TRANSPORTATION RESEARCH RECORD 999

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# The Asphalt Triangle: Supply, Demand, and Technology; and Asphalt Durability

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# Refinery Processing of Asphalt Cement

LUKE W. CORBETT

## ABSTRACT

Crude petroleum varies in its makeup of distillable fractions as well as in its bitumen content. Initially, it is separated by distillation with the major volume of asphalt cement manufactured today prepared by straight reduction to grade. Other processing methods, such as solvent deasphalting, supercritical extraction, blending, and continuous air-blowing, supply fractions that are usable in asphalt cement within the limitations of specification compliance. Crude oils may be arbitrarily classified according to their API (American Petroleum Institute) gravity, which is shown to relate to composition, physical properties, and the viscosity-penetration relationship of the asphalt cement therefrom. It is also related to distillation cut-points and how that crude might best be processed. The viscosity-penetration relationship is shown to correlate with temperature susceptibility and may be used directly in determining specification compliance. The viscosity graded (Table 2) specifications as used in the United States are more rational than the penetration-softening point control systems used in Europe and Eastern countries.

It is generally believed that asphalt cement specification quality is closely dependent on the crude oil being processed as well as on the refinery processes applied. It is not as well-known how these two variables are controlled in meeting product standards.

The inherent differences found in crude petroleum are first discussed followed by a discussion of the reason it is initially processed by distillation. The other refinery processes and methods that may be applied and how they may be worked into the scheme of manufacture are described. An arbitrary classification of crudes is suggested and shown to be related to product test characteristics as well as to the processing method applied. The viscosity-penetration relationship is suggested as a means for controlling the effect of the crude as well as adapting it to the processing route used. The difference between the viscosity graded system used in the United States is compared with that used in European and Eastern countries.

## CRUDE PETROLEUM VARIES

The compositional makeup of crude petroleum varies appreciably, especially with respect to its content of distillable fractions as well as its content of residual bitumen. This is illustrated by the three examples in Figure 1 showing typical volume percentages of those fractions that are distillable compared with the bitumen content shown by the shaded areas. Low American Petroleum Institute (API) (1) gravity crudes contain relatively low percentages of distillable overhead fractions with a high percentage of bitumen, whereas the high API gravity crudes contain a relatively high percentage of overhead fraction with a low percentage of bitumen. The low gravity crudes are generally referred to as heavy crudes or as sour crudes if their sulfur content is high. Conversely, the high gravity crudes are known as light crudes, or sweet crudes if their sulfur content is low. The fractional makeup of a crude thus becomes an important consideration to the refiner because he must balance his product yield with sales movement. For reference purposes, each crude is always identified by name or source along with its API gravity.

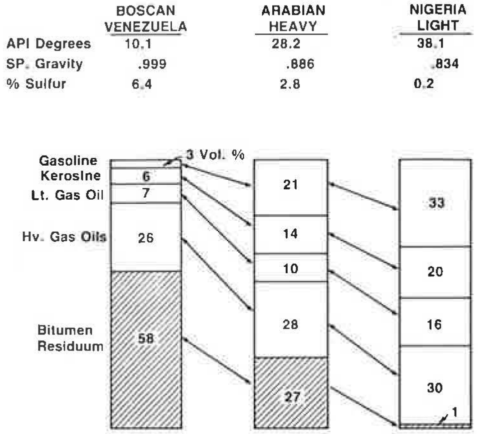

FIGURE 1 Make-up of crude petroleum.

## DISTILLATION IS FIRST STEP

Straight reduction by distillation is a necessary first step in the processing of all crude petroleum (2). As shown in Figure 2, the distillation principle is used to separate the lower boiling points, or boiling ranges of the hydrocarbons contained in the crude petroleum. Because bitumen or asphalt is

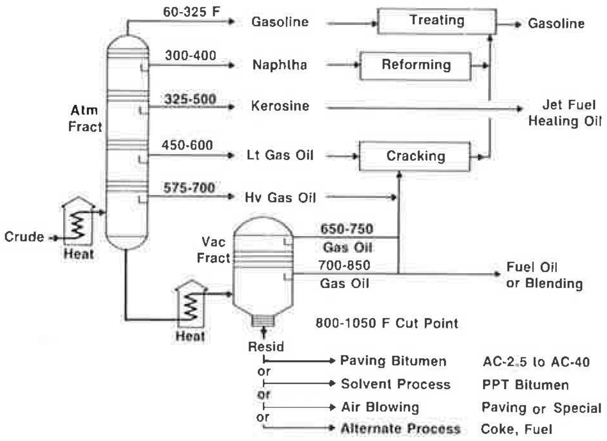

FIGURE 2 Crudes initially separated by distillation.

primarily made up of the highest boiling fractions, it becomes the residuum from the atmospheric fractionator. Usually a second stage of distillation, under vacuum, is needed to yield a residuum of suitable consistency for use as an asphalt cement. All of this is done by a continuous flow operation.

A typical range in distillation temperature is shown for the different overhead fractions, noting that the asphalt residuum from the vacuum fractionator is identified by a cut-point, which is the atmospheric equivalent vapor temperature needed to fractionate the residuum from the overhead fractions above it. Most refineries are designed to yield high percentages of fuel type products. Treating, reforming, cracking, and solvent processing are thus part of the overall scheme, although they have little bearing on the asphalt manufactured. Where the characteristics of the crude feed permit, asphalt cements are commonly prepared by straight reduction to grade, as indicated by the bold lines in this figure.

## SOLVENT DEASPHALTING

Solvent deasphalting (SDA) is sometimes applied to a vacuum residua in order to extract additional quantities of high boiling fractions (deasphalted oil) for either lube manufacture or as a feed for catalytic cracking (3). Propane and butane are usually used as the extracting solvent in a flow process such as that shown in Figure 3. Vacuum residuum is fed into an extracting (EXT) tower where it is contacted at 100 to 150°F with the solvent in a countercurrent fashion. This process yields a high softening point bitumen (precipitated asphalt) that may be used as a blending component for asphalt cements. As discussed later, the use of precipitated bitumen is often limited because it often downgrades temperature susceptibility. It does represent a source of bitumen, which at times can be used in minor proportions in asphalt cement.

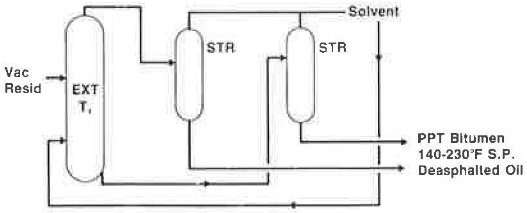

FIGURE 3 Solvent deasphalting (SDA).

## SOLVENT EXTRACTION

The Residuum Oil Supercritical Extraction (ROSE) is a newer process (4,5), which provides a wider flexibility in resid fraction characteristics. Figure 4 shows the processing scheme that is initiated by admixing a resid feed with any one of a variety of low-boiling hydrocarbon solvents, for example, normal pentane. This mixture is then fed into a separator (SEP) at a predetermined controlled temperature ($T_1$) and pressure, which causes the separation of an asphaltene concentrate, subsequently recovered by stripping (STR) off the solvent. The extract portion from above is then taken to a second separator where at a controlled higher temperature ($T_2$) and pressure, a decrease in solubility is effected, causing the precipitation of a second fraction (resins). Similarly, a third fraction (oils) is separated and recovered. The ROSE process thus offers either the asphaltene or the resin fraction as a blending component for asphalt cements, subject to specification compliance, as will be explained later.

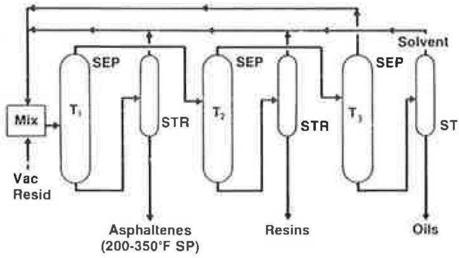

FIGURE 4 Supercritical extraction (ROSE).

## CONTINUOUS AIR-BLOWING

This process is used only when vacuum resids must be increased in viscosity or are in need of improved temperature susceptibility (6). As shown in Figure 5, this process involves the continuous pumping of a vacuum resid (flux) through an oxidation tower held within the temperature range of 450 to 525°F, while air is passed through the hot flux. This causes a chemical conversion (7) within the flux, yielding a product of higher viscosity and softening point and improved temperature susceptibility. Batch air-blowing is a common process in the manufacture of roofing asphalts, whereas continuous air-blowing involves a lesser degree of conversion and thus is more applicable for asphalt cement manufacture. Continuous air-blowing is sometimes used in Europe and in Eastern countries, whereas it is infrequently used in the Americas.

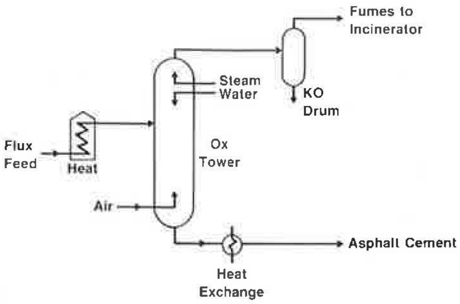

FIGURE 5 Continuous air-blowing.

## CRUDES CLASSIFIED

After first arbitrarily classifying crudes according to their API gravity, it will be shown how the crude type correlates with the specification quality of the asphalt cement derived from the crude. Table 1 lists examples of the arbitrary type classification and some of the sources that are typical of those types.

Also related to crude types is its cut-point at a given viscosity level of asphalt residua. The cut-point is the atmospheric equivalent vapor temperature (AEVT) required to separate overhead fractions from a residuum as shown in Figure 6. To the refiner, this is an important consideration because it indicates the temperature equivalence that must be attained if asphalt cement is manufactured by straight reduction to grade. For example, to yield an AC-20 from crude type A, a cut-point temperature of about 1,190°F must be reached, whereas for crude

TABLE 1 Arbitrary Crude Types and Typical Sources

| TYPE | °API | SOURCE |
|---|---|---|
| A | 34 | ARABIAN LT.,SA |
|  | 32 | KUWAIT, KU |
| B | 28 | HAWKINS, US |
|  | 26 | TIAJUANA, VN |
| C | 19 | GALAN, CO |
|  | 18 | CYRUS, IR |
| D | 16 | LLOYDMINSTER,CA |
|  | 15 | OBEJA, VN |
| E | 12 | PANUCO, MX |
|  | 10 | BOSCAN, VN |

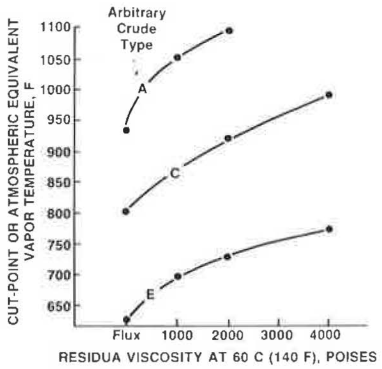

FIGURE 6 Distillation cut-point relates to crude type.

type E, a temperature equivalence of about 730°F is needed. The use of vacuum in the second stage of distillation aids in attaining the equivalent of these high temperatures.

