

# Effects of Asphaltenes on Asphalt Recycling and Aging

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Blends made using n-hexane asphaltenes from asphalts, SHRP AAG-1, AAD-1, and AAK-2 and maltenes from SHRP AAG-1 and AAD-1 were laboratory-aged to study the effects of asphaltenes on rheological properties. For comparison, maltenes from SHRP AAG-1 and AAD-1 as well as their parent asphalts were aged at the same aging conditions as those of blends. The laboratory oxidation conditions were pure oxygen pressure at 20.7 bar absolute, temperatures of 71.1, 82.2, and 93.3°C with aging times from 1 to 24 days depending on aging temperature. The changes due to oxidative aging were monitored by asphaltene precipitation in n-hexane, Fourier transform infrared spectroscopy, and dynamic mechanical analysis at 60°C. Oxidative aging of asphalts and maltenes results in the formation of carbonyl compounds, the production of asphaltenes, and an increase in viscosity. The change in asphaltene content with respect to the change in carbonyl content is quantified by defining the asphaltene formation susceptibility (AFS). The type of asphaltenes, regardless of their sources, have no effect on AFS. Therefore, it appears that AFS is a strong function of maltene composition. However, the effect of asphaltenes on viscosity is only moderately dependent on the asphalt source of the asphaltenes. The results of this study show that the maltene composition has the dominant effect on the oxidation behavior of an asphalt. For recycling of road pavement, the results also suggest that a recycling agent should be chosen so that the mixture of the recycling agent and the maltene from the old pavement possesses good oxidation properties.

It is well documented that a major factor in asphalt aging and hardening is the formation of asphaltenes by oxidation of aromatic components in the maltene fraction. It has been proposed (1-3) that asphalt consists of asphaltene micelles, or clusters, solubilized by polar aromatics. If so, it is reasonable to expect asphaltenes to obey a modified Pal-Rhodes model (4) for dispersion of particles in a liquid. Lin et al. (5) recently showed that a two-parameter version of the model represented very well the increase in asphalt viscosity as the asphaltene content increased.

It has been shown (6) that the logarithm of the zero frequency limiting viscosity ( $\eta_0^*$ ) increases linearly with the growth of the infrared carbonyl peak area (CA) as the asphalt oxidizes. Furthermore, this relationship has been shown to be independent of aging temperature for temperatures up to 93.3°C (200°F). This function, known as hardening susceptibility (HS), is a characteristic of each asphalt and, mathematically, is  $(d \log \eta_0^*/dCA)$ .

Lin et al. (5) hypothesized that carbonyl growth itself does not cause a viscosity increase, but rather causes an increase in asphaltenes which in turn increases viscosity. Hence,  $\log \eta_0^* = f[\%A(CA)]$ ; viscosity increases with asphaltenes which in turn increase with oxidative carbonyl growth. Therefore, HS can be

divided into two quantities, one the increase in log viscosity with asphaltene content and the other the increase in asphaltene content with carbonyl peak growth.

$$HS = \left( \frac{d \log \eta_0^*}{dCA} \right) = \left( \frac{d \log \eta_0^*}{d\%A} \right) \left( \frac{d\%A}{dCA} \right) \quad (1)$$

where

$\eta_0^*$  = zero frequency limit viscosity,

$\%A$  = weight fraction asphaltene, and

CA = carbonyl peak area.

The second term in Equation 1, the increase in asphaltene with carbonyl, was defined as the asphaltene formation susceptibility (AFS) by Lin et al. (5).

Lin et al. (5) concluded that AFS was the same for a given asphalt whether whole asphalts or maltenes were oxidized, at least to the level of asphaltene studied. In other words, the existing asphaltenes have little, if any, effect in the formation of new asphaltenes. However, this function is quite different in different asphalts and maltenes.

The present study was undertaken to explain the interaction of asphaltene and maltene from different sources, as would occur in recycling, to better understand (a) the difference, if any, between the original asphaltenes and those produced by oxidation, and (b) the importance of higher concentrations of asphaltene, continuing the work begun by Lin et al. (5).

## EXPERIMENTAL METHOD

Four asphaltenes fractionated from SHRP AAD-1, AAG-1, AAK-2 and a supercritical fraction of SHRP ABM-1 were blended with the maltenes fractionated from SHRP AAD-1 in 10-90, 20-80 and 40-60 asphaltene-maltene ratios by weight. In addition, three asphaltenes (from SHRP AAD-1, AAG-1, and AAK-2) were also blended with the maltenes from SHRP AAG-1 in the same ratios as those described previously. A total of 21 blends were produced by this blending scheme. Blends of 10, 20 and 40 percent asphaltenes from SHRP AAG-1 into the maltene from SHRP AAD-1 were designated GD1, GD2, and GD4, respectively. Similarly, blends of AAK-2 asphaltene in AAD-1 maltene were designated KD1, KD2, and KD4. Also formed were blends DD1, DD2, and DD4 by blending D asphaltenes with D maltenes. Other blends were (BMD1, BMD2, BMD4), (DG1, DG2, DG4), (KG1, KG2, KG4), and (GG1, GG2, GG4).

In the solvent fractionation procedure, approximately 160 g of whole asphalt were mixed with 16 L of n-hexane. The solution was stirred overnight and the asphaltenes were collected by filtering the solution through Whatman No. 41 filter paper. The asphaltenes were dried in an oven at 140°C for 30 min and stored for producing blends. The maltene solution was recovered from n-hexane in a Buchi rotary evaporation apparatus. This recovery method was used to diminish the effect of the solvent on the maltene properties (7). Blend components were dissolved in toluene and recovered as described previously. The recovered samples were analyzed by gel permeation chromatography (GPC) to confirm complete solvent removal (8).

The changes in compositional, chemical, and rheological properties of the aged blends were measured by solvent fractionation using n-hexane, Fourier transform infrared spectroscopy (FT-IR), and dynamic mechanical analysis (DMA). Furthermore, GPC was used to characterize the difference between the molecular weight distribution of aging-produced asphaltenes and original asphaltenes from unaged asphalts.

All blends except DD1, DD2, and DD4 were laboratory-aged in a pressure oxidation vessel at 20.7 bar pure oxygen, at temperatures of 71.1, 82.2, and 93.3°C for aging times from 1 to 24 days depending on the aging temperature. Samples of 1.5 g were weighed into aluminum trays giving an effective film thickness of 0.6 mm. These thin films minimized oxygen diffusion effects on the samples (6).

