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7. Author(s) H. Plancher, E. L. Green*, and J. C. Petersen				10. Work Unit No. (TRAIS) FCP Code 39A6-051	
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16. Abstract This study showed that lime treatment removes polar, viscosity-building components and reduces the susceptibility of the asphalt to laboratory oxidative hardening. The beneficial effects of lime treatment in reducing asphalt oxidative hardening were attributed to two synergistic effects: (1) lime reduces the formation of oxidation products by the removal of oxidation catalysts or promoters and (2) lime reduces the sensitivity of the asphalt to these oxidation products by removing polar molecules that would otherwise interact with the oxidation products to cause an increase in viscosity. Relationships were observed between polar functional group interactions and changes in asphaltene content and viscosity.					
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INTRODUCTION*

Oxidative aging in asphalts (1-10)** and its effects on asphalt pavements (11-18) have been the subject of numerous papers. A Utah State Department of Highways report (17) showed that the addition of one percent hydrated lime to bituminous mixtures was beneficial because it reduced the hardening rate of the asphalts. We surmised that this effect was caused by the adsorption on the lime surface of certain asphaltic components that normally contribute to the viscosity increase on aging and/or from the inactivation of oxidation catalysts naturally present in asphalts. The Utah report and our interest in the mechanism of asphalt oxidative aging (10, 19-20) and in the polar functional groups and molecular interactions (21-28) of asphalt prompted the present investigation.

The objectives of this study were to compare the susceptibility of the untreated and lime-treated asphalts to oxidative hardening when subjected to laboratory aging and to suggest a mechanism explaining the action of lime.

EXPERIMENTAL

Materials

Asphalts. - The four asphalts, identified by code numbers B-2959, B-3036, B-3051, and B-3602, were supplied by the Materials Division, Office of Research and Development, Federal Highway Administration (FHWA). These four viscosity-graded AC-10 asphalts, which have been used in other studies (10, 24, 26, 29-32), were selected because they varied widely in chemical composition.

Aggregates. - Four aggregates, native to the Washington, D. C., area, were supplied by the FHWA's Materials Division. These aggregates, (quartzite, Hol limestone, Riverton limestone, and granite), used in previous studies (10, 24, 26), were crushed in a Bico-Braun disk grinder equipped with ceramic plates. The crushed aggregates were wet screened to 20-42 mesh size, rinsed with distilled water, and dried at 150°C for 24 hours. Surface area measurements were made by Micromeritics Instrument Corporation, using the BET method with krypton as the adsorbate.

Solvents. - Reagent-grade solvents obtained from standard suppliers were used throughout this study. Benzene and pyridine were dried by refluxing them for 8 hours over calcium hydride before final distillation through a Vigreux column. Peroxide-free tetrahydrofuran (THF) (22, 28) was kept dry by storing it over a small quantity of 4-A molecular sieve. n-Pentane was distilled and then passed through an adsorption column filled with activated alumina.

*Presented in part at the Fifty-first Annual Meeting of the Association of Asphalt Paving Technologists at New Orleans, La. Feb. 16-18, 1976.

**Underlined numbers in parentheses refer to items in the list of references.

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

Procedures

Lime-Treatment of Asphalts. - Lime-treated asphalts were prepared by slurring a 1:1:600 weight mixture of hydrated lime, asphalt, and benzene, respectively, for 24 hours. The asphalt-benzene solution was separated from the lime by centrifugation. The recovered lime was washed several times with benzene, and the centrifuged filtrates were combined. Solvent was removed from the lime-treated asphalts in a rotary evaporator at 92°C and 2 mm Hg pressure.

Recovery of Adsorbed Materials. - Asphaltic components strongly adsorbed on the lime were recovered in two sequential fractions. The first fraction was obtained by Soxhlet extraction of the lime with pyridine. The second fraction was recovered from the pyridine-extracted lime as follows. The pyridine-extracted lime was digested with aqueous hydrochloric acid in contact with benzene. The digested mixture was filtered through a 0.9- to 1.4-micron fritted glass funnel, and the filtrate was neutralized to pH 7 with sodium hydroxide. Trace amounts of organic material present in the filtrate were recovered from the benzene after azeotropeing off the water. Organic material in the residue from the filtration was recovered by repeated washings with boiling pyridine. The filtered pyridine washings were then combined with the trace material recovered from the benzene step before final solvent removal.

Laboratory Oxidative Aging of Asphalts. - Five-gram samples of the four untreated and four lime-treated asphalts were dissolved in benzene and deposited as a thin film on 225-g samples of the four aggregates by evaporation of the benzene while the mixture was lightly stirred. Each asphalt-coated aggregate sample was packed into two 1/4-in. by 22-ft aluminum columns, and the columns were simultaneously oxidized for 24 hours at 130° C by a 30 cc/min flow of air through the columns, using established column-oxidation techniques (5, 33). The asphalts were also aged in asphalt-aggregate briquets as described in a subsequent section of the "Experimental."

The untreated and lime-treated asphalts were also aged in the absence of aggregates, using the rolling thin-film oven (RTFO) (ASTM-D-2872-74) and the rolling microfilm-circulating oven (RMF-C) (34) test methods. The RTFO procedure requires that 35 g of asphalt, contained in a specially designed RTFO sample bottle, be aged as a moving film for 75 minutes at 163°C. Because of insufficient material, the RTFO test was run on a 10-gram sample. In the RMF-C test, 0.5 g of asphalt is deposited from a benzene solution into an RTFO sample bottle as a 20-micron-film and aged for 48 hours at 98.9°C.

Recovery of Aged Asphalts from Aggregates. - The aged asphalts were recovered from the aggregates by a cold benzene wash followed by an 8-hr pyridine extraction in the modified Soxhlet extractor shown in Figure 1. This all-glass extractor has the following features: (1) the aggregate in the thimble is totally submerged at all times in the hot extracting solvent, (2) the extracting solvent is continuously displaced by fresh, incoming solvent, (3) the solvent retained in the thimble can be removed by opening the stopcock, and (4) there is negligible solvent hold-up when the run is completed. After extraction, the pyridine was removed from the asphalt in a rotary evaporator at 92°C and 2 mm Hg pressure. Final traces of pyridine were removed by repeated benzene flushings. The absence of benzene and pyridine in the recovered asphalts was established by the absence of the intense infrared absorption bands at 670 and 700 cm^{-1} , respectively.

Asphaltene Determination. - n-Pentane-insoluble asphaltenes were determined on the asphalts before and after lime treatment and after the RTFO and column aging procedures. The asphalt (1.000 g) was stirred in 40 cc of n-pentane for 24 hours at room temperature and then filtered through a 4- to 8-micron fritted glass funnel. The asphaltene precipitate was washed with 50 cc of n-pentane, dried, and weighed. The maltene fraction or pentane-soluble material was recovered by evaporation of the solvent.

Chemical Analyses. - Ketones, carboxylic acids, dicarboxylic anhydrides, and 2-quinolone types were quantitatively determined by a differential infrared spectrometric technique previously described (28). Sulfoxide concentrations were determined from the area of the 1030 cm^{-1} infrared absorption band (S-O stretching₃ vibration) in carbon disulfide solution (0.25 g/5.00 cc) using 5.8×10^3 liters/mole. cm^2 for the integrated absorption intensity (B) of the sulfoxide band. Procedures for determining the band area and calculating the concentration of sulfoxides were similar to those reported (28) for carbonyl compounds.

The percentages of carbon, hydrogen, and nitrogen were determined with a Carlo Erba analyzer and the percentage of sulfur by the Parr Bomb method. Vanadium content was determined by atomic absorption. Mineral analyses of the aggregates were made by X-ray fluorescence and X-ray diffraction.

Viscosity Measurement. - Viscosities were determined either at 60°F or at 77°F (25°C) using a sliding-plate viscometer and are reported at 0.05 sec^{-1} shear rate.

