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VISCOELASTIC MEASUREMENTS AND THEIR RELATIONSHIP TO BITUMEN PROPERTIES

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VISCOELASTIC MEASUREMENTS AND THEIR RELATIONSHIP TO BITUMEN PROPERTIES

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Viscoelastic measurements of bitumens made on a mechanical spectrometer assisted in providing insight into phenomena associated with bitumen-aging characteristics, adsorption of bitumen components on mineral surfaces, and the effect of moisture on the bitumen-aggregate interactions. Irregular transitions believed related to changes in molecular structuring in bitumens were observed in the viscoelastic and asphaltene settling times data following time-dependent oxidative aging of the bitumens.

INTRODUCTION

Measurements such as penetration, viscosity, ductility, and softening point are widely used by the paving industry to determine rheological properties of bitumens. These measurements provide data for preparing, classifying, and grading (specifying) bitumens; for designing and testing paving mixtures; and for evaluating bitumen-aging characteristics. Rheological properties of bitumens are dependent on intra- and intermolecular interactions related to the compositional makeup of the bitumen. A better understanding of the interactions involved could be beneficial in producing better products that would ultimately lead to prolonged service life of our streets and highways. To assist in developing this understanding, it may often be necessary to make rheological measurements over a broad range of temperatures, rates of shear, and stress levels. Unfortunately, this is not easily accomplished because most rheological measuring instruments or devices lack the versatility to measure flow properties precisely over broad temperature ranges, rates of shear, and stress levels.

Recent developments in viscoelastic testers have overcome some of the limitations associated with versatility. These developments have facilitated the study of bitumens and bitumen-mineral mixtures using dynamic viscoelastic measurements. Examples are studies of the properties of bitumen-silica composites ([1,2]), bitumen aging characteristics ([3]), and changes in bitumen properties under changing conditions of shear, stress, and temperature ([4–10]). In the present study dynamic viscoelastic data in conjunction with other test results and compositional data obtained in previous studies were used to develop a better understanding of the effects of molecular interactions on the properties of bitumens and bitumen-aggregate mixtures.

EXPERIMENTAL SECTION

Materials

Bitumens. - Several different paving-grade bitumens including two experimental syncrude bitumens derived from tar sand and shale oil residues were used. Pertinent data on the various bitumens are included in the text.

Aggregate. - An aggregate from Utah was crushed in a Bico-Braun disk grinder* equipped with ceramic plates. The crushed aggregate was dry sieved to pass a 38-μm screen (400 mesh).

Hydrated Lime. - Hydrated lime was prepared by adding small amounts of distilled water to calcium oxide. After the exothermic reaction had subsided, additional water was added to the lime to produce a creamy texture. The lime slurry was dried overnight at 150°C, and the resulting caked lime was powdered in a mortar prior to use.

Solvents. - Reagent-grade solvents were used. Benzene and pyridine were dried by refluxing them for 8 hours over calcium hydride before distillation through a Vigreaux column.

Sample Preparation

Lime-Treated Bitumens. - Eight bitumens were heated to a semifluid state, freshly prepared hydrated lime was added in the quantities specified in the text, and the mixtures were thoroughly mixed. All samples received the same thermal treatment and exposure to air during mixing.

Laboratory-Aged Bitumens. - Several bitumens were artificially aged in the laboratory using the column-oxidation technique (12) and a rolling thin film oven (RTFO). Column-oxidation involved first coating Fluoropak 80 (Teflon), 850- to 500-μm particle size, with a bitumen-benzene solution followed by solvent evaporation of the benzene while continually stirring the mixture. Sufficient bitumen was used to give 2.5 and 5 weight percent coatings on the Teflon. Bitumen-coated particles were then packed into separate 6.35-mm o.d. x 6.7-m aluminum tubes prior to oxidizing the contents for 2 hours at 163°C by passing 30 cm^3/min air through the tube. Time-dependent bitumen aging studies were conducted in the RTFO utilizing the procedures described in ASTM METHOD D 2872. The first of a series of seven samples of each bitumen oxidized was removed from the oven after 35 minutes aging; subsequent samples were removed every 25 minutes thereafter up to 185 minutes.

Recovery of Column-Oxidized Bitumens. - Column-oxidized bitumens were recovered from inert Teflon particles by a cold benzene wash followed by an 8-hour pyridine extraction in a modified Soxhlet extractor (12,13). Solvent removal was accomplished with a rotary evaporator using vacuum and a hot water bath. Complete removal of benzene and pyridine from the recovered bitumens was indicated by the absence of their intense infrared absorption bands at 670 and 700 cm^{-1}, respectively.

Preparation of Moisture-Treated Aggregates. - One sample of Utah aggregate fines was humidified at ambient temperature for 24 hours in a desiccator containing a

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*Mention of specific brand names or models of equipment is for information only and does not imply endorsement by the U. S. Department of Energy.

beaker of water. A second sample of fines was heated overnight at 150°C to serve as a dry control. Two bituminous mixtures containing 10 weight percent of the conditioned aggregate fines were prepared using an AC-5 bitumen and employing the same experimental procedures described for preparing lime-treated bitumens. The bituminous mixtures were sealed in ointment cans for two weeks prior to measuring viscoelastic properties.

Rheological Measurements.

All viscoelastic (VE) data were obtained using a Mechanical Spectrometer (Model RMS-605) manufactured by Rheometrics, Inc. Description of the spectrometer has been reported elsewhere ([6,14]). VE measurements were obtained using 25-mm parallel plates and 1-mm sample-film thickness. Other conditions such as temperature, rate of shear (frequency), and percent strain amplitude are reported in the tables.

