	0.22
F ₃	-0.49	-0.58	0.34	0.03	0.75	-0.04
MMS*	-0.73***	-0.61	0.32	0.09	0.87	-0.18
F ₄	-0.25	-0.46	0.17	0.15	0.78	-0.36
F ₅ or SMS	-0.19	-0.02	-0.19	0.29	0.27	-0.26

* LMS = F₁ + F₂; MMS = F₃ + F₄

** The correlation coefficient, r , for LMS and PVN, 135°C, ...etc.

*** The correlation coefficient, r , for MMS and PVN, 135°C, ...etc.

TABLE 7 MSD DATA FOR ASPHALTS EXTRACTED FROM FIELD CORES

	82- 1332	82- 1522	85- 4116	86- 3063	87- 2040	88- 2483	88- 3680
LMS	35.8	46.0	41.3	43.2	41.2	42.4	45.5
MMS	54.6	50.1	53.2	50.9	53.8	55.8	47.1
SMS	9.6	3.8	5.4	5.8	5.0	1.8	7.4

TABLE 8 CORRELATION COEFFICIENTS (r) FOR MSD DATA AND SOME PHYSICAL PROPERTIES FOR SEVEN FIELD-AGED ASPHALTS

Fraction	PVN 135°C	Kine- matic Visc- osity, 135°C	Abs. Vis., 60°C	VTS	pen., 25°C
LMS (F ₁ +F ₂)	0.84	0.04	0.37	-0.49	0.44
MMS (F ₃ +F ₄)	-0.43	-0.08	-0.10	0.53	-0.61
SMS (F ₅)	-0.64	-0.46	-0.40	0.02	0.15

Correlation Between MSD Data and Viscosity Ratio

For virgin asphalts, the viscosity ratio at 60°C showed a weak correlation with MSD (Table 6). Excluding SMS because of its small content and hence limited effect, the direction of association between the two variables was opposite of that reported for PVN at 135°C. Because good field performance is believed to accompany a low viscosity ratio, it then follows

that a high LMS percentage and a low MMS percentage are desirable features in an asphalt.

The weak correlation between MSD and viscosity ratio may be attributable to shortcomings of the TFOT method (15).

Correlation Between MSD Data and Kinematic Viscosity

For virgin asphalts, r has the same direction and nearly the same strength as that calculated for correlation between MSD and PVN at 135°C (Table 6). Field-aged samples showed a weaker correlation between the two variables, but the direction of association was maintained (Table 8).

Correlation Between MSD Data and Absolute Viscosity

A weak correlation exists between the two variables for virgin asphalts (Table 6). This agrees with Glover et al. (6), who studied the same relationship for 18 virgin asphalts from different Texas refineries. That conclusion does not contradict that of Garrick and Wood (5), who report an excellent correlation between MSD and absolute viscosity, because they used blended asphalts obtained from the same source and refinery process. In the present investigation, comparing MSD for pairs of samples (83-3203 and 88-3719, 86-3063 and 88-2192, 88-2570 and 88-2787), received from the same refinery but showing a different viscosity grade, confirms the conclusion of Garrick and Wood (5).

Field-aged asphalts showed r values that have the same direction and practically the same strength as those reported for correlation between MSD and kinematic viscosity (Table 8). This similarity is probably attributable to the fact that field-aged asphalts, having been subjected to hot mixing conditions during paving, have already undergone molecular interactions to the point where heating to 60°C or 135°C does not create any net effect, and r is maintained at essentially the same level. Virgin asphalts, on the other hand, showed a marked difference in the value of r to the point of having opposite directions of association between MSD and each of the two types of viscosity (Table 6).

Correlation Between MSD and VTS

A strong to excellent correlation exists between the MSD and VTS variables (Table 6). From the direction of association, a low VTS (low temperature susceptibility) is expected for asphalts with a high percentage of LMS components and a low percentage of MMS components. The correlation between SMS and VTS is weak (0.27) and does not allow a definite conclusion to be reached; the positive association, however, favors a low SMS percentage.