Crude Type is Relevant

It has been shown (8) that crude type relates both to composition and to the physical properties of the asphalt cement. This is shown in Figure 7 where crude type A asphalt is found to be relatively high in saturates and naphthene-aromatics and low in polar-aromatics and asphaltenes (9). It will also be noted that type E asphalt typically displays the reverse of that, namely, low saturates and naphthene-aromatics and high polar-aromatics and asphaltenes. The physical properties of mid-range AC-20 from each of these types also show a pattern of differences. Asphalt from type A crude has a relatively low penetration, low viscosity at 275°F, low penetration ratio, and low viscosity after thin film oven testing. Asphalts from type E crude are relatively high for the same test characteristics with type C intermediate. The average molecular weights of the numbers (measured with a Mechrolab vapor pres- sure osmometer with benzene) for each of the four fractions show high values for type A fractions and low values for type E. This is directionally con- sistent with the data shown in Figure 6 relating cut-points to crude type. That is, high cut-points mean higher hydrocarbon boiling points and higher molecular weights, and low cut-points have the op- posite effect. There are, of course, exceptions to any arbitrary classification and its correlations, but for the most part, these relationships hold true.

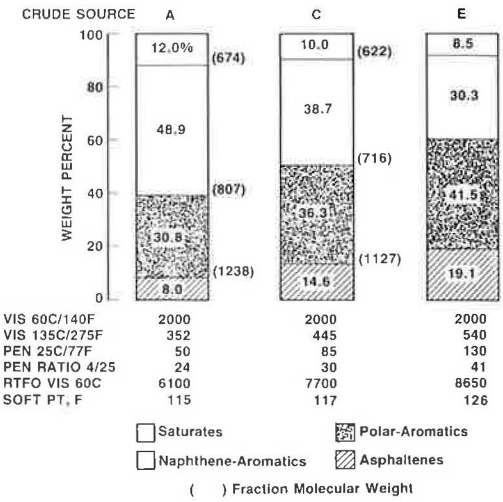

FIGURE 7 Crude type versus composition.

SEVERAL MANUFACTURING ROUTES

Asphalt cements may be prepared by any one of several routes depending on the crude type being used. If the crude feed permits, straight reduction to grade is the most direct and most commonly practiced route. Figure 8 shows the different routes that may be selected. Blending or mixing the crude feed is one route often selected. If two or more crudes were processed separately with one yielding a low viscosity residuum and the other yielding a high viscosity residuum, the resids could be blended. If only a low viscosity resid was made, it could be blended with a precipitated bitumen or air-blown. If only a high viscosity type resid was made, it could be regulated to asphalt cement during distillation, or it could be blended back with a gas oil or a similar fraction. Thus, the refiner has several choices, but his choice is largely dictated by the crude type or crude mix being used.

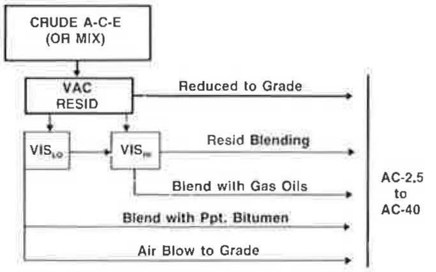

FIGURE 8 Asphalt cement prepared by several routes.

VISCOSITY PENETRATION RELATIONSHIPS

The relationship between viscosity at 140°F in poises and penetration at 77°F is an important and useful characteristic when considering the manufacture of asphalt cement. This is related to crude type as based on the finding (10) that straight reduced asphalts, including those made by blending, may be represented by a straight line when plotting viscosity at 140°F in poises against penetration at 77°F on a log-log chart. Figure 9 shows that this results in a nesting of lines varying slightly in slope but differing considerably in level between a maximum and minimum, based on a survey of free world sources of crudes. At a viscosity level of 2,000 poises, asphalt cements from crude A have a penetra-

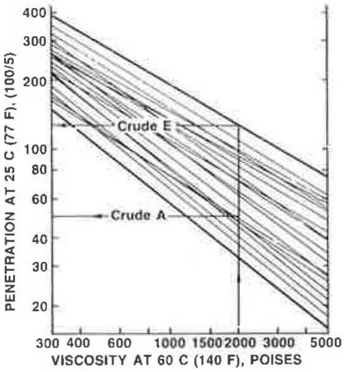

FIGURE 9 Viscosity-penetration relationship.

tion of 50 and a penetration of 130 for asphalt from crude E. Viscosity levels could also be related for a common penetration of 90, which would be about 500 poises for asphalt from crude A and about 3,600 poises for asphalt from crude E. Thus asphalts from crude A would be termed low viscosity asphalts and those from crude E would be termed high viscosity asphalts.

## Viscosity Penetration Guides

The selection of crudes as well as the fitting into specifications is dependent on the viscosity-penetration relationship. For example, Figure 10 shows that asphalts from crude type A have little chance of meeting either an AC-10 or AC-20 specification under AASHTO (11) or ASTM (12) (Table 2). Asphalts from crude type C, D, or E will easily comply, however. Generally if the asphalt meets grade AC-20 specifications, the higher and lower viscosity grades from that crude will also meet specifications.

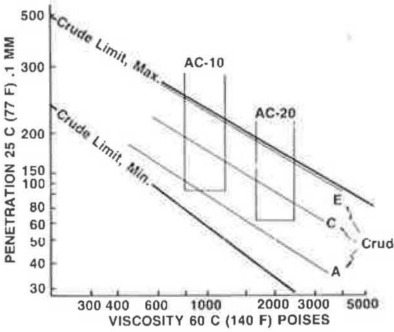

FIGURE 10 Viscosity-penetration relationship guides.

TABLE 2 AASHTO, Table 2, Specifications

| | AC-20 | PURPOSE |
|---|---|---|
| Vis 140 F, Poises | 1600-2400 | Grade Control |
| Pen 77 F, .1 mm | 60 + | Temp. Susceptibility |
| Vis 275 F, cSt | 300+ | Hot-Mix Guide |
| Flash, F | 450+ | Contamination |
| Solubility, TCE | 99+ | Purity |
| TFO, Loss | 0.5- | Optional |
| TFO, Vis Ratio | 4- | Hardening Quality |
| TFO, Duct Res | 50+ | Crude Suitability |

## Viscosity Penetration Indicates Temperature Susceptibility

If the often-used penetration index (13,14) can be accepted as a measure of temperature susceptibility, it can be shown that the viscosity-penetration relationship does the same. If the penetration at a given viscosity level (i.e., 2,000 poises) is plotted against penetration index (pen/pen 45-77°F) (15), a good correlation can be found (see Figure 11). To support this, refer to the high temperature viscosity (275°F) and the penetration ratios shown in Figure 7. Low viscosity at high temperatures and low penetration ratios relate to type A asphalts and the opposite effect to type E asphalts.

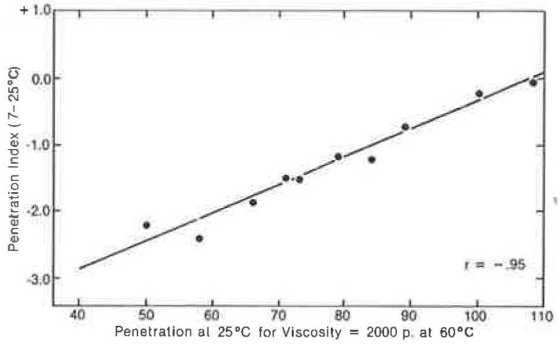

FIGURE 11 Viscosity-penetration relationship relates to temperature susceptibility.

SPECIFICATIONS GOVERN

Under AASHTO and ASTM specifications, a minimum penetration is required for each grade, which is simply another way of stating the viscosity-penetration relationship previously described. Knowing this relationship for the specific crude or crude mix, the refiner can quickly determine compliance by using the log-log plot shown in Figure 12. If the viscosity-penetration requirements pass, the other test requirements will normally conform. This, of course, is subject to laboratory verification for the specific crude or mix involved. In Table 2 the viscosity grade and the penetration at 77°F are underlined to emphasize their prime consideration in specification compliance.

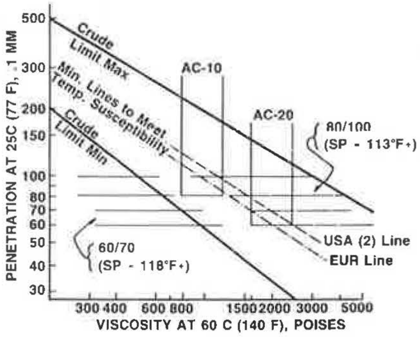

FIGURE 12 USA system is more rational.

If the viscosity-penetration requirements are a problem, the refiner will ordinarily take steps to effect a change in the asphalt cement product. As previously indicated, he may blend crudes, blend mately eight different authors in this paper's reference list who have used this same or a very similar correlation in their study of asphalt cement. Furthermore, it has a very practical value in refinery planning as well as in meeting current specifications.

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# Refinery Economics

K. W. HOLBROOK

## ABSTRACT

The following aspects of refinery economics are covered: relation to asphalt-cement production; the outlook for crude-oil supply and demand; refinery data and the statistics of refining operations; past, current, and future changes in the economics; the effect of those changes on asphalt-cement supply, price, and availability; and a review of the general outlook for asphalt production.

Refinery economics is a subject about which there are many questions. Some assumptions can be made as to what we think is going to happen in the refining industry, but the economics changes rapidly. The subject of this paper is not just refinery economics but also how refinery economics relates to asphalt-cement production. The paper will cover the outlook for crude-oil supply and demand; refinery data and the statistics of refining operations; past, current, and future changes in the economics; the effect of those changes on asphalt-cement supply, price, and availability; and a review of the general outlook for asphalt production.

It can be seen from the data in Table 1 on world oil consumption that the 1960s was the decade of

**TABLE 1** World Oil Consumption

| Time Period | Percentage of Growth | Characteristics |
|---|---|---|
| 1960s | 6/year | Expanding world economies |
| 1970s | 3/year | Slowing growth and energy conservation |
| 1980-1985 | 0/year | Flat world economies and greater energy conservation |
| 1985-1990 | 1-2/year | Improved economic conditions |

resids, use fluxants, or even air-blow if necessary, all of which may be predetermined through a laboratory effort.

### Viscosity Graded Specifications are More Rational

Based on temperature susceptibility alone, the AASHTO Table 2 specification is more critical than those specifications used in European and Eastern countries. Figure 12 shows a comparison between the viscosity graded system and a typical European specification for two penetration grades. Whereas the viscosity grades are controlled by the viscosity-penetration relationship, the European specifications rely on a softening point-penetration relationship or penetration index (13). By translating other data, it is possible to plot the two systems together, which shows that the viscosity-penetration line must be at a higher level in the Figure 12 plot when meeting an AC-20 specification (Table 2) compared with a 60/70 penetration grade under the European specifications.