Asphaltene Settling Test

Details of the asphaltene settling test have been published elsewhere ([11]). Briefly, the test procedure involves digesting 2 g of bitumen in 50-cm^3 n-hexane for 24 hours using a magnetic stirring apparatus. After digestion, the resultant mixture is transferred into a 50-cm^3 graduated cylinder, and the rate at which the asphaltenes settle in the hexane solution is determined. The test result is reported as that time in minutes required for the asphaltene meniscus to reach the 25-cm^3 mark on the graduated cylinder.

RESULTS AND DISCUSSION

The objectives of this investigation were to develop a better understanding of bitumen-aggregate adsorption effects, bituminous mixture sensitivity to moisture damage, and bitumen age-hardening processes. Viscoelastic data were used in the present study to evaluate changes in the properties of bitumen and bitumen-aggregate mixtures. The adsorption of bitumen components on mineral surfaces is important in determining the stability and durability of bituminous mixtures. A small amount of hydrated lime, a very active adsorbent, was added to eight paving-grade bitumens to determine its effect on the flow properties of the treated bitumens at 25° and 0°C. The effects of moist and dry aggregate fines on bitumen flow properties were also evaluated. Finally, changes in bitumen VE behavior and asphaltene settling rate ([11]) in time-dependent oxidative-aging studies were related to possible transitions in the molecular structuring of bitumen components.

Effects of Hydrated Lime on Bitumen Properties

Previous studies at the Utah Department of Transportation and in our laboratory showed that addition of hydrated lime to bituminous mixtures ([15]) or pretreatment of bitumens with hydrated lime ([12]) affected the physical and chemical properties of bitumens. We previously explained ([12]) the beneficial effects of reducing age hardening of bitumens by lime pretreatment as follows: (1) lime reduced the formation of oxidation products by removing oxidation catalysts or promoters and (2) lime reduced the sensitivity of the bitumens to these oxidation products by removing reactive polar molecules that would otherwise interact with the oxidation products to cause an increase in viscosity. In these studies, the lime was removed after treatment prior to evaluation of the bitumen. The major polar, viscosity-building components removed by lime included carboxylic acids, 2-quinolone types, and other nitrogen compounds ([12]). The effect of carboxylic acids on viscosity was demonstrated ([16]) by the introduction of carboxyl groups by an unambiguous chemical route into an aromatic fraction obtained from a Wilmington, California, bitumen; viscosity of the aromatic fraction increased from 900 to 3000 Pa·s.

VE measurements reported in this paper on the various bitumens were obtained using a mechanical spectrometer operated in a sinusoidal oscillatory stress mode. Because of the sinusoidal stress imposed on the sample, the resulting stress and strain responses are not in phase. In perfect elastic solids the stress and strain would be in phase and in perfect viscous liquids the stress and strain are 90° out of phase. In bitumens, part of the stress input is stored (elastic energy) by the samples and part of it is dissipated (viscous flow or heat loss) in each stress-strain cycle.

Figure 1 illustrates a portion of the VE data obtained on bitumen B-3051 before and after addition of 3 weight percent hydrated lime. VE measurements were performed on the control (untreated) bitumen and on the lime-containing bitumen at 3, 10, and 24 hours after lime addition. Shown in the upper right portion of the figure are four dots representing the frequency (rate of shear) where G', the shear storage modulus (stored energy or elasticity), and G", the shear loss modulus (viscous flow), curves would have intersected had these curves been drawn on the figure. The four curves labeled control and lime-treated bitumen are the complex shear viscosity curves (η^*) calculated from G' and G" values at their respective frequencies. The significance of the point where the G' and G" curves intersect is directly related to the flow properties of the test specimen. Ideally, for pavement applications G", the viscous flow modulus, should have a larger value (Pa) than G', the storage modulus. This allows the bitumen to dissipate most of the stress energy imposed on the sample through flow.

The gradual reduction in viscosity values from 5.80 x 10^4 to 1.45 x 10^4 Pa·s at 0.410 rad/sec observed over the 24-hour period and the corresponding increase in frequency of the G', G" intersection points from 13 to 75 rad/sec (dots) is attributed to the action of lime on the bitumen. These changes in VE behavior showed that the flow properties of the bitumen improved upon addition of the hydrated lime. Perhaps more important than the observed decrease in viscosity values was the shifting of G', G" intersecting points to a higher frequency. This means that the bitumen is capable of dissipating more stress energy through viscous flow or heat loss than the untreated bitumen, and that the lime-treated sample can absorb the stress energy equally well at higher shear rates. The action of hydrated lime suggests that viscosity-building components in the bitumen slowly migrated to and interacted with the lime during this room-temperature experiment. Their potential viscosity-building effect on the bitumen was therefore reduced. This interpretation is based on results of the lime study previously cited (12), which showed that removing these components caused a reduction in viscosity.

