

# Correlation Between Performance-Related Characteristics of Asphalt Cement and Its Physicochemical Parameters Using Corbett's Fractions and HPGPC

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The study of a set of 20 asphalt cements reported in a recent publication is modified and extended to cover additional parameters and a precise statistical evaluation of correlations. For a given asphalt, the whole, original material is subjected to high performance gel permeation chromatography (HPGPC) using a gravimetric finish. The experimental conditions used are kept uniform for all molecular size distribution (MSD) analyses in this study. Another part of asphalt is fractionated by ASTM D 4124. Each Corbett fraction is subjected to HPGPC analysis. The asphaltene compatibility index (ACI) is determined as proposed by Branthaver et al. A part of original asphalt is subjected to 16-hr TFOT, and MSD of the aged sample is determined. Two asphalts from the same refinery showed MSD and ACI data that are outliers with respect to the other 18 asphalts. For many correlations, excluding these two asphalts causes the correlation coefficient,  $r$ , to change appreciably because  $r$  is not resistant (i.e., one or more extreme entries can be influential). Several correlations are evaluated. Depending on the number of asphalts involved,  $n$ , the numerical value of  $r$  indicates whether a correlation is not significant, significant, or highly significant; the sign of  $r$  indicates the direction of slope of the regression line. Considering only the significant and highly significant correlations, the sign of associations tested indicate that a high LMS/MMS ratio [the molecular size index (MSI)] for original asphalt accompanies a low ACI, a minimum temperature susceptibility, a high resistance to aging (minimum change of MSI due to 16-hr TFOT), and a high viscosity, 135°C. From the MSD of original asphalt, eight with the highest MSI show common parameters that predict a promising field performance.

Fourteen out of every 15 mi of surfaced roads in the United States is topped with asphalt. The amount spent annually on asphalt pavement is \$10 billion, of which \$3 billion is for the binder itself (1).

Asphalt is an extremely complex material with no specifications for its chemical composition or structure. There is mounting evidence that the physical properties by themselves are not sufficient to predict pavement performance (2). Garrick and Wood (3) reported having asphalts with similar rheological properties but different chemical composition. Other investigators (4,5) pointed out asphalt cements with same specifications but different chemical compositions.

An important property of asphalt (and other polymers) is the molecular size distribution (MSD). In a previous inves-

tigation (6), a set of 20 original asphalt cements ( $n = 20$ ) was studied. The set covers a wide viscosity range (500 to 2,200 poises) and was collected from 14 different refineries. The rheological properties were measured. The MSD of the whole set was carried out; the chemical analysis of 11 out of the 20 samples was achieved using Corbett (7) ASTM D4124, Method B. Although some parameters [e.g., penetration viscosity number (PVN), 135°C; viscosity, 135°C; and viscosity temperature susceptibility (VTS)] indicated correlations with MSD that are highly significant, other parameters, such as penetration, 25°C; viscosity, 60°C; viscosity ratio, 60°C; and colloidal instability index (8) indicated nonsignificant correlations with MSD. Classification of a correlation between two variables as highly significant, significant, or not significant follows the generally accepted practice of considering a correlation highly significant if for a given number of pairs of variables ( $n-2$ ) the value of  $r$ , irrespective of the sign, is beyond its tabulated value at the 1 percent level of significance ( $p = 0.01$ ). The correlation is not significant if the value of  $r$  is less than its reported value at the 5 percent level of significance ( $p = 0.05$ ); the correlation is significant if the value of  $r$  exceeds the value reported at the 5 percent level (9-11).

The previous study (6) has dealt with the MSD of whole asphalt samples. To better understand the structure of asphalt cement, however, fractionation by various procedures may be involved (12-15). Branthaver et al. (12) analyzed asphalts by ion-exchange chromatography (IEC). The neutral (non-polar) fraction from IEC was then analyzed by preparative high performance gel permeation chromatography (HPGPC) (13) into seven fractions; each of the two middle fractions was separated into saturate and aromatic components by chromatography on silica gel (14). Each of the two parts, saturate and aromatic, was then analyzed by supercritical fluid chromatography (SFC) to get the range of carbon numbers. Stegeman et al. (15) applied residual oil supercritical extraction (ROSE) to fractionate asphalt. Each fraction was then analyzed by ASTM D4124, Method B. Ramond et al. (16) reported that the grade of asphaltenes and their tendency to associate to form agglomerates (interaction index) are behind the changes of rheological properties that occur during hot mixing.

In the present work, the Corbett method was used to fractionate the 20 original asphalts used previously (6). Each fraction was then analyzed by semipreparative HPGPC according

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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	VIS	** 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.

$$\text{**PNV, } 60^{\circ}\text{C} = \frac{-1.5(6.489 - 1.59 \log_{10} \text{Pen } 25^{\circ}\text{C} - \log_{10} n \text{ } 60^{\circ}\text{C})}{1.05 - 0.2234 \log_{10} \text{Pen } 25^{\circ}\text{C}} \quad \text{Ref. (25)}$$

$$\text{***PNV, } 135^{\circ}\text{C} = \frac{-1.5(4.258 - 0.79674 \log_{10} \text{Pen } 25^{\circ}\text{C} - \log_{10} n \text{ } 135^{\circ}\text{C})}{0.795 - 0.1858 \log_{10} \text{Pen } 25^{\circ}\text{C}} \quad \text{Ref. (3)}$$

to the method described earlier (6,17). Compatibility tests were carried out on the whole, original asphalt samples according to Branthaver et al. (18). The original asphalts were aged by the 16-hr TFOT method (ASTM D1754), then subjected to semipreparative HPGPC analysis. Physical properties of the whole asphalts before and after aging are given in Tables 1 and 2. The reasonably large number of asphalt cements studied and the fact that they are randomly selected (random here means that the asphalts cover a wide viscosity range and a large number of refineries) make it possible to consider the correlation coefficient,  $r$ , to be an unbiased estimate of  $\mu$ , the correlation coefficient for the population of asphalt cements, that is, generalize the association relationships to cover the wide range of asphalt cements. Another objective is to use MSD data to pinpoint from among the 20 asphalt cements those with potential for good field performance.

## EXPERIMENTAL

### 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- $\mu\text{m}$ , 500-Å phenogel semipreparative column (300  $\times$  22.5 mm) with THF as solvent was used.

### Procedure

#### Fractionation of Original Asphalts

Carried out by ASTM D4124, Method B. n-Hexane was used instead of n-Heptane.

#### Molecular Size Distribution Analysis

**Preparation of Sample Solution** For whole, original or laboratory-aged asphalt, weigh accurately (to within 0.01 mg) an asphalt sample in the range of 2.0 to 2.5 g. Add about 25 mL of THF and sonify for 15 min at room temperature. Transfer quantitatively to a 50-mL volumetric flask and complete to volume with THF. An aliquot is then filtered through 0.2- $\mu\text{m}$  membrane. An exact volume (100 to 200  $\mu\text{L}$ ) chosen

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

Sample	Pen 25°C, mm	Vis. 60°C, poises	Vis. 135°C, cst	VIS	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

to contain 6 to 7 mg of the asphalt material is injected in the HPGPC system.