That the MSD of virgin asphalts correlates strongly with VTS has also been noted by Glover et al. (6); they, too, report weaker correlation for asphalts extracted from field cores. The findings of this paper (Tables 6 and 8) favor the same conclusion.

Correlation Between MSD Data and Penetration at 25°C

In agreement with previous research, virgin asphalts demonstrated weak correlation between MSD and penetration (Table 6). For field-aged samples, correlation is stronger for the two major parts: LMS and MMS (Table 8).

The above correlations share the following: (a) a linear fit is assumed; other forms of curve fit—for example, logarithmic, exponential, or power—did not improve correlation; (b) because the virgin asphalts studied were randomly selected (“random” here refers to asphalts covering a wide range of viscosity and a large number of sources and being received over a long period of time) it then follows that the correlation coefficient (r) calculated herein is an unbiased estimate of the correlation coefficient (μ) for population of asphalt cements (17).

The high value of r , and consequently the high value of the coefficient of determination (r^2) for correlation of MSD and PVN at 135°C, MSD and kinematic viscosity, and MSD and VTS suggests the possibility of using MSD data to predict these physical parameters.

Chemical Analysis

Eleven of the 20 virgin asphalts were randomly selected and analyzed into four fractions according to ASTM D4124, Method B. The results—together with the colloidal instability index (I_c), as suggested by Gaestel et al. (18)—are given in Table 9. The higher the value of I_c , the lower the colloidal stability and the more an asphalt will be of the gel type (4). It is shown that four out of the five samples with a high colloidal stability ($I_c < 0.35$) appear in the upper left corner of Figure 1.

The colloidal instability index correlates fairly well with MSD (Table 10). The direction of association suggests that a

TABLE 9 CHEMICAL ANALYSIS OF VIRGIN ASPHALTS INTO FOUR FRACTIONS ACCORDING TO ASTM D4124, METHOD B

Sample	Asphaltenes	Saturates	Naphthene Aromatics	Polar Aromatics	I_c^*
82-1332	13.19	9.98	46.84	29.04	0.305
82-1522	15.48	16.32	38.18	28.97	0.474
83-3284	20.54	10.79	38.42	28.82	0.466
85-3695	17.92	10.77	41.66	28.06	0.411
85-3890	10.27	10.33	42.57	34.95	0.266
86-3063	15.60	17.11	36.87	29.36	0.494
87-2040	14.31	15.91	38.89	29.90	0.439
88-2483	17.75	17.02	36.62	27.04	0.546
88-2570	6.19	13.09	43.58	35.78	0.243
88-2787	5.21	8.63	43.78	41.17	0.163
88-3680	11.27	13.61	39.50	34.74	0.335

$$*I_c = \frac{\text{Asphaltenes} + \text{Saturates}}{\text{Naphthene Aromatics} + \text{Polar Aromatics}}$$

TABLE 10 CORRELATION COEFFICIENTS FOR FRACTION CONTENT AND EACH OF THE COLLOIDAL INSTABILITY INDEX AND ASPHALTENE CONTENT

Fraction	I_c	% Asphaltene
LMS	-0.51	-0.66
MMS	0.47	0.60
SMS	0.28	0.45

high colloidal stability is satisfied by a high LMS proportion, together with low MMS and SMS proportions. Glover et al. (6) and Iattingh (19) reported that a high LMS content is a feature of nontender asphalts.

Table 10 also reveals that MSD correlates well with asphaltene content; r has same direction and a higher strength compared with that reported for I_c . This is not surprising, because asphaltene content is directly proportional to I_c (18). Brulé (20) using HPGPC, reports that—contrary to general belief—asphaltenes are not composed of only large molecules but that practically the whole range of molecular sizes present in asphalt is found in asphaltenes.

Relationship Between MSD and Physicochemical Parameters

To sum up the foregoing strong correlations: a high PVN at 135°C and a low VTS (low temperature susceptibility), a low viscosity ratio (high resistance to aging), a high colloidal stability, and a low asphaltene content would all be favored by a high LMS, together with a low MMS percentage. The SMS fraction demonstrated a weak correlation with most variables and constituted less than 11 percent of any of the virgin samples. Direction of associations, nevertheless, favors a low SMS percentage.