In another experiment, seven different paving-grade bitumens were examined rheologically to determine how the addition of 2 weight percent hydrated lime altered the low-temperature flow properties of each bitumen. VE measurements were performed on untreated samples and on lime-treated samples 90 to 100 hours after lime addition. Measurements were made at 0°C, and results are shown in Table 1. Six of the seven bitumens examined showed a decrease in viscosity (η^*) after lime treatment. Except for one bitumen system, T-3 (17), these results are consistent with the lime-treatment experiment discussed previously and indicate again that polar, viscosity-building materials are removed from the bitumens by adsorption on the lime surface. The increase in viscosity seen for bitumen T-3 after treatment with 2 percent lime probably results because the

TABLE 1. - Viscoelastic properties of lime-treated bitumens at 0°C, 0.25 percent strain

	Frequency,	Torque		Pa, x10^6			
Bitumen	rad/sec	g-cm	% reduction	G'	G"	Tan δ	η*, Pa·s, x 10^7
B-2959	0.01585	50.4		0.602	0.601	0.998	5.37
(Lime)	0.01585	46.8	7.1	0.538	0.576	1.070	4.97
B-3036	0.01585	185.0		2.676	1.613	0.603	19.71
(Lime)	0.01585	141.2	23.7	1.939	1.393	0.718	15.06
T-1[1]	0.01585	253.7		4.172	1.020	0.245	27.10
(Lime)	0.01585	232.0	8.6	3.801	0.908	0.239	24.66
T-2[1]	0.01585	150.9		2.535	0.256	0.101	16.08
(Lime)	0.01585	126.7	16.0	1.925	0.926	0.481	13.48
T-3[1]	0.01585	146.6		2.017	1.428	0.708	15.59
(Lime)	0.01585	156.3	+6.2	2.264	1.332	0.588	16.57
Shale Oil	0.01585	123.6		1.666	1.259	0.756	13.17
(Lime)	0.01585	92.5	25.2	1.195	1.015	0.849	9.89
Tar Sands	0.1585[2]	79.1		0.870	1.011	1.162	0.84
(Lime)	0.1585	64.8	18.1	0.696	0.847	1.217	0.69

[1] Used in Pennsylvania study (19).

[2] 0.1585 shear rate used because tar sands bitumen was too soft for measurements at 0.01585 rad/sec.

"filler effect," normally seen when larger amounts of mineral fines are added to bitumens, offsets the effects of adsorption of polar components on the lime surface.

The observed reductions in torque values (Table 1) for six of the seven bitumens corresponded with the reductions found in the η*, G' and G" values as was expected since torque, the force required to deform a sample, must correspond with the measured flow properties of the bitumen. The decrease in torque values following lime treatment varied from a low of 7.1 percent to a high of 25.2 percent. Bitumen T-3 described above showed a 6.3 percent increase in torque after lime treatment, which is consistent with its increase in viscosity for reasons already cited. Shale oil- and tar sand-derived bitumens, following lime treatment, showed a torque reduction of 25.2 and 18.1 percent, respectively.

Tan δ, also known as the loss tangent, is a damping term or a relative measure of the energy dissipated through viscous flow, and is calculated from the ratio of G"/G'. δ is called the dissipation factor and reflects the time lag between the applied stress and the resulting strain. Bitumens having larger Tan δ numbers are considered better for pavement applications because of their greater ability to flow under stress relative to their ability to store energy (elasticity) which may reflect itself as pavement stress that could lead to pavement cracking. The absolute values of the G' and G" which are used to calculate Tan δ and η* must also be considered in assessing the potential performance of bitumens in pavements.

Five of the seven bitumens showed an increase in Tan δ following lime treatment. Tar sand and B-2959 bitumens had the largest Tan δ's following lime treatment (1.217 and 1.070, respectively). T-1 and T-2 bitumens had the smallest Tan δ's 0.239 and 0.481, respectively. The largest and smallest changes in Tan δ values observed as a result of the lime treatment were for bitumen T-2 (0.101 to 0.481) and bitumen T-1 (0.245 to 0.239), respectively. The magnitude of the increases indicates the degree to which lime interacted with the bitumen components as discussed previously for bitumen B-3051. Bitumen T-3 showed an increase in G' and η^* and a reduction in G" and Tan δ following lime treatment. This increase for T-3 implies that interactions of T-3 components with lime which would increase viscous flow were offset by the stiffening or "filler effect" of the lime which would increase elasticity and restrict the viscous flow of associated bitumen components. In polymer rheology, Tan δ numbers in the neighborhood of 1 are associated with amorphous polymers and numbers around 0.1 are associated with glassy or crystalline polymers.

Bitumen Interactions with Moist and Dry Aggregate Surfaces

The properties of the adhesive interactions between bitumen and aggregate in bituminous mixtures play an important role in determining mixture performance properties. These interactions can be deleteriously affected by moisture because most mineral surfaces have great affinity for water. Considerable work has been done to evaluate the effect of water on the bitumen components strongly adsorbed on the aggregate surfaces ([13]). In the present study we conducted an experiment to compare the relative effects of moist and dry aggregate on bitumen properties when the aggregate material was added to the bitumen as a filler. The effects of the mineral addition on bitumen properties were followed using rheological measurements.

In the study, two bituminous mixtures, each containing 10 weight percent of 38-μm Utah aggregate fines, were prepared using an AC-5 bitumen. Prior to addition to the bitumen, one aggregate sample was heated in air for 16 hours at 150°C and the other was humidified overnight at ambient temperature in a closed vessel containing moisture-saturated air. VE measurements were obtained after curing the two mixtures for two weeks in closed ointment tins. Three complex dynamic shear viscosity (η^*) curves derived from the untreated AC-5 bitumen and the two mixtures prepared from dry and humidified aggregate fines are shown in Figure 2. The viscosity increase from 1030 to 2100 Pa·s at at 1.0 rad/sec as a result of addition of dry aggregate fines to the bitumen was probably a net result of two offsetting effects, adsorption of polar components and a "filler effect." Adsorption of polar, viscosity-building bitumen components on the aggregate surface would tend to reduce mixture viscosity (as reported in the previous section); however, 10 weight-percent aggregate filler was apparently sufficient to create a more than offsetting "filler effect" that produced a net increase in viscosity. The addition of humidified aggregate to the bitumen produced an even greater increase in viscosity from 1030 to 5200 Pa·s at 1.0 rad/sec (Figure 2). The additional viscosity increase produced by the humidified, as compared with dried,aggregate could have resulted from the net effect of 1) inhibition of the adsorption of polar, viscosity-building components by the moist aggregate surface and/or 2) hydrogen-bonding interactions between bitumen components and water molecules released from the moist aggregate. While the relative contributions of these two effects could not be deduced from this experiment, other studies in our laboratory have shown that water inhibits strong bond formation between bitumen components and mineral surfaces ([13]).

