Variations in Molecular Size Distribution of Virgin and Recycled Asphalt Binders Associated with Aging

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The relative amounts and characteristics of asphaltenes, oils, and resins in a given asphalt have an important effect on its physical characteristics and value as a paving material. A more recent procedure to separate asphalt into fractions of various molecular sizes makes use of high pressure liquid chromatography in the gel permeation mode, referred to as high pressure-gel permeation chromatography (HP-GPC). This procedure can be used to classify asphalt molecules into three groups according to their molecular size: large molecular size (LMS) component, medium molecular size (MMS) component, and small molecular size (SMS) component. The balance between the relative amounts of these molecules is an important attribute of asphalt durability and its ability to perform properly in paving mixtures. This paper presents a study in which the changes in properties of a virgin AC-20 (ASTM designated) due to aging are characterized by means of the HP-GPC. Furthermore, molecular size distribution analysis was used to characterize Mobilsol-30 (a recycling agent) and to determine the proper amount required to restore salvaged binders to an AC-20 specification range. In addition, the changes in properties due to aging of the weathered binder that had been restored to an AC-20 specification range were also characterized by means of the HP-GPC. It was concluded that the weathering actions (simulated in the laboratory) would cause increases in LMS and decreases in MMS and SMS. These changes may be detrimental to asphalt characteristics because they result in drastic changes in asphalt consistency. A greater amount of a specific recycling agent is required to restore a more age-hardened binder to its original consistency; hence, the more the molecular size distribution moves away from the original balance. This could be resolved, however, by using different types of recycling agents for different hardening levels of salvaged asphalt or by using more than one recycling agent in proper proportions. Temperature susceptibility may be affected when high percentages of recycling agents are required because of severe hardening characteristics of the salvaged asphalt binder. The high pressure gel-permeation chromatography analysis for the virgin and recycled asphalt binders may be recommended as a criterion for the choice of the proper amount and characteristics of a recycling agent to be used to rejuvenate salvaged asphalt.

Asphalt is considered a combination of asphaltenes, resins, and oils. Many other fractional classifications have been reported about asphalt composition. However, this classification is still considered the simplest and most understandable one. Asphaltenes are more viscous than the resins and oils, respectively. They play a major role in determining asphalt viscosity (*1*). Chemical reactions take place inside asphalt when it is exposed to heat, air (oxygen), light, or other environmental physical actions. Oxidation causes the oils to convert to resins and the resins to asphaltenes (*2*). Heating an asphalt causes volatilization of the oil fraction and also assists oxidation. This convention process increases with time in the field, causing aged asphalt to have a high asphaltene content and, hence, to be more viscous. The selective absorption of the oil fraction caused by the presence of mineral aggregate may result in more hardening (*3*). Furthermore, mineral aggregate surfaces may act as a catalyst for the oxidation process and aggravate the age-hardening process (*4*).

Rejuvenating agents are used (a) to bring the asphalt to a suitable chemical composition for durability and (b) to restore the asphalt characteristics to a consistency level appropriate to the mix (*5*). Dunning and Mendenhall (*6*) suggested that the approach best suited to recycling asphalt is to improve the ability of the maltene fraction (resins and oils) of a recycled asphalt to disperse the asphaltene fraction. They suggested that a minimum of 69 percent of the maltene fraction needs to be present to disperse a maximum of 31 percent asphaltenes. Terrel and Fritchen (*7*) suggested a similar approach by selecting a recycling agent to keep the asphaltene-to-maltene ratio at a certain level. Noureldin (*1*) suggested that a maltene content of 70 percent minimum and 80 percent maximum is the best to disperse the asphaltenes without causing the AC-20 to be highly susceptible to temperature.

A high percentage of asphaltenes (more than 30 percent) present in asphalt would result in a pavement with potential cracking problems (*6,8*), whereas low percentages of asphaltenes (less than 20 percent) present in asphalt would result in a highly temperature susceptible paving mixture with potential rutting problems (*1*). Similar effects would be expected from asphalts with low or high percentages of maltenes (oils + resins), respectively. Optimum percentages for an AC 60/70 penetration grade (similar to AC-20, ASTM) were found to be 25 ± 5 percent asphaltenes, 50 ± 5 percent resins, and 25 ± 5 percent oils, respectively, in a previous study conducted by the author (*1*).