To further illustrate the differences between the two systems, Table 3 was prepared to present the range in test values, first, when meeting the minimum specification requirements, and second, when all crude sources were involved. If the reasoning can be accepted (16,17) that viscosity at 140°F is a more appropriate control of asphalt-aggregate mix qualities than penetration hardness, then it can be rationalized that grading by viscosity offers a better opportunity for controlling mix qualities than when using the penetration system as permitted under crude source limitations.

TABLE 3 Differences Between Grading Systems

| AREA | GRADE | VISCOSITY DEPENDS ON CRUDE SOURCE |  | PENETRATION DEPENDS ON CRUDE SOURCE |  |
|---|---|---|---|---|---|
|  |  | MIN | ALL | MIN | ALL |
| USA | AC-10(2) | 800-1200 | 800-1200 | 80-105 | 80-200 |
| USA | AC-20(2) | 1600-2400 | 1600-2400 | 60-77 | 60-130 |
| EUR | 80/100 | 790-1100 | 790-4200 | 80-100 | 80-100 |
| EUR | 60/70 | 1300-1600 | 1600-6700 | 60-70 | 60-70 |

Additionally, the viscosity graded system includes controls on hardening through the use of thin film oven tests, with its limitation on viscosity increase and minimum ductility. The European system is still based on the loss-on-heating test and a decrease in penetration, which is appreciably less limiting.

### SUMMARY

1. Crude petroleum varies in its make-up distillable fractions as well as in its bitumen content. These differences are considerable and are an important consideration in the manufacture of asphalt cement.
2. Straight reduction by distillation is a necessary first step in the processing of all crudes. Solvent deasphalting and supercritical extraction are other processes that yield fractions that are sometimes used in asphalt cement. Continuous air-blowing is applied only when low viscosity resids need to be adjusted or upgraded.
3. The largest volume of asphalt cement manufactured in the United States is manufactured by straight reduction to grade from either a single crude or from a mixture of crudes. Blending of fractions is done under the limitation of meeting specification requirements.
4. Crudes may be arbitrarily classified according to API gravity, which is relatable to distillation cut-points as well as to the composition of the asphalt derived therefrom and their physical properties.
5. The viscosity-penetration relationship, identified with temperature susceptibility, is a very useful characteristic when selecting crude feeds for asphalt cement specification compliance.
6. Viscosity graded (Table 2) specifications as used in the United States are more rational than the penetration-softening point controlled system practiced in European and Eastern countries.

## Discussion

Richard L. Davis*

The author is to be complimented on a very fine and informative presentation. During his presentation, he mentioned that viscosity determinations at 140°F showed considerable variation when run on asphalts that had nearly the same penetration at 77°F. This statement points out a major problem in the asphalt industry.

The dangers of extrapolation are well-known. In the case of viscosity measurements of asphalt, there are a number of sources of variation. The viscosity of different asphalts are affected to a greater or lesser extent by both temperature and stress. In addition to the variations due to temperature and stress, the random error variations of the test methods used to measure viscosity, such as the capillary tube and penetration device, are rather large. When the test results of these methods are extrapolated to other temperatures and stresses, the precision limits are greatly expanded. This means that we should extrapolate as little as possible and that we should not be surprised when test results at different temperatures show considerable variation.

## Author's Closure

Thank you for your comments in which you pointed out the dangers of extrapolating viscosity and penetration values to other temperatures and under different conditions of stress. You suggested that the relationship as used may not be as real as apparent because some of the true causative factors are not being subject to measurement.

Whereas you choose to use the term "extrapolation," that is, going beyond the limiting degree of measurement, the writer believes that the term "correlation" or "correspondence" between test values is more appropriate to the case in point. Seldom can we control all of the independent variables, either in testing or, more important, in the composition or crude source involved. That, however, does not mean that we should not investigate some of the more apparent causes and effects, which would lead to a better understanding of the complexities of this subject. As evidence of this, you will find approxi-

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greatest growth. The growth in consumption was about 6 percent per year because the economies were expanding both in the United States and overseas. Economies looked good, cars were getting bigger, people were driving further, and there were no carpools or vanpools; consequently, demand grew rapidly. In the 1970s, helped by the Arab oil embargo, that growth slowed to about 3 percent per year. Energy conservation became a fact of life; carpooling became more common and even though the economies were stable, there was significant reduction in the demand for crude oil and petroleum products. In the first half of the 1980s there was basically no growth at all, or possibly even a decline: It has been a no-growth period because of the significant energy conservation that everyone is practicing.

Poor economies overseas and only a moderately improving economy in the United States have kept refinery economics in the doldrums. For the last half of the 1980s some improvement has been projected--possibly 1 to 2 percent growth in petroleum products and crude oil. Of course, this projection is based on some significant assumptions: The world economies are going to improve, there will be relative stability within the Organization of Petroleum Exporting Countries (OPEC) on crude-oil production and pricing, and the political climates in the world will remain stable. The primary concern, of course, is the Middle East.

## REFINERY OPERATIONS AND UTILIZATION

Refinery operations slowed dramatically in the early 1980s because of the poor world economy. Refinery operations have also been affected by government regulations. Before the 1980s, the U.S. government assisted small refineries and the refinery industry, support that has now been eliminated in many cases. This has had a detrimental effect on the refining industry, particularly small operations. Further, energy conservation has resulted in significant reduction in petroleum product demand.

Refinery utilization was at a low of 62 percent in 1982, whereas in the late 1970s refineries operated in the range of 80 to 90 percent utilization. Because of this low utilization more refineries have shut down. As a result, 35 percent of the 324 refineries have been shut down in the last 4 years, and more shutdowns can be expected in the next year or so. Many of those refineries were the smaller ones. In excess of 20 percent of the U.S. refining capacity has been affected by the economy and the economics of refining.

## DOMESTIC ASPHALT-CEMENT PRODUCTION

About 36 percent of all U.S. refineries produce asphalt cement. However, not all crudes yield heavy bottoms that make asphalt and as a result only about 4.2 percent of the crude that is processed results in asphalt cement. The United States has a refining capacity of 18 million barrels per day of crude; 4.2 percent of that is 756,000 barrels per day of asphalt cement, which is equal to 50 million tons of product a year. Demand in the United States is in the range of 25 to 30 million tons annually, so in 1982 there was a more than adequate supply of asphalt-cement capacity to meet the needs of the industry. With the refinery shutdowns mentioned earlier, that capacity of 50 million tons or 756,000 barrels per day has been reduced significantly. Nevertheless, there is still adequate refinery capacity to meet the annual demand.

Asphalt cement is a major product of small refineries but only a small part of the production of many large refineries. Refineries with less than 10,000 barrels per day of crude capacity yield 7 percent asphalt production. On the other hand, the larger refineries, in general, yield only 2 percent asphalt production. The smaller refineries were the ones hit hardest by the fluctuations in the economy and by the change in government legislation. Their closings significantly affected the asphalt-cement supply.

## OUTLOOK

Refineries, as a result of the change in economics, have begun modifying their processes to meet changing market conditions and also to meet changing crude availability. The increasing price of crude and petroleum products has made residual heating oil uneconomical as compared with coal and natural gas. A recent statistic illustrates that 1 million Btu's of heat generated by a petroleum product cost about \$5. A comparable amount of Btu's generated by coal is about one-third of that, or \$1.50. The incentive to convert from petroleum products to nonpetroleum energy sources is clear. Of course, that conversion does not automatically result in a \$3.50 savings because the user will incur some conversion cost in changing a facility from a petroleum to a nonpetroleum energy user. Nonetheless, there is significant incentive to convert and that has caused changes in petroleum product demand.

Crude quality is also changing. A variety of different gravities of crude are available in the world. Right now the crude processed in the United States is about 60 percent light with 40 percent of the heavier type. The known reserves in the world are the heavier crudes such as those from Venezuela, Mexico, and a number of other countries. The crude that is being discovered is also of the heavier nature. As a result, it is predicted that by 1990 there will be a significant switch from lighter to heavier crudes. That means more bottoms available to convert to asphalt cement.

Pricing of the crudes certainly has an effect on availability and what the refinery is going to process. In the past, the light crudes have sold at a premium. With the decline in price of the light products recently and the improvement in the price of the bottom of the barrel, demand for heavier crude has increased. This phenomenon is expected to continue for a short period of time. So it may be seen that there are many factors that go into the overall analysis of refinery economics.

## RESIDUAL UPGRADING PROJECTS

Because of changing economics, refineries are modifying their methods of operation by upgrading the bottom of the barrel with conversion projects. In the past 3 or 4 years more than 30 major conversion projects have been started, which will be completed soon. These new projects will be capable of converting in excess of 500,000 barrels per day of bottoms to light products, reducing the asphalt supply. However, soon after these projects were in operation, the economics changed, making these residual-conversion projects much less attractive than they had appeared to be a year earlier.

Economics dictates the operations of a refinery. In the following discussion crude costs are related to refined products and asphalt-concrete prices, and two cases in which a refiner has to decide whether to produce another barrel of asphalt or to convert that asphalt to light products are reviewed. Two types of refining methods are compared:

- A refinery producing asphalt and
- A refinery capable of converting all the asphalt into light products using a coker (no asphalt is produced).

## Case 1

Historically the price of asphalt concrete has been an economic loss to the refinery and was propped up by the higher value of the lighter products. By a simple arithmetic calculation one can determine whether asphalt will recover raw material costs. As an example, sour crude is delivered to the refinery at about $33.50 per barrel; the average selling price for asphalt cement is $143 per ton, which, when converted to barrels, is $25.58 per barrel. In this case the refinery is losing $7.92 per barrel on the asphalt cement. In other words, the refiner must recover that $7.92 in the high value of other products or that refinery is not going to be in existence for long. In this case the refinery is not even making raw material costs, much less operating costs or profit, on that particular segment of the refinery operation.

To illustrate this point a little better, a typical refinery (Table 2) that yields 43,479 barrels per day with an investment of $52 million will be used. These products are yielded: motor gasoline, jet fuel, diesel fuel, and other products. As can be seen, in addition to this yield of various products, this refinery produces 10,000 barrels per day of asphalt (23 percent of the crude) valued at $140 per ton or $25 per barrel; gasoline sells for $1.02 per gallon, diesel fuel for $0.98 per gallon. On a daily basis this refinery generates revenue of $1,643,702. After operating expenses of $103,514 per day have been deducted, the net amount available to pay for the crude is $1.5 million. Dividing this amount by 43,479 barrels per day yields $35.41, which is the amount available per barrel. The crude costs $33.50 per barrel, so this refinery, on a before-tax basis, is making about $2 per barrel, covering costs, and making some money.