Preparation and Testing of Laboratory Briquets. - A modified version of Schmidt's resilient modulus instrument (35), built in the Laramie laboratory, was used to measure the resilient modulus of small briquets. Briquets (2.5 cm thick and 4.0 cm in diameter) were prepared from untreated and lime-treated asphalts as follows: 47.5 grams of 20-42 mesh aggregate and 2.5 g of asphalt, preheated to 150°C, were mixed until the aggregate was uniformly coated. The mixture was then transferred to a preheated 4.0-cm diameter mold and pressed into a briquet at

150°C under 4000 psi pressure for 15 minutes. The briquets were removed from the mold, annealed in an oven at 150°C for 1 hour to relieve internal strains caused during the fabrication of the briquets, and stored at 25°C for at least 72 hours before the resilient modulus (M_R) was measured. The briquets were then placed in a laboratory oven at 150°C for an additional 5 hours. After this accelerated aging, the briquets were cooled to 25°C for 72 hours and the M_R was again measured.

RESULTS

Surface areas and composition of the major components present in the aggregates are shown in Table 1. Riverton limestone, a mixture of dolomite and calcite, had six times more surface area than Ho1 limestone and five times more than granite or quartzite. Three of the aggregates were relatively simple mixtures, but granite was a composite of quartz, albite, biotite, and hornblende.

Elemental analyses of the four untreated and four lime-treated asphalts are shown in Table 2.

Viscosities and aging indexes of the untreated and lime-treated asphalts both before and after the asphalts were subjected to several laboratory oxidative aging methods are tabulated in Table 3. The aging index is the ratio of the viscosity after aging to the initial viscosity.

Aging index data in Table 3 are averaged in Table 4. These data were averaged to simplify the comparison of asphalt and aggregate effects. The percentage decrease in aging indexes resulting from lime treatment, obtained by averaging the percentage decrease for the individual asphalt-aggregate systems in Table 4, is also reported.

The resilient moduli (M_R) of briquets prepared from untreated and lime-treated asphalts after a 1-hour annealing period and after an additional 5 hours accelerated laboratory oxidative aging at 150°C are presented in Table 5. Modulus aging indexes (ratio of M_R after 5 hours of aging to M_R after 1 hour of aging) are also included. The last column in the table shows the percentage decrease in the modulus aging index resulting from lime treatment of the asphalt.

The concentrations of functional group types in the asphalts before and after lime treatment are shown in Table 6. Table 7 shows the concentrations of functional group types in the untreated and lime-treated asphalts after both column and briquet aging. To facilitate evaluating the effects of lime treatment on the various asphalt-aggregate systems, a percent decrease calculation based on the sum of the ketones and dicarboxylic anhydrides is included near the center of the table. Data in Table 8, computed from the column-aging data in Table 7, fit both averages for all aggregates on each asphalt (to show differences in asphalts) and for all asphalts on each aggregate (to show aggregate effects). Functional group type analyses of asphalts aged in the RTFO and RMF-C tests are given in Table 9.

Elemental analyses of asphaltic components adsorbed on the hydrated lime and subsequently removed as two separate fractions are tabulated in Table 10. Included in the table are the extracts' weight percentages of the original, untreated asphalts.

The asphaltene contents of unaged asphalts and asphalts recovered after laboratory aging are reported in Table 11 for both untreated and lime-treated asphalts. Also shown in the table are the net increases in asphaltene content resulting from laboratory aging. The viscosities of the maltene fractions obtained from the asphalts listed in Table 11 are shown in Table 12 together with the corresponding percent asphaltenes.

DISCUSSION

Effect of Lime Treatment on Oxidative Hardening

The beneficial effects of lime treatment in reducing the oxidative hardening of asphalts is demonstrated by the viscosity and aging index data in Table 3. These data show that all lime-treated asphalts, whether aged on aggregates (column aging or briquet aging procedures) or aged in the absence of aggregate (RMF-C and RTFO tests), have lower viscosities after laboratory aging than do their untreated counterparts. The largest amount of oxidative hardening was produced by the column- and briquet-aging procedures. This aging, based on comparison of asphalts recovered from road cores and laboratory aging tests, is roughly equivalent to the amount produced during normal hot-mix and laydown operations plus about 5 years of road service. Approximately the same amount of age hardening of the asphalts occurred during either the column or briquet aging procedure; however, the data on column-aged asphalts is more reliable for comparative purposes because exposure conditions are more uniform and controllable in the column than in briquets. The void volume of briquets, and thus their permeability to air, is dependent on the physical properties of the materials and may vary from one asphalt-aggregate system to another. The RMF-C test, designed by Schmidt to correlate with field hardening, produced a hardening level intermediate between those produced by the column- and briquet-aging procedures and the RTFO test. The RTFO test, which produced the least amount of hardening, was designed to simulate the aging during the hot-mix operation. Because a limited sample size forced the use of smaller-than-specified samples in the RTFO test, the asphalt hardening from this test was probably slightly greater than would have been encountered had the full-sized sample been used.

Aging index data averaged for all asphalts on each aggregate (top of Table 4) show that lime treatment reduced the aging indexes for asphalts oxidized on all aggregates; the averaged percentage decrease in the aging index after lime treatment was similar for all of the aggregates (54 to 59 percent for column-aged asphalts and 49 to 67 percent for the briquet-aged asphalts). The column-oxidized data suggest that Riverton limestone has an adsorption effect similar to lime itself in reducing asphalt hardening; averaged aging indexes of column-aged asphalts on Riverton limestone, both before and after lime treatment, were considerably lower than those of asphalts aged on the other aggregates.

Thus, in addition to the effect of lime treatment, an effect of the aggregate on oxidative hardening was apparent.

The effect of degree of compaction was observed in the briquet aging index data. For example, Ho1 limestone briquets were less susceptible to oxidative aging than Riverton limestone briquets because briquets made from Ho1 limestone were less permeable to the oxidizing atmosphere. This effect results from greater compaction as evidenced by the larger modulus values for Ho1 limestone briquets, Table 5. Variations in briquet compaction and their effect on asphalt hardening are discussed later.

A comparison of the column-aging indexes of the four asphalts averaged on all aggregates showed that the asphalts responded differently to lime treatment; the decrease in the indexes ranged from 73 percent for the asphalt most benefitted by lime treatment (B-3051) to 40 percent for the asphalt least benefitted (B-3602). The greater susceptibility of asphalt B-3051 to oxidative aging is evidenced by its greater aging index both before and after lime treatment. Briquet-aging indexes are not used here for comparative purposes because of variability in asphalt exposure conditions explained above.

The decreases in the averaged aging index caused by lime treatment of asphalts aged in the RTFO and the RMF-C tests were similar to those found for the column-aged asphalts. Therefore, even though the severity of the test conditions imposed by the various aging methods is quite different, as indicated by the differences in the magnitude of the aging indexes, the effect of lime treatment in reducing asphalt hardening is apparent in each instance.

Resilient Modulus (M_R) Measurements on Compacted Mixes

A modified version of Schmidt's resilient modulus testing device was used to compare the aging properties of briquets prepared from both untreated and lime-treated asphalts. A narrow range of aggregate sizes (20-42 mesh) was chosen to reduce the mechanical interlocking of aggregate particles and thus increase the sensitivity of the M_R measurements to the properties of the asphalt. M_R data are shown in Table 5. The lower M_R values of briquets prepared from lime-treated asphalts when compared with values for briquets prepared from the untreated asphalts are attributed to the lower initial viscosities of the lime-treated asphalts.

Effect of Lime Treatment on M_R . - Modulus aging indexes (Table 5) of all briquets prepared from lime-treated asphalts were lower than those prepared from untreated asphalts. The decrease in the modulus aging indexes caused by lime treatment, as shown in the last column of the table, ranged from 6 to 29 percent. Briquets made from asphalt B-3051 showed the greatest overall benefit from lime treatment. Thus, the beneficial effect of the lime treatment in reducing the stiffness of the briquets is similar to the effect on the asphalt aging index (Table 4), although not of the same magnitude.