In another study, a bitumen was coated separately on wet and dry aggregates and the mixtures were allowed to stand in foil-covered dishes for 4 days, after which the mixtures were extracted with benzene. Bitumen components strongly adsorbed on the aggregate and not desorbed with benzene were subsequently desorbed with pyridine. Sixty percent less bitumen components were found strongly adsorbed on the wet-coated aggregate than on the dry-coated aggregate, indicating that moisture had inhibited adsorption of polar-bitumen components. In another detailed study ([13]) of the effects of moisture on bitumen-mineral interactions, we found that water displaced a portion of the strongly adsorbed bitumen fraction not extractable with benzene. Viscosity-building components such as carboxylic acids were found to be selectively adsorbed by mineral surfaces and selectively displaced by water, thus showing that water can interfere with their bonding to the mineral surface.

The effects of moisture on the interactions between polar bitumen components and aggregate surfaces and the effects of polar components on bitumen viscosity provided an explanation for a frequently observed seasonal effect on the measured viscosity or penetration of bitumens recovered from pavement cores. This phenomenon using penetration data was reported by Gotolski and co-workers ([18]), but a satisfactory explanation for the phenomenon to our knowledge has not been reported. The effect is demonstrated in Figure 3 which was reproduced from Gotolski's report and shows the penetration values of bitumens recovered from pavement cores taken biannually over a 42-month pavement-aging study. The designations April and October were added to Gotolski's figure to indicate the months of the year in which pavement cores were taken.

As can be seen in Figure 3, the expected decrease in penetration with time was observed for each recovered bitumen; however, the October and April samplings produced a sawtooth curve with the October samplings showing abnormally high penetrations compared with the April samplings. We propose the following explanation for this behavior. In October the pavements were relatively dry following hot summer temperatures. As a result there was relatively good bonding between the polar bitumen components and the aggregate surfaces. Thus, on recovery of the bitumen from the core samplings with benzene, a relatively large amount of strongly adsorbed polar, viscosity-building components were left adsorbed on the aggregate surfaces following benzene extraction. (Depending on aggregate and asphalt characteristics, we have found that polar components amounting to 1 to 4 percent of the total bitumen were not extracted from road cores by benzene ([12,13])). In April, however, the pavements in Gotolski's study had been exposed to wet, cold winter conditions, providing ample opportunity for water to disrupt bonding of polar bitumen constituents with the aggregate surface. During subsequent benzene extraction of the "moisture-conditioned" cores, polar components normally adhering to the aggregate surfaces during extraction of dry cores were displaceable by the action of water and thus were extracted with the benzene. These polar materials increased the viscosity of the recovered bitumen producing the lower-than-normal penetrations for the April samplings. If a more polar solvent such as pyridine had been used for extracting the bitumens from the pavement cores, a more regular pattern of decrease in penetration values with time would be expected because pyridine extracts nearly all strongly adsorbed materials from aggregate surfaces.

Irregular Transitions in Viscoelastic and Asphaltene Settling Time Data on Oxidative Aging of Bitumens

Age-hardening and embrittlement of bituminous pavement binders is a well known cause of pavement failure. The age-hardening phenomenon is largely a result of atmospheric oxygen reacting with components of the bitumen to form oxygen-containing functional groups. These newly formed groups are polar and interact with other molecules through hydrogen bonding, dipole-dipole interactions, π complexes, etc., to cause an increase in molecular associations. Reactions such as rearrangement of molecular structures, aromatization, and loss of alkyl side chains may also occur. These changes in composition and molecular interactions are thus reflected in the physical properties of the bitumen. The qualitative and quantitative aspects of these changes are a function of the composition of each individual bitumen and the level of age-hardening attained. Recent results from bitumen VE measurements and from an asphaltene settling test (AST) developed in our laboratory ([11]) showed nonregular transitions in the data as the time of oxidative aging increased. These transitions are related to changes in molecular interactions of bitumen components.

Shear-frequency dependent transitions in the VE data were observed in several paving-grade bitumens known to be comprised of different petroleum crude stocks. These transitions were observed under varying conditions from 40° to 80°C and from 35 to 85 percent strain-amplitude levels while obtaining frequency sweep (shear) measurements from 0.01 to 100 rad/sec. The most pronounced transitions which were evident from VE data plots were sudden decreases in such VE properties as η^*, G' and G", when measured at 60°C and 70 percent strain amplitude. These transitions are believed to be related to the breakdown of molecular structures in the bitumen during shear. Figure 4 illustrates the VE data for unaged bitumen A and for bitumen A after 35 minutes oxidative aging in a rolling thin film oven (RTFO). Note that the transitions in the VE data are visible in all three VE curves (η^*, G' and G") at a shear frequency of 32 rad/sec for the unaged bitumen and shifts to 20 rad/sec for the aged bitumen.