TABLE 2 Case 1: Typical Refinery Economics

| Item | Unit Amount and Price | Amount ($) |
|---|---|---|
| Products | | |
| Motor gasoline (25%) | 10,870 barrels/day at $1.02/gal | 465,671 |
| Turbine jet fuel (15%) | 6,522 barrels/day at $1.00/gal | 273,024 |
| Diesel fuel (15%) | 6,522 barrels/day at $0.98/gal | 268,446 |
| Catalyst cracker feedstock (22%) | 9,565 barrels/day at $0.96/gal | 385,661 |
| Asphalt (23%) | 10,000 barrels/day at $140.00/ton | 250,000 |
| Total | 43,479 barrels/day | 1,643,702 |
| Operating expenses | | −103,514 |
| Net available to pay for crude | | 1,540,188[a] |
| Crude cost | | −1,457,250[b] |
| Before-tax profit or loss | | 82,938[c] |

Note: Investment, $52,163,600; capacity, 43,500 barrels/day.

[a] $35.41/barrel.

[b] $33.50/barrel.

[c] $1.91/barrel.

The economic effect on this refinery when a 10,000-barrel-a-day coker is installed to convert the asphalt into lighter products is presented in Table 3. Again, a large investment of $30 million is needed; this equipment is not inexpensive. The refiner produces the range of products shown in Table 3, resulting in income of $363,442. Operating costs for this little coker are $51,400 per day, which leaves $312,042 to pay for feedstock, or $31 per barrel. Again, the feedstock cost was equivalent to the value of the asphalt that this refinery was selling for $140 per ton or $25 per barrel. Therefore, on that portion of the asphalt for which the costs were barely covered, the refinery is now making $6.20 per barrel more. Therefore, refinery operators say, why sell asphalt at $140 per ton if the asphalt can be upgraded to produce these products and bring that much more profit? The answer is obvious in this particular case. Again, all cases are not quite so simple and every refinery is different, depending on changes in product prices and crude prices.

TABLE 3 Case 1: Typical Refinery Economics with Addition of Coker

| Item | Unit Amount and Price | Amount ($) |
|---|---|---|
| Products | | |
| Fuel gas (5.2%) | 520 barrels/day at $25.00/barrel | 13,000 |
| Light ends and gasoline (17.5%) | 1,750 barrels/day at $0.96/gal | 70,560 |
| Blend oil (10.5%) | 1,050 barrels/day at $0.98/gal | 43,218 |
| Catalyst feed (52.0%) | 5,200 barrels/day at $0.96/gal | 209,664 |
| Coke (27.0%) | 2,700 barrels/day at $60.00/ton | 27,000 |
| Total | | 363,442 |
| Operating expenses | | −51,400 |
| Net available to pay for feedstock | | 312,042[a] |
| Feedstock cost | | −250,000[b] |
| Before-tax profit or loss | | 62,042[c] |

Note: Data are for 10,000-barrel/day delayed coker; investment, $30 million.

[a] $31.20/barrel.

[b] $25.00/barrel.

[c] $6.20/barrel.

## Case 2

Actually, the economics in Case 2 may be more current than that for Case 1. The problem is the same: Asphalt is a loser. In Case 2, crude is delivered to the refinery at $29.50 per barrel, which is about $4 per barrel lower than in Case 1. In this case asphalt cement is selling for about $150 per ton, a little higher than in Case 1. The loss per barrel is $2.70 versus $7.92 in Case 1; the lower crude costs and the slightly higher asphalt sales price improve the situation significantly.

In Table 4 the specifics of the value of the light products are given; note that motor gasoline sells for $0.82 per gallon compared with $1.02 in

TABLE 4 Case 2: Typical Refinery Economics

| Item | Unit Amount and Price | Amount ($) |
|---|---|---|
| Products | | |
| Motor gasoline (25%) | 10,870 barrels/day at $0.82/gal | 374,363 |
| Turbine jet fuel (15%) | 6,522 barrels/day at $0.87/gal | 238,314 |
| Diesel fuel (15%) | 6,522 barrels/day at $0.75/gal | 205,443 |
| Catalyst cracker feedstock (22%) | 9,565 barrels/day at $0.79/gal | 317,367 |
| Asphalt (23%) | 10,000 barrels/day at $150.00/ton | 27,000 |
| Total | 43,479 barrels/day | 1,403,487 |
| Operating expenses | | −103,514 |
| Net available to pay for crude | | 1,299,973[a] |
| Crude cost | | −1,283,250[b] |
| Before-tax profit or loss | | 16,723[c] |

Note: Investment, $52,173,600; capacity, 43,500 barrels/day.

[a] $29.88/barrel.

[b] $29.50/barrel.

[c] $0.38/barrel.

Case 1. This price is probably more typical of what is happening locally, where gasoline pump prices are about $0.96 per gallon. As before, the revenue from the range of products plus asphalt at $150 per ton totals $1.4 million daily. Again daily operating costs are $103,514, which are deducted from the daily revenue to give a net amount for crude of $1.3 million or $29.88 per barrel. The crude cost mentioned was $19.50 per barrel; therefore, this operation is making $0.38 per barrel on a daily basis. This is less than the refiner in Case 1, who was marginally successful, made. The refiner in Case 2 is barely able to break even.

The effect of adding a coker in this case to convert the 10,000 barrels per day of asphalt into light products is presented in Table 5. Again, $30 million is invested. The same operating costs of $51,400 apply, which gives $24.42 per barrel to pay for the feedstock. In this case, the feedstock was $150 per ton or $26.80 per barrel. Therefore, in this particular case, the refinery operator decides not to spend $30 million on a coker and to continue to market the asphalt, which will yield a higher value than if it were converted to light products. In today's environment, this is probably a more realistic situation than Case 1. Cokers do not appear to be as attractive as they were when they were designed or even when they were first put into operation 2 to 5 years ago. Again, the situation may change dramatically and the original economics may have to be discarded. The purpose of this discussion has been to explain the range of alternatives that exists for a refinery and to explain how decisions may be made regarding one method of operation versus another.

**TABLE 5 Case 2: Typical Refinery Economics with Addition of Coker**

| Item | Unit Amount and Price | Amount ($) |
|---|---|---|
| Products | | |
| Fuel gas (5.2%) | 520 barrels/day at $25.00/barrel | 13,000 |
| Light ends and gasoline (17.5%) | 1,750 barrels/day at $0.77/barrel | 56,595 |
| Blend oil (10.5%) | 1,050 barrels/day at $0.83/gal | 36,603 |
| Catalyst feed (52.0%) | 5,200 barrels/day at $0.79/gal | 172,536 |
| Coke (27.0%) | 2,700 barrels/day at $35.00/ton | 16,875 |
| Total | | 295,609 |
| Operating expenses | | –51,400 |
| Net available to pay for feedstock | | 244,209[a] |
| Feedstock cost | | –268,000[b] |
| Before-tax profit or loss | | –23,791[c] |

Note: Data are for 10,000-barrel/day delayed coker; investment, $30 million.

[a] $24.42/barrel.

[b] $26.80/barrel.

[c] $2.38/barrel.

## SUMMARY

The data in Tables 2-5 show that the refiner can make more money refining crude to make asphalt under the following conditions:

1. Crude costs are low ($28 to $31 per barrel),
2. Asphalt prices are high ($150 per ton), and
3. Gasoline, jet, and turbine fuels are low ($0.75 to $0.87 per gallon). (The foregoing are refinery costs, not pump prices.)

Conversely, not making asphalt but converting it to light products is profitable under the following conditions:

1. Crude costs are high ($33 to $34 per barrel),
2. Asphalt prices are low ($140 per ton), and
3. Gasoline, jet, and turbine fuels are high ($0.96 to $1.02 per gallon). (The foregoing are refinery costs, not pump prices.)

Although each refinery is unique, the basic economics to stay in the asphalt business is as follows:

1. Asphalt must recover at least the costs of the crudes.
2. Asphalt is a valuable refinery resource; it is no longer a waste product.
3. In modern refineries, asphalt competes with light products, and the economics is determined by the selling price of all products produced.
4. A uniform, consistent, long-range highway program without drastic swings in demand for asphalt is beneficial to both users and producers. It permits refiners to plan.

Asphalt prices have not equalled crude costs in the past and they are not equal to crude costs now, and that is part of the problem. Asphalt prices must go up in order for the product to carry its own weight. Refinery operations need to recover crude costs from asphalt or more of them are going to cease asphalt production in the future. Strong light-product prices and low asphalt-cement prices have stimulated the interest in alternative manufacturing methods such as cokers, which produce no asphalt. As long as low asphalt prices continue, asphalt availability is going to be a problem because refineries would rather convert the bottoms to lighter products and generate higher revenue.

Refinery economics is changing, and cokers will not appear as attractive when asphalt demand and prices are high and gasoline prices are low. On the assumption that there will be a reasonably strong asphalt-cement demand in the future, and that as a result the prices should improve, it is expected that industry will be assured of an adequate supply of asphalt cement to meet the needs of this country's road programs.

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# Changes in Asphalts

**ROY S. HODGSON**

ABSTRACT

A review of recently published literature indicates that changes in asphalts are of considerable concern to those responsible for designing, constructing, and managing pavements. Data indicate that the ranges of properties of asphalts have not changed significantly, but recent world petroleum supply and economic climate may have caused more rapid changes in asphalt from certain sources. New refining or manufacturing techniques may also affect asphalt properties, but these causes probably account for a smaller portion of reported changes than variations in feedstocks that are primarily petroleum crude oils. There appears to have been a statistically significant but small change to a population of more temperature-susceptible asphalts, which may have been a result of specification changes and greater use of high smoke point asphalts (that may generally have higher temperature susceptibilities) with the use of increased mixing temperatures in drum mixers. Preferred methods of measuring low temperature performance are through the use of low temperature consistency measurements. Chemical analyses reported to date have not correlated well with performance because of the complex nature of asphalts. The changes in asphalt properties with use of antistripping additives is discussed and some factors affecting paving construction and pavement performance, which may be perceived as changes in asphalts, are listed.

Do asphalts really change? This probably depends on what is perceived as the material called asphalt. To the extent that most asphalts are sold to meet an accepted specification, it might be said that asphalts do not change, only specifications change. However, to the contractor, engineer, supervisor, or laborer responsible for constructing an asphalt concrete pavement, the mixture does change. This mixture of about 95 percent aggregate and 5 percent asphalt does have different behaviors at times, and, because the mixture is generally black in appearance, it might appear logical to say that the asphalt has changed. Not only are the persons responsible for constructing the pavement concerned about possible changes in asphalts, but the persons responsible for the management of the pavements are concerned that these reported changes in asphalts may have some harmful effect on the pavement's performance. The literature abounds with articles on this subject of changes in asphalts and also confirms the significance of the subject to the industry.