Asphaltenes were measured by precipitation in n-hexane as described by Pearson et al. (9). Approximately 0.2 g of aged material was weighed into a scintillation vial, 20 mL of n-hexane was added, and the solutions were sonicated until the sample was completely dispersed. After overnight equilibration, the asphaltenes were separated by filtering the solutions through a pre-weighed polytetrafluoroethylene (PTFE) membrane, 0.4-micron syringe filters. After filtration, the filters were dried in an oven at 140°C for 1 hr and post-weighed 2 hr after removal from the oven. The weight percentage asphaltene (%A) is defined as the difference in the filter weight divided by the sample weight. Asphaltene trapped in filters were washed out using 10 mL tetrahydrofuran (THF), and the resulting asphaltene solutions were analyzed using FT-IR and GPC.

Infrared spectra were measured using a Mattson galaxy 5000 FT-IR with the attenuated total reflectance (ATR) method described by Jemison et al. (10). Progress of the oxidation was monitored by the peak area in the carbonyl region. The carbonyl area of the aged blends is defined as the integrated area from 1650 to 1820  $\text{cm}^{-1}$  relative to the integrated area over the same region of their unaged blends. The unaged maltene has no distinctive carbonyl band and this is defined to be zero carbonyl area. For asphaltenes, infrared spectra were measured by casting asphaltene solutions on an ATR prism. For asphaltenes from whole asphalts, approximately 0.07 g of asphaltene was dissolved in 10 mL THF and the solution was spread on the ATR prism drop by drop to allow THF to evaporate. When the asphaltene film was of sufficient thickness, it was further dried with a heat gun. However, for asphaltenes produced by maltenes upon aging, the asphaltene solutions obtained from the filter wash were used.

The rheological property of zero frequency limiting viscosity ( $\eta_0^*$ ) was determined from data measured at 60°C with a Carri-Med CSL 500 control stress rheometer using a 2.5-cm composite parallel plate with a 500- $\mu\text{m}$  gap. A 0.1-rad/sec frequency was used to approximate the  $\eta_0^*$  for materials less than 100,000 poise at 60°C. For materials with higher viscosities at 60°C, dynamic rheological measurements were performed at 60, 85, and 90°C, and the  $\eta_0^*$  at

60°C was calculated by time-temperature superposition as described by Ferry (11).

The change in molecular weight distribution was determined using GPC. To achieve good separation, three columns with pore size 50, 500, and 1000 Å were connected in series to accommodate the wide range of molecular sizes commonly found in asphalts. A flow rate of 1.0 mL/min, a column temperature of 40°C, and a 100- $\mu\text{L}$  injection volume were used for the samples. For maltenes, original asphaltenes, whole asphalts, and blends,  $0.07 \pm 0.005$  g of sample was dissolved in 10 mL THF and filtered using a 0.45- $\mu$  PTFE syringe filter before injection. For produced asphaltenes, the filter-washed solution was injected directly into the column. Molecular weight and molecular weight distribution were calculated based on a calibration using polystyrene standards.

## DISCUSSION OF RESULTS

For the unaged whole asphalts, maltenes, and blends, Table 1 shows the percent asphaltenes, absolute  $\eta_0^*$ , and the relative viscosity ( $\eta_r$ ) (defined as the  $\eta_0^*$  for a blend divided by the  $\eta_0^*$  for the maltene from which the blend is made). The carbonyl areas are not shown because they are defined to be zero.

The following observations were made about the unaged blend viscosities:

1. For a given unaged asphaltene-maltene blend, the absolute viscosities increase with the amount of asphaltene blended (12,13).
2. The relative viscosity of all blends, regardless of the sources of asphaltenes and maltenes, behaves similarly with respect to the total asphaltene content (Figure 1).
3. In addition to the maltene viscosity, the maltene solvent power, or ability to disperse the asphaltenes, would affect the rise in viscosity with asphaltene content.

Figure 1 suggests that although they are very different in chemical nature, the SHRP AAD-1 and AAG-1 maltenes may have similar solvation power. The data of Figure 1 also show that the asphaltene-maltene interactions do not vary widely for all materials in this study. Figure 2 shows a plot of absolute  $\eta_0^*$  versus CA for SHRP AAD-1 and AAG-1 whole asphalt aged at 20.7 bar pure oxygen and various temperatures from 60°C to 104.4°C. The HS ( $d \log \eta_0^* / dCA$ ) of AAD-1 asphalt is clearly higher than that of AAG-1 asphalt. That is, for the same amount of carbonyl increase, AAD-1 will harden much more than AAG-1. Many investigators (14–17) have shown that the increases in viscosity as an asphalt ages result from the formation of asphaltenes produced by oxidation. Figure 1 also suggests that the increase in asphaltene content directly results in the increase in the viscosity of blends with only relatively slight dependence on asphaltene sources. As mentioned earlier, the HS of an asphalt material can be further studied by considering separately the increase in viscosity due to the increase in asphaltene content, and the increase in asphaltene content due to the increase in carbonyl formation defined earlier as AFS.

### Asphaltene-Carbonyl Relationship (AFS)

Asphaltenes produced by oxidation have been shown to have higher oxygen content than those originally present in asphalt (18). This is substantiated in Figure 3, which shows that the FT-IR absorbance

**TABLE 1** Weight Percentage of n-Hexane Asphaltenes (%A), Low Frequency Limiting Viscosities ( $\eta_0^*$ ), and Relative Viscosity of Maltenes, Whole Asphalts, and Blends