A more recent procedure to separate asphalt into various molecular size fractions makes use of high pressure liquid chromatography in the gel permeation mode referred to as HP-GPC (*9*). Jennings et al. (*10*) classified asphalt constituents into three groups according to their molecular size: large

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molecular size (LMS) component, medium molecular size (MMS) component, and small molecular size (SMS) component. Asphalts with smaller amounts of LMS material were found to perform better (with respect to cracking potential) than do those with larger amounts (*11*).

This paper presents a study in which the molecular size distributions were obtained and compared for virgin AC-20, artificially hardened AC-20, a more severely artificially hardened AC-20, a field-aged AC-20 present in recycled asphalt pavement (RAP), and asphaltenes separated from a virgin AC-20. This comparison helped in understanding the changes in molecular size distribution of an asphalt binder present in an asphalt mixture throughout the pavement life span. In addition, the molecular size distributions of Mobilsol-30 (a rejuvenating agent) and the hardened binders rejuvenated by Mobilsol-30 were also obtained in order to investigate the changes in molecular size distributions of aged binders after a rejuvenator has been used.

MOLECULAR SIZE DISTRIBUTION TEST PROCEDURE

The HP-GPC testing equipment consists mainly of a solution injection unit connected to six silica gel porous columns through which the sample solution is pumped. The silica gel pore arrangement allows larger molecules of a sample to flow through a differential refractometer detector, followed by progressively smaller molecules. The detector continuously scales the amount of molecules flowing through as a function of time. The system is connected to a recorder that gives a continuous tracing of time versus amount of flowing molecules. A general view of this system is shown in Figure 1. The test procedure used, reported by Garrick (*12*), can be summarized as follows.

1. An asphalt sample is weighed on a sensitive scale and is allowed to dissolve in a tetrahydrofuran (THF) solvent. Asphalt concentration in solvent is adjusted to be 1 percent. This is achieved by dissolving 0.0527 g of asphalt in a 5.223-g (6-mL) solvent.
2. The solution is drawn by a 6-mL injector and then pushed out to a clean glass container through a filter (fixed inside the injector) to ensure the purity of the solution.
3. A 0.5-mL quantity of the solution is then immediately drawn by a smaller injector and injected into the HP-GPC system through its injection unit.
4. The solution is drawn through the gel permeation columns and allowed to flow at a rate of 2 mL/min. This is achieved by increasing or decreasing the pump pressure gauge until 10 mL of THF solution can be drawn out of the system in a 5-min period before the sample injection.

The gel permeation columns separate constituents of asphalt by molecular size. The columns contain porous silica gel that permits the largest molecules to pass first and successively retards the progress of the smaller molecules. A detector and a recorder within the system produce a chromatogram depicting the relative amount of molecules being eluted from the HP-GPC system at different times. The plot of the relative quantity of molecules versus time represents the molecular size distribution (MSD) of the asphalt sample being analyzed. It must be remembered that the resulting distribution is a function of both the solvent and the column used in the determination.

SAMPLING PLAN AND MATERIAL

The following 10 binders were analyzed by the HP-GPC for comparison purposes.

Binder 1. Virgin AC-20, H_o. A virgin AC-20 was obtained from Amoco Oil Company. Its characteristics are given in Table 1.

Binder 2. AC-20, H_1. An artificially weathered AC-20 was obtained by heating a sample of virgin AC-20 (H_o) in an oven at 140°F for 8 days.