For asphaltene, polar aromatics, naphthene aromatics, and saturates, after fractionation of an original whole asphalt by ASTM D4124, each of the four fractions is kept in a small vial under helium. The dried material is dissolved in THF. An aliquot is filtered through 0.2- $\mu$ m membrane, and a suitable volume (100 to 200  $\mu$ L) is injected.

**HPGPC Analysis** The following conditions were maintained for analysis of all types of material, that is, whole asphalts (original and aged) as well as the four fractions generated by the ASTM D4124 method. The mobile phase consisted of 90 percent (v/v) THF plus 10 percent (v/v) pyridine flowing at a rate of 6 mL/min. The semipreparative phenogel column is maintained at 50°C. (For analysis of saturates, a Waters LC Spectrophotometer, Model 481, was used to check whether absorption of UV light at 345 nm would occur with any of the 20 samples studied.)

The material eluting from the column is collected in a series of small, glass, accurately weighed (to within 0.01 mg) petri dishes at 4.5 to 8.0, 8.0 to 11.0, and 11.0 to 14.5 min from injection. These designate the large molecular size fraction (LMS), medium molecular size fraction (MMS), and small molecular size fraction (SMS), respectively. Repeat the injection and collect each fraction in the corresponding petri dish.

The petri dishes are set aside to allow the mobile-phase solvents to evaporate at room temperature, then heated in an oven for 90 min at 200°C. The petri dishes are then cooled in a desiccator to constant weight.

The time required to equilibrate the column and consequently eliminate "tailing" effects increases from naphthene aromatics to polar aromatics to asphaltene.

#### Determination of Compatibility

The asphaltene compatibility index (ACI) was determined as recommended by Branthaver et al. (18).

#### Aging of Original Asphalts

This was achieved by 16-hr TFOT (ASTM D1754).

## RESULTS AND DISCUSSION

A previous Kansas investigation (6) dealt mainly with whole asphalt cements. The MSD was found to correlate, at different levels of significance, with the performance-related properties studied. The direction (sign) of association between MSD (considered as the independent variable) and any of the parameters tested (considered as the dependent variable) always favors a high percentage of LMS, together with low percentages for each of MMS and SMS in order to attain the desirable performance properties of low temperature susceptibility and high resistance to aging. Since the SMS content was found to be small (less than 10 percent), a high LMS/MMS ratio [the molecular size index (MSI)] appears to be an optimum characteristic.

However, the highly complex nature of asphalt has long suggested its fractionation to permit a better understanding of asphalt behavior. In the present study, the whole asphalt was fractionated by ASTM D4124, then HPGPC was used to analyze each fraction. Table 3 gives the results of the analysis of whole asphalts by the Corbett method (7) together with the colloidal instability index,  $I_c$  (8).

Of the four Corbett fractions, asphaltene has received the most attention. Because it is composed mainly of highly polar compounds, or associations thereof, asphaltene is believed to have a significant role in asphalt behavior. To study MSD of asphaltene, and to establish comparisons with MSD of the whole asphalts, the conditions applied previously (6) for the whole asphalts were first used. But the following modifications were deemed necessary:

1. The mobile phase used in the previous study (95 percent THF + 5 percent pyridine) could not overcome the tendency of the smaller, polar molecules of asphaltene to be retained within the column—probably by an adsorption mechanism—and elute after the total permeation volume (19). Increasing the pyridine content of the mobile phase to 10 percent, together with maintaining the GPC column at 50°C, eliminated the phenomenon almost entirely.

2. The time periods reported earlier (6) for collecting the fractions were selected to provide nearly equal weight of material in each fraction. However, for these fractions to more

TABLE 3 ANALYSIS OF 20 ORIGINAL, WHOLE ASPHALTS INTO FOUR FRACTIONS ACCORDING TO ASTM D4124, METHOD B, USING n-HEXANE AS SOLVENT INSTEAD OF n-HEPTANE

Sample Number	Fraction, %				I <sub>c</sub> **
	Asphaltenes	Polar Aromatics	Naphthene Aromatics	Saturates	
82-1214	16.0	28.1	37.7	16.8	0.50
1332	13.5	30.5	46.1	9.8	0.30
1522	16.2	28.0	35.5	17.1	0.52
2746	12.1	37.3	37.4	12.0	0.32
83-3203	20.2	32.2	35.6	11.4	0.47
3284	21.2	29.8	37.1	11.1	0.48
85-1230	8.9	38.8	39.7	10.6	0.25
3695	20.0	29.1	38.2	11.9	0.47
3890	12.8	33.0	38.5	13.5	0.37
4116	20.0	26.9	35.1	15.9	0.58
86-3063	16.7	29.0	36.1	17.7	0.53
3113	17.4	31.0	34.5	15.5	0.50
87-2040	15.2	29.7	38.0	16.5	0.47
88-2381	15.6	34.5	38.2	8.7	0.33
2192	15.2	27.2	36.0	21.0	0.57
2483	18.7	26.2	36.0	17.6	0.58
2570	6.8	42.4	38.2	9.6	0.20
2787	5.9	44.8	39.8	6.8	0.15
3680	12.3	34.8	37.4	14.1	0.37
3719	18.8	29.6	39.3	11.0	0.43

\*Average of two results.

\*\*The colloidal instability index,

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

accurately represent LMS, MMS, and SMS components, the cut points are adjusted so that the selective permeation region (between total exclusion and total permeation) is divided into three more or less equal time periods—4.5 to 8.0, 8.0 to 11.0, and 11.0 to 14.5 min from injection, to represent LMS, MMS, and SMS contents, respectively.

Because these modifications proved suitable to study MSD of the asphaltenes fraction (and hence the other three less polar fractions), the set of 20 whole, original asphalts was subjected to MSD analysis under the new conditions, which were then applied all over the present work (i.e., for each of the four Corbett fractions and the laboratory-aged asphalts).

#### MSD of Whole, Original Asphalts

As expected, changing conditions of analysis caused the MSI to be different from that reported previously for the same set of samples (6). Decreasing (by ½ min) the period over which the LMS fraction is collected, while increasing (by ½ min) the period of collecting the MMS fraction caused the MSI for any given asphalt to be smaller than that reported earlier (6). However, Table 4 indicates that the group of samples that

possess the highest MSI is nearly the same for the two studies. Under the present conditions, excluding sample numbers 88-2570 and 2787 for reasons mentioned later, eight asphalts with MSI of  $\geq 0.42$  have the common parameters:  $I_c$  between 0.25 and 0.58; viscosity, 60°C, between 1,200 and 1,700 poises; viscosity, 135°C, between 300 and 420 cst; viscosity ratio, 60°C, from 2.3 to 2.9; VTS from 3.45 to 3.59; PVN, 60°C, between -0.33 and -0.79; and PVN, 135°C, between -0.25 and -0.80. Interestingly, these ranges are essentially the same as those reported previously (6). The only detectable change is in the lower limit of absolute viscosity, which increased from 1,100 to 1,200 poises. This and other evidence (20) confirm the statement that absolute viscosity appears to be a function of asphalt preparation, because it is a "made to order" property (18). This work and others (6,21) have found that correlation between viscosity, 60°C and MSD is not significant (Table 5).