Effect of Aggregate Type on M_R . - An effect of aggregate type on the M_R , independent of lime treatment, is apparent from the data in Table 5. M_R values of briquets prepared from the two limestones are much larger than M_R values for corresponding briquets prepared from granite; values for granite are in turn larger than those for quartzite. These differences are believed to result primarily from differences in the physical properties of the aggregate; i.e., the softer aggregates are crushed or abraded at contact points during compaction to produce a briquet with interlocking aggregate particles that has larger M_R values. The relative quantities of fines produced during the compaction process for the four aggregates were directly related to the magnitude of the M_R values, thus supporting this contention. Viscosity and aging-index data in Table 3 and averaged aging-index data in Table 4 showed that the asphalts aged in briquets made from limestones generally exhibited less hardening than those made from granite or quartzite. This general decrease in hardening of the asphalts in the limestone briquets is apparently caused by the increased compaction and reduced permeability of the briquets to air, further supporting the proposition that the larger modulus values for limestone briquets result largely from mechanical properties of the aggregates.

Reversible hardening induced in the asphalts by the polar aggregate surface might also have contributed to the differences in modulus. An investigation of this reversible hardening phenomenon would require that briquets be made without causing significant mechanical damage to the aggregate during compaction.

Chemistry of Lime Action

Having established that the lime treatment significantly reduced the oxidative aging of laboratory-aged asphalts, we directed the major thrust of this study toward gaining an understanding of the mechanism by which asphalt hardening was reduced.

Effect of Lime Treatment on Oxidation Product Formation. - Asphalts were examined for the effect of lime treatment on the formation of polar oxidation products that might promote an increase in viscosity through molecular interactions. Polar functional group types that are readily determined by infrared spectroscopy are ketones, carboxylic acids, dicarboxylic anhydrides, 2-quinolone types, and sulfoxides. Functional group determinations reported in Tables 6, 7, 8, and 9 show that ketones and sulfoxides were the major types formed during the laboratory aging tests. Moderate amounts of dicarboxylic anhydrides and smaller amounts of carboxylic acids were also formed. A comparison of the data on untreated and lime-treated asphalts shows that lime-treated asphalts contained smaller amounts of the determined oxidation products than the untreated asphalts. Sulfoxides were an exception to this generality, but earlier studies in the Laramie laboratory indicated that sulfoxide concentration reaches a constant level in asphalts during the early stages of oxidation; therefore the constant amount of sulfoxide observed independent of lime treatment is not surprising. The 2-quinolone types reported in the tables are naturally occurring in asphalt and are not

affected by oxidation (28). Thus it is concluded that lime treatment reduced the formation of carbonyl-type compounds--ketones, carboxylic acids, and dicarboxylic anhydrides--during laboratory aging.

The amounts of functional group types formed on aging (Tables 7-9) rank the severity of the laboratory aging procedures as follows: column aging approximately equal to briquet aging RMF-C RTFO. This agrees with the ranking based on aging index data previously discussed and supports the conclusion that oxidation is a major contributor to asphalt hardening. Further, column-aged data in Tables 7 and 8 show that less oxidation products are formed in asphalts aged on Riverton limestone than on any of the other aggregates, thus supporting the previously discussed data in Table 3 that show less hardening of asphalts aged on Riverton limestone.

Naturally occurring catalysts or promoters of asphalt oxidation are suggested by the reduced amounts of polar, oxygen-containing functional groups produced on aging in lime-treated asphalts; i.e., lime treatment may remove components that promote or catalyze asphalt oxidation. Because reports in the literature (36) and work in our laboratories have indicated a correlation between vanadium content and oxidative hardening, we examined the vanadium content of the asphalts before and after lime treatment. Data in Table 2 show only a slight reduction in vanadium content from lime treatment and suggest that vanadium compounds are not the principal catalyst removed by lime.

Although lime treatment reduced the amount of carbonyl-type oxidation products formed in asphalt, this reduction was relatively small when compared with the reduction in hardening as measured by the aging index. Table 8 shows that the sum of the ketones and dicarboxylic anhydrides formed on oxidation was reduced about 12 percent by lime treatment in contrast to an average decrease in the aging index of about 60 percent (Table 4). The large disparity in these figures suggests that lime treatment acts in additional ways to reduce the age hardening of the asphalts.

Polar Components Removed by Lime. - To find additional ways that lime treatment might reduce asphalt hardening, we examined the polar components removed by the lime. Recall that the components removed by the lime were separated from the asphalt prior to oxidative aging and should not be confused with the polar oxidation products. Table 10 shows that lime treatment removed 4.34, 4.88, and 5.96 percent of the components from asphalts B-2959, B-3036, and B-3051, respectively. The exact amount removed from asphalt B-3602 is not known because of an accidental sample loss; however, it is known to be over 3 percent. Elemental analyses of the components adsorbed on, and thus removed by, the lime (Table 10) show that 8 to 19 percent of the adsorbed material is not accounted for as carbon, hydrogen, or nitrogen and so must be largely sulfur and oxygen. Infrared data obtained on the material recovered from lime showed that carboxylic acids and 2-quinolone types were the predominant compound types adsorbed. The major portion of the deficit in the elemental analysis data described above can be accounted

for by the oxygen in these compound types. The two- to fourfold increase in nitrogen content in the material adsorbed on lime cannot be totally accounted for as 2-quinolones and pyrrole-type nitrogen compounds; therefore, other nitrogen types not readily measurable by infrared spectroscopy must account for the additional nitrogen in the adsorbed material.

Another way to characterize the material removed by the lime is to look for differences in asphalt composition before and after lime treatment. Infrared functional group analyses of the asphalts before and after lime treatment (Table 6) confirm that carboxylic acids and 2-quinolone types are removed by lime. These data also show that when the concentration of carboxylic acids was high enough to compel the acids and 2-quinolone types to compete for the lime surface the acids were preferentially adsorbed. For all asphalts except B-3602, the carboxylic acids were virtually removed by the lime.

These analyses show that the components removed by the lime are polar molecules that are capable of exhibiting strong molecular interaction forces (21, 22, 27). Thus, these components probably play an important role in asphalt hardening.

Relationship Between Polar Functional Groups and Asphaltenes. - A relationship between the concentration of carbonyl-type oxidation products and the asphaltene content and the effect of lime treatment on this relationship is illustrated in Figure 2. In this plot, derived from data in Tables 6, 8, and 11, lines were drawn connecting the points corresponding to unaged and column-aged asphalts. Data points for aged asphalts were obtained by averaging the data for each asphalt aged on all aggregates. The plot shows two distinct lines with different slopes for each asphalt. The greater slope for the lime-treated asphalts as compared with the corresponding untreated asphalts shows that fewer asphaltenes are formed for a given amount of carbonyl-type oxidation product in the lime-treated asphalts. These results suggest that lime removed polar functional group types from the unoxidized asphalts that would otherwise interact with the oxidation products to form asphaltenes.

The ability of molecules containing polar functional groups to interact with asphalt components to form asphaltenes was demonstrated by a study of Neuman and Roesler (37). Their study showed that asphaltenes were formed in asphaltene-free bitumens when water-soluble substances containing polar functional groups were added; compounds containing functional groups similar to those formed on oxidation or removed by lime were included in their study. These substances were later recovered as structural units in the newly formed asphaltenes, but the additives were no longer water extractable. Thus, this study supports our proposal that the removal of the carboxylic acids, 2-quinolone types, and other polar substances from asphalts by the lime treatment is directly related to the reduction of asphaltene formation on aging.

Relationship Between Polar Functional Groups and Viscosity. - Evidence for the viscosity-building properties of the components removed by lime is apparent from the viscosities of the untreated and lime-

treated asphalt (Table 3). In all cases, lime treatment reduced the viscosity of the asphalts, demonstrating that the polar materials removed by the lime are viscosity-building components.