Binder 3. AC-20, H_2. An AC-20 (H_o) was weathered under actual field conditions. The recycled asphalt pavement (RAP) used was milled from US-52 (south of Indianapolis, Indiana)

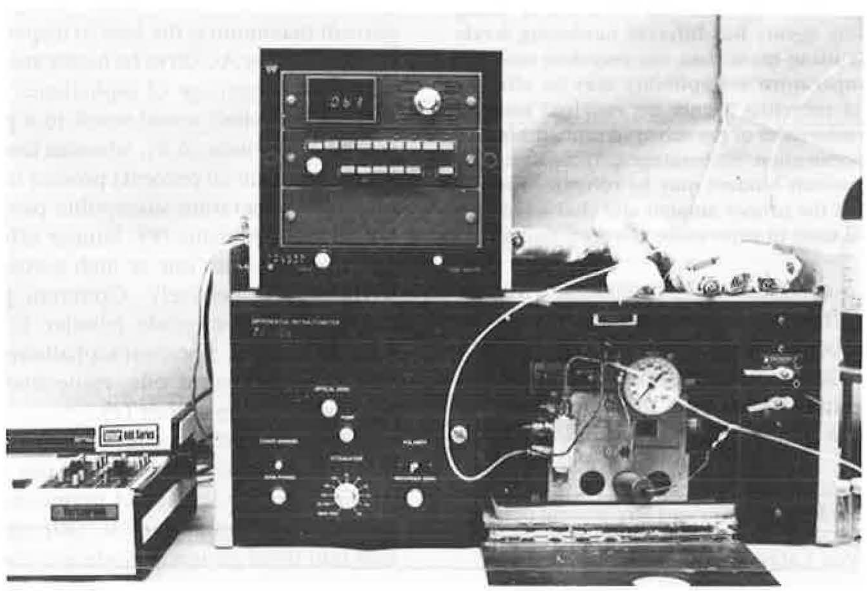

FIGURE 1 HP-GPC equipment.

and selected under the supervision of Indiana Department of Highways personnel. Samples of the RAP were reduced in size for laboratory evaluation. Asphalt extraction and recovery were conducted using ASTM D2172 Method A and Abson Method ASTM D1856. The salvaged binder was characterized by means of penetration, softening point, and viscosity tests. Table 2 gives the amount and physical characteristics of the extracted hard asphalt.

Binder 4. AC-20, H_3. An artificially weathered AC-20 (H_o) was obtained by heating a sample of virgin AC-20 in an oven at 250°F for 24 hr.

Binder 5. Asphaltenes. The asphaltene fraction of a virgin AC-20 (H_o) was separated using heptane solvent and the standard method of separating asphalt into fractions, ASTM D4124.

Binder 6. Mobilsol-30. A rejuvenating agent produced by McConnaughy, Inc., Mobilsol-30 is an ASTM-designated type 101 oil. Table 3 gives the characteristics of Mobilsol-30. This is a softening agent used for rejuvenating the hardened asphalt present in RAP. The selection of this softening agent was based on its previous usage in pavement recycling operations.

Binder 7. Recycled AC-20, 1. This binder consists of 85 percent of Binder 3 (RAP) and 15 percent of Binder 6 (Mobilsol-30). It represents the recycled binder after it has been restored to AC-20 consistency range. The percentages required to obtain a binder with a viscosity and a penetration within the AC-20 specification range were 85 percent and 15 percent.

TABLE 1 CHARACTERISTICS OF AC-20

Test	Value
Penetration (100 gm, 5 sec, 77°F, 0.1 mm)	65
Absolute viscosity (140°F, poise)	1890
Softening point (°F)	122
Ductility (77°F, 5 cm/min, cm)	150+

TABLE 2 CHARACTERISTICS OF EXTRACTED HARD ASPHALT

Test	Value
Penetration (77°F, 100 gm, 5 sec)	28
Viscosity (140°F, poises)	20,888
Kinematic viscosity (275°F, c. st.)	726
Softening point (°F)	137
Asphalt content (total weight, %)	6

TABLE 3 CHARACTERISTICS OF MOBILSOL-30

	Value
Asphaltenes (%)	0
Polar compounds (%)	8
Aromatics (%)	79
Saturates (%)	13
Flash point (°F)	505
Kinematic viscosity at 140°F (c. st.)	164
Specific gravity	0.974

NOTE: Constituents were obtained using Clay-Gel Analysis (ASTM D2007-75).