The Asphalt Institute's laboratory conducted a comprehensive survey of 68 asphalt cements supplied from several different crude sources, manufacturers, and refineries in 1977. The results of their evaluations of these 1977 asphalts were reported by Puzinauskas at the 1979 Association of Asphalt Paving Technologists meeting (1) and compared with asphalts manufactured in 1960 and others manufactured from 1965 to 1973. Puzinauskas concluded from this work that asphalts did not differ substantially over these periods of time. However, he also concluded that asphalts, within a given grade, differ substantially in their properties but the magnitudes of these differences appear to be similar for the asphalts manufactured during the different time periods. Puzinauskas also concluded that (a) the source of parent oil from which the asphalt is produced and its method of manufacture affect the physical properties of the asphalt; (b) asphalts' response to heating is highly variable; (c) different methods used to evaluate temperature susceptibility correlate rather poorly; and (d) measurement of paving mixture properties may be a more rational approach than measurement of individual components to explain behavior in mixes.

Puzinauskas' work showed that the physical properties of asphalts have remained within the ranges experienced for many years and that the 1973 Arab oil embargo and other effects on crude supply did not significantly alter this range of physical properties. However, his work did show that if two asphalts of the same grade, but manufactured from different crude sources, were employed on the same job, significant differences in the physical properties of the asphalt on hot mixed aggregate could be experienced. Puzinauskas reported a range of thin film oven (TFO) heat aging indexes of 1.55 to 3.80 for the viscosity at 140°F of samples, which would have complied with the original 140°F viscosity range of 800 to 1,200 poises specified for AC-10. Assuming that the TFO test simulates the heat hardening that can be experienced when mixing at 325°F, a difference of 2,300 poises with a range of 1,422 to 3,722 poises of viscosity on the aggregate could have been experienced for the 15 different asphalts reported in the AC-10 range of original viscosity. Using the 275°F viscosity data from Puzinauskas' work, the ranges of TFO residue viscosity are 247 to 492 centistokes or differences of 323 centistokes for the AC-10 grade samples.

Considered individually, these numbers probably do not mean much, but they do indicate that the different heat hardening effects between sources may be of a similar magnitude to a grade change from the same source. Use of mixing temperatures of less than 325°F would lessen these differences for original grading systems, but then the problem occurs with residue grading systems. Although differences in manufacturing technique may have an effect, most single sources do not change their manufacturing techniques frequently; therefore, the largest single influence on the properties of an asphalt are the feedstocks used to produce the asphalt. For the most part, these feedstocks are crude oils. Some new solvent extraction resid refining processes, notably the ROSE process, have recently been developed. These processes may permit asphalt manufacture from crudes that have not previously been used to produce asphalt, but because the asphalts must meet commonly accepted specifications, their physical properties will probably not be outside the ranges of asphalts produced in the past.

Corbett (2) advised in 1980 that there were more than 1,500 different crude sources of which about 1,100 were being used in North America, and of these sources, about 260 were possibly suitable for the production of asphalts. The Oil and Gas Journal reported in 1983 that of 223 refineries in the United States, 78 (or 35 percent) report the production of asphalt (3). This would appear to confirm that in many refineries, more than one crude stream is used to produce asphalts. [The 78 refineries had a reported total use of 260 crudes (2,3).] It is also apparent that certain refineries may operate on the same crude source or sources for many years, and the properties of asphalts from this refinery may change little with time.

Anderson and Dukatz (4) reported in 1980 on a statistical evaluation of the properties of asphalts obtained by different laboratories from 1950 to 1980 with specific emphasis on changes in physical and chemical properties before and after the 1973 Arab oil embargo. They concluded that there were statistically significant differences in chemical and physical properties of asphalt sampled between 1950 and 1980, and that temperature susceptibility of the sampled asphalts increased over this same period. The methodologies of statistical comparison and the precision of the multi-laboratory data used in this study are the subject of much contention by asphalt technologists, especially regarding the significance of the chemical tests. These same authors (with Rosenberger) used these data, and data they had gained from additional samples during the interim, in a 1983 report (5) to conclude that except for an increase in temperature susceptibility, they did not measure any asphalt properties relating to a decrease in asphalt quality from 1950 to 1981. (This period included the time before and after the 1973 Arab oil embargo.) The conclusion by Anderson et al. that temperature susceptibility has changed is based on their calculations showing an increase in the average penetration-viscosity number (PVN) of -0.39 to -0.79 from 1950 to 1981. They do not believe this change warrants the inclusion of a PVN requirement in current general specifications, but they do believe some control of temperature susceptibility may be justified in regions of the country where thermal cracking may be a problem. They calculate that this difference in PVN may equate to a difference of 6°C (11°F) in limiting stiffness temperatures.

It is unfortunate that the data bank does not include penetration measurements at two temperatures so that the stiffness could be measured according to procedures reported by Gaw (6), which indicated that the PVN method is suitable only for predicting low temperature performance for asphalts for which the penetration-temperature and viscosity-temperature consistency relationship is linear. This is not the case with asphalts having wax contents greater than 2 percent and for air-blown asphalts. A procedure for predicting asphalt stiffness at low temperatures from penetration measurements at two different temperatures is recommended by the Asphalt Institute (7), especially if waxy or air-blown asphalts are involved such as could be expected from the large samplings involved in these studies.

The effect that changing of specifications from penetration grading systems in 1950 to largely viscosity-based systems by 1981 may have had on these reported changes is unknown. Temperature susceptibility was controlled in penetration-based specifications in some regions and not in others. For example, the Uniform Pacific Coast penetration grading system used before January 1974, contained a penetration ratio as well as a minimum viscosity at the 275°F requirement. Current AASHTO and ASTM penetration grading systems do not have controls on temperature susceptibility. Most viscosity grading systems that grade at 140°F do have controls on consistency at 77°F and viscosity at 275°F.

Button et al. (8) evaluated the effect of temperature susceptibility of asphalts on the tenderness of the pavements and concluded that highly temperature-susceptible asphalts have been related to tender pavements, but that both aggregate (grading, top size, particle shape, and particle surface characteristics) and the asphalt binder (viscosity, temperature susceptibility, and chemical make-up) contribute to tenderness.

The increased use of drum mixers has had an effect in increasing the average population of asphalts toward more temperature susceptibility by eliminating from use some of the low smoke point asphalts that also may have low temperature susceptibility. Asphalts represented by Corbett's (see elsewhere in this Record) crude type A would have high smoke points and perform quite satisfactorily from a blue smoke emissions standpoint when used in a drum mixer; however, many asphalts in crude type A tend to have high temperature susceptibilities. On the other hand, asphalts represented by Corbett's crude type E may have lower smoke points and their use may result in the generation of blue smoke emissions in drum mixers operating in the range of 300°F mixing temperatures. Therefore, use of drum mixers at high mixing temperatures--approximately 300°F or higher--may exclude use of many of the less temperature-susceptible group of asphalts represented by Corbett's crude type E in order to comply with air pollution control regulations.

The use of antistripping additives has been prevalent in many areas recently. Mixes using these additives may demonstrate tenderness due to the effect of the additives in lowering the original viscosity of the asphalt and the heat aging characteristics of the additive-asphalt mixture (9). This effect may be perceived as a change in the asphalt supply, especially in the many instances where the additives are required to be added by the asphalt supplier.

Two comprehensive studies (10,11) were conducted to determine, among other things, the procedures for accommodating or controlling temperature susceptibility of asphalts, assuming temperature susceptibility is a major problem. The results of this study are eagerly anticipated.

From a review of this literature, it becomes apparent that there have been no significant changes in the range of physical properties of asphalts over the past 30 years, and that the perceived belief that asphalts have changed is probably the result of differences in the temperature susceptibilities of asphalts produced from different crudes or blends of crudes as certain refineries make changes in their crude slates. Because the type of crude slate chosen by a refiner is generally an economic decision, tighter controls placed on the refiner in terms of restrictive asphalt specifications will, in all probability, have economic consequences. The controls applied, if any, should therefore be meaningful.

Relationships of performance with chemical tests may be found for a limited number of asphalts; however, the complex nature of all asphalts produced is such that generalized correlations have been found to be difficult to make. Perhaps this is aptly stated by Anderson et al. (5):

> A significant lesson to be learned from analyzing the massive amount of data in the files is that asphalt cement is a very complicated material, and it is not likely that its behavior will be pre-

> dicted from one or two simplistic tests. Correlations made with limited data sets, data from a specific region, or data from a particular crude do not extrapolate with acceptable precision to large data sets as studied in this paper.

It is not intended here to reduce efforts to find good generalized correlations of any type of analysis with performance, but it should be understood that asphalt is very complex chemically and is also only a part of the paving system.

Perhaps, as suggested by Puzinauskas, more effort should be spent on how all aspects of the paving system affect performance of asphalt pavements. Because the mixture is black, the effect of other factors on performance may often be overlooked. Some factors affecting paving construction and pavement performance that may be perceived as changes in asphalts could be:

1. The effect of antistripping additives on asphalt consistency, temperature susceptibility, and hardening, especially during mixing.
2. The effect of mixing temperatures on asphalt consistency when combined with asphalts of different heat hardening characteristics, and the lack of understanding of the effect of mix temperature on mix consistency and its effect on placing and compaction characteristics of the mix.
3. The effect of insufficient aggregate gradation control and asphalt content.
4. The effect of mix characteristics of higher moisture contents sometimes permitted in field mixes that are not considered in the mix design, and the interaction of moisture and asphalt on compactive effort and performance.
5. The effect of different fuels and improperly adjusted burners that may leave unburned fuel in the mix.
6. The effect of the fine and coarse portion of fillers on the asphalt film consistency and durability.
7. The effect of the frequent use of low-cost rounded sands resulting in tender mixes that may be very sensitive to asphalt content.

A summary of the possible factors (real or perceived) affecting changes in asphalt follows:

1. Crude oil economics and availability,
2. Refining processing methods,
3. Specifications,
4. Low temperature performance requirements,
5. Antistrip additives,
6. Condensed fuels during aggregate heating,
7. Drum mixer blue smoke requirements,
8. Fine particulate management,
9. Mixing and laying mix temperatures,
10. Mix moisture contents, and
11. Oversanded mixes.

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# Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art

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## ABSTRACT

The literature on asphalt chemical composition and asphalt durability has been reviewed and interpreted relative to the current state of the art. Two major chemical factors affecting asphalt durability are the compatibility of the interacting components of asphalt and the resistance of the asphalt to change from oxidative aging. Historically, studies of the chemical components of asphalt have been facilitated by separation of asphalt into component fractions, sometimes called generic fractions; however, these fractions are still complex mixtures the composition of which can vary significantly among asphalts of different sources. The reaction of asphalt with atmospheric oxygen is a major factor leading to the hardening and embrittlement of asphalt. The hardening phenomenon is primarily a result of the formation in asphalt of polar oxygen-containing functional groups that increase asphalt consistency through strong molecular interaction forces. The identification and characterization of the chemical functional types normally present in asphalt or formed on oxidative aging that influence molecular interactions afford a fundamental approach to relating asphalt composition with asphalt properties and thus the performance of both asphalts and asphalt-aggregate mixtures. In addition to the polar chemical functional groups formed on oxidation, asphalt properties can also be significantly altered by molecular structuring, sometimes called steric hardening. This potentially reversible phenomenon, although highly elusive and difficult to quantify in asphalt pavement mixtures, may also be a major factor contributing to pavement embrittlement.