#### Correlation Between MSD of Whole Original Asphalts and Their Physicochemical Parameters

The correlation coefficient,  $r$ , for the relationship between MSD (LMS, MMS, or LMS/MMS) and some physicochemical



TABLE 4 MSD OF 20 ORIGINAL, WHOLE ASPHALT CEMENTS

Sample Number	Fraction, %			(LMS/MMS)
	IMS	MMS	SMS	
82-1214	29.5	69.4	1.1	0.43
1332	20.9	77.8	1.3	0.27
1522	31.0	66.7	2.3	0.47
2746	29.3	69.3	1.5	0.42
83-3203	27.5	70.0	2.5	0.39
3284	33.7	64.3	2.0	0.52
85-1230	30.4	68.0	1.6	0.45
3695	32.8	65.3	2.0	0.50
3890	20.4	75.8	3.7	0.27
4116	30.4	65.8	3.9	0.46
86-3063	30.9	67.5	1.6	0.46
3113	26.8	72.4	0.8	0.37
87-2040	24.6	72.5	2.9	0.34
88-2381	25.3	72.2	2.6	0.35
2192	28.3	70.2	1.5	0.40
2483	26.1	72.5	1.4	0.36
2570	41.3	57.9	0.7	0.71
2787	46.9	52.3	0.7	0.90
3680	25.7	70.1	4.1	0.37
3719	25.9	71.2	2.8	0.36

parameters of the 20 original asphalts is given in Table 5. To judge how credible a correlation might be, the numerical value of  $r$  has to pass the  $t$  test (9-11). The following equation is used to calculate  $t$ .

$$t = r[(n-2)/(1-r^2)]^{1/2} \quad (1)$$

where  $n$  is the number of individual samples and  $(n-2)$  represents the degrees of freedom,  $df$ . If the calculated value of  $t$  for  $(n-2)$   $df$  is greater than the tabulated value of  $t^*$  at the critical value of  $p = 0.05$ , then the correlation is significant (i.e., there is less than a 5 percent chance that the set of samples studied has been selected from a noncorrelated population). If  $t$  is greater than  $t^*$  at  $p = 0.01$ , the correlation is highly significant with less than a 1 percent chance that the population is noncorrelated. An easier way, however, is to consult tables that list values of  $r$  at various levels of significance for a given  $df$  (9,10). For 20 samples,  $df = 18$  and  $r$  is equal to 0.444 and 0.561 at the 5 percent and 1 percent levels of significance, respectively. Table 5 indicates the following:

1. For the significant and highly significant correlations, the numerical value of  $r$  under the MSI for a given parameter is usually higher than, or at least equal to, the  $r$  value for either the LMS or MMS fraction alone. The correlation between asphaltenes content and MSI is significant, but correlation of asphaltenes content with each of the LMS or MMS fraction is not significant. The same observation is true for the colloidal instability index. On the other hand, for those correlations that are nonsignificant (e.g., penetration, 25°C; viscosity, 60°C;

TABLE 5 CORRELATION COEFFICIENT,  $r^*$ , FOR THE MSD DATA AND SOME PHYSICOCHEMICAL PARAMETERS FOR 20 ORIGINAL ASPHALTS

Physicochemical Parameter	MSD Data**		
	IMS	MMS	(IMS/MMS)=MSI
Penetration, 25°C	0.17 <sup>a</sup>	-0.15 <sup>a</sup>	0.14 <sup>a</sup>
Viscosity, 60°C	0.03 <sup>a</sup>	-0.04 <sup>a</sup>	-0.01 <sup>a</sup>
Viscosity, 135°C	0.69 <sup>c</sup>	-0.68 <sup>c</sup>	0.67 <sup>c</sup>
Viscosity Ratio, 60°C	-0.14 <sup>a</sup>	0.19 <sup>a</sup>	-0.18 <sup>a</sup>
VIS	-0.83 <sup>c</sup>	0.81 <sup>c</sup>	-0.83 <sup>c</sup>
FTN, 60°C	0.32 <sup>a</sup>	-0.32 <sup>a</sup>	0.24 <sup>a</sup>
FTN, 135°C	0.78 <sup>c</sup>	-0.77 <sup>c</sup>	0.75 <sup>c</sup>
Asphaltenes, %***	-0.41 <sup>a</sup>	0.39 <sup>a</sup>	-0.48 <sup>b</sup>
Polar Aromatics, %	0.57 <sup>c</sup>	-0.57 <sup>c</sup>	0.62 <sup>c</sup>
Naphthene Aromatics, %	-0.11 <sup>a</sup>	0.14 <sup>a</sup>	-0.04 <sup>a</sup>
Saturates, %	-0.34 <sup>a</sup>	0.34 <sup>a</sup>	-0.39 <sup>a</sup>
Colloidal Instability, I <sub>c</sub>	-0.39 <sup>a</sup>	0.38 <sup>a</sup>	-0.47 <sup>b</sup>

\*In calculating the value of  $r$ , the IMS (MMS or IMS/MMS) is considered the independent variable, and the physicochemical parameter is considered the dependent variable.

\*\*The SMS content hardly exceeded 4% and therefore correlation coefficients for this fraction were not calculated.

\*\*\*n-Hexane insolubles.

<sup>a</sup>Not significant correlation.

<sup>b</sup>Significant correlation.

<sup>c</sup>Highly significant correlation.

TABLE 6 MSD OF THE SATURATES FRACTION OF 19 ORIGINAL ASPHALT CEMENTS

Sample Number	Fraction, %			MSI
	LMS	MMS	SMS	
82-1214	12.5	86.2	1.2	0.15
1332	0.0	100.0	0.0	0.00
1522	10.3	89.7	0.0	0.12
2746	6.0	91.5	2.4	0.07
83-3203	5.3	94.7	0.0	0.06
3284	1.4	97.8	0.8	0.01
85-1230	11.3	87.7	1.0	0.13
3695	2.7	94.3	3.0	0.03
3890	5.8	92.6	1.6	0.06
4116	10.5	86.6	2.8	0.12
86-3063	8.5	89.2	2.2	0.10
3113	11.5	86.7	1.8	0.13
87-2040	5.1	93.5	1.4	0.06
88-2381	8.9	91.1	0.0	0.10
2192	4.4	94.7	0.9	0.05
2570	16.0	81.3	2.7	0.20
2787	19.9	80.1	0.0	0.25
3680	8.4	91.6	0.0	0.09
3719	0.0	100.0	0.0	0.00

PVN, 60°C; and naphthene aromatics, percent) the numerical value of  $r$  under MSI is even smaller than the corresponding value under LMS or MMS fraction. Therefore, the use of MSI to describe the MSD is advantageous.

2. The physical parameters measured, or derived from measurements, at the high temperature (135°C) show highly significant correlations with MSI. Physical parameters measured, or derived from measurements, at low temperature (25°C for penetration, 60°C for the rest) show correlations with MSI that are not significant.