Binder 8. Recycled AC-20, 2. This binder consists of 70 percent Binder 4 and 30 percent Binder 6. It also represents the recycled asphalt after it has been restored to AC-20 consistency range as Binder 7. The only difference is that the weathered binder to be restored is harder and requires more softening agent for the AC-20 specification range.

Binders 9 and 10. Artificial weathering conditions to which Binder 1 (virgin AC-20) was subjected and that resulted in the production of Binder 2 were repeated for Binders 7 and 8. Binders 9 and 10 are those obtained from those artificial hardening conditions.

The layout and the procedure for producing the 10 binders to be analyzed by the HP-GPC equipment are given in Figure 2. It should be noted that 7 of these 10 binders were created from the other 3 (virgin AC-20, Mobilsol-30, and salvaged asphalt present in the RAP).

EXPERIMENTAL DESIGN

This study was statistically designed in order to investigate the effect of binder types. This factor consists of 10 levels (10 binder types). The following model was used to introduce the data in a mathematical form:

$$P = M + B_i + E_{ij}$$

where

P is the percentage of LMS, MMS, or SMS present in the binder;
M is an overall mean,
B_i is the binder type effect (fixed); and
E_{ij} is the experimental error (random).

A completely randomized design with one factor having 10 levels and three replications for each level was applied *(13)*.

HP-GPC TEST RESULTS AND ANALYSIS

Molecular size distribution (MSD) plots were obtained for the 10 binders. Figure 3 illustrates the MSD for the virgin AC-20 (Binder 1). The area under the curve, which represents the relative amount of molecules present in the AC-20 sample, was divided into three parts: LMS area, MMS area, and SMS area. The elution times separating the three areas were chosen to be 26.5 and 28.8 min, respectively. The choice was made to obtain 25 percent, 50 percent, and 25 percent as the percentages of LMS, MMS, and SMS present in an AC-20. The same separating times were used to compare the 10 binders.

Tables 4 and 5 present the LMS, MMS, and SMS percentages (average of three replications) present in the 10 binders identified previously. The penetration and absolute viscosity values of the 10 binders are also included. It should be noted that the results for the three replications were almost identical, suggesting the precision of the HP-GPC system in analyzing asphalt samples.

A complete analysis of variance (ANOVA) was conducted to detect significant differences between the molecular size distributions of the 10 binders. The least significant difference between each of two means was found to be 1.37, 1.32, and 1.48 for LMS, MMS, and SMS, respectively.