Further evidence for a relationship between polar functional group interactions and the viscosity of asphalts was indicated by a study at the Laramie laboratory (38). The effect of carboxylic acid groups on asphalt viscosity was demonstrated by introducing carboxylic acid groups (0.125 moles/liter) into molecules of highly aromatic fraction from a Wilmington, Calif., asphalt by an unambiguous chemical route. Two identical samples of Wilmington maltenes were spiked with the aromatic fraction or with the carboxylated aromatic fraction. The viscosity of the uncarboxylated blend was 9,000 poise compared to 30,000 poise for the carboxylated blend.

Relationship Between Asphaltenes and Viscosity

The previous two sections of this paper have shown an apparent relationship between polar functional group interactions and both asphaltene formation and changes in viscosity. These relationships, therefore, suggest a relationship between asphaltene content and viscosity. If each asphalt is considered as an individual system, some correlations can be made. These correlations are shown in Figure 3, which includes all viscosity and asphaltene data for untreated and lime-treated asphalts, both before and after column aging on aggregates and in the RTFO test. For each asphalt studied an excellent correlation exists between asphaltenes formed on aging and the corresponding increase in viscosity. The deviations from the best-fit line for three of the asphalts are within the precision of the experimental methods. The two curves designated by the broken lines for asphalt B-3602 in Figure 3 are drawn through the two sets of points representing untreated and lime-treated asphalts. The displacement of these two curves suggests that the removal of polar components by lime altered the composition of this asphalt sufficiently to produce a "new" asphalt with a slightly different asphaltene-viscosity relationship than that of the untreated asphalt.

Asphalts of similar viscosity, as used in this study, may have widely differing asphaltene contents. These differences can be explained if it is assumed that polar functional group interactions (or, more generally speaking, molecular interaction forces of polar or polarizable molecules) contribute significantly to both viscosity increase and asphaltene formation. Asphaltenes are defined as those components in asphalt that are precipitated by pentane; however, during the asphaltene determination pentane makes an arbitrary separation of the polar, viscosity-building components between the insoluble asphaltene and the soluble maltene (resin, oil) fractions. The solubility of the polar components in pentane is governed by such factors as functional group type and content, molecular weight, molecular structure, etc. These factors characteristically vary from one asphalt to another. Many polar resin components of the maltene fraction have functionality similar to that of asphaltenes but remain soluble in the pentane during the asphaltene determination. The similarity of the molecular interaction forces

of resins and asphaltenes has been demonstrated using inverse gas-liquid chromatography (39).

Additional evidence that pentane splits the viscosity-building components between the asphaltene and maltene phases is provided by data in Table 12 and Figure 4. As shown in Figure 4 by the unbracketed data points for unoxidized asphalts, an excellent inverse correlation was found between the maltene viscosity and asphaltene contents of the column-aged asphalts. Because all asphalts are of the same viscosity grade, those asphalts exhibiting lower asphaltene contents should exhibit higher maltene viscosities and vice versa. Thus the viscosity-building components in asphalt B-3602 (which has only 10.6 percent asphaltenes) are much more soluble in pentane than are the viscosity-building components in asphalt B-2959 (which has 27.6 percent asphaltenes).

The viscosity-composition data clearly reflect the differences in chemical composition of the asphaltene and maltene fractions from one asphalt to another and that each asphalt has its own asphaltene-viscosity relationship as determined by its own individual chemical makeup.

Some additional comments should be made relative to the data in Figure 4. With the exception of asphalt B-3602 (which developed carbonyl components during the lime treatment), lime treatment produced an asphalt with lower maltene viscosity. This lower viscosity probably resulted from the removal of carboxylic acids and other viscosity-building polar groups by the lime treatment that would otherwise be found in the maltene fraction. These are components that, as previously suggested, interact with oxidation products to form asphaltenes and increase viscosity. This view is supported by the bracketed data points in Figure 4. These data points are averaged values for the asphalts aged on four different aggregates prior to fractionation and are connected to the values for unaged asphalts by the dashed lines. Note that in all cases maltenes separated after oxidative aging have lower viscosities than the maltene fraction from unaged asphalts and that much less change in maltene viscosity and asphaltene formation occurred in the lime-treated asphalts on aging. These results support the proposition that polar-viscosity building components in the maltene fraction are being converted to asphaltenes during aging and that lime treatment removes components that contribute to this process.

Mechanism of Lime Action

These studies have shown that lime treatment

1. reduces the viscosity increases upon aging
2. removes reactive polar compounds
3. reduces the formation of carbonyl-type oxidation products on aging
4. reduces the ratio of asphaltenes formed to oxidation products formed on aging
5. reduces asphaltene formation

These facts suggest that the mechanism of the action of lime in reducing the asphalt hardening rate involves a combination of factors. Less oxidation products are produced in lime-treated asphalts than in untreated asphalts, thus reducing the viscosity-building interactions. The effect of this reduction in oxidation products on viscosity is enhanced by an additional factor. In untreated asphalt, oxidation products interact readily with reactive polar compounds to increase viscosity and asphaltene formation. In the absence of the reactive polar compounds removed by lime, the oxidation products have less opportunity to participate in viscosity-building or asphaltene-producing interactions, thus the sensitivity of the asphalt to their presence is reduced.

In summary, it is proposed that the beneficial effect of lime treatment in reducing asphalt oxidative hardening is due to two synergistic effects: (1) lime reduces the formation of oxidation products by the removal of oxidation catalysts or promoters and (2) lime reduces the sensitivity of the asphalt to these oxidation products by removing reactive polar molecules that would otherwise interact with the oxidation products to cause an increase in viscosity.

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TABLE 1. - Properties of aggregates

Aggregate	Surface area, m ² /g	Composition, wt. percent
Riverton limestone	0.655	Dolomite, 18 Calcite, 78
Hol limestone	0.104	Calcite, 93
Quartzite	0.145	Quartz, 94
Granite	0.141	Quartz, 78 Albite Biotite Hornblende] 18

TABLE 2. - Composition of untreated and lime-treated asphalts

Asphalts	Weight percent				V, ppm
	C	H	N	S	
B-2959, untreated	83.77	9.91	0.28	5.25	180
B-2959, lime-treated	83.18	10.20	0.24	5.30	174
B-3036, untreated	85.78	10.19	0.26	3.41	7
B-3036, lime-treated	85.21	10.49	0.25	3.18	7
B-3051, untreated	82.90	10.45	0.78	5.43	1380
B-3051, lime-treated	82.27	10.01	0.72	5.68	1137
B-3602, untreated	86.77	10.94	1.10	0.99	40
B-3602, lime-treated	86.57	10.75	1.04	1.38	40

TABLE 3. - Viscosity and aging index of untreated and lime-treated asphalts after oxidative aging

Asphalt	Oxidative aging	Untreated				Lime-treated			
		Viscosity, megapoise		Aging index*		Viscosity, megapoise		Aging index	
		Column**	Briquet***	Column	Briquet	Column	Briquet	Column	Briquet
B-2959	None	0.749				0.362			
	On Hol limestone	27.5	43.3	37	58	6.14	3.52	17	10
	On Riverton limestone	22.9	51.6	31	69	4.37	3.33	12	9
	On quartzite	30.6	37.1	41	50	6.79	7.28	19	20
	On granite	30.1	145	41	194	7.57	4.01	21	11
	In RTFO	7.44		10		1.82		5	
	In RMF-C	15.2		20		2.23		6	

B-3036	None	1.39				.783			
	On Hol limestone	38.7	24.0	28	17	6.99	3.64	9	5
	On Riverton limestone	28.2	18.3	20	13	4.94	5.83	6	7
	On quartzite	39.2	57.2	28	41	7.69	10.9	10	14
	On granite	42.6	30.6	31	22	11.3	6.43	14	8
	In RTFO	4.01		3		1.76		2	
	In RMF-C	11.1		8		1.87		2	