LMS Versus MMS

In Figure 5, MMS is plotted versus LMS for the 20 virgin asphalts, and it has a correlation coefficient of -0.97 . The two Shamrock asphalts are far from the others and appear in the extreme lower right corner. Figure 6 represents the same relationship after the two unique asphalts are excluded. The seven samples appearing in the lower right corner of Figure 6 are arranged according to the LMS/MMS ratio in Table 11.

It is interesting to note that all seven asphalts (35 percent of the whole set) with high LMS/MMS ratios appear in—or at the periphery of—the upper left corner of Figure 1, which includes other samples as well (75 percent of the whole set). Using MSD, it is thus possible to further screen asphalts with potential for good field performance. This set of seven asphalts has common characteristics: absolute viscosity of 1,100 to 1,700 poises, kinematic viscosity of 300 to 400 cst, a viscosity ratio of 2.1 to 2.9, a VTS of 3.43 to 3.58, a PVN at 60°C of -0.3 to -0.8 , and a PVN at 135°C of -0.3 to -0.8 .

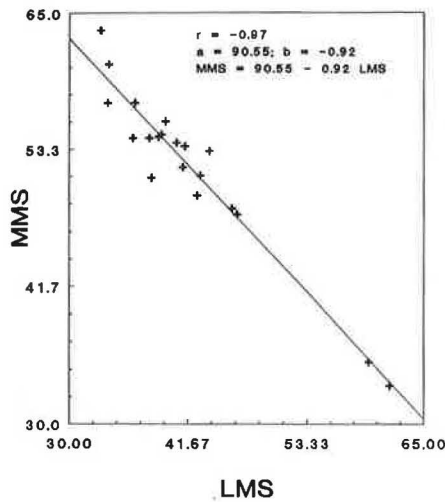


FIGURE 5 MMS versus LMS for 20 virgin asphalts.

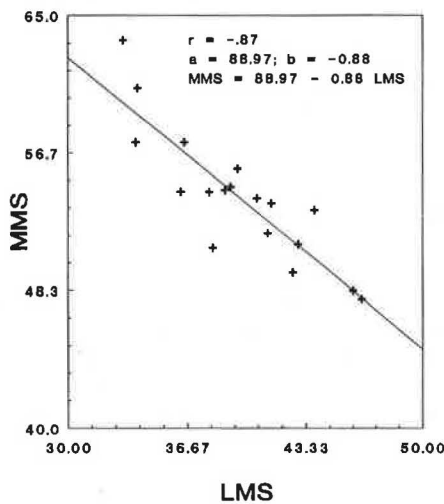


FIGURE 6 MMS versus LMS for 18 of the asphalts shown in Figure 5.

TABLE 11 ASPHALTS WITH HIGH LMS AND LOW MMS FRACTIONS

Sample	LMS, %	MMS, %
88-3680	0.97	
85-1230	0.95	
82-2746	0.86	
82-1522	0.84	
86-3063	0.82	
83-3284	0.80	
82-1214	0.77	

Laboratory Aging Versus Field Aging

To compare the effects of the two types of aging, the change in MSD for some asphalts was calculated (Table 12). In agreement with other investigators' findings, both types of aging caused the LMS proportion to increase and the MMS proportion to decrease. The only exceptions were three field-aged samples, none of which had more than 3 years of service. The odd change (LMS decreased, and MMS increased) was within the accuracy of data (± 1 percent of the original) (11). The SMS proportion showed mixed response; however, the small percentage of SMS (< 6.5 percent) limits the role of this fraction.

CONCLUSIONS

First, 2 asphalts supplied by Diamond Shamrock demonstrated unique characteristics as opposed to the other 18: They have high penetration at 25°C, low absolute viscosity, low viscosity of residue after TFOT, highest kinematic viscosity, lowest viscosity ratio, lowest VTS, highest PVN at 135°C, highest LMS, lowest MMS, lowest asphaltene content, and highest colloidal stability.