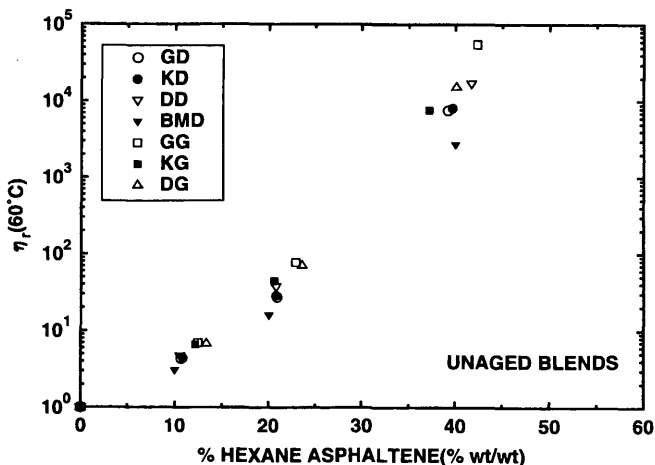
	10%			20%			40%			Maltene or Asphalt		
	%A <sup>a</sup>	$\eta_0^b$	$\eta_r^c$	%A <sup>a</sup>	$\eta_0^b$	$\eta_r^c$	%A <sup>a</sup>	$\eta_0^b$	$\eta_r^c$	%A <sup>a</sup>	$\eta_0^b$	$\eta_r^c$
AAD-1 Maltene										0.7	2.3	1.0
AAD-1 Asphalt										23.2	133.2	57.9
GD	10.7	9.88	4.3	20.9	62.1	27.0	39.2	17400	7565.2			
KD	10.9	10.0	4.3	20.8	65.0	28.3	39.7	18700	8130.4			
DD	10.6	10.7	4.7	20.8	85.2	37.0	41.7	39300	17087.0			
BMD	10.0	7.0	3.0	20.0	36.3	15.8	40.0	6260	2721.7			
AAG-1 Maltene										0.3	73.0	1.0
AAG-1 Asphalt										6.2	192.5	2.6
GG	12.5	503.7	6.9	22.9	5610	76.8	42.3	4.0x10 <sup>6</sup>	54794.5			
KG	12.2	478.7	6.6	20.6	3190	43.7	37.2	5.58x10 <sup>5</sup>	6643.8			
DG	13.4	496.0	6.8	23.6	5160	70.7	40.1	1.13x10 <sup>6</sup>	15479.5			

<sup>a</sup> %A weight percentage  
<sup>b</sup>  $\eta_0^*$  in Pa·s at 60°C  
<sup>c</sup>  $\eta_r$  dimensionless at 60°C

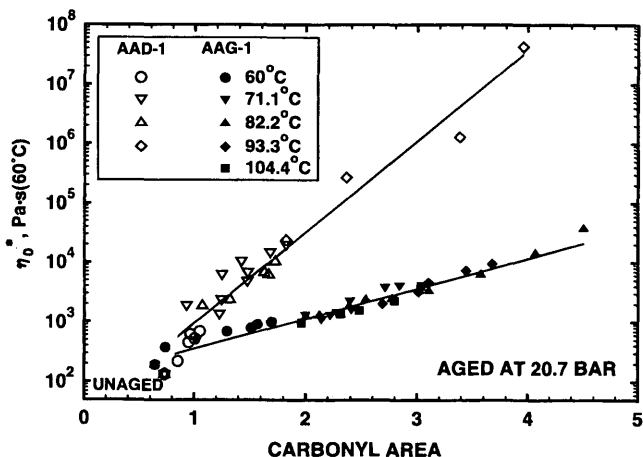
in the carbonyl region of asphaltenes from aged SHRP AAD-1 maltene is much higher than that of the original AAD-1 whole asphalt asphaltenes. This is direct evidence that the carbonyl formation is at least partially responsible for asphaltene formation in aged maltenes. Figure 4 shows a plot of asphaltenes produced during aging versus carbonyl area for AAD-1 maltene, AAD-1 whole asphalt, and blends made by adding various asphaltenes into AAD-1 maltene. It is difficult to distinguish one material from another for carbonyl areas less than 2. However, upon careful examination of the data for carbonyl areas above 2, it is apparent that the AFS ( $d\%A/dCA$ ) for each material is different. The AFS increases as original unaged blend asphaltene content decreases. For example, the AFS of KD4 is smaller than that of KD2, the AFS of KD2 is

smaller than that of KD1, and the AFS of KD1 is smaller than that of AAD-1 maltene. Additionally, the AFS is not constant and decreases as asphaltene content increases for a given aged blend. This result suggests that the AFS is a function of total asphaltene content. This phenomenon was also observed by Lin et al. (5).

To compare the difference in AFS, the carbonyl areas for the unaged blends were adjusted to be the same as that of the aged maltene with the same asphaltene content. All of the data points for the aged blends were adjusted by the same amount as the unaged blend. The result of this data manipulation is shown in Figure 5. For all of the blends, asphalts, and maltenes studied, all AFSs overlap and form a single curve for materials from the same maltene. This indicates that the AFS is not affected by the type of asphaltene, either



**FIGURE 1** Relative viscosity versus asphaltene content for all unaged blends studied.



**FIGURE 2** Hardening susceptibilities of SHRP AAG-1 and AAD-1 whole asphalt.

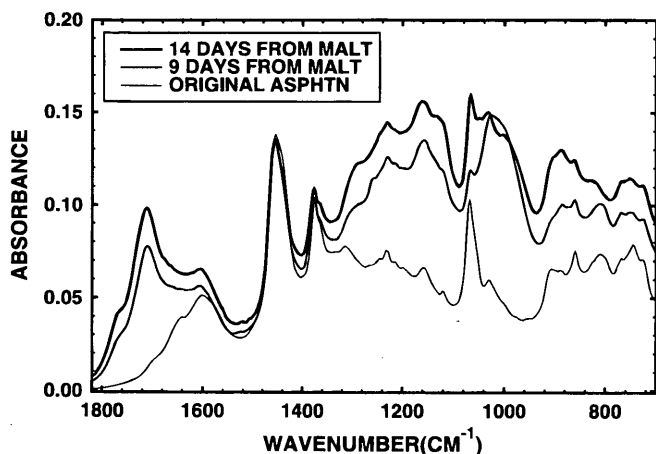


FIGURE 3 Infrared spectra of SHRP AAD-1 original asphaltene and asphaltenes produced by aging SHRP AAD-1 maltene at 93.3°C and 20.7 bar.

produced by aging or originally present from different sources. However, the AFS clearly is a function of the type of maltene. The AFS of SHRP AAG-1 maltene is much lower than that of SHRP AAD-1 maltene. Thus, the AFS is a strong function of the type of maltene in the blend and is a function of the total asphaltene content but is not a strong function of the type of asphaltene.