Differences in the quality of asphalts from different sources (different composition) and relationships between composition and performance properties have long been recognized, as shown by the many publications on the subject, a few of which are cited (1-13). Asphalts meeting the same specifications often produce pavements with widely differing performance and serviceability. Admittedly such factors as aggregate characteristics, design, construction variables, and environment play major roles in determining pavement performance and often overshadow the contribution to performance made by variabilities in asphalt cement quality. However, such studies as the well-known Zaca-Wigmore Experimental Road Test (4,9), in which construction variables were carefully controlled and asphalt source was intentionally varied, clearly demonstrate the importance of asphalt chemical composition in pavement durability.

For the purposes of this review, a durable asphalt is defined as one that (a) possesses the physical properties necessary to produce the desired initial product performance properties and (b) is resistant to change in physical properties during long-term in-service environmental aging. Although design and construction variables are major factors in pavement durability, more durable asphalts will produce more durable pavements.

The importance of chemical composition to asphalt durability, although not well understood, cannot be disputed. Durability is determined by the physical properties of the asphalt, which in turn are determined directly by chemical composition. An understanding of the chemical factors affecting physical properties is thus fundamental to an understanding of the factors that control asphalt durability.

The purpose of this paper is to examine the literature dealing with the chemical composition of asphalt and changes in composition during environmental aging that affect durability-related properties. Both past and recent research important to the state of the art will be considered. Because of the extreme breadth of the subject and the voluminous literature related to durability, a complete bibliography will not be attempted, but sufficient references will be cited to allow the serious researcher to find additional literature. The author's approach to the fundamental chemical factors affecting asphalt properties and durability will also be presented.

## PRELIMINARY CONSIDERATION OF FACTORS AFFECTING ASPHALT DURABILITY

To provide a background for the documented discussions that follow, the major composition-related factors affecting durability are briefly outlined. The most important aspect of a durable asphalt, assuming that it meets initial performance requirements, is its resistance to change while in service. The dominant physical change leading to reduced asphalt durability is a change in flow properties related to excessive stiffening or hardening of the asphalt. Three fundamental composition-related factors govern the changes that could cause hardening of asphalts in pavements:

1. Loss of the oily components of asphalt by volatility or absorption by porous aggregates,
2. Changes in the chemical composition of asphalt molecules from reaction with atmospheric oxygen, and
3. Molecular structuring that produces thixotropic effects (steric hardening).

With current specifications and construction practices, volatility loss is probably not a significant contributor to pavement hardening. Reaction with atmospheric oxygen is probably the major and best understood cause. Molecular structuring, although elusive and difficult to quantify, may also be a significant contributor.

Irreversible adsorption of polar asphalt components by mineral aggregate surfaces, although not a factor that might be expected to harden asphalt, will produce compositional changes in the asphalt that may also significantly affect asphalt properties and aging characteristics. Finally, it is recognized that environmental factors affecting the properties of the asphalt-aggregate bond, particularly water, can seriously affect the performance and durability of asphalt pavements; however, even though moisture-induced damage may be related to asphalt composition and adsorption of asphalt components on aggregate surfaces, it is primarily an interfacial phenomenon and beyond the scope of this paper.

## CHEMICAL COMPOSITION OF ASPHALT

### Elemental and Molecular Composition

Before an attempt is made to discuss relationships between chemical composition and asphalt properties affecting durability, the chemical composition of asphalt will be reviewed. Asphalt is not composed of a single chemical species but is rather a complex mixture of organic molecules that vary widely in composition from nonpolar saturated hydrocarbons to highly polar, highly condensed aromatic ring systems. Elemental analyses of several representative petroleum asphalts are presented in Table 1. Although asphalt molecules are composed predominantly of carbon and hydrogen, most molecules contain one or more of the so-called heteroatoms nitrogen, sulfur, and oxygen together with trace amounts of metals, principally vanadium and nickel. As seen in Table 1, the heteroatoms, although a minor component compared to the hydrocarbon moiety, can vary in concentration over a wide range depending on the source of the asphalt. Because the heteroatoms often impart functionality and polarity to the molecules, their presence may make a disproportionately large contribution to the differences in physical properties among asphalts from different sources.

**TABLE 1 Elemental Analyses of Representative Petroleum Asphalts (*14*)**

| | Asphalt[a] | | | |
|---|---|---|---|---|
| Element | B-2959 (Mexican) | B-3036 (Ark.-La.) | B-3051 (Boscan) | B-3602 (Calif.) |
| Carbon (%) | 83.77 | 85.78 | 82.90 | 86.77 |
| Hydrogen (%) | 9.91 | 10.19 | 10.45 | 10.94 |
| Nitrogen (%) | 0.28 | 0.26 | 0.78 | 1.10 |
| Sulfur (%) | 5.25 | 3.41 | 5.43 | 0.99 |
| Oxygen[b] (%) | 0.77 | 0.36 | 0.29 | 0.20 |
| Vanadium (ppm) | 180 | 7 | 1,380 | 4 |
| Nickel (ppm) | 22 | 0.4 | 109 | 6 |

[a] From study by Welborn et al. (*15*).
[b] By difference.

Elemental analyses are average values and reveal little information about how the atoms are incorporated in the molecules or what type of molecular structures are present. Molecular type and structure information is necessary for a fundamental understanding of how composition affects physical properties and chemical reactivity. The molecular structures in asphalt will be discussed in more detail in subsequent sections; however, an overview is important at this point.

Because asphalt was undoubtedly produced from living organic matter by maturation in the earth for millions of years, the molecular structures of the compounds present are highly diverse. Carbon in aromatic ring systems has been estimated by correlations based on carbon-hydrogen analyses and densities (16,17) and directly by nuclear magnetic resonance (NMR) (18). Concentrations of aromatic carbon determined by NMR typically run from 25 to 35 percent for petroleum asphalts. The aromatic carbon is incorporated in condensed aromatic ring systems containing from 1 to possibly 10 rings per aromatic moiety (18). These ring systems may be associated with saturated naphthenic (cycloalkyl) ring systems, and both the aromatic and naphthenic ring systems may have attachments composed of a variety of types of normal or branched hydrocarbon side chains. By NMR, carbon associated with naphthenic ring systems typically ranges from 15 to 30 percent (18). Normal and branched chain hydrocarbons are present either as individual molecules or as the previously mentioned moieties associated with naphthenic or aromatic rings. The nonaromatic and nonnaphthenic carbon content of asphalt would typically range from 35 to 60 percent. It should be emphasized that examples outside these ranges may be found and the variety of possible combinations of molecular structures in an asphalt is astronomically large and may vary widely from one crude source to another. The hydrocarbon molecular structures are further complicated by the heteroatoms sulfur, nitrogen, and oxygen, which are often present in sufficient combined amounts so that, on the average, one or more heteroatom(s) per molecule may be present. These may be incorporated within the ring or nonring components or in more discrete chemical functional groups attached to these components.

The heteroatoms, particularly nitrogen and oxygen, and the aromatic ring systems contribute considerable polarity or polarizability to the molecules that produce the major association forces affecting physical properties. This will be discussed in more detail in a later section.

Because the number of molecules in asphalt with different chemical structures and reactivities is extremely large, chemists have not seriously considered attempts to separate and identify them. Considerable progress, however, has been made in the study of asphalt composition by separation or characterization of asphalt based on the reactivity or polarity or both of the various molecular types present. The molecules in asphalt can be conveniently separated or grouped into classes of molecular types or fractions based on their chemical functionality. This separation and classification of molecular types has been useful to provide simpler component fractions that permit further characterization and has aided in determining how different molecular types affect the physical and chemical properties of the whole asphalt.

### Asphalt Composition as Defined by Fractionation

A variety of procedures has been employed in attempts to fractionate asphalt into less complex and more homogeneous fractions. Some are simple (19) and others are more complex (20,21). Many are specialized and unique to a given research endeavor in which they were used to prepare fractions for further characterization. Several, however, have found more general use to characterize and classify asphalts. These separation schemes can be classified into three general types based on the procedure used: (a) partitioning with partial solvents (22-24), (b) selective adsorption-desorption (10,19,25), and (c) chemical precipitation (5,6). Gel permeation chromatography (GPC) is also an important separation method; however, because the method as normally used makes separations primarily on the basis of molecular size rather than type, its relationship to chemical composition is not well-defined. Therefore, it will not be discussed further in this review. Relationships between GPC data and asphalt properties and performance characteristics, however, have been suggested and the reader is referred to the literature for more details on this separation technique (26-30).

Schematic diagrams illustrating the three types of component fractionation schemes are shown in Figure 1. Partitioning with selective solvents (scheme 1-A) has not been widely used. Although it avoids contact with reactive adsorbants and chemicals that might irreversibly adsorb or alter asphalt components, the fractions obtained are usually not as distinctively different as with the other separation types. In general, one sequentially treats the asphalt with increasingly polar solvents precipitating a series of fractions with decreasing polarity.

Selective adsorption-desorption chromatography has probably found the widest use as a research separation technique. This technique is typified by scheme 1-B in Figure 1. The asphaltenes are separated first based on their insolubility in a nonpolar paraffinic solvent. This removes the most polar and least soluble asphalt components and generally facilitates further separation. The remaining petrolene (maltene) fraction, which is dissolved in the paraffinic solvent, is then adsorbed on a chromatographic column and sequentially desorbed with solvents of increasing polarity. By proper selection of the adsorbant and desorption solvents, a series of fractions with increasing polarity is obtained. The fractions obtained will be described in some detail to provide background for discussion in later sections of this paper.

The saturate fraction, because it lacks polar chemical functional groups, is not adsorbed on the column and is first to emerge. (It is important to note that although the names of component fractions were often intended to describe the predominant chemical types, component fractions are still complex mixtures and do not represent clear-cut compound-type separations.) The saturate fraction may contain saturated normal and branched-chain hydrocarbons, saturated cyclic hydrocarbons (sometimes called naphthenic hydrocarbons), and possibly a small amount of mono-ring aromatic hydrocarbons; however, those molecules containing ring systems are dominated by attached saturated hydrocarbon side chains. Sulfur is often found incorporated in molecules of the saturate fraction. Addition to the chromatographic column of a more polar aromatic solvent such as benzene (now usually replaced by toluene), which competes for the polar sites on the adsorbants, displaces the more weakly adsorbed asphalt molecules. These molecules usually contain condensed nonaromatic and aromatic ring systems, and in addition to sulfur, the heteoratoms oxygen and nitrogen may also be part of the molecule. In scheme 1-B, this fraction has been called the naphthene-aromatic fraction.