Second, \log_{10} of absolute viscosity correlates strongly with each of \log_{10} kinematic viscosity ($r = 0.87$, excluding the two Shamrock asphalts), and just as strongly ($r = -0.81$) with \log_{10} penetration at 25°C for the 20 virgin asphalts.

Third, a 16-hr TFOT causes penetration and MMS components to decrease but absolute viscosity, kinematic viscosity, VTS, PVN at 60°C, PVN at 135°C, and LMS components to increase. Field aging (up to 7 years) caused changes that are similar in direction but less drastic in magnitude.

Fourth, MSD correlates strongly with PVN at 135°C, viscosity at 135°C, VTS, colloidal instability, and asphaltene content but less strongly with viscosity ratio at 60°C. For all

TABLE 12 COMPARISON BETWEEN LABORATORY AGING AND FIELD AGING AS REVEALED BY HPGPC ANALYSIS

Sample #	82-1332	82-1522	85-4116	86-3063	87-2040	88-2483	88-3680
Years of Service	7	7	4	3	2	1	1
δ LMS	+1.9	+3.1	+1.8	-0.6	+4.7	+3.3	-1.0
δ LMS'	+3.0	+1.7	+4.5	+4.1	+3.3	+5.0	+3.9
δ MMS	-6.0	-1.0	-2.5	-2.3	-3.5	+1.2	-0.7
δ MMS'	-5.2	-3.7	-4.2	-2.9	-2.6	-5.2	-1.4
δ SMS	+4.1	-2.2	+0.6	+2.8	-1.2	-4.6	+1.7
δ SMS'	+2.1	+1.9	-0.4	-1.1	-0.7	0.0	-2.6

δ LMS = LMS% of field aged sample - LMS,% of original.

δ LMS' = LMS% after TFOT - LMS,% of original.

correlations, direction of associations points out that high PVN at 135°C and low VTS (low temperature susceptibility), low viscosity ratio (high resistance to aging), high colloidal stability, and low asphaltene content are all favored by high LMS and low MMS proportions. The SMS fraction correlates weakly with most variables investigated and constitutes less than about 10 percent of any of the asphalts under consideration. Direction of associations, however, favors a low SMS proportion.

Fifth, among those studied, virgin asphalts with high LMS/MMS ratio (> 0.75) are characterized by low temperature susceptibility and high resistance to aging.

Sixth, because asphalts with low temperature susceptibility and high resistance to aging are expected to exhibit good field performance, and because the LMS/MMS ratio provides a further screening characteristic, it is recommended that HPGPC be used to determine the MSD of a given asphalt. However, further work to tie the optimum MSD to actual field performance is needed.

Finally, from the 20 virgin asphalts tested, those with the highest LMS/MMS ratio have common features: viscosity at 60°C between 1,100 and 1,700 poises, viscosity at 135°C between 300 and 400 cst, viscosity ratio from 2.1 to 2.9, VTS from 3.43 to 3.58, PVN at 60°C between -0.3 and -0.8 , and PVN at 135°C between -0.3 and -0.8 .

ACKNOWLEDGMENTS

This work was accomplished in cooperation with FHWA and its Kansas division. Thanks are due to Hope Alban and Condie Erwin for entering text on the word processors.