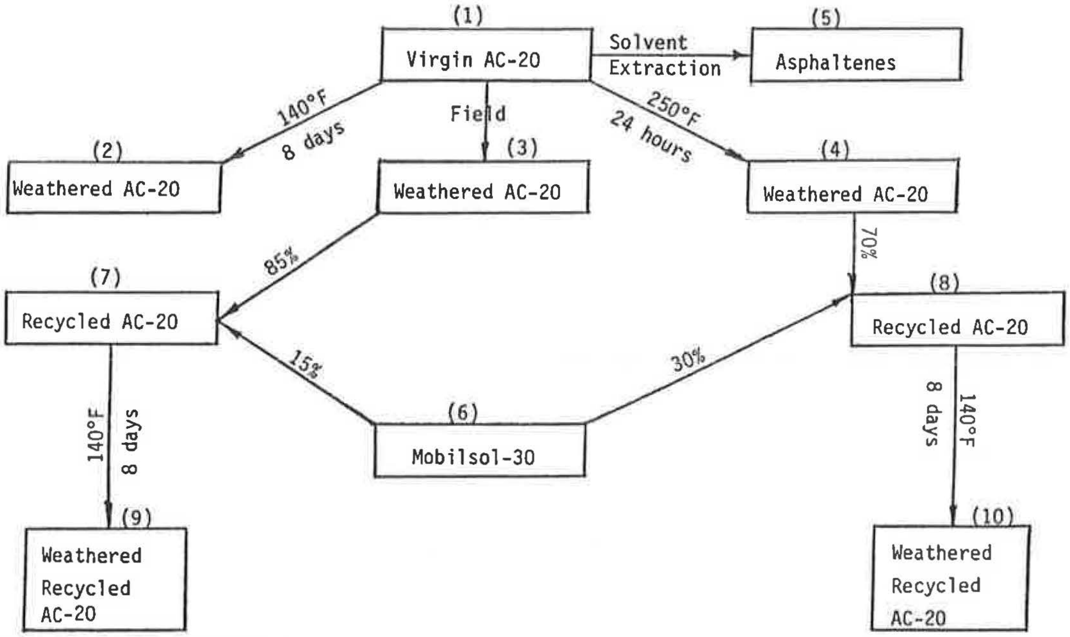

FIGURE 2 Layout of the 10 binders analyzed by HP-GPC.

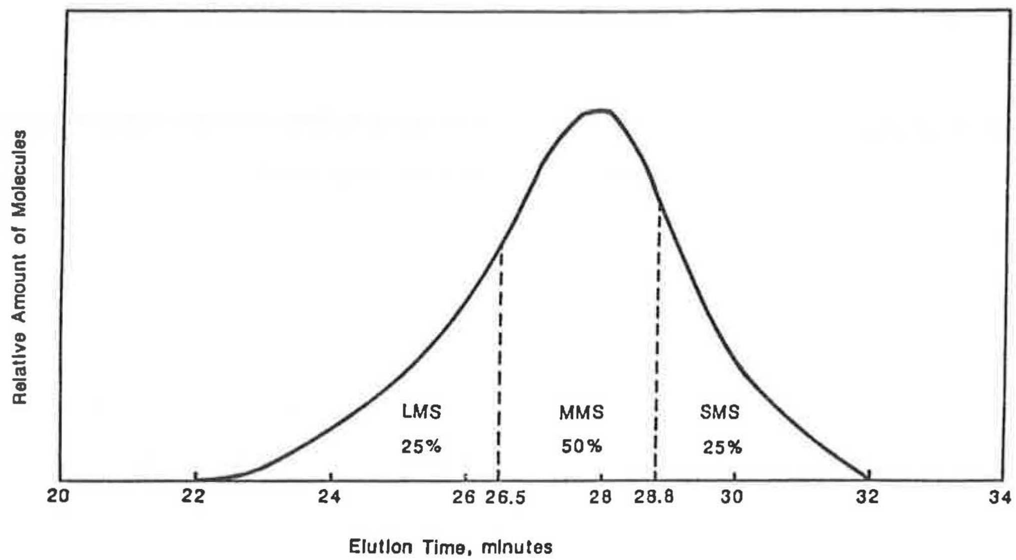

FIGURE 3 Molecular size distribution plot of AC-20 obtained by HP-GPC system.

Time-Temperature Effect on Molecular Size Distribution (MSD) of Virgin AC-20

Data presented in Table 4 suggest that the artificial weathering actions to which virgin AC-20 (Binder 1) was subjected would result in a significant increase in the IMS component together with a significant decrease in the MMS and SMS components, as can be observed from MSD values for Binder 2. The more severe the artificial hardening process, the greater is the increase in IMS components and the decrease in MMS and SMS components, as can be seen from MSD values for Binder 4. However, the decrease in the SMS component becomes less substantial than that of the MMS component. The changes in MSD by the artificial laboratory hardening process were also accompanied by an increase in the viscosity and a decrease in the penetration values.

HP-GPC analysis for Binder 3, which is AC-20 subjected to actual environmental and weathering actions in the field, resulted in an MSD, penetration, and viscosity values between Binder 2 and Binder 4.

It can be concluded that, generally, time and temperature would cause AC-20 (Binder 1) to transform to Binder 2, then to Binder 3, and then to Binder 4 (from a molecular size distribution standpoint).