**Viscosity-Asphaltene Relationship**

Lin et al. (5) showed that, for a given asphalt, the asphaltenes naturally present and those produced by oxidation have similar effects on the increase in the viscosity of the asphalt; the effect of asphaltenes from different asphalts on the viscosity for a given maltene before and after aging was not addressed. However, these

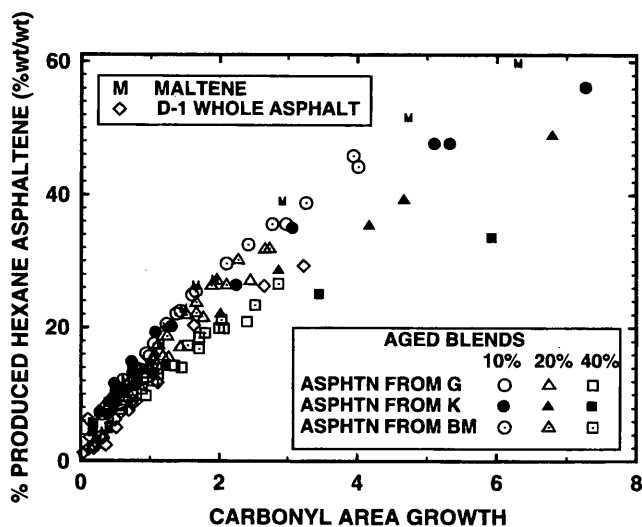


FIGURE 4 Produced asphaltene content versus carbonyl area for blends made by adding asphaltenes from SHRP AAG-1, AAK-2, and supercritical fraction of ABM-1 into AAD-1 maltene.

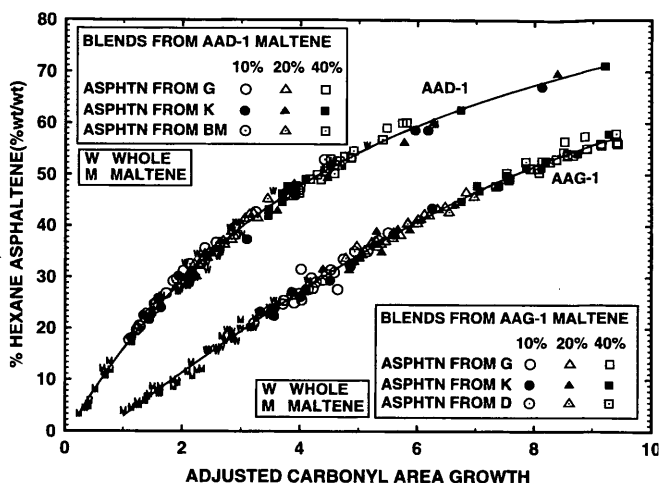


FIGURE 5 Asphaltene formation susceptibility for all maltenes, whole asphalts, and blends studied.

effects were investigated in the current study. The viscosity-asphaltene relationship for aged AAD-1 maltene and the viscosity-asphaltene relationship for AAD-1 maltene blended with multiple levels of AAD-1 asphaltenes is shown in Figure 6. The symbols D1, D2, and D4 represent the blends of AAD-1 maltene with approximately 10, 20, and 40 percent asphaltenes, respectively. The exact asphaltene contents, as determined by precipitation after blending, are tabulated in Table 1. The symbol M in Figure 6 represents data obtained by aging AAD-1 maltene.

For the same amount of asphaltene content, the viscosity of aged maltene is consistently lower than that of blends DD. To further understand the cause of this difference, GPC was implemented to measure the molecular size distribution of the AAD-1 original asphaltene and the maltene-produced asphaltene. Figure 7 shows that the AAD-1 maltene-produced asphaltenes have a significantly lower molecular size than the AAD-1 original asphaltenes. Yen et al. (3) showed that asphaltenes form aggregates through aromatic stacking. Upon oxidative aging, the aging-produced asphaltenes contain large numbers of carbonyl group that can produce polar-

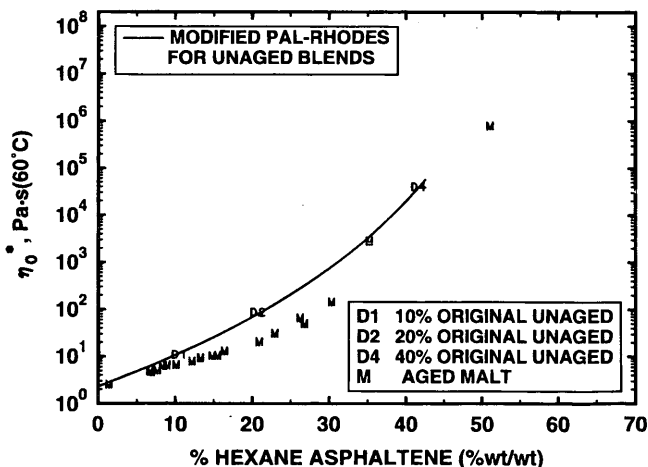


FIGURE 6 Viscosity versus asphaltene content for blends made by adding asphaltenes from SHRP AAD-1 into AAD-1 maltene.

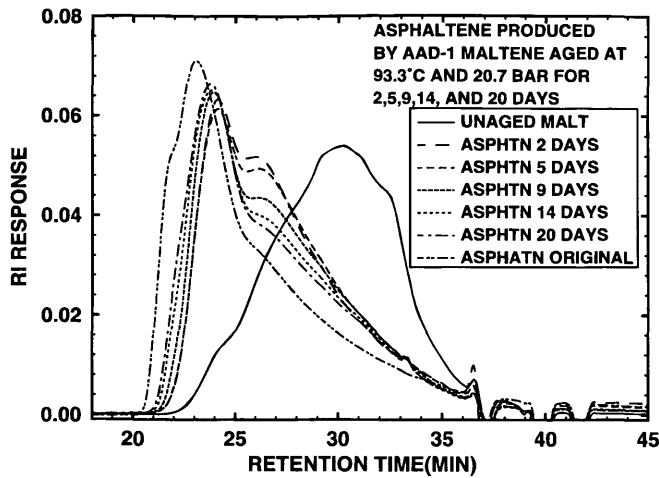


FIGURE 7 GPC chromatogram for SHRP AAD-1 maltene, AAD-1 original asphaltene, and asphaltenes produced by AAD-1 maltene.

polar aggregation (Figure 3). Furthermore, Storm et al. (19) indicate that the asphaltene molecular weight measured by mass spectroscopy is usually significantly lower than that measured by GPC or vapor osmometry. Therefore, the molecular size of the asphaltene determined by GPC can be used as a measure of the severity of the asphaltene aggregation. Furthermore, for viscosity of suspensions that form aggregates, Pal and Rhodes (4) and Graham et al. (20) showed that the effects of particle concentration on the suspension viscosity increase as the average number of particles per aggregate increases. This explains that the viscosity of aged maltene is somewhat lower than that of DD blends due to lower molecular weight of the produced asphaltene.