3. The MSI shows a highly significant correlation with polar aromatics content, a significant correlation with asphaltenes content as well as with colloidal instability index, but a non-significant correlation with naphthene aromatics and saturates content. However, the correlation with saturates content is significant at the 10 percent level of significance. Thus, if we can accept the situation that there is less than a 10 percent chance that the saturates content and MSI for the population of asphalt cements are noncorrelated (i.e., there is more than a 90 percent chance they are correlated), this leaves only the naphthene aromatics fraction with a correlation that is not significant. At the other extreme, polar aromatics seem to have the strongest influence on MSI of whole asphalt.

#### MSD of Saturates

In accordance with the gravimetric procedure used for analysis of this and all the other types of fractions, the milligram amounts of material eluting from the HPGPC column were

heated in an oven for 90 min. But only the material collected from the saturates fraction generated the distinct odor of burning asphalt. None of the other fraction types behaved similarly.

One of the main advantages of a gravimetric finish (17) over an UV absorption method for MSD analysis is inability of the latter to account for components of the saturates fraction—usually 10 to 25 percent of an asphalt. For the set of 20 samples investigated, the maximum absorbance reading at 345 nm was practically zero; saturates of only two asphalts showed a maximum absorbance of 0.024. However, this slight absorbance might be attributed to a trace of naphthene aromatics contaminating the saturates (22).

The MSD of saturates is given in Table 6; the saturates from one asphalt sample were lightly colored, indicating presence of a minute quantity of naphthene aromatics, and therefore were not included. For any given asphalt, the MSI of saturates is smaller than the corresponding value for whole asphalt. Table 6 indicates that saturates are composed mainly (85 to 100 percent) of medium-size molecules; the only exception is the two unique asphalts 88-2570 and 2787.

#### MSD of Naphthene Aromatics

The naphthene aromatics fraction of one asphalt cement was accidentally lost. Table 7 gives MSD of 19 naphthene aromatics fractions. The MSI for naphthene aromatics of any given asphalt is always larger than that obtained for saturates (Table 6) but still smaller than that of the whole asphalt cement (Table 4).

TABLE 7 MSD OF THE NAPHTHENE AROMATICS FRACTION OF 19 ORIGINAL ASPHALT CEMENTS

Sample Number	Fraction, %			MSI
	LMS	MMS	SMS	
82-1214	18.3	81.4	0.3	0.22
1332	12.1	87.1	0.8	0.14
1522	17.2	81.4	1.4	0.21
2746	26.2	72.8	1.0	0.36
83-3203	10.2	88.2	1.6	0.12
3284	11.3	87.0	1.7	0.13
85-1230	16.8	81.4	1.8	0.21
3695	11.1	88.2	0.7	0.13
3890	14.2	84.6	1.2	0.17
4116	15.0	84.6	0.4	0.18
86-3063	16.8	81.3	1.9	0.21
87-2040	13.2	85.9	0.9	0.15
88-2381	18.0	80.1	1.9	0.22
2192	27.1	71.7	1.2	0.38
2483	12.9	87.2	0.0	0.15
2570	35.7	63.3	1.1	0.56
2787	42.1	56.3	1.6	0.75
3680	17.5	80.3	2.1	0.22
3719	8.1	91.6	0.3	0.09

### MSD of Polar Aromatics

Table 8 gives MSD of the polar aromatics of 19 asphalt cements. In comparison with the three other Corbett fractions, MSI of the polar aromatics fraction is the closest to MSI of the whole asphalt material (Table 4).

### MSD of Asphaltenes

Tables 9 and 10 indicate the following:

1. The MSI of an asphaltene fraction is higher than the corresponding value of any of the other Corbett fractions. Typically, about two-thirds (60 to 70 percent) of an asphaltene fraction is composed of large-size molecules.

2. For any given asphalt, the MSI increases going from saturates to naphthene aromatics to polar aromatics to asphaltenes. Thus, as the polarity increases, the MSI also increases. All of the fractions of the 20 asphalts investigated met this criterion.

Stegeman et al. (15), using ROSE method for fractionation, reported a progressive increase in molecular size with fraction number. They also found that the asphaltenes content is highest in the bottom fraction, whereas saturates are highest in the first fraction; the naphthene aromatics content peaks in a lighter fraction than polar aromatics. Although the fractionation techniques and the routes followed are different (Stegeman et al. used ROSE then Corbett, this study used

TABLE 8 MSD OF THE POLAR AROMATICS FRACTION OF 19 ORIGINAL ASPHALT CEMENTS

Sample Number	Fraction, %			MSI
	LMS	MMS	SMS	
82-1214	31.6	66.3	2.2	0.48
1332	31.3	67.8	0.9	0.46
1522	36.9	60.2	2.9	0.61
2746	28.2	71.1	0.7	0.40
83-3203	29.5	68.4	2.1	0.43
3284	34.3	57.9	7.7	0.59
85-1230	36.8	61.6	1.5	0.60
3695	29.4	69.2	1.4	0.42
3890	33.2	63.6	3.1	0.52
4116	34.6	63.9	1.5	0.54
86-3063	28.9	68.6	2.5	0.42
87-2040	26.8	70.8	2.4	0.38
88-2381	29.5	67.0	3.5	0.44
2192	30.3	66.5	3.3	0.46
2483	29.4	69.6	1.1	0.42
2570	61.7	38.0	0.3	1.62
2787	43.6	52.7	3.6	0.83
3680	37.2	61.4	1.5	0.61
3719	27.5	72.1	0.4	0.38

TABLE 9 MSD OF THE ASPHALTENES FRACTION OF 20 ORIGINAL ASPHALT CEMENTS

Sample Number	Fraction, %			MSI
	LMS	MMS	SMS	
82-1214	71.7	24.3	4.0	2.95
1332	57.8	37.2	5.0	1.55
1522	67.9	27.4	4.7	2.48
2746	59.7	32.1	8.0	1.86
83-3203	61.6	32.0	6.4	1.93
3284	66.8	26.5	6.7	2.52
85-1230	63.0	32.0	4.9	1.97
3695	64.9	31.7	3.3	2.05
3890	60.7	33.9	5.5	1.79
4116	67.7	28.5	3.8	2.38
86-3063	68.8	26.2	5.0	2.63
3113	60.9	30.7	8.4	1.98
87-2040	61.9	32.8	5.2	1.89
88-2381	61.4	35.1	3.5	1.75
2192	69.1	25.0	5.9	2.76
2483	61.5	31.4	7.0	1.96
2570	59.7	29.7	10.6	2.01
2787	62.4	28.3	9.3	2.20
3680	57.1	33.4	9.4	1.71
3719	65.1	29.0	5.9	2.24

Corbett then HPGPC), the two studies come to the same conclusion about the interrelationship between MSD of asphalt and polarity of constituents.

3. For a given asphalt, the MSI for polar aromatics is the nearest in magnitude to the corresponding value of the whole asphalt (Table 4). From the four fractions, MSI of polar aromatics is the closest to the MSI of whole asphalt (compare Tables 4 and 10).