TABLE 4 MOLECULAR SIZE DISTRIBUTION FOR THE 10 BINDERS

	Binder									
	1	2	3	4	5	6	7	8	9	10
LMS (%)	25.2	30.6	33.2	37.8	91.1	0.0	26.1	27.0	31.1	33.3
MMS (%)	50.1	48.0	46.1	42.4	8.9	40.9	47.3	41.2	43.8	42.5
SMS (%)	24.6	21.5	20.7	19.8	0.0	59.1	26.6	31.8	25.1	24.2
Penetration	65	34	28	17	–[a]	–[b]	69	72	44	32
Viscosity (140°F, poise)	1,890	9,158	20,888	72,186	–[a]	–[b]	1,974	1,797	5,580	10,791

[a]Binder 5 (asphaltenes) was too brittle to run penetration or viscosity tests.
[b]Binder 6 (Mobilsol-30) was too soft to run penetration. Its kinematic viscosity at 140°F was 164 C.st.

TABLE 5 MOLECULAR SIZE DISTRIBUTION FOR THE 10 BINDERS: REPLICATION VALUES

Binder	(1)	(2)	(3)	(4)	(5)
LMS, %	25.2*	30.6	33.2	37.8	91.1
MMS, %	50.2	48.0	46.1	42.4	8.9
SMS, %	24.6	21.4	20.7	19.8	0.0
Binder	**(6)**	**(7)**	**(8)**	**(9)**	**(10)**
LMS, %	0.0	26.1	27.0	31.1	33.3
MMS, %	40.9	47.3	41.2	43.8	42.5
SMS, %	59.1	26.6	31.8	25.1	24.2

*Note: Percentage represents the average of 3 replications.

Asphaltenes Versus Mobilsol-30

Figure 4 illustrates the MSD for asphaltenes (Binder 5) and Mobilsol-30 (Binder 6), and Table 4 gives the IMS, MMS, and SMS percentages present in these two binders. Binder 5 has 0.0 percent SMS, whereas Binder 6 has 0.0 percent IMS. These results suggest that Binder 6 may be used as an additive (softening agent) for binders containing high percentages of IMS (hardened binders) and that Binder 5 may be used as an additive to those binders containing very low percentages of IMS.

Molecular Size Distribution for Recycled Binders

Binder 7 is composed of 15 percent Mobilsol-30 (Binder 6) and 85 percent RAP (Binder 3), and Binder 8 is composed of 30 percent Mobilsol-30 and 70 percent Binder 4. These compositions were used to obtain recycled binders having consistency characteristics similar to those of Binder 1 (AC-20). Specification limits for AC-20 are 60+ (AASHTO M226, Table 2) for penetration and 2,000 ± 400 poises for viscosity at 140°F.

It can be observed, from Table 4, that although the consistency characteristics (penetration and viscosity) of Binders 7 and 8 were restored to AC-20 classification range, significant differences exist between their MSD and that of AC-20 (Binder 1). Assuming that the MSD of AC-20 is the target distribution, Binder 7 has a slightly (but not significantly) higher percentage of LMS, a significantly higher percentage of SMS, and a significantly lower percentage of MMS. Binder 8 followed the same trend but with more drastic differences. This implies that the recycling process may restore the hardened asphalt back to the proper consistency requirements but may not at the same time restore the balance of the LMS, MMS, and SMS. In addition, the more an asphalt was hardened, the greater the amount of rejuvenating agent was required to fulfill proper consistency requirements and, hence, the more the MSD moves away from the original balance.

Time-Temperature Effect on the MSD of Recycled Binders

The MSDs of Binders 7 and 8 were transformed to Binders 9 and 10, respectively, under the same artificial hardening conditions causing Binder 1 to transform to Binder 2. A significant increase in IMS and a significant decrease in MMS were obtained when Binder 9 was compared with Binder 7. Similar trends were obtained when Binder 10 was compared with Binder 8 except for MMS, where a slight nonsignificant increase was noted. Penetration and viscosity values for Bind-