B-3051	None	.605				.378			
	On Hol limestone	78.3	27.5	129	45	16.2	11.5	43	30
	On Riverton limestone	41.6	50.3	69	83	6.34	20.4	17	54
	On quartzite	81.6	140	135	231	16.7	44.4	44	117
	On granite	118	116	195	192	14.3	36.3	38	96
	In RTFO	8.87		15		3.14		8	
	In RMF-C	17.5		29		5.33		14	

B-3602	None	1.46				1.10			
	On Hol limestone	56.8	50.4	39	35	23.4	23.8	21	22
	On Riverton limestone	33.0	59.9	23	41	19.0	34.2	17	31
	On quartzite	35.8	65.3	25	45	18.8	38.3	17	35
	On granite	46.4	49.8	32	34	17.6	32.2	16	29
	In RTFO	7.38		5		5.24		5	
	In RMF-C	17.1		12		11.3		10	

*Ratio of viscosity after oxidative aging to initial viscosity

**Aged in stream of air in column at 130°C for 24 hours

***Aged in briquets in air oven at 150°C for 5 hours

TABLE 4. - Effect of lime treatment on asphalt hardening

Aging Method	Aggregate or asphalt	Aging index					
		Untreated		Lime treated		Decrease on lime treatment, percent	
		Column	Briquet	Column	Briquet	Column	Briquet
<u>Averaged for all asphalts on each aggregate</u>							
Column or briquet	Quartzite	57	92	23	47	54	49
	Hol limestone	58	39	23	17	59	57
	Riverton limestone	36	52	13	25	58	51
	Granite	75	111	22	36	59	67
<u>Averaged for all aggregates on each asphalt</u>							
Column or briquet	B-2959	38	93	17	13	54	87
	B-3036	27	23	10	9	64	63
	B-3051	132	138	36	74	73	46
	B-3602	30	39	18	29	40	25
<u>Averaged for all asphalts for each test method</u>							
RTFO			8		5		33
RMF-C			17		8		54

TABLE 5.- Resilient modulus data on briquets prepared from untreated and lime-treated asphalts and subjected to accelerated oxidative aging

Asphalt	Aggregate	$M_R \times 1000, \text{psi}^*, \text{at } 25^\circ\text{C}$				Modulus aging index**		
		Aging time at 150°C				Untreated	Lime-treated	Decrease on lime treatment, percent
		Untreated		Lime-treated				
		1 hr***	5 hr***	1 hr***	5 hr***			
B-2959	Quartzite	12	29	6	10	2.4	1.7	29
	Hol limestone	89	158	36	54	1.8	1.5	17
	Riverton limestone	76	124	31	45	1.6	1.5	6
	Granite	27	41	9	12	1.5	1.3	13
B-3036	Quartzite	25	46	10	15	1.8	1.5	17
	Hol limestone	121	173	71	86	1.4	1.2	14
	Riverton limestone	109	158	54	76	1.5	1.4	7
	Granite	38	56	20	28	1.5	1.4	7
B-3051	Quartzite	11	32	8	17	2.9	2.1	28
	Hol limestone	78	149	41	60	1.9	1.5	21
	Riverton limestone	70	136	40	60	1.9	1.5	21
	Granite	26	44	16	21	1.7	1.3	24
B-3602	Quartzite	27	66	23	47	2.4	2.0	17
	Hol limestone	146	244	144	184	1.7	1.3	24
	Riverton limestone	114	205	109	184	1.8	1.7	6
	Granite	52	84	47	72	1.5	1.6	6

*To convert from psi to pascal (Pa), multiply by 6.894757×10^3

**Ratio of 5-hr M_R /1-hr M_R

***Total hours briquets heated at 150°C

TABLE 6. - Concentration of functional groups in asphalts before and after lime treatment

Asphalts	Concentration, moles/liter				
	Ketones	Carboxylic acids	Dicarboxylic anhydrides	2-Quinolone types	Sulf-oxides
B-2959					
Untreated	0.015	trace	0.0014	0.003	0.015
Lime-treated	.039	*	*	*	.013
B-3036					
Untreated	.021	trace	.0014	.001	.022
Lime-treated	.039	*	*	*	.019
B-3051					
Untreated	.017	.014	.003	.009	.010
Lime-treated	.039	*	.001	.004	.008
B-3602					
Untreated	.045	.06**	*	.011	.015
Lime-treated	.10	.014**	.007	.006	.015

*Below level of detection

**Present as carboxylate salts

TABLE 7. - Concentration of functional group types in untreated and lime-treated asphalts oxidized on mineral aggregates in columns and briquets

		Concentration, moles/liter													
		Ketones		Dicarboxylic anhydrides		Ketones and anhydrides			Carboxylic acids		2-Quinolones		Sulfoxides		
Aggregate	Asphalt	Type of aging	Not treated	Lime treated	Not treated	Lime treated	Not treated	Lime treated	% De-crease on treatment	Not treated	Lime treated	Not treated	Lime treated	Not treated	Lime treated
Quartzite	B-2959	Column	.51	.44	.014	.011	.524	.451	14	.009	.004	.003	Trace	.27	.26
		Briquet	.52	.45	.016	.011	.536	.461	14	.007	.004	.002	.003	.26	.27
	B-3036	Column	.57	.47	.017	.012	.587	.482	18	.005	.004	.001	Trace	.29	.27
		Briquet	.62	.52	.020	.015	.640	.535	16	.007	.004	Trace	Trace	.25	.27
	B-3051	Column	.58	.46	.022	.018	.602	.478	21	.023	.004	.007	.004	.26	.26
		Briquet	.64	.56	.026	.019	.666	.579	13	.021	.011	Trace	.004	.24	.25
	B-3602	Column	.76	.74	.049	.039	.809	.779	4	.058*	.016	.010	.006	.17	.17
		Briquet	.81	.76	.057	.039	.867	.799	8	.044*	.012	.006	.005	.14	.15
Hol limestone	B-2959	Column	.51	.42	.014	.010	.524	.430	18	.009	Trace	.002	Trace	.31	.27
		Briquet	.53	.37	.012	.005	.542	.375	31	.005	.002	.001	.001	.30	.27
	B-3036	Column	.54	.48	.014	.009	.554	.489	12	.005	.002	.001	Trace	.29	.27
		Briquet	.50	.43	.007	.006	.507	.436	14	.004	Trace	Trace	Trace	.28	.27
	B-3051	Column	.59	.50	.017	.017	.607	.517	15	.024	.004	.005	.003	.27	.27
		Briquet	.50	.50	.022	.017	.522	.517	16	.016	.007	.009	.003	.28	.28
	B-3602	Column	.78	.77	.042	.042	.822	.812	1	.061*	.014	.010	.006	.18	.17
		Briquet	.80	.72	.031	.026	.831	.746	10	.070*	.012	.007	.006	.18	.18
Riverton limestone	B-2959	Column	.47	.40	.012	.009	.482	.409	15	.007	Trace	.002	Trace	.31	.29
		Briquet	.53	.39	.016	.009	.546	.399	27	.005	.002	.002	Trace	.29	.27
	B-3036	Column	.53	.45	.010	.008	.540	.458	15	.005	.002	.001	Trace	.29	.30
		Briquet	.50	.46	.012	.008	.512	.468	9	.004	.002	Trace	Trace	.28	.26
	B-3051	Column	.56	.45	.017	.018	.577	.468	19	.021	.006	.007	.005	.30	.27
		Briquet	.55	.52	.019	.017	.569	.537	6	.012	.005	.004	.004	.26	.24
	B-3602	Column	.77	.72	.039	.037	.809	.757	6	.061*	.014	.010	.006	.18	.17
		Briquet	.80	.78	.040	.028	.840	.808	4	.032*	.011	.008	.004	.14	.15
Granite	B-2959	Column	.51	.44	.014	.011	.524	.451	14	.007	.004	.003	Trace	.32	.30
		Briquet	.66	.42	.020	.009	.680	.429	37	.011	Trace	.001	Trace	.26	.27
	B-3036	Column	.55	.51	.019	.012	.569	.522	8	.005	.002	.001	Trace	.30	.29
		Briquet	.59	.51	.015	.010	.605	.520	14	.004	Trace	Trace	Trace	.27	.26
	B-3051	Column	.58	.51	.022	.017	.602	.527	12	.023	.005	.008	.005	.30	.29
		Briquet	.62	.55	.023	.022	.643	.572	11	.016	.009	.006	.004	.29	.27
	B-3602	Column	.78	.74	.041	.042	.821	.782	5	.063*	.012	.010	.006	.17	.18
		Briquet	.84	.84	.047	.030	.887	.870	2	.064*	.014	.010	.007	.17	.16