To further investigate the transitions, VE data were obtained on two bitumens (A and B) that had been subjected to a time-dependent RTFO aging study in which the first aged sample of each bitumen was removed from the oven after 35 minutes aging and subsequent samples were removed every 25 minutes thereafter up to 185 minutes of aging. VE data similar to that shown in Figure 4 were obtained on each sample, and the molecular structure breakdown transition (shear frequency transition) frequencies were determined. The results are summarized in Figure 5. (Figure 5 also contains data from asphaltene settling test results obtained on the same samples). In the figure, molecular structure breakdown transition frequencies are shown in brackets and the corresponding RTFO aging times are shown in circles. Note that for both bitumens the transition frequencies decreased with increasing aging time and increased viscosity (η^*) of the bitumen, although the magnitude of the transition frequency was different for each bitumen.

Analysis of the transition frequencies indicated an irregularity in the rate of change during oxidative aging that seemed generally to correspond with irregularities in the asphaltene settling test (AST) results obtained on the same samples. The AST is a rapid, simple, sensitive procedure proposed to be related to the dispersibility of asphaltenes in paving bitumens. Because asphaltenes are formed from bitumen components as the bitumen is partially dissolved in the hydrocarbon solvent, n-hexane; the size, shape, density, charge, etc., of the asphaltene particles should be influenced by the state of molecular interaction or structuring in the original bitumen. These factors affect the asphaltene settling time. Thus, it is reasonable to expect that changes in the state of molecular structuring in a bitumen should be reflected in asphaltene settling test data. Results shown in Figure 5 appear to support this proposition.

Asphaltene settling times data, calculated as the percent increase from the unaged bitumen to the aged bitumen, versus η^* at 1.0 rad/sec are shown in Figure 5. Corresponding RTFO aging times are shown in circles. Bitumen A showed a break or discontinuity in the viscosity-settling time data between 110 and 135 minutes aging time; however, the discontinuity was much more apparent in the results shown for bitumen B. During the first 85 minutes of bitumen B aging time, a general increase in settling time was seen with increasing aging time. A large discontinuity, however, was seen between 85 and 110 minutes of aging time in which the change in settling time decreased from 35.3 to 12.4 percent. Thus, both VE and asphaltene settling time data reflect nonregular transitions as a function of level of oxidative aging, suggesting, as discussed earlier, changes in the molecular structuring of bitumen components.

An irregular change in the viscosity was also observed for bitumen B (Figure 5) in which the viscosity decreased from 103 to 86 Pa·s with an increase of RTFO aging time from 160 to 185 minutes. This unusual event may be related to a change in molecular structuring. This interpretation is supported by the corresponding increase in the molecular structure breakdown transition frequency (20 to 25 rad/sec) and a large increase in the percent change in asphaltene settling times (40 to 65 percent). The increase in the frequency of the molecular structure breakdown transition indicates a reduced shear susceptibility and an improvement in viscous flow properties of the bitumen. The increase in asphaltene settling time indicates an increased dispersibility of the asphaltenes. Thus an increase in the "state of peptization" ($^{19-21}$) of the bitumen is suggested to account for the observed decrease in viscosity between 160- and 185-minute aging times.

Another example of an unusual aging level-viscosity relationship is shown by the data in Figure 6. Bitumen B-3051 was aged as both 2.5 and 5 percent coatings on Teflon particles for 2 hours at 163°C, using the column-oxidation technique described in the Experimental Section. One would expect the thinner 2.5 percent coating to age at a faster rate than the thicker 5 percent coating because the oxidation rate of bitumens is highly dependent on oxygen diffusion into the bitumen. VE data in Figure 6, however, show that the bitumen aged as a 5 percent coating was more viscous than the bitumen aged as a 2.5 percent coating. Also, the G' and G" intersection points for the 2.5 percent coating occurred at a higher shear frequency than the 5 percent coating, indicating a reduction of the shear susceptibility and increased viscous flow properties. Again, differences in molecular structuring and dispersion of polar components in the two samples which resulted in differences in the "state of peptization" are probably responsible for the unexpected reversal of flow properties with level of oxidative aging.

CONCLUSIONS

Rheological data, compositional data, and results from other tests provided insight into phenomena associated with adsorption of bitumen components on lime surfaces, bitumen-aging characteristics, and the effects of moisture on the properties of bitumen-aggregate mixtures. Seven of eight lime-treated bitumens, including two syncrude-derived bitumens, showed a reduction in viscosity and improved low-temperature flow following lime treatment, probably as a result of adsorption of polar, viscosity-building components on the lime surface. VE measurements on bituminous mixtures containing both moist and dry mineral aggregate fines showed that moisture increased the viscosity of the mixture because water may have inhibited strong adsorption of polar components on the mineral surface and/or interacted (e.g., by hydrogen bonding) with components of the bitumen. Irregular changes in VE and asphaltene settling time data on time-dependent aging of bitumens provided evidence of changes in molecular interactions of bitumen components. Unexpected changes in the VE properties with increased oxidative aging time were attributed to changes in the dispersion of polar components in the bitumen and differences in molecular structuring.