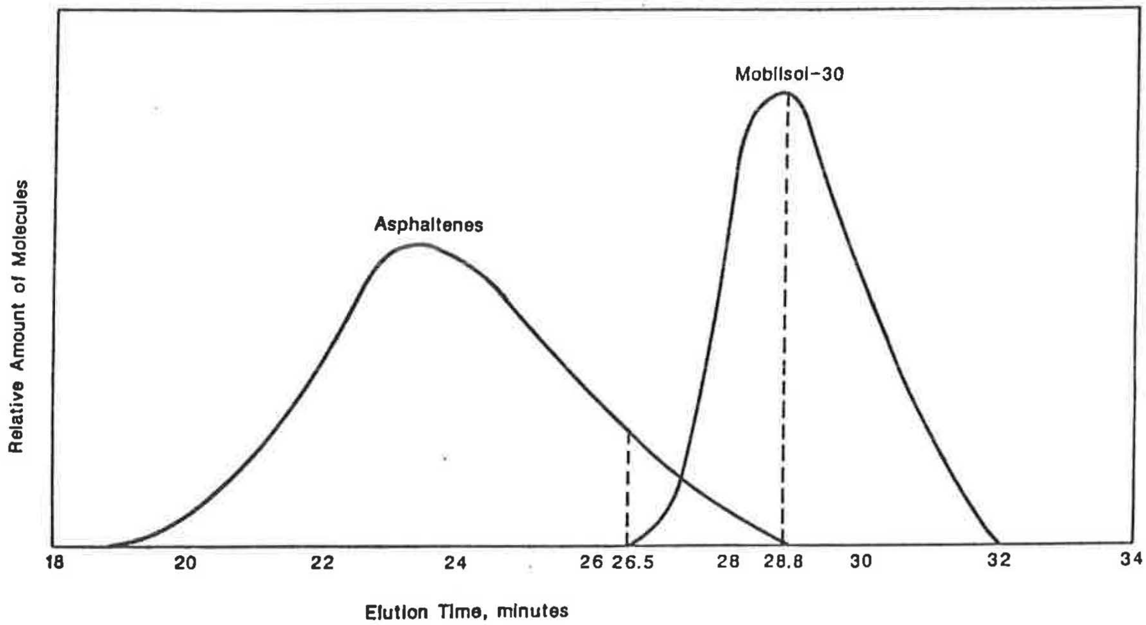

FIGURE 4 Molecular size distribution plot of asphaltenes and Mobilsol-30.

ers 7 through 10 indicate that Binder 7 may be less temperature susceptible than Binder 8. Binder 8 possesses a greater reduction in penetration value and an increase in viscosity when transformed to Binder 10 than when Binder 7 was transformed to Binder 9.

Approach for Choice of Proper Type and Amount of Recycling Agent

Most of the recycling operations involving the addition of virgin asphalt and/or a recycling agent are based on achieving a target consistency (based on viscosity) for determining the type and amount of the virgin binder. In other words, to restore a salvaged binder with a viscosity of 21,000 poises at 140°F to an AC-20 classification range (viscosity of 2,000 ± 400 poises at 140°F), a virgin asphalt and/or a softening agent with a lower viscosity is used. The required amount of this softening agent is determined on the basis of the target viscosity of the resulting binder (2,000 ± 400 poises). This may not be the proper approach because it does not assure the balance between molecules present in that resulting binder.

A more promising approach can be to choose a rejuvenating agent with a certain MSD to be added to the salvage binder to restore its MSD close to that of the target binder. In other words, if the target binder was AC-20 with an MSD of 25 percent—50 percent—25 percent for the LMS, MMS, and SMS and the old asphalt MSD was 35 percent—45 percent—20 percent for the LMS, MMS, and SMS, the amount of rejuvenating agent to be used in combination with the old asphalt is that required to obtain an MSD of 25 percent—50 percent—25 percent (or close to it) for the recycled binder. If there is no such amount to achieve that MSD, another recycling agent can be selected.

SUMMARY OF RESULTS

Asphalt binders are composed of molecules that can be divided by size into LMS, MMS, and SMS. A balance between the relative amounts of these molecules could be an important attribute relating to its durability and its ability to perform properly as an asphaltic binder. The main findings of this study can be summarized as follows.