4. The 88-2570 and 2787 asphalts have the highest MSI for the first three fractions but not for asphaltenes. The dominance of large molecules in these two whole, original asphalts as opposed to other asphalts (6,21) may then be mainly attributed to a higher-than-normal percentage of large molecules in the naphthene aromatics and polar aromatics fractions; the same is true but to a lesser degree in the saturates fraction.

### Correlation Between MSI of Corbett Fractions and Physicochemical Parameters of Original Asphalts

To find  $r$  for these relationships, the MSD of a Corbett fraction is considered the independent variable, and the physicochemical property is considered the dependent variable. Table 11, like Table 5, indicates that the MSI has generally nonsignificant correlations with parameters measured, or derived from measurements, at low temperature (25°C for pen-

TABLE 10 VARIATION OF MSI ACROSS THE CORBETT FRACTIONS OF ORIGINAL ASPHALT CEMENTS

Sample Number	MSI			
	Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
82-1214	0.15	0.22	0.48	2.95
1332	0.00	0.14	0.46	1.55
1522	0.12	0.21	0.61	2.48
2746	0.07	0.36	0.40	1.86
83-3203	0.06	0.12	0.43	1.93
3284	0.01	0.13	0.59	2.52
85-1230	0.13	0.21	0.60	1.97
3695	0.03	0.13	0.42	2.05
3890	0.06	0.17	0.52	1.79
4116	0.12	0.18	0.54	2.38
86-3063	0.10	0.21	0.42	2.63
3113	0.13	----	----	1.98
87-2040	0.06	0.15	0.38	1.89
88-2381	0.10	0.22	0.44	1.75
2192	0.05	0.38	0.46	2.76
2483	----	0.15	0.42	1.96
2570	0.20	0.56	1.62	2.01
2787	0.25	0.75	0.83	2.20
3680	0.09	0.22	0.61	1.71
3719	0.00	0.09	0.38	2.24

etration, 60°C for the rest). Parameters measured, or derived from measurements, at high temperature (135°C) show highly significant correlations with MSI of at least some of the fractions. For example, only MSI of saturates correlates with viscosity, 135°C; MSI of saturates, polar aromatics, and asphaltenes correlates with PVN, 135°C; and MSI of saturates, naphthene aromatics, and polar aromatics correlates with VTS. The MSI of each of the fractions, except asphaltenes, correlates with MSI of the whole asphalt. However, if the asphaltenes fraction of the two unique asphalts (88-2570 and 2787) is excluded,  $r$  increases to 0.61, indicating a highly significant correlation.

#### Correlation Between Corbett Fractions' Content and Physicochemical Parameters of Original Asphalts

It is interesting to note that MSI of whole asphalt correlates with MSI of naphthene aromatics ( $r = 0.82$ , Table 11) but does not correlate with the content of naphthene aromatics ( $r = -0.04$ , Table 5). Table 12 gives the correlation between Corbett's fraction content (independent variable) and the physicochemical parameter (dependent variable). The fraction content generally correlates with some of the parameters measured, or derived from measurements, at low temperature (60°C). The asphaltenes fraction content contributes much to temperature susceptibility, as evidenced by the significant and highly significant correlations with PVN, 60°C and VTS, respectively. Shiau et al. (23) have also reported that the asphaltenes content contributes much to temperature susceptibility. Polar aromatics correlate highly significantly with VTS. The naphthene aromatics percentage correlates with PVN, 60°C.

TABLE 11 CORRELATION COEFFICIENT,  $r$ , FOR THE RELATIONSHIP BETWEEN MSI OF EACH CORBETT FRACTION AND SOME PHYSICOCHEMICAL PARAMETERS OF ORIGINAL ASPHALTS

Physicochemical Parameter	MSI			
	Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
Penetration, 25°C	0.06	0.33	0.32	0.34
Viscosity, 60°C	0.00	-0.34	-0.27	0.16
Viscosity, 135°C	0.59*	0.35	0.33	0.33
Viscosity Ratio, 60°C	0.10	-0.36	-0.31	0.15
VTS	-0.71*	-0.79*	-0.75*	-0.30
PVN, 60°C	0.16	-0.14	0.00	0.63*
PVN, 135°C	0.63*	0.03	0.58*	0.63*
MSI of Whole Asphalt	0.72*	0.82*	0.66*	0.28
				(0.61)* <sup>a</sup>

\*Indicates a highly significant correlation; the rest are not significant correlations.

<sup>a</sup>Obtained after excluding the two asphalts 88-2570 and 2787.

TABLE 12 CORRELATION COEFFICIENT,  $r$ , FOR THE RELATIONSHIP BETWEEN CORBETT'S FRACTION CONTENT AND SOME PHYSICOCHEMICAL PARAMETERS OF ORIGINAL ASPHALTS

Physicochemical Parameter	Fraction, %			
	Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes
Penetration, 25°C	0.44	-0.22	-0.10	-0.13
Viscosity, 60°C	-0.11	-0.22	-0.17	0.43
Viscosity, 135°C	-0.31	-0.15	0.35	0.03
Viscosity Ratio, 60°C	0.48*	-0.35	-0.46*	0.43
VTS	0.21	0.06	-0.59**	0.57**
PVN, 60°C	0.29	-0.56*	-0.36	0.48*
PVN, 135°C	-0.03	-0.31	0.00	-0.21

\*Significant correlation.

\*\*Highly significant correlation; the rest are not significant.

From Tables 11 and 12, neither the penetration, 25°C, nor the viscosity, 60°C is correlated with the content or with MSI of any of the four Corbett fractions. The viscosity, 135°C does not correlate with the percentage of any of the fractions, but it correlates with MSI of saturates. Viscosity ratio does not correlate with MSI of any of the four fractions, but it correlates with saturates and polar aromatics content. The VTS correlates with polar aromatics content as well as its MSI. It also correlates with MSI of saturates and naphthene aromatics, as well as with asphaltenes content. Not surprisingly, VTS correlates with both the MSI and the content of some of Corbett fractions, since VTS involves measurements at the two temperatures of 60°C and 135°C. The PVN, 60°C correlates with asphaltenes content as well as its MSI; it also correlates with naphthene aromatics content. The PVN, 135°C correlates with MSI of saturates, polar aromatics, and asphaltenes.

The positive association between viscosity ratio and saturates content (Table 12) indicates that a small percentage of saturates favors a low viscosity ratio. The polar aromatics content is negatively associated with viscosity ratio, and therefore a low viscosity ratio would be favored by a high percentage of polar aromatics. A low VTS would be favored by

a high content of polar aromatics (negative association) and by a low asphaltene percentage (positive association). Therefore, a low percentage of saturates and of asphaltenes together with a high percentage of polar aromatics would favor the desired properties of low viscosity ratio and low VTS. Interestingly, the same requirements would automatically favor a low colloidal instability index,  $I_c$  (8). The fourth term in the equation that describes  $I_c$ , namely naphthene aromatics content, has nonsignificant correlation with each of the viscosity ratio and VTS (Table 12).