Figures 8, 9, and 10 show the viscosity-asphaltene relationships for aged and unaged blends made by adding the original asphaltene from SHRP AAG-1, SHRP AAK-2, and the supercritical fraction of SHRP ABM-1 to SHRP AAD-1 maltene. Again, the viscosity of unaged blends is higher than that of maltene aged to the same level of asphaltene. Furthermore, the difference between the viscosity of

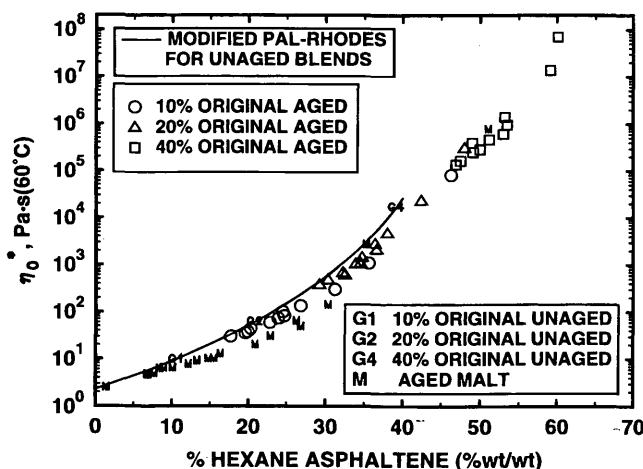


FIGURE 8 Viscosity versus asphaltene content for blends made by adding asphaltenes from SHRP AAG-1 into AAD-1 maltene.

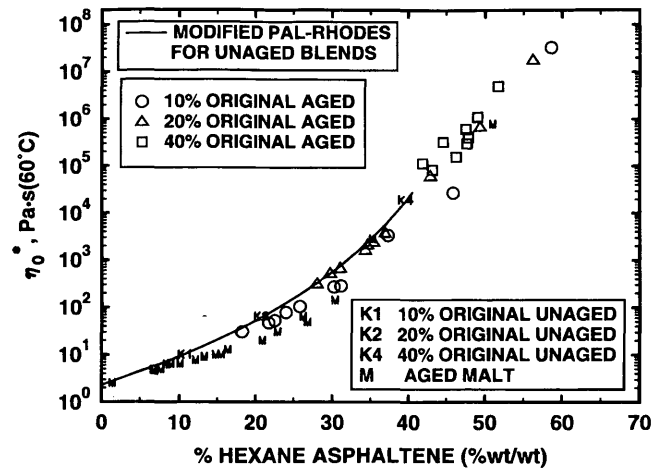


FIGURE 9 Viscosity versus asphaltene content for blends made by adding asphaltenes from SHRP AAK-2 into AAD-1 maltene.

unaged blends and that of aged maltene is greatest for blends DD and follows the order of DD > KD > GD > BMD. This is consistent with the ranking of the GPC molecular weights of the original asphaltenes, SHRP AAD-1 > AAK-2 > AAG-1 > ABM-1 SF, shown in Figure 11. However, for aged blends, the viscosities lie between the unaged blends and aged maltene because the asphaltenes of aged blends contain both original asphaltenes and produced asphaltenes. Figure 12 shows all the viscosity-asphaltene data for the blends made by adding the original asphaltenes into SHRP AAD-1 maltene. Although there are differences in the viscosity-asphaltene relationships for different blends, all data lie in a narrow band in the practical viscosity range of 1,000 to 500,000 poise. Figure 13 shows that blends made from AAG-1 maltene exhibit similar behavior. However, for blend GG, the viscosity of the aged blend is essentially identical to that of the unaged blend. This is consistent with the fact, as shown in Figure 14, that the molecular weight distribution of asphaltene produced by AAG-1 maltene is very similar to that of the original asphaltenes as determined

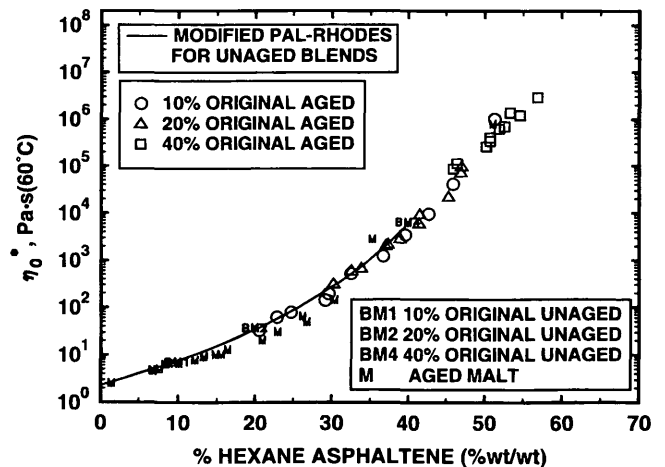


FIGURE 10 Viscosity versus asphaltene content for blends made by adding asphaltenes from supercritical fraction of SHRP ABM-1 into AAD-1 maltene.

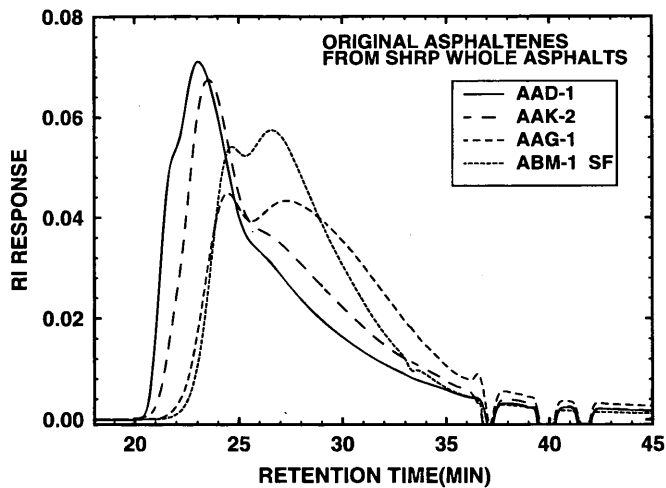


FIGURE 11 GPC chromatogram for original asphaltenes from SHRP AAG-1, AAD-1, AAK-2, and supercritical fraction of ABM-1.