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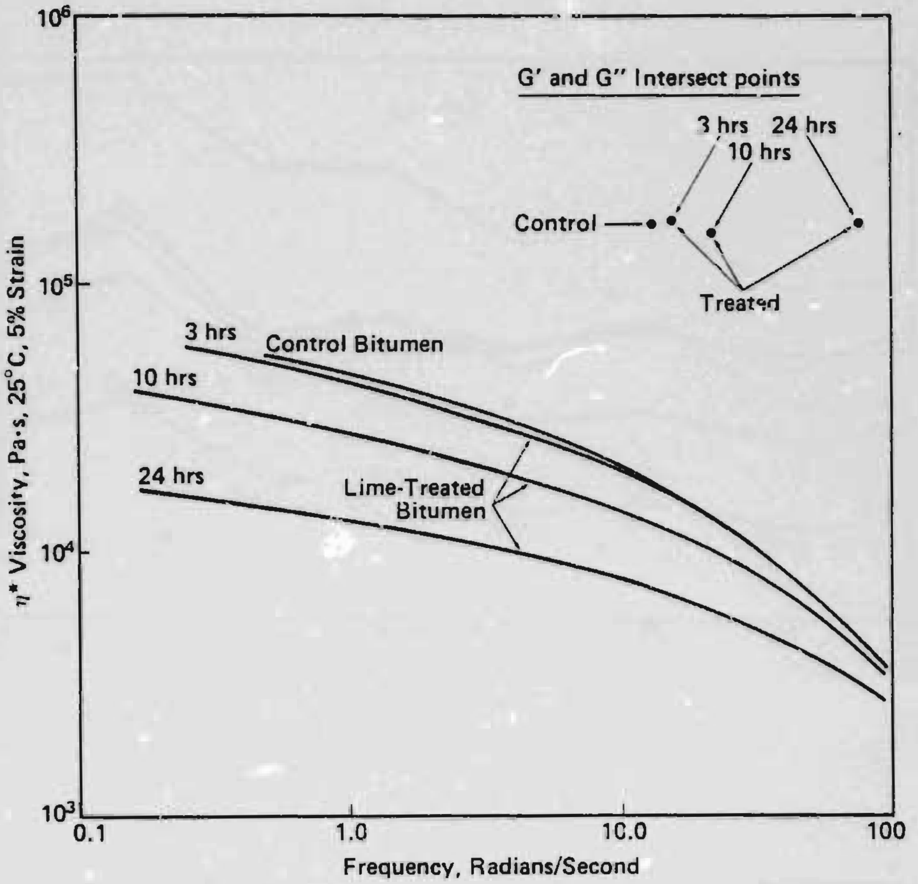