Finally, a highly polar solvent such as an alcohol is added to the benzene to displace the most strongly adsorbed and most polar components of the petrolene fraction. The alcohol debonds these components, which are held strongly to the adsorbant by highly polar functional groups, and the benzene provides solubility for these components as they elute from the column. This fraction, called polar aromatics, contains more highly condensed aromatic ring systems and functional groups containing hetero-

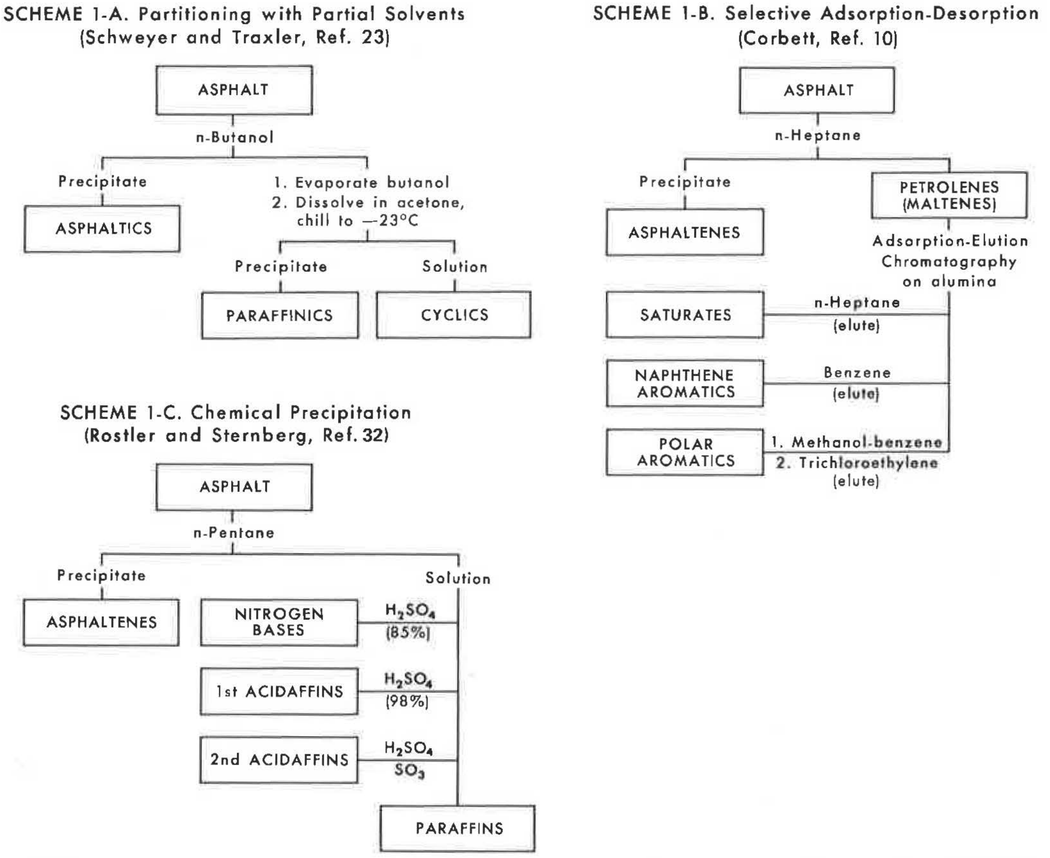


**FIGURE 1** Schematic diagrams illustrating three types of fractionation schemes used to separate asphalt into component fractions.

atoms. It should be noted here, and will be important later when durability and oxidation susceptibility are discussed, that all fractions contain, to a greater or lesser degree, cyclic and noncyclic saturated hydrocarbon fragments either as individual molecules in the saturate fraction or as moieties attached to the aromatic ring fragments in the more polar fractions. Sulfur is usually found in a large percentage of the individual asphalt molecules, but in unoxidized asphalt, it is rather nonpolar and thus is found distributed among all the component fractions. The so-called asphaltene fraction is chemically similar to the more resinous or polar components of the petrolene fraction (31). Although the asphaltene fraction may contain small amounts of occluded or insoluble saturate-type material, the significant differentiating feature of this fraction is the preponderance of molecules with highly condensed planar and polarizable aromatic ring systems together with a high concentration of polar, heteroatom-containing functional groups. Because of these features, molecules of this fraction are strongly attracted to each other, associate strongly, and are difficult to disperse even in polar solvents.

The last fractionation scheme to be considered is that of chemical precipitation (scheme 1-C in Figure 1). This scheme and its modifications are based on a fractionation procedure developed by Rostler and Sternberg (32) and later applied to asphalts (5,6). It may not be exactly correct to call this fractionation procedure a separation scheme because it is really a method of analysis. Some of the steps are destructive and the method does not require the recovery of the altered fractions for further analysis. After separation of the asphaltenes, the remaining components are sequentially separated into fractions based on their reactivity with sulfuric acid of increasing acid strengths (decreasing degree of hydration). In practice, the sulfuric acid phase is added to a nonpolar hydrocarbon solution of the components to be separated, thus forming a second polar acid phase containing those components reactive with the sulfuric acid together with other components sufficiently polar or polarizable to partition toward the sulfuric acid phase. In the first step, an 85 percent sulfuric acid solution is used to remove the most polar components, including most of the basic and nonbasic nitrogen compounds and many of the oxygenated molecules. This fraction is called nitrogen bases. Because the nitrogen in asphalt is usually associated with condensed aromatic ring systems, the so-called nitrogen base fraction is quite aromatic. Concentrated sulfuric acid (98 percent) is used next to precipitate the first acidaffin fraction, which has been reported as containing unsaturated hydrocarbons (5). The use of the term "unsaturated" is unfortunate because the term is usually reserved for the designation of double and triple carbon-carbon bonds in nonaromatic ring structures (olefinic and acetylenic types), which have not been found in significant amounts, if at all, in petroleum residues. The first acidaffin fraction is quite aromatic and low in nitrogen content. The most likely reaction leading to separation of this fraction is sulfonation or complex formation involving the aromatic ring systems. Sulfuric acid containing 30 percent $SO_3$, which is a powerful sulfonating and complexing agent, is used to precipitate those components with less reactive or polarizable aromatic ring systems. Analysis of this fraction, called second acidaffins, indicates that it is considerably less aromatic than the nitrogen bases or first acidaffins (5). The final remaining fraction is called paraffins. This fraction is the oily component of asphalt and is composed primarily of molecules embodying straight-chain, branched, and cyclic alkanes.

Although any of the fractionation schemes discussed separate asphalt into less complex and more homogeneous fractions, the generic fractions obtained are in themselves still complex mixtures and not well-defined chemical species. In all the separation methods, equilibria are involved. This may be solid-liquid equilibria in the chromatographic separation or liquid-liquid partitioning in the chemical precipitation method. The same generic fraction can vary considerably in composition and properties from one asphalt source to another; however, the separations are often sufficiently definitive to provide useful information in studies relating chemical composition with physical properties.

## INTERACTIONS AMONG ASPHALT COMPONENT FRACTIONS AND RELATIONSHIPS WITH DURABILITY

As is shown from the results of component fractionation, a wide spectrum of molecular types is present in asphalt. The most nonpolar or oily fraction, in the absence of the resinous components, is so unlike the asphaltene fraction that the two fractions are not mutually soluble; yet, these extremes in molecular types must coexist in neat asphalt as a microscopically homogeneous mixture. This is made possible by the interaction of various components of asphalt with each other to form a balanced or compatible system. It is this balance of components that gives asphalt its unique viscoelastic properties that are so important to its application as a pavement binder. Lack of compatibility or balance, as sometimes manifested by component phase separation, leads to undesirable properties. The role of the various component fractions in contributing to asphalt component compatibility, and thus durability, will be considered next.

It has long been recognized that asphalts exhibit properties that deviate from those of a true solution. The colloidal nature of asphalt was first recognized by Nellenstyn (33,34), who considered asphalt a dispersion of micelles in an oily medium. The asphaltene fraction was early associated with the dispersed or micelle phase (35). It was also recognized that the inability of the resinous components to keep these highly associated asphaltene components dispersed in the oily phase largely determined the gel or non-Newtonian flow characteristics of the asphalt (36,37). Rostler (5) described the asphaltene fraction as the component of asphalt primarily responsible for asphalt viscosity and colloidal behavior because of its limited solubility in the remaining components. He concluded that the asphaltenes are kept dispersed by the peptizing ability of the nitrogen bases. The peptized asphaltenes are in turn solvated by the resinous acidaffin fractions and gelled by the paraffins. Corbett (38) described the effects on physical properties of the four fractions separated by his procedure: the asphaltenes function as solution thickeners; fluidity is imparted by the saturate and naphthene aromatic fractions, which plasticize the solid polar aromatic and asphaltene fractions; the polar aromatic fraction imparts ductility to the asphalt; and the saturates and naphthene-aromatics in combination with asphaltenes produce complex flow properties in the asphalt. In summary, he concluded that "each fraction or combination of fractions perform separate functions in respect to physical properties, and it is logical to assume that the overall physical properties of one asphalt are thus dependent upon the combined effect of these fractions and the proportions in which they are present."

For purposes of comparison, the polar aromatic fraction from the Corbett separation (10, scheme 1-B in Figure 1) might be considered to contain many of the components found in the Rostler nitrogen base fraction plus possibly part of the first acidaffin fraction. The Corbett naphthene aromatic fraction may be roughly compared with the Rostler second acidaffin fraction plus some components found also in the Rostler first acidaffin fraction. The saturate and paraffin fractions from the two schemes might also be somewhat comparable.

It has been widely recognized (6,7,12,39-43) that a proper balance of chemical components is necessary in a durable asphalt. Not only may too much or too little of a given generic type as defined by the fractionation schemes be detrimental to the compatibility of the system, but so also may variations in chemical composition within the same generic type classification be detrimental. For example, the presence of waxes in the oily fraction, which tend to crystallize and cause phase separation, can be detrimental (39). Asphaltenes that are not properly dispersed, either because of their inherent solubility properties or because of the solvent properties or dispersing power of the resinous components of the petrolenes, will have reduced compatibility with the oily fraction and thus reduce asphalt durability (5,42). Exudation of oil may occur and undesirable gel characteristics thus be imparted.

Rostler and coworkers (6,43,44) showed that the balance of the component fractions, as indicated by the ratio of the most reactive fractions (nitrogen bases plus first acidaffins) to the least reactive fractions (paraffins plus second acidaffins), was important to the resistance of pellets of asphalt and Ottawa sand to abrasion loss in laboratory testing. Although the Rostler fractionation scheme has been used by many materials laboratories and correlations with field performance have been attempted (45,46), it has generally not been accepted as an accurate predictor of field performance. Lack of consideration of the asphaltene fraction, which contributes so significantly to flow properties, in the Rostler durability parameter may be unfortunate and a serious omission. In field tests conducted in California (46), the Heithaus parameter (P) (state of peptization), which is an attempt to measure the internal compatibility of an asphalt by evaluating the peptizability of the asphaltenes and the dispersing power of the petrolenes (42), was found to correlate better with pavement field hardening than the Rostler durability parameter. Using six asphalts of widely differing composition, Traxler (47) found a correlation between his coefficient of dispersion (resins plus cyclics divided by asphaltenes plus saturates) and the rate of hardening during laboratory oxidative aging. Better-dispersed asphalts hardened more slowly. He further suggested that the degree of dispersion of the asphalt components is inversely related to the complex (non-Newtonian) flow properties of the asphalt and is indicative of the asphalt's colloidal characteristics.