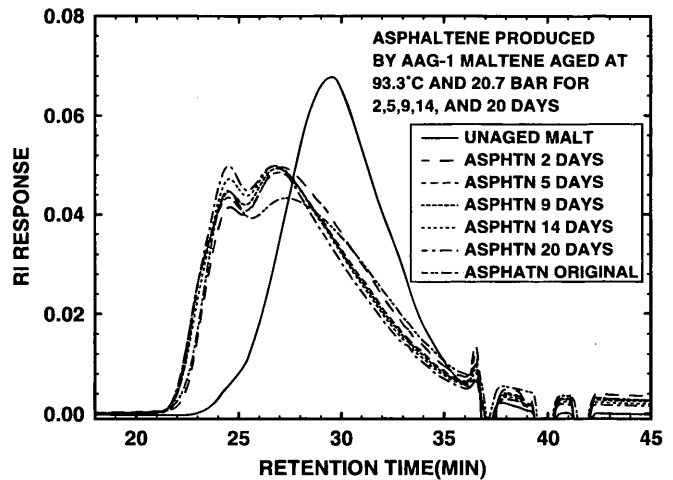


FIGURE 14 GPC chromatogram for SHRP AAG-1 maltene, AAG-1 original asphaltene and asphaltenes produced by AAG-1 maltene.

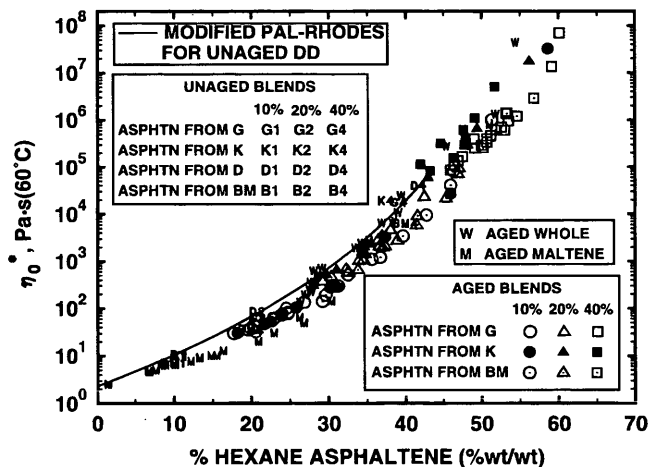


FIGURE 12 Viscosity versus asphaltene content for blends made by adding various original asphaltenes into AAD-1 maltene.

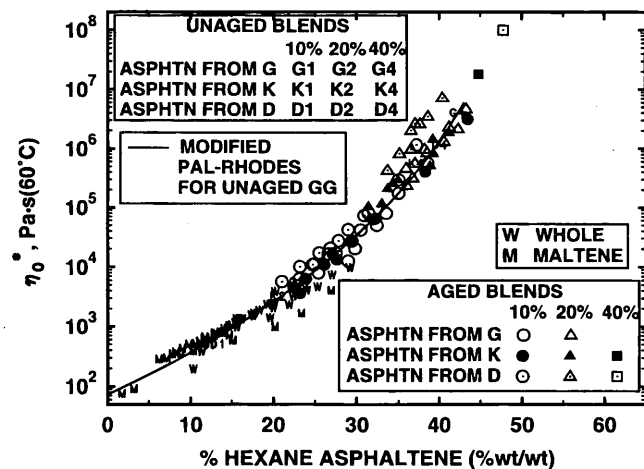


FIGURE 13 Viscosity versus asphaltene content for blends made by adding various original asphaltenes into AAG-1 maltene.

by GPC. Figure 15 shows all the relative viscosity-asphaltene data for all blends in this study. For aged blends, the maltene source alters the behavior of the increase in relative viscosity with asphaltene content. However, for a given maltene, all aged blends do not show significant differences with respect to asphaltene sources.

As stated in Equation 1, HS can be considered the product of two functions. Based on the results presented in this study, the first term in Equation 1 does not vary greatly with asphaltene sources for the two maltenes studied. However, the second term, AFS, is very different for AAD-1 maltene compared with AAG-1 maltene. This indicates that the main difference in HS for different asphalt is due to different AFS. Therefore, for recycling, the recycling agent should be designed or selected to have a low AFS. Recycled pavement with a low AFS rejuvenator can significantly suppress the formation of asphaltenes during oxidation, and therefore improve the service life of the recycled pavement. However, for blends from different maltenes, the difference in the increase in relative viscosity

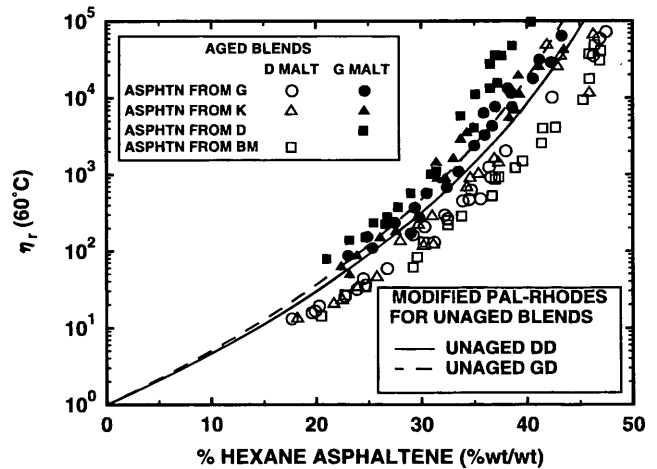


FIGURE 15 Relative viscosity versus asphaltene content for all aged blends studied.

with asphaltene content is less significant compared with the difference in AFS. Furthermore, dilution of asphaltene by the agent will improve the increase in viscosity because the increase in viscosity is much less for low asphaltene content than for high asphaltene content. As shown in Figure 16, although the  $d \log \eta^*/d\%A$  for AAG-1 asphalt is larger than that for AAD-1 asphalt at the same amount of asphaltene content, the  $d \log \eta^*/d\%A$  for AAG-1 asphalt is actually smaller than that for AAD-1 asphalt due to the lower starting asphaltene content and the lower level of asphaltene content throughout the entire service life.

## CONCLUSIONS

Based on the research, the following conclusions can be made:

1. With oxidative aging, n-hexane asphaltene content increases in whole asphalts and maltenes as a result of carbonyl formation. The presence of asphaltenes has no effect on the AFS of a given maltene.
2. The asphaltenes produced by aging exhibit rheological effects very similar to those of the original asphaltenes present in a given maltene, regardless of the asphaltene source. However, the relative viscosity is a strong function of asphaltene content. This implies that maltene solvation power is much more important than asphaltene source.
3. AFS is an extremely important property to consider in asphalt recycling.
4. Asphaltene dilution also should be a major goal in asphalt recycling.