FIGURE 1. CHANGES IN VISCOSITY, G', AND G'' OF BITUMEN B-3051 FROM LIME TREATMENT

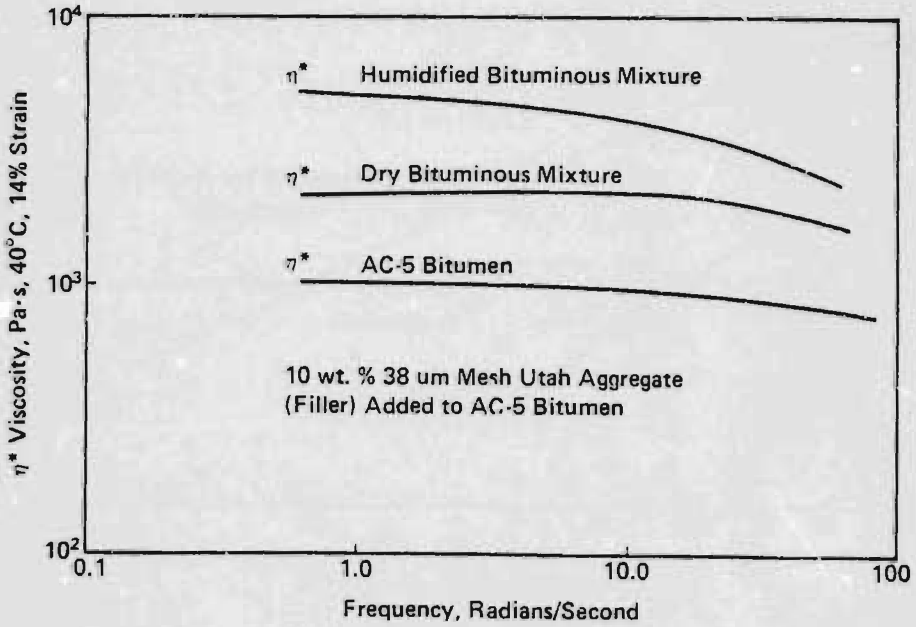

FIGURE 2. EFFECTS OF MOISTURE ON BITUMINOUS MIXTURE PROPERTIES

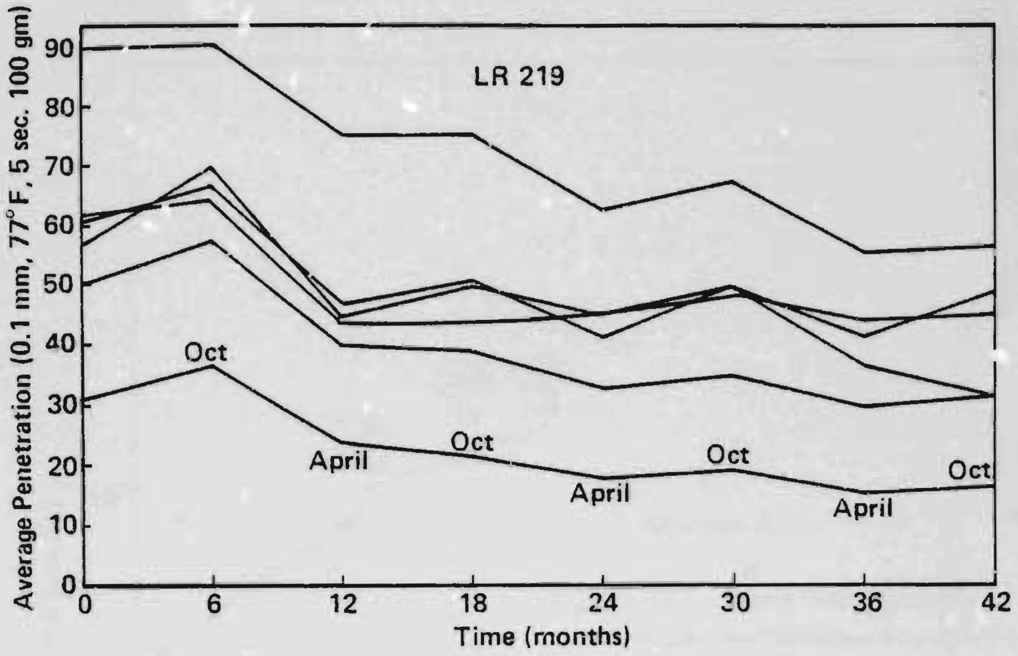

FIGURE 3. EFFECTS OF RESIDUAL MOISTURE ON PROPERTIES OF RECOVERED BITUMENS [13]