1. Environmental and weathering actions in the field or simulated in the laboratory would cause changes in the relative amounts of LMS, MMS, and SMS present in the asphalt binder. These changes can be described as increases in LMS and corresponding decreases in MMS and SMS. They may be detrimental to asphalt characteristics because they result in drastic changes in asphalt consistency.
2. A recycling agent can restore the consistency characteristics of the weathered asphalt. However, the balance between LMS, MMS, and SMS may not be restored exactly.
3. The more age hardened an asphalt is, the greater the amount of recycling agent is required to restore original consistency and, hence, the more the MSD moves away from the original balance. It may be recommended, however, that this could be resolved by using different types of recycling agents for different hardening levels of asphalt or by using more than one recycling agent.
4. Temperature susceptibility may be affected when using high percentages of recycling agents required because of the severe hardening characteristics of an asphalt binder. This was noted for Mobilsol-30, which was the type of recycling agent used in this study.
5. Achieving a target MSD for the recycled binder may be considered as an approach to select the proper type and amount of virgin asphalt or recycling agent required for the recycling

operation. It is yet to be investigated, however, whether restoring asphalt consistency, restoring a certain MSD, or restoring both would result in better performance by recycled asphalt.

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REFERENCES

1. A. S. Noureldin. *Experimental and Statistical Evaluation and Improvements of Local 60/70 Asphalt Cement*. M.Sc. thesis. Faculty of Engineering, Cairo University, December 1982.
2. F. S. Rostler and R. M. White. Composition and Changes in Composition of Highway Asphalts, 85-100 Penetration Grade. *Proc., Association of Asphalt Paving Technologists*, Vol. 31, 1962, pp. 35–89.
3. J. A. Epps, D. N. Little, R. J. O'Neal, and B. M. Gallaway. *Mixture Properties of Recycled Central Plant Materials*. STP662, ASTM (L. E. Wood, ed.), Nov. 1978.
4. J. C. Petersen, F. A. Barbour, and S. M. Dorrence. Catalysis of Asphalt Oxidation by Mineral Aggregate Surfaces and Asphalt Components. *Proc., Association of Asphalt Paving Technologists*, Vol. 43, 1974, pp. 162–177.
5. D. D. Davidson, W. Canessa, and S. J. Escobar. Recycling of Substandard or Deteriorated Asphalt Pavements—A Guideline for Design Procedures. *Proc., Association of Asphalt Paving Technologists*, Vol. 46, 1977, pp. 496–525.
6. R. L. Dunning and R. L. Mendenhall. *Design of Recycled Asphalt Pavements and Selection of Modifiers*. STP662, ASTM (L. E. Wood, ed.), Nov. 1978.
7. R. L. Terrel and D. R. Fritchen. *Laboratory Performance of Recycled Asphalt Concrete*. STP662, ASTM (L. E. Wood, ed.), Nov. 1978.
8. H. Kuroda, S. Inui, and H. Tokuda. An Example of Reuse of Asphalt Mixture (in Japanese). *Hoso* (Pavement), Oct. 1976, References.
9. P. W. Jennings. Use of High Pressure Liquid Chromatography to Determine the Effects of Various Additives and Fillers on the Characteristics of Asphalt. Research Project FHWA/MT-82/001. Helena, Montana; FHWA, U.S. Department of Transportation, June 1982.
10. P. W. Jennings, J. A. S. Pribanic, D. R. Dawson, and C. E. Bricca. *Use of the HPLC and NMR Spectroscopy to Characterize Asphaltic Materials*. American Chemical Society, Division of Petroleum Chemistry, Washington, D.C., Aug. 1981, p. 915.
11. P. W. Jennings and J. A. S. Pribanic. The Expanded Montana Asphalt Quality Study Using High Pressure Liquid Chromatography. Research Report FHWA/MT-85/001. Montana DOH Research Program, Helena, April 1985.
12. N. W. Garrick. *Using High Pressure-Gel Permeation Chromatography to Evaluate the Influence of the Chemical Composition of Blended Asphalts*. Ph.D. thesis. Purdue University, West Lafayette, Ind., Aug. 1986.
13. V. L. Anderson and R. A. McLean. *Design of Experiments: A Realistic Approach*. Marcel Dekker, Inc., New York, 1974.

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