*Part of acid exists as carboxylate salts

TABLE 8. - Concentration of functional group types in untreated and lime-treated asphalts oxidized by the column method on mineral aggregates

Asphalt	Concentration, mole/liter					Decrease in ketones and anhydrides resulting from lime treatment, percent
	Ketones	Carboxylic acids (Averaged for all aggregates on each asphalt)	Dicarboxylic anhydrides	2-Quinolone types	Sulfoxides	
<u>Untreated</u>						
B-2959	0.50	0.008	0.014	0.003	0.30	
B-3036	.55	.005	.015	.001	.29	
B-3051	.58	.023	.020	.007	.29	
B-3602	.77	.061	.043	.010	.18	
<u>Lime-treated</u>						
B-2959	.43	.002	.010	*	.28	15
B-3036	.48	.003	.010	*	.28	13
B-3051	.48	.005	.018	.004	.27	17
B-3602	.74	.014	.040	.006	.17	4
(Averaged for all asphalts on each aggregate)						
<u>Untreated</u>						
Quartzite	0.61	0.024	0.026	0.005	0.25	
Hol limestone	.61	.025	.022	.005	.27	
Riverton limestone	.58	.024	.020	.005	.27	
Granite	.61	.025	.024	.006	.27	
<u>Lime-treated</u>						
Quartzite	.53	.007	.020	.003	.24	14
Hol limestone	.54	.005	.021	.002	.25	10
Riverton limestone	.51	.006	.018	.003	.26	13
Granite	.55	.008	.021	.003	.27	9

Below level of detection

TABLE 9. - Concentration of functional group types in untreated and lime-treated asphalts from the RTFO and RMF-C tests

Test method	Asphalt	Concentration, moles/liter				
		Ketones	Carboxylic acids	Dicarboxylic anhydrides	2-Quinolone types	Sulfoxides
<u>Untreated</u>						
RTFO	B-2959	0.31	trace	0.003	0.003	0.16
	B-3036	.30	trace	.003	.001	.20
	B-3051	.34	0.018	.003	.007	.15
	B-3602	.49	.075	.009	.010	.10
RMF-C	B-2959	.38	.008	.003	.002	.28
	B-3036	.37	.008	.003	.001	.26
	B-3051	.43	.014	.004	.005	.28
	B-3602	.63	.020	.016	.009	.20
<u>Lime-treated</u>						
RTFO	B-2959	.25	trace	.002	*	.15
	B-3036	.31	trace	.001	*	.21
	B-3051	.35	trace	.005	.005	.14
	B-3602	.55	.018	.020	.006	.12
RMF-C	B-2959	.32	trace	.003	*	.25
	B-3036	.33	trace	.002	*	.26
	B-3051	.38	trace	.009	.003	.25
	B-3602	.56	.018	.030	.006	.18

*Below level of detection

TABLE 10. - Composition of asphaltic components adsorbed on hydrated lime

	Pyridine extract				Acid-digestion extract			
	Wt. percent				Wt. percent			
	Of original asphalt	C	H	N	Of original asphalt	C	H	N
B-2959	2.59	80.28	7.73	1.02	1.75	76.61	7.56	1.10
B-3036	2.60	83.86	7.54	0.76	2.28	79.22	9.54	0.72
B-3051	2.06	80.65	8.41	1.75	3.90	77.02	8.30	1.49
B-3602	*	81.45	8.30	1.99	2.50	71.08	8.52	1.56

*Lost during laboratory workup

TABLE 11.- Asphaltene determinations

Asphalt	Asphaltenes											
	Unoxidized Wt. %	Oxidized on solid supports*									Oxidized in RTFO test**	
		Hol limestone			Riverton limestone		Quartzite		Granite			
	Wt. %	Wt. %	Δ^{***}	Wt. %	Δ^{***}	Wt. %	Δ^{***}	Wt. %	Δ^{***}	Wt. %	Δ^{***}	
B-2959												
Untreated	27.6	38.1	10.5	37.6	10.0	38.5	10.9	38.6	11.0	33.5	5.9	
Lime-treated	26.4	32.0	5.6	31.5	5.1	33.2	6.8	33.3	6.9	28.2	1.8	
B-3036												
Untreated	17.9	28.6	10.7	26.9	9.0	29.4	11.5	29.6	11.7	22.2	4.3	
Lime-treated	16.2	22.0	5.8	21.6	5.4	22.2	6.0	24.4	8.2	18.6	2.4	
B-3051												
Untreated	25.9	39.5	13.6	38.6	12.7	40.3	14.4	41.2	15.3	31.8	5.9	
Lime-Treated	26.7	33.5	6.8	32.1	5.4	34.0	7.3	33.8	7.1	29.3	2.6	
B-3602												
Untreated	10.6	24.5	13.9	23.4	12.8	23.7	13.1	23.9	13.3	15.7	5.1	
Lime-treated	13.3	21.6	8.3	19.8	6.5	20.4	7.1	20.9	7.6	16.2	2.9	

*Air oxidized, 130°C, 24 hours in column as 5 percent coating on solid supports

**10 g oxidized as rolling film, 163°C for 75 minutes

***Increase in percent asphaltene resulting from laboratory aging

TABLE 12. - Viscosity of maltenes from column-aged, untreated, and lime-treated asphalts

Asphalt	Method of oxidative aging	Support used	Untreated		Lime-treated	
			Asphalt-tenes, percent	Viscosity, 60°F, poise x 10 ⁻³	Asphalt-tenes, percent	Viscosity, 60°F, poise x 10 ⁻³
B-2959	None		27.6	11.3	26.4	6.45
	Column	Hol	38.1	4.27	32.0	4.47
	Column	Riverton	37.6	3.15	31.5	3.04
	Column	Quartzite	38.5	8.12	33.2	5.52
	Column	Granite	38.6	3.69	33.3	3.56
	RTFO		33.5	3.95	28.2	4.49
B-3036	None		17.9	367	16.2	197
	Column	Hol	28.6	78.3	22.0	66.6
	Column	Riverton	26.9	102	21.6	136
	Column	Quartzite	29.4	81.9	22.2	122
	Column	Granite	29.6	69.5	24.4	91.6
	RTFO		22.2	146	18.6	176
B-3051	None		25.9	23.1	26.7	10.0
	Column	Hol	39.5	10.3	33.5	7.00
	Column	Riverton	38.6	17.4	32.1	8.50
	Column	Quartzite	40.3	4.83	34.0	6.28
	Column	Granite	41.2	4.83	33.8	5.72
	RTFO		31.8	14.4	29.3	12.6
B-3602	None		10.6	1290	13.3	2070
	Column	Hol	24.5	590	21.6	776
	Column	Riverton	23.4	697	19.8	919
	Column	Quartzite	23.7	400	20.4	607
	Column	Granite	23.9	777	20.9	787
	RTFO		15.7	2080	16.2	1270