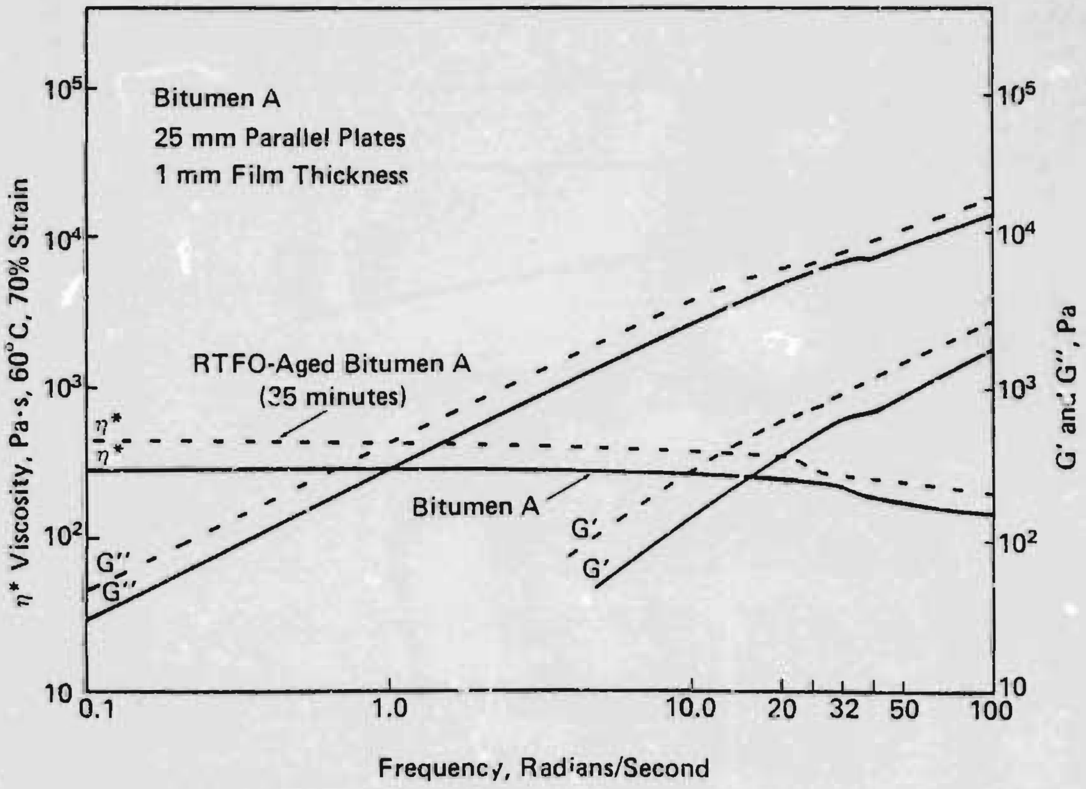

FIGURE 4. VISCOELASTIC PROPERTIES OF ORIGINAL BITUMEN AND BITUMEN AFTER 35 MINUTES OF RTFO AGING

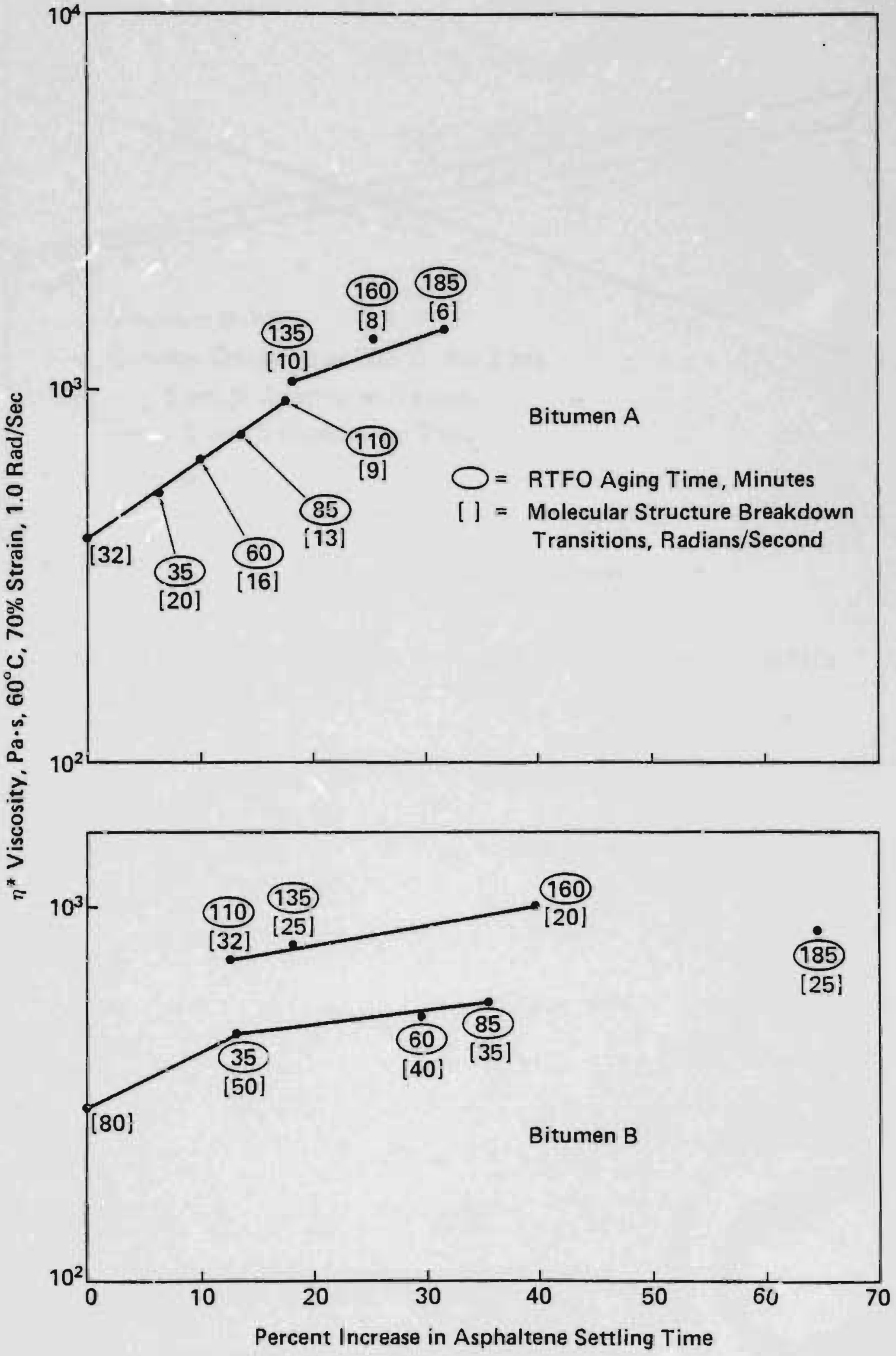

FIGURE 5. TIME-DEPENDENT RTFO AGING STUDY

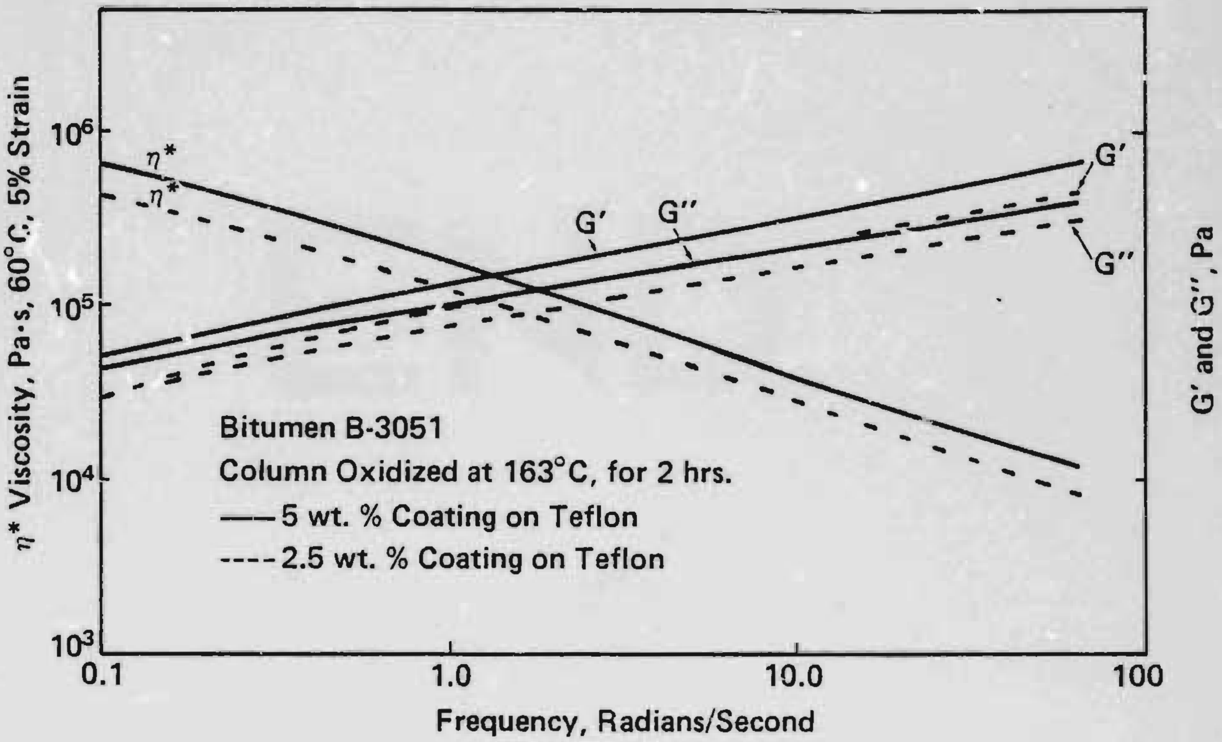

FIGURE 6. EFFECTS OF FILM THICKNESS ON BITUMEN AGING CHARACTERISTICS

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