#### Correlation Between MSI and Percentage of Corbett Fractions

Table 13 indicates that the polar aromatics fraction content has a highly significant correlation with its MSI. The other three fractions have nonsignificant correlations. In further contrast to the other fractions, the polar aromatics fraction has the following features: (a) the content has a highly significant correlation with MSI of the whole asphalt, and (b) the content correlates significantly with the resistance to aging (viscosity ratio) and highly significantly with temperature sus-

TABLE 13 CORRELATION COEFFICIENT,  $r$ , FOR THE RELATIONSHIP BETWEEN MSI AND PERCENTAGE OF CORBETT FRACTIONS—COMPARISON WITH THE VALUE OF  $r$  FOR WHOLE ASPHALT

Fraction Content	MSI of Corbett Fraction	MSI of Whole Asphalt
Saturates	-0.14	-0.39
Naphthene Aromatics	0.06	-0.04
Polar Aromatics	0.62**	0.62**
Asphaltenes	0.27	-0.48*

\*Significant correlation.

\*\*Highly significant correlation; the rest are not significant.



TABLE 14 COMPATIBILITY OF 20 ORIGINAL ASPHALTS

Sample Number	ACI*
82-1214	0.938**
1332	1.712
1522	0.827
2746	1.619
83-3203	0.959
3284	0.717
85-1230	2.004
3695	0.964
3890	1.726
4116	0.730
86-3063	0.879
3113	1.220
87-2040	1.061
88-2381	1.317
2192	0.760
2483	1.068
2570	3.188
2787	3.641
3680	1.090
3719	1.217

\*Asphaltene compatibility index as defined by Branthaver et al. (18);

$$ACI = \left[ \frac{\text{Isooctane Asphaltenes, \%}}{\text{Isooctane Asphaltenes, \%} + \text{n-Heptane Asphaltenes, \%}} \right] \times 10$$

\*\*Each entry is the average of two determinations.

ceptibility (VTS) [i.e., polar aromatics is the only fraction that correlates with both the susceptibility and aging resistance (Table 12)].

### Compatibility of Asphalts

According to the widely accepted micellar model, associations of polar, aromatic molecules are dispersed in a nonpolar solvent phase. The physical properties of asphalt appear to be largely determined by the ability of the solvent phase to disperse the associated phase. The state of dispersion (compatibility) is one way of characterizing each of these phases (14). Table 14 indicates that the majority of asphalts investigated have an ACI in the range of 0.7 to 2.0. Only the two unique asphalts 88-2570 and 2787 have an ACI well beyond this range. As expected, these two asphalts have the lowest n-heptane asphaltenes.

### Effect of Some Physicochemical Parameters on ACI

Table 15 (top part) indicates that, excluding the two unique asphalts, the percentage of each of the four Corbett fractions

is at least significantly correlated with ACI; those of naphthene aromatics and asphaltenes demonstrate a highly significant correlation. Although not directly included in the calculation of ACI, the content of saturates, naphthene aromatics, and polar aromatics appears to affect the state of dispersion. On the other hand, MSI of the same three fractions does not seem to influence ACI ( $r$  is practically zero); only MSI of asphaltenes shows a highly significant correlation with ACI ( $r = -0.65$ ). The direction of association predicts that a low ACI would be favored by a high MSI for asphaltenes (i.e., the predominance of large asphaltene molecules would favor a relatively incompatible system). Branthaver et al. (18) reported that the asphaltene molecular weight, obtained by vapor phase osmometry in toluene or pyridine at 60°C, does not relate to compatibility. The conclusion may then be that distribution of molecular sizes within asphaltenes, rather than asphaltene molecular weight, affects compatibility. In GPC analysis, the size parameter that is important is not molecular weight, but the average volume that a molecule assumes in a dynamic-flowing environment.

$$V_h = [\eta]M \quad (2)$$

TABLE 15 CORRELATION BETWEEN ACI AND SOME PHYSICOCHEMICAL PARAMETERS OF ASPHALTS—INFLUENCE OF TWO UNIQUE ASPHALTS

Physicochemical Parameter	n		Correlation Coefficient, <i>r</i>	
	*	**	*	**
Saturates	Percentage	20 18	-0.66	-0.55 <sup>α</sup>
	MSI	19 17	0.64	-0.03
Naphthene Aromatics	Percentage	20 18	0.44	0.62 <sup>αα</sup>
	MSI	19 17	0.80	0.05
Polar Aromatics	Percentage	20 18	0.90	0.56 <sup>α</sup>
	MSI	19 17	0.70	0.00
n-Hexane Asphaltenes	Percentage	20 18	-0.86	-0.75 <sup>αα</sup>
	MSI	19 17	-0.26	-0.65 <sup>αα</sup>
n-Heptane Asphaltenes (Percentage)		20 18	-0.84	-0.68 <sup>αα</sup>
I <sub>c</sub>		20 18	-0.88	0.56 <sup>α</sup>
MSI Whole Asphalt		20 18	0.67	-0.52 <sup>α</sup>
Penetration, 25°C		20 18	0.03	-0.34
Viscosity, 60°C		20 18	-0.33	-0.22
Viscosity, 135°C		20 18	0.28	-0.28
Viscosity Ratio, 60°C		20 18	-0.34	-0.22
VIS		20 18	-0.64	0.26
PVN, 60°C		20 18	-0.42	-0.66 <sup>αα</sup>
PVN, 135°C		20 18	0.29	-0.53 <sup>α</sup>
Including 88-2570 and 2787 asphalts.			Excluding 88-2570 and 2787 asphalts.	

<sup>α</sup>Denotes significant correlation; <sup>αα</sup>denotes highly significant correlation. Correlations involving the two unique asphalts are not marked, and reported only for comparison.

The correlation coefficient, *r*, for the parameters above the dividing line was obtained by considering the physicochemical parameter as independent variable, and ACI as dependent variable; the opposite applies for parameters below dividing line.

where  $V_h$  is the hydrodynamic volume,  $\eta$  the intrinsic viscosity, and  $M$  the molecular weight. The molecular volume is determined by molecular weight, structure, configuration, and solute associations (24). An aromatic molecule with rather long, not highly branched side chains would have a large molecular volume but a relatively small molecular weight.

The colloidal instability index,  $I_c$ , shows a significant correlation with ACI; the positive association implies that a low  $I_c$  favors a low ACI. The MSI of whole asphalt correlates significantly with ACI; a high MSI favors a low ACI. The significant correlation and negative association between MSI of whole asphalt and ACI mutually confirm the validity and significance of the two new parameters.

The two parameters of MSI and ACI indicate that the values obtained for two asphalts 88-2570 and 2787 are out of the range found for the 18 other asphalts. One common rule of thumb for identifying suspected outliers (11) singles out values falling at least 1.5 times the interquartile range (IQR) above the third quartile,  $Q_3$  (75th percentile) or below the first quartile,  $Q_1$  (25th percentile). Applying the  $1.5 \times \text{IQR}$  rule to the set of 20 asphalts indicates that an  $\text{MSI} > 0.62$  and an  $\text{ACI} > 2.422$  is an outlier. Each of the two asphalts have an MSI and an ACI that is higher than the calculated value.