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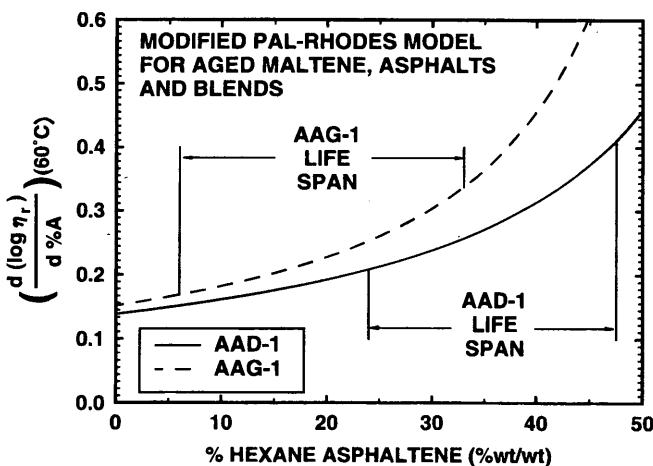


FIGURE 16  $(d \log \eta_r/d\%A)$  versus %A for all aged blends studied.

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## DISCUSSION

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We wish to take exception to the authors' suggestion that the solvent powers of the maltenes of asphalt AAD-1 and AAG-1 are sim-

ilar. Consider the data presented in Table 1. Focus attention on the AAG-1 asphaltenes "dissolved" in AAD-1 and AAG-1 maltenes. At 10 percent asphaltenes,  $\eta_r$  values are 4.3 and 6.9. The difference is greater (27.0 versus 76.8) at 20 percent asphaltenes. At 40 percent asphaltenes, the ratio of  $\eta_r$  for AAG-1 asphaltenes in AAD-1 maltenes versus AAG-1 maltenes is 7,565 versus 54,794, or 7.25 to 1. The same data, shown in Figure 17, plotted on a log scale also indicate a greater than 7:1 ratio of  $\eta_r$  for the same blends.

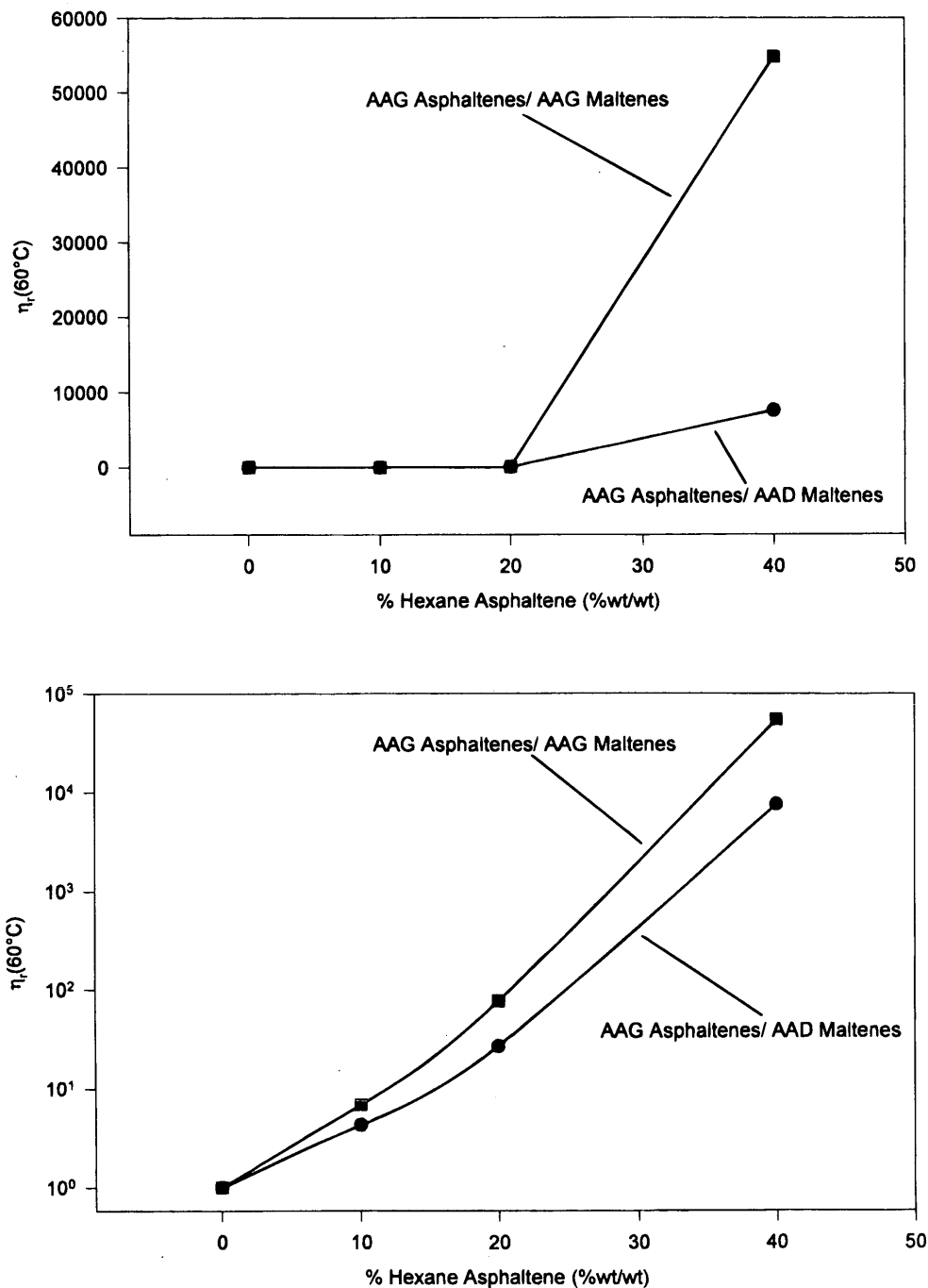


FIGURE 17 Relative viscosity versus asphaltene content for indicated unaged blends: *top*, linear scale; *bottom*, log scale.