## CHANGES IN CHEMICAL COMPOSITION ON AGING

The discussion thus far has addressed chemical compositional factors that determine the physical properties of asphalts. Without question, a durable asphalt must possess acceptable physical properties to produce a pavement with initially acceptable performance properties. The companion requirement of a durable asphalt is that these initial properties be resistant to change during environmental aging in field service. However, asphalt composition changes with time when the asphalt is exposed as a thin film to atmospheric oxygen in the pavement. That asphalt reacts with atmospheric oxygen, which stiffens or hardens the asphalt, has been recognized for more than 50 years, and the literature in this area is voluminous. Atmospheric oxidation is the major factor responsible for the irreversible hardening of asphalts (2) and is the reason why pavement void content (which allows access to atmospheric oxygen) correlates so strongly with asphalt pavement hardening (48,49). Hardening from loss of volatile components, the physical factor that might affect the correlation of hardening and void content, is not considered a significant factor when asphalts meeting current specifications are used. The potentially volatile components would be part of the saturate fraction; Corbett and Merz showed that the amount of this fraction remained virtually constant during 18 years of service in the well-known Michigan Road Test (50). Thus, in dealing with asphalt durability a major factor that must be addressed is change that takes place in asphalt composition from oxidative aging.

The change in the amounts of fractional components of asphalt generally seen on oxidative aging is a movement of components from the more nonpolar to the more polar fractions. The saturates in the Corbett analysis (50) and the paraffins in the Rostler analysis (6) show the least change on oxidation. There is usually some loss of the Rostler second acidaffins and a greater loss of the more reactive first acidaffins and these losses are offset by a significant increase in the asphaltene fraction. Similarly, the Corbett naphthene aromatics and the polar aromatics decrease as asphaltenes increase.

King and Corbett (51) using thin films at 150°C and Knotnerus (11) using dilute toluene solutions showed that the saturate fraction is relatively inert to reaction with oxygen as measured by oxygen uptake. The naphthene aromatic (King and Corbett) and aromatic (Knotnerus) fractions showed slight and no reactivity, respectively. However, the Corbett polar aromatic fraction and the Knotnerus resin and asphaltene fractions were highly reactive with oxygen. Corbett's asphaltene fraction showed intermediate reactivity. Direct measurement of the formation of oxygen-containing functional groups by Petersen et al. (52) ranks the relative reactivity with atmospheric oxygen of the saturate, aromatic, polar aromatic, and asphaltene fractions as 1:7:32:40, respectively, for a Wilmington (California) asphalt when the fractions were oxidized separately at 130°C. However, evidence was found that in neat asphalt, components of the more polar fractions may promote more oxidation of components of the less polar fractions than when they are oxidized separately.

The asphaltene fraction has been considered by some (5) to be chemically almost inert; however, the foregoing data indicate that asphaltenes are quite reactive with oxygen. This supports the author's criticism made earlier that it may not have been justified to eliminate the asphaltene fraction from the Rostler durability ratio. The apparent contradiction regarding the chemical reactivity of asphaltenes might be explained by the following observations made by the author. Isolated asphaltenes are brittle solids and in this state at ambient temperatures are indeed quite unreactive with atmospheric oxygen, probably because their solid, highly structured state reduces molecular mobility, which in turn reduces reactivity with oxygen. However, when the asphaltenes are melted (as in the 130 and 150°C oxidations) or in solution in solvents, their mobility is increased and thus so is their apparent reactivity. One might assume that if asphaltene components are well dispersed in neat asphalt, they might also be chemically quite active. Their chemical structure, highly condensed ring systems with alkyl attachments, also suggests a system sensitive to hydrocarbon-type oxidation.

More recent studies (14,52-57) have yielded considerable information on the specific chemical changes that take place in asphalt on oxidative aging by reaction with atmospheric oxygen. The major oxygen-containing functional groups formed on aging are listed in Table 2 for four asphalts of different crude sources and aged under identical conditions (air, 130°C, thin film). The data (14) represent averages for the four asphalts aged on four different aggregates and are for the same asphalts shown in Table 1. The level of oxidation has been judged to be equivalent to that typically found in asphalts after 5 years or more of pavement service (9). That the chemical functionality developed during laboratory oxidation at 130°C is similar to that developed during normal pavement aging at ambient temperatures is supported by data given in Table 3 (59). Reasons for the lower levels of oxidation in some pavement samples compared with laboratory oxidation are discussed elsewhere (59), but they relate to the inaccessibility of some of the asphalt in the pavement to atmospheric oxygen.

**TABLE 2 Chemical Functional Groups Formed in Asphalts During Oxidative Aging (*14*)**

| | Concentration (mol · liter$^{-1}$) | | | | Average |
|---|---|---|---|---|---|
| Asphalt | Ketone | Anhydride | Carboxylic Acid[a] | Sulfoxide | Hardening Index[b] |
| B-2959 | 0.50 | 0.014 | 0.008 | 0.30 | 38.0 |
| B-3036 | 0.55 | 0.015 | 0.005 | 0.29 | 27.0 |
| B-3051 | 0.58 | 0.020 | 0.009 | 0.29 | 132.0 |
| B-3602 | 0.77 | 0.043 | 0.005 | 0.18 | 30.0 |

Note: Column oxidation (*58*), 130°C, 24 hr, 15-micron film.

[a] Naturally occurring acids have been subtracted from reported value.

[b] Ratio of viscosity after oxidative aging to viscosity before oxidative aging.

**TABLE 3 Comparison of Oxidation Products in Column-Oxidized and Pavement-Aged Samples**

| | Concentration (mol · liter$^{-1}$) | | | |
|---|---|---|---|---|
| | Column Oxidized[a] | | Pavement Aged[b] | |
| Asphalt | Ketone | Anhydride | Ketone | Anhydride |
| 60 | 0.76 | 0.024 | 0.53 | 0.018 |
| 25 | 0.70 | 0.025 | 0.53 | 0.022 |
| 30 | 0.64 | 0.027 | 0.64 | 0.038 |
| 61 | 0.67 | 0.022 | 0.44 | 0.020 |
| 67 | 0.43 | 0.013 | 0.32 | 0.010 |
| 71 | 0.76 | 0.026 | 0.51 | 0.022 |
| 72 | 0.82 | 0.033 | 0.68 | 0.029 |
| 73 | 0.49 | 0.013 | 0.35 | 0.011 |
| 74 | 0.72 | 0.027 | 0.43 | 0.017 |

[a] Thin film oxidation, 130°C, 24 hr (*58*).

[b] Recovered from 11- to 13-year-old pavements (*15*).

**TABLE 4 Carbonyl Functional Groups Formed in Wilmington Asphalt Fractions During Column Oxidation (*52*)**

| | Concentration (mol · liter$^{-1}$) | | |
|---|---|---|---|
| Fraction | Ketone | Anhydride | Carboxylic Acid |
| Saturate | 0.045 | 0.010 | Trace |
| Aromatic | 0.32 | 0.017 | —[a] |
| Polar aromatic | 1.48 | 0.088 | —[a] |
| Asphaltene | 1.82 | 0.080 | ND[b] |
| Whole asphalt | 1.02 | 0.052 | 0.007 |

[a] Some acids lost on alumina column during component fractionation.

[b] Not determined.

Data in Table 2 show that ketones and sulfoxides are the major oxidation products formed during oxidative aging; anhydrides and carboxylic acids are formed in smaller amounts. In some asphalts, the summed concentrations approach 1 mole per liter. If a molecular weight of 1,000 is assumed for an asphalt molecule, on the average one functional group is formed for each asphalt molecule. Of course, not all molecules of asphalt have the same reactivity. Data in Table 4 show that ketones are formed in the highest concentrations in the asphaltene and polar aromatic fractions; lesser amounts are formed in the aromatic fraction, and considerably less in the saturate fraction. These data are consistent with the earlier-cited oxygen uptake experiments (11,51).

The oxidation products formed are consistent and in good agreement with what is known about the hydrocarbon types in asphalt and the general chemistry of hydrocarbon oxidation. The major reaction pathway of hydrocarbon air oxidation is the formation of carbonyl compounds via the hydroperoxide intermediate (53,54). The most sensitive hydrocarbon moiety expected to be present in asphalt is that associated with the carbon atom adjacent to an aromatic ring system, commonly called a benzylic carbon. The hydrogen attached to the carbon in this position is relatively easy to displace, forming a free radical on the carbon. Branching in the attached hydrocarbon chains also increases the sensitivity of the asphalt to oxidation.

A simplified, generalized scheme proposed by the author for the oxidation of the hydrocarbon moieties in asphalt is proposed in Figure 2, which shows ketones as the major functional group formed, consistent with the data in Tables 2 and 3. In the reaction scheme presented, the symbol R may represent either a hydrogen atom or an alkyl group. The reaction is initiated by the abstraction of a hydrogen atom attached to a benzylic carbon of an asphalt molecule (I) to form a free radical (II). The free radical reacts with atmospheric oxygen to form a peroxy radical (III). This in turn rapidly decomposes to form a ketone (IV) or, more likely, abstracts a hydrogen atom from the benzylic carbon of another asphalt molecule (V) to form a hydroperoxide (VII). The asphalt-free radical formed (VI) can react with atmospheric oxygen to repeat the process. The hydroperoxide is rather unstable and may decompose to form either a ketone (VIII) or an alkoxy radical (IX). The alkoxy radical may rapidly decompose to form a ketone (X). This mechanism is admittedly oversimplified and minor amounts of other oxidation products not shown are undoubtedly formed. However, it adequately accounts for the major hydrocarbon oxidation product, ketones. Ketones as the major oxidation product in oxidized asphalt have been positively verified (53). Smaller amounts of anhydrides are formed (54) through what is believed by the author to be an alternate hydroperoxide decomposition route in certain asphalt molecules having stereospecific ring systems associated with the oxidizable alkyl moieties. Under certain conditions, the alkyl moiety may oxidize to the carboxylic acid; however, only small amounts of carboxylic acids [and no measurable esters (54)] have been found in laboratory- or pavement-aged asphalts. It appears that the oxidation reaction almost always stops at the ketone stage.

Because the polar aromatics (or nitrogen bases and first acidaffins) and asphaltene fractions are known to contain the highest concentrations of aromatic ring systems, and thus benzylic carbons via the alkyl moieties attached, they have the highest content of hydrocarbon types sensitive to air oxidation. It is then not surprising that the polar aro-