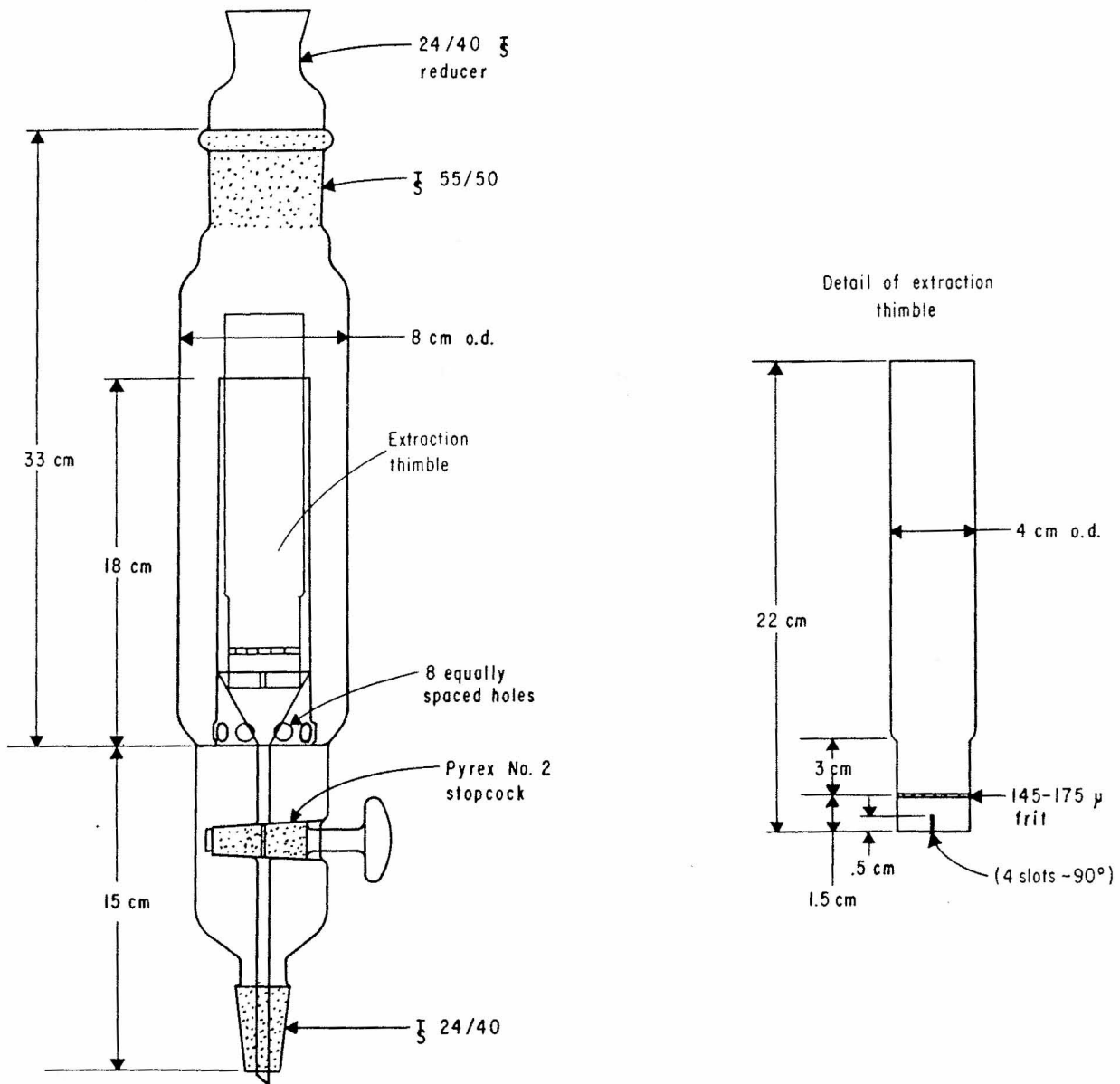


FIGURE I.- All glass modified Soxhlet extractor used to recover asphalts from aggregates.

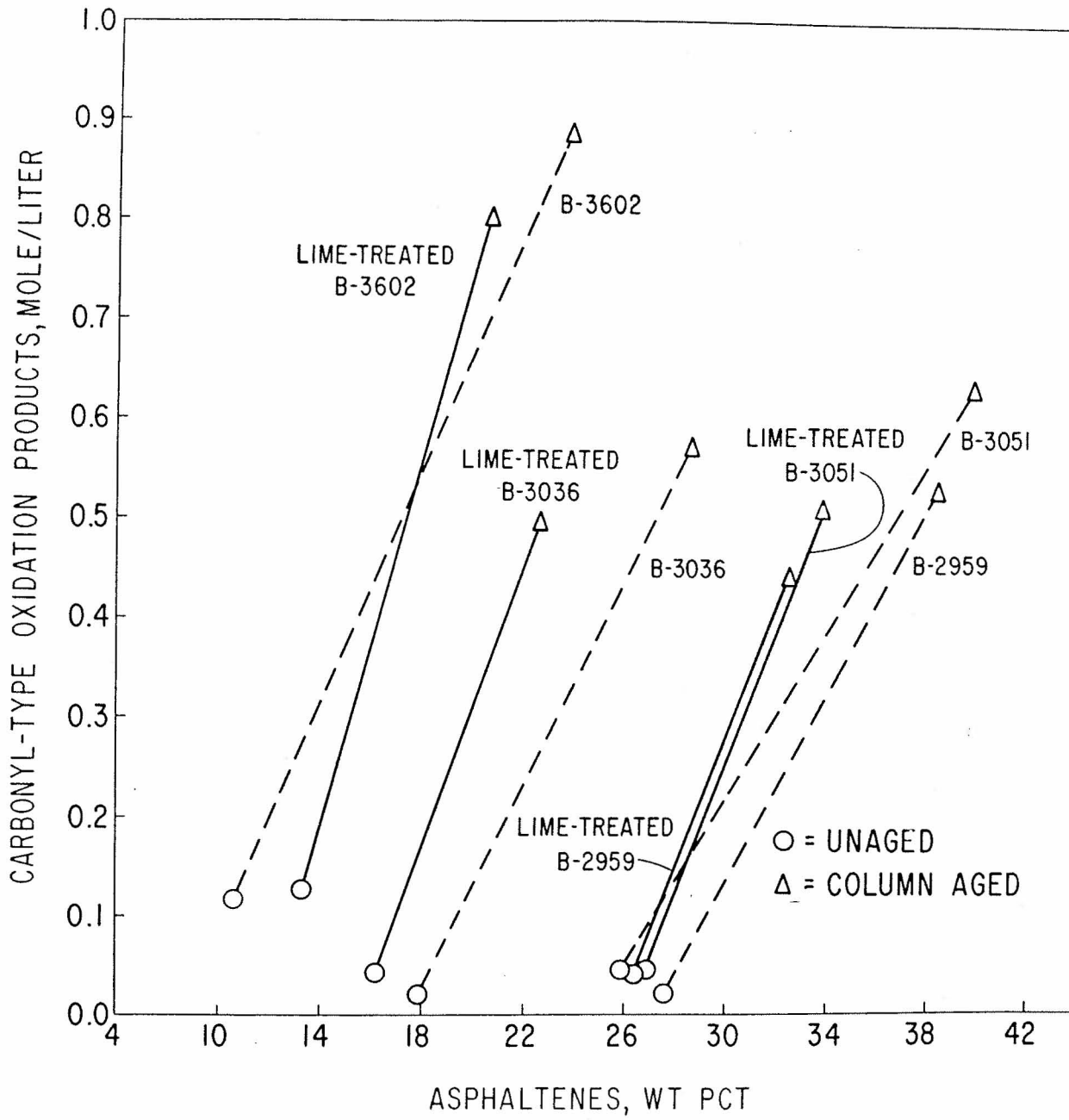


FIGURE 2. - Relationship Between Carbonyl-Type Oxidation Products and Asphaltene Content of Untreated and Lime-Treated Asphalts