When outliers exist, the first option (11) is to search for a cause and have the data corrected. In the present case, however, outliers are caused by factors associated with crude source, refinery processes, additives, or some other related criteria that are beyond the scope or control of this study. Moore and McCabe (11) state, "If some other abnormal condition caused the outlier, we can delete it from the data with a clear conscience."

Calculating *r* after excluding the two asphalts 88-2570 and 2787 (Table 15, top part) shows that the correlation coefficient can be significantly affected, to the point where the sign of association is reversed, that is, correlation between ACI and each of  $I_c$  and MSI of whole asphalt. The effect of excluding the two asphalts is also evident from the correlation between ACI and MSI of Corbett fractions. The least affected are correlations between ACI and Corbett fraction's content. The two asphalts have fraction contents that are generally not much different from the whole set (Table 3), but MSI of their Corbett fractions (except asphaltene) is quite different (Tables 6 through 9). That the value of *r* after excluding the two asphalts is different from that obtained for the whole set is not unexpected, however, because *r* is not resistant [i.e., one or more entries can greatly influence the correlation coefficient].

cient (11)]. A basic scatter plot of  $Y$  versus  $X$  shows that the two asphalts possess physicochemical parameters data (MSI of whole asphalt, ACI,  $I_c$ , MSI of saturates, naphthene aromatics, and polar aromatics) that are extreme in value. Such data may therefore be influential, and removing them would markedly change the position of regression line (11).

### Effect of ACI on Some Physical Parameters

Branthaver et al. (18) reported that parameters that measure compatibility should correlate with variations in viscosity with temperature, but not necessarily with absolute viscosity. Our findings confirm this statement. Table 15 (lower part) indicates that correlation between ACI and both the absolute viscosity and kinematic viscosity is not significant. On the other hand, ACI correlates significantly with PVN, 135°C and highly significantly with PVN, 60°C; a low ACI favors a high PVN.

Excluding 88-2570 and 2787 caused  $r$  to change, sometimes markedly as for the correlation between ACI and each of viscosity, 135°C; VTS; and PVN, 135°C. From Table 15 (lower part), excluding the two asphalts significantly changes correlations involving parameters measured, or derived from measurements, at high temperature (135°C). These parameters have been shown to correlate highly significantly with MSI of whole asphalt (Table 5). Indeed, the two asphalts have proved to possess a unique MSD as opposed to the other 18 asphalts (Table 4).

### Viscosity Ratio as a Measure of Resistance to Aging

The correlation between ACI and viscosity ratio is not significant (Table 15). Furthermore, viscosity ratio proved to be the least correlated to any of the parameters studied [e.g., it is not significantly correlated to MSI of whole asphalt (Table 5), MSI of any of Corbett fractions (Table 11), or the naphthene aromatics or asphaltene content (Table 12)]. Resistance to aging may alternatively be evaluated by another parameter, such as MSI before and after aging, as shown later.

### Effect of Laboratory Aging on MSI

As expected, the 16-hr TFOT caused MSI of original asphalt to increase (compare Tables 4 and 16). The rate of change (MSI of aged asphalt divided by MSI of original asphalt) may serve as a measure of the resistance to aging. The 10 original asphalts with MSI of  $\geq 0.42$  suffer the least change in MSD (rate of increase ranging from 1.10 to 1.50).

### Correlation Between Resistance To Aging and Some Physicochemical Parameters for 18 Asphalts

The correlation between MSI of original asphalt as independent variable and rate of change of MSI as dependent variable has a coefficient of  $-0.55$  (Table 17). The numerical value reflects a significant correlation even at the 2 percent level; the negative association indicates that original asphalts with

TABLE 16 MSI OF LABORATORY-AGED ASPHALT; RATE OF CHANGE OF MSI DUE TO 16-hr TFOT

Sample Number	MSI	MSI aged MSI original
82-1214	0.66	1.53
1332	0.46	1.70
1522	0.59	1.26
2746	0.63	1.50
83-3203	0.57	1.46
3284	0.71	1.37
85-1230	0.67	1.49
3695	0.56	1.12
3890	0.40	1.48
4116	0.67	1.46
86-3063	0.58	1.26
3113	0.86	2.32
87-2040	0.58	1.71
88-2381	0.61	1.74
2192	0.59	1.48
2483	0.65	1.81
2570	1.00	1.41
2787	1.28	1.42
3680	0.52	1.41
3719	0.63	1.75

a high MSI tend to have a minimum change in their MSD due to aging (i.e., manifest a high resistance to aging).

Table 17 indicates that resistance to aging (expressed as rate of change of MSD) is not correlated with either the percentage or the MSI of any of Corbett fractions. However, the MSI of polar aromatics and asphaltene content manifest  $r$  values that are not too small; the sign of association suggests that a high MSI for either fraction should accompany a low rate of change of MSD. The temperature susceptibility parameters are not correlated with the rate of change of MSD or with viscosity ratio. Viscosity ratio correlates significantly with  $I_c$ .

### Correlation Between Temperature Susceptibility and Some Physicochemical Parameters for 18 Asphalts

The MSI of whole asphalt correlates significantly with VTS and highly significantly with PVN, 135°C; a high MSI favors a low VTS and a high PVN, 135°C (Table 18). The  $I_c$  correlates nonsignificantly with VTS and PVN. No correlation exists between temperature susceptibility and content of any of Corbett fractions except that of naphthene aromatics, which correlates significantly with PVN, 135°C. A low naphthene aromatics content favors a high PVN. Only MSI of asphaltene content correlates with temperature susceptibility; it correlates significantly with VTS and highly significantly with PVN, 135°C.

TABLE 17 CORRELATION COEFFICIENT,  $r$ , FOR SOME PHYSICOCHEMICAL PARAMETERS AND THE RESISTANCE TO AGING FOR 18\* ASPHALT CEMENTS

Physicochemical Parameter**	Resistance to Aging	
	Rate of Change of MSD	Viscosity Ratio
MSI of Whole Asphalt	-0.55 <sup>α</sup>	0.11
ACI	0.26	-0.22
I <sub>C</sub>	-0.04	0.52 <sup>α</sup>
Saturates	Percentage	-0.03
	MSI	0.42
Naphthene Aromatics	Percentage	0.11
	MSI	0.12
Polar Aromatics	Percentage	0.02
	MSI	-0.33
Asphaltenes	Percentage	-0.13
	MSI	-0.28
Penetration, 25°C	Percentage	0.03
	MSI	-0.42
Viscosity, 60°C	Percentage	-0.40
	MSI	-0.11
Viscosity, 135°C	Percentage	-0.03
	MSI	0.34
VTS	0.06	0.14
PVN, 60°C	-0.27	0.12
PVN, 135°C	-0.36	-0.03
	0.29	0.28
	-0.22	0.16

\*For  $n=18$ ;  $df=16$  and  $r=0.468$  and  $0.590$  at the 5% and 1% levels of significance, respectively.

\*\*The physicochemical parameter is considered the independent variable, and resistance to aging as the dependent variable.