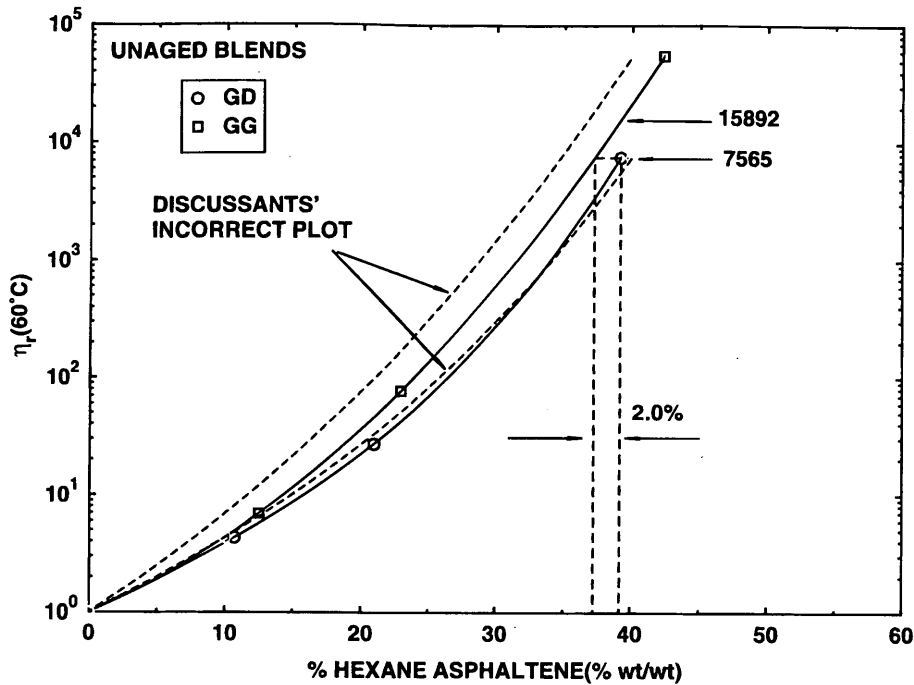


FIGURE 18 Relative viscosity versus asphaltene content for indicated unaged blends, authors' data.

We suggest that this near order of magnitude difference in solvent power of AAD-1 maltenes versus AAG-1 maltenes is hardly convincing evidence that "SHRP AAD-1 and AAG-1 maltenes have similar solvation power." We maintain that the solvent powers are substantially different and that the authors' own data tell the same story.

Also, under the section on viscosity-asphaltene relationships, it is stated that it was previously reported by the authors (5) that "asphaltenes naturally present and those produced on oxidation have similar effects on the increase in the viscosity of the asphalt." However, this fact has previously been reported for four different asphalts and discussed in detail by Plancher et al. (16).

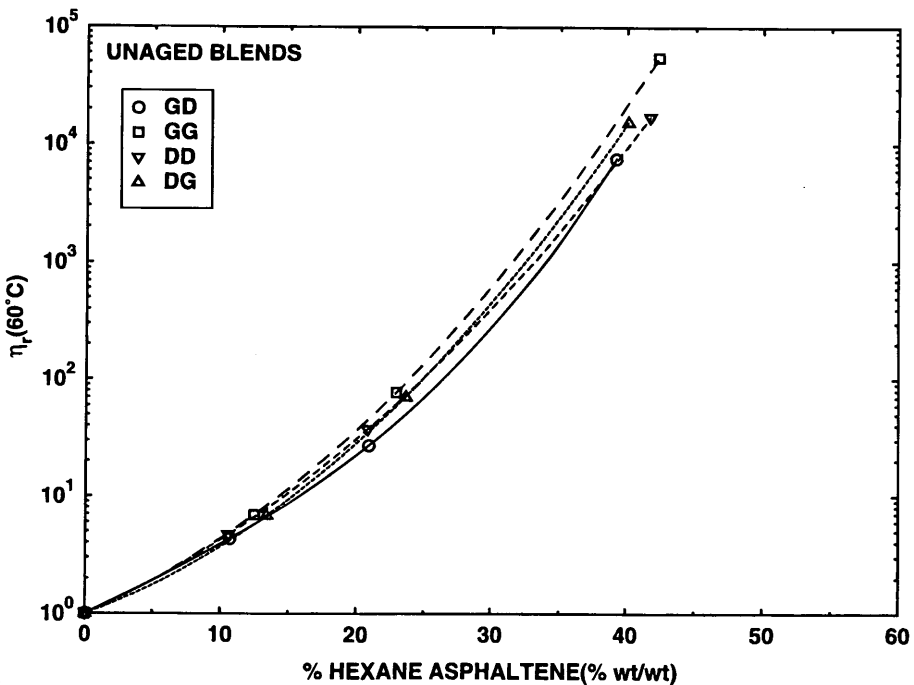


FIGURE 19 Reported data for AAD-1 asphaltenes compared with AAD-1 and AAG-1 maltene blends.

## AUTHORS' CLOSURE

The discussants' point that our Figure 1 shows a "near order of magnitude difference in AAD-1 versus AAG-1 maltene" is incorrect. One must use the actual reprecipitated (measured) value of asphaltene content for reliable comparison rather than the nominal ("theoretical") target value of 10, 20, and 40 percent. The data points that were not questioned by the discussants have been removed and a curve fit has been plotted through the actual data reported in Table 1 in Figure 18. The annotations in Figure 18 show that the ratio of reduced viscosities at the 40 percent asphaltene level is much closer to 2 than to 7. Furthermore, the difference in asphaltene content that would give the same relative viscosity is only 2 percentage points at the 40 percent level. We still assert that "Figure 1 suggests that the SHRP AAD-1 and AAG-1 maltenes may have similar solvation power." We further confirm our statement by comparing our reported data for AAD-1 asphaltenes with AAD-1 and AAG-1 maltenes blends as shown in Figure 19. Figure 19 shows that all of the blends behave similarly. Note that we did not say that they are the same, just similar. Furthermore, we conclude that neither our

data nor their data support the characterization of AAD-1 maltenes as "a much better solvent" than AAG-1 maltenes.

The discussants' last point concerning the similar effect of naturally present asphaltenes and those produced by oxidation on viscosity leaves us puzzled. We can find neither a statement to this effect nor experimental data supporting this conclusion in the discussants' reference (16). They discuss the effect of asphaltenes produced by aging on viscosity, but they report no experiments in which the asphaltene content was varied by spiking with original asphaltenes.

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