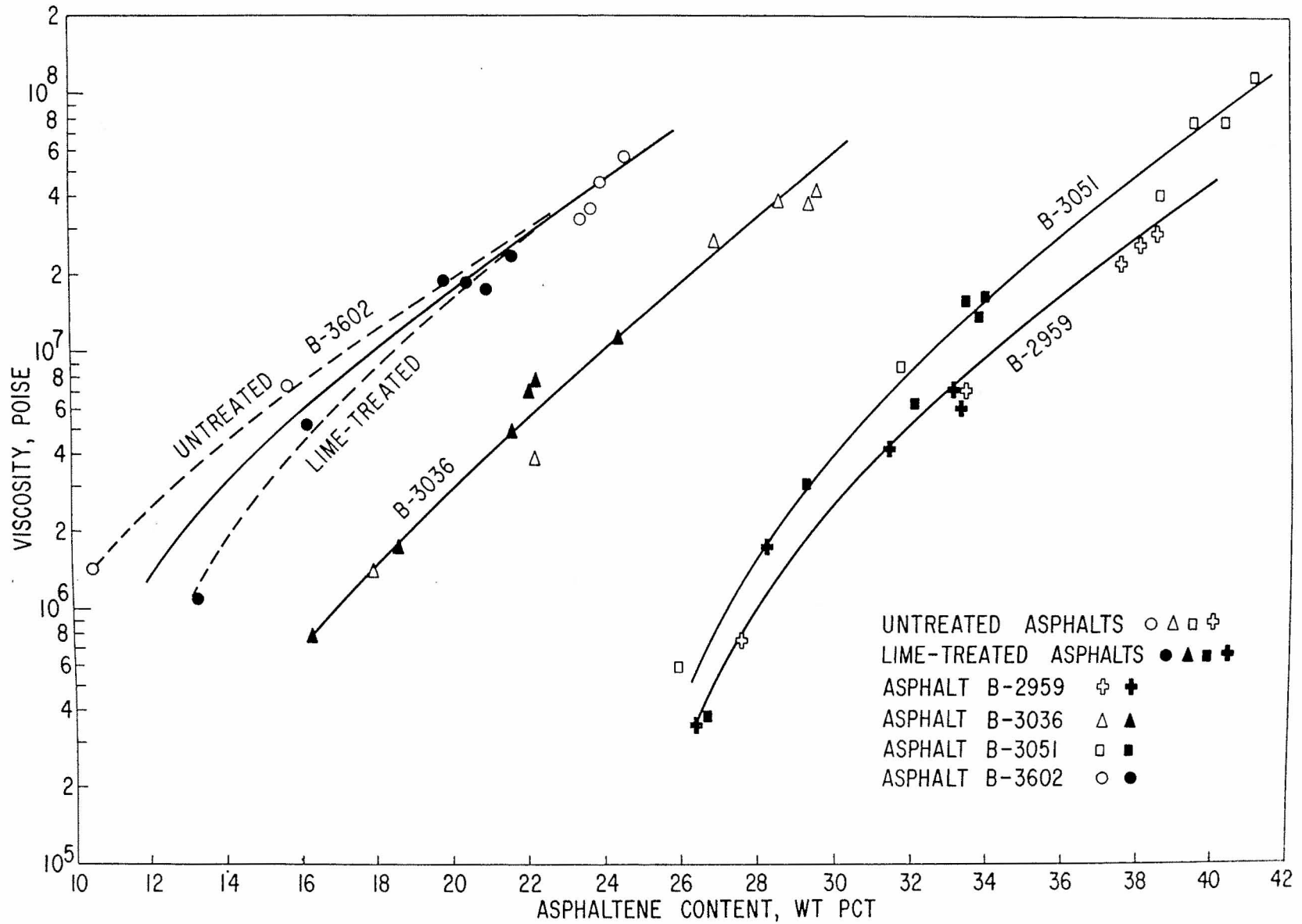


FIGURE 3. - Relationship Between Viscosity and Asphaltene of Untreated and Lime-Treated Asphalts Aged by Different Laboratory Methods

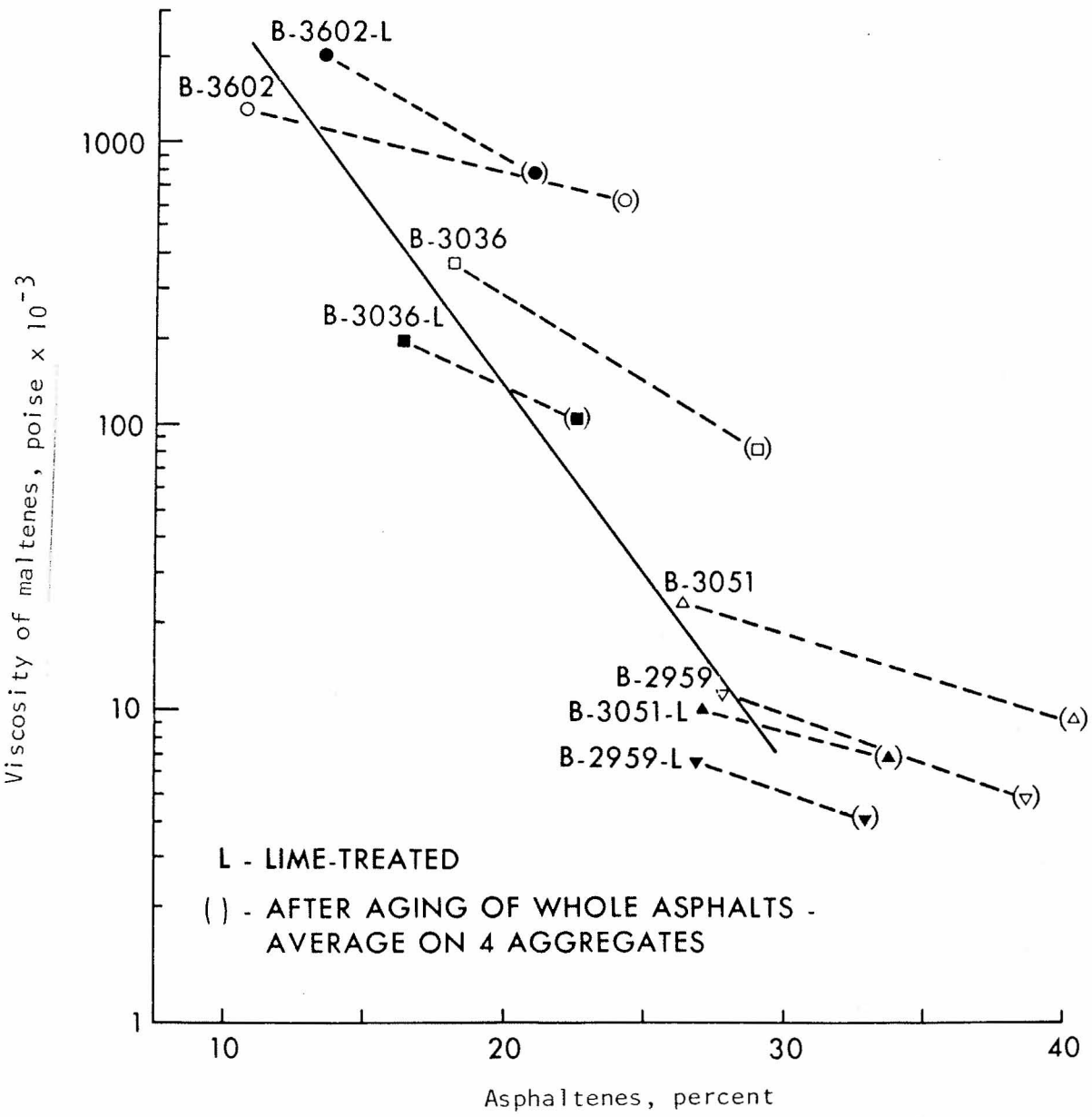


FIGURE 4. - Relationship Between Percent Asphaltenes and Maltene Viscosity for Untreated and Lime-Treated Asphalts Before and After Column Aging on Aggregates