<sup>α</sup>Denotes a significant correlation.

A high MSI for asphaltenes favors a low temperature susceptibility. Correlation between the two temperature susceptibility parameters and MSI of polar aromatics is significant at the 10 percent level; a high MSI favors a low temperature susceptibility.

The penetration, 25°C and viscosity, 60°C do not correlate with susceptibility, whereas viscosity, 135°C correlates significantly with VTS and highly significantly with PVN, 135°C—in exactly the same way that the MSI of whole asphalt correlates with susceptibility (Table 18). Table 5 has also indicated that viscosity, 135°C and MSI of whole asphalt show a highly significant correlation. Thus, viscosity, 135°C; MSI of whole asphalt; and temperature susceptibility are all at least significantly intercorrelated.

## CONCLUSION

For the set of 20 asphalts studied, the following conclusions are drawn:

1. MSD (expressed as MSI or LMS/MMS) of whole asphalt correlates significantly with I<sub>C</sub> and highly significantly with ACI; viscosity, 135°C; VTS; and PVN, 135°C.

2. For any given asphalt, there is a continuous increase in MSI of Corbett fractions going from saturates to naphthene aromatics to polar aromatics to asphaltenes. None of the 20 asphalts is an exception. Therefore, a direct relationship exists between MSI and polarity.

3. Some of the parameters measured, or derived from measurements, at 60°C (e.g., viscosity ratio; VTS; and PVN, 60°C) correlates significantly with the percentages of some Corbett fractions. Parameters measured, or derived from measurements, at 135°C (e.g., VTS; PVN, 135°C; and viscosity, 135°C) correlate highly significantly with MSI of some Corbett fractions. A high MSI for asphaltenes favors a low temperature susceptibility.

4. Polar aromatics fraction has some distinct features. It is the only fraction that shows a correlation between content and MSI. The content is highly significantly correlated with MSI of whole asphalt, with VTS, and significantly correlated with viscosity ratio. The MSI is the closest to that of whole asphalt.

5. Two asphalts, 88-2570 and 2787, showed MSI, ACI, as well as MSI of Corbett fractions (except asphaltenes) that are markedly different from the 18 other asphalts. Applying the 1.5 times IQR rule for detecting outliers to the set of 20 samples shows that whole asphalts with MSI and ACI > 0.62

TABLE 18 CORRELATION COEFFICIENT,  $r$ , FOR SOME PHYSICOCHEMICAL PARAMETERS AND THE TEMPERATURE SUSCEPTIBILITY FOR 18 ASPHALT CEMENTS

Physicochemical Parameter*	Temperature Susceptibility	
	VTS	PVN, 135°C
MSI of Whole Asphalt	-0.52 <sup>α</sup>	0.71 <sup>αα</sup>
I <sub>c</sub>	-0.13	-0.45
Saturates { Percentage	-0.33	0.33
MSI	-0.34	0.39
Naphthene { Percentage	0.34	-0.50 <sup>α</sup>
Aromatics { MSI	-0.36	0.15
Polar { Percentage	0.04	-0.27
Aromatics { MSI	-0.45	0.42
Asphaltenes { Percentage	0.06	0.30
MSI	-0.53 <sup>α</sup>	0.65 <sup>αα</sup>
Penetration, 25°C	-0.45	0.28
Viscosity, 60°C	-0.06	0.34
Viscosity, 135°C	-0.50 <sup>α</sup>	0.71 <sup>αα</sup>

\*The physicochemical parameter is considered the independent variable, and the temperature susceptibility the dependent variable.

<sup>α</sup>Denotes a significant correlation.

<sup>αα</sup>Denotes a highly significant correlation.

and 2.422, respectively, are outliers—a condition that applies to the two asphalts. Furthermore, data for MSI of saturates, naphthene aromatics, and polar aromatics fractions indicate that at least one of the two asphalts is an outlier. Consequently, many correlations change appreciably after excluding the two asphalts. The most noticeable change occurs for correlations between ACI and each of MSI (of whole asphalt and of Corbett fractions) and parameters measured, or derived from measurements, at 135°C.

Excluding the two asphalts (i.e.,  $n = 18$ ), the following conclusions are drawn:

6. Of the MSI of Corbett fractions, only that of asphaltenes correlates with ACI and with temperature susceptibility. A high MSI for asphaltenes favors a low ACI and a low temperature susceptibility (VTS and PVN, 135°C).

7. Of the percentage of Corbett fractions, only that of naphthene aromatics correlates with PVN, 135°C. None correlates with VTS or with resistance to aging.

8. The ACI correlates significantly with each of MSI of whole asphalt; PVN, 60°C; PVN, 135°C; and I<sub>c</sub>. A low ACI accompanies a high MSI for whole asphalt; a high PVN, 60°C; PVN, 135°C; and a low I<sub>c</sub>.

9. MSI of whole asphalt correlates significantly with ACI, temperature susceptibility, and resistance to aging (expressed as rate of change of MSD due to 16-hr TFOT), and correlates highly significantly ( $r = 0.65$ ) with viscosity, 135°C. A high MSI ( $>0.62$ ) for whole asphalt favors a minimum temperature susceptibility; a high resistance to aging; and a high viscosity, 135°C.

10. Viscosity, 60°C and penetration, 25°C do not correlate with any of the parameters studied: temperature susceptibility, resistance to aging, ACI, MSI of whole asphalt, or the percentage, the MSI of any of Corbett fractions.

11. Viscosity ratio correlates only with I<sub>c</sub> (at the 5 percent level) but not with any of the other parameters. The rate of change of MSD of an asphalt due to aging may also serve as a measure of aging—a primarily chemical process. Rate of change of MSD due to 16-hr TFOT correlates significantly (at the 2 percent level) with MSI of whole asphalt; a high MSI for whole asphalt favors a minimum rate of change of MSI.

12. Because  $n$  is reasonably large and the original asphalts tested are randomly selected (random here refers to the fact that samples cover a wide range of viscosity and a large number of sources), the value of  $r$  calculated herein for a given correlation is an unbiased estimate of  $\mu$ , the correlation coefficient for population of asphalt cements.

13. To put the preceding significant/highly significant associations together and select from among the set of 18 asphalt cements those with potential for good field performance, the analysis started with MSI of whole asphalt, because it correlates at least significantly with temperature susceptibility and resistance to aging (as expressed by rate of change of MSI). Eight asphalts with MSI  $\geq 0.42$  have the following characteristics: MSI of 0.42 to 0.52; ACI of 0.72 to 2.00; I<sub>c</sub> of 0.25 to 0.58; viscosity, 135°C of 305 to 416 cst; VTS of 3.45 to 3.59; PVN, 135°C of -0.25 to -0.81; rate of change of MSI from 1.12 to 1.53; and MSI of asphaltenes from 1.86 to 2.95. To use the specified ranges for selection from among a



wider collection of asphalts, the  $1.5 \times \text{IQR}$  rule for identifying outliers may be used to find upper and lower permissible limits of variation (e.g.,  $\text{MSI} \geq 0.62$  and  $\text{ACI} \geq 2.422$ ).

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