REFERENCES

1. J. L. Goodrich and L. H. Dimpfi. Performance and Supply Factors to Consider in Paving Asphalt Specifications. *Proc., Association of Asphalt Paving Technologists*, Vol. 55, 1986.
2. F. S. Rostler and R. M. White. *Influence of Chemical Composition of Asphalts on Performance, Particularly Durability*. ASTM STP, 1959.
3. R. P. Price and J. L. Burati, Jr. A Quantitative Method Using HP-GPC to Predict Laboratory Results of Asphalt Cement Tests. *Proc., Association of Asphalt Paving Technologists*, Vol. 58, 1989, pp. 182–219.
4. B. Brulé, G. Ramond, and C. Such. Relationships Between Composition, Structure, and Properties of Road Asphalts: State of Research at the French Public Works Central Laboratory. In *Transportation Research Record 1096*, TRB, National Research Council, Washington, D.C., 1986, pp. 22–34.
5. N. W. Garrick and L. E. Wood. Relationship Between High-Pressure Gel Permeation Chromatography Data and the Rheological Properties of Asphalts. In *Transportation Research Record 1096*, TRB, National Research Council, Washington, D.C., 1986, pp. 35–41.
6. C. J. Glover, R. R. Davison, J. A. Bullin, J. W. Button, and G. R. Donaldson. Chemical Characterization of Asphalt Cement and Performance-Related Properties. In *Transportation Research Record 1171*, TRB, National Research Council, Washington, D.C., 1988, pp. 71–81.
7. P. W. Jennings, J. A. S. Pribanic, J. Smith, and T. M. Mendes. Predicting the Performance of Montana Test Sections by Physical and Chemical Testing. In *Transportation Research Record 1171*, TRB, National Research Council, Washington, D.C., 1988, pp. 59–65.
8. G. R. Donaldson, M. W. Hlavinka, J. A. Bullin, C. J. Glover, and R. R. Davison. The Use of Toluene as a Carrier Solvent for Gel Permeation Chromatography Analysis of Asphalt. *Journal of Liquid Chromatography*, Vol. 11, 1988, pp. 749–765.
9. B. V. Enustun, S. S. Kim, and D. Y. Lee. *Correlation of Locally-based Performance of Asphalts with their Physicochemical Parameters*. Final Report on Project HR-298. Iowa Department of Transportation, Des Moines, March 1990, pp. 1–107.
10. S. W. Bishara and R. L. McReynolds. Use of HPGPC with UV Detection for Determination of Molecular Size Distribution of Asphalt Cement After Quantitative Corrections for Molar Absorptivity Variation and Saturated Oils. In *Transportation Research Record 1269*, TRB, National Research Council, Washington, D.C., 1990, pp. 40–47.
11. S. W. Bishara and R. L. McReynolds. The Use of HPGPC for Determination of MSD of Asphalt Cement: A Spectrophotometric vs. Gravimetric Finish. *Proc., 200th National Meeting*, American Chemical Society, Vol. 35, No. 3, 1990, pp. 396–406.
12. *Recovery of Asphalt from Methylene Chloride and Trichloroethylene by the Abson Method*. Publication FHWA-RD-89-207. FHWA, U.S. Department of Transportation, Nov. 1989.
13. L. W. Corbett and H. E. Schwyer. Viscosity Characterization of Asphalt Cement. In *Viscosity Testing of Asphalt and Experience with Viscosity Graded Specifications*, ASTM STP 532, 1973, pp. 40–49.
14. D. S. Moore and G. P. McCabe. *Introduction to the Practice of Statistics*. W. H. Freeman and Company, New York, N.Y., 1989, pp. 197–212.
15. Asphalt Binder Specification "Hypothesis" Developed. *Focus*, Strategic Highway Research Program, National Research Council, Washington, D.C., Sept. 1989.
16. B. Brulé. Contribution of Gel Permeation Chromatography (GPC) to the Characterization of Asphalts. In *Liquid Chromatography of Polymers and Related Materials II* (J. Cazes and X. Delamare, eds.), Marcel Dekker, Inc., New York, N.Y., 1980, pp. 215–248.
17. R. L. Anderson. *Practical Statistics for Analytical Chemists*. Van Nostrand Reinhold Company, New York, N.Y., 1987, pp. 118–120.
18. C. Gaestel, R. Smadja, and K. A. Lamminan. Contribution à la Connaissance des Propriétés des Bitumes Routiers. *Revue Générale des Routes et Aéroports*, Vol. 466, 1971, pp. 85–94.
19. M. M. Hattingh. The Fractionation of Asphalt. Presented at the Annual Meeting of Association of Asphalt Paving Technologists, Scottsdale, Ariz., 1984.
20. B. Brulé. Characterization of Bituminous Compounds by Gel Permeation Chromatography (GPC). *Journal of Liquid Chromatography*, Vol. 2, 1979, pp. 165–192.
21. D. W. Christensen and D. A. Anderson. Effect of Amine Additive on the Properties of Asphalt Cement. *Journal, Association of Asphalt Paving Technologists*, Vol. 54, 1985, pp. 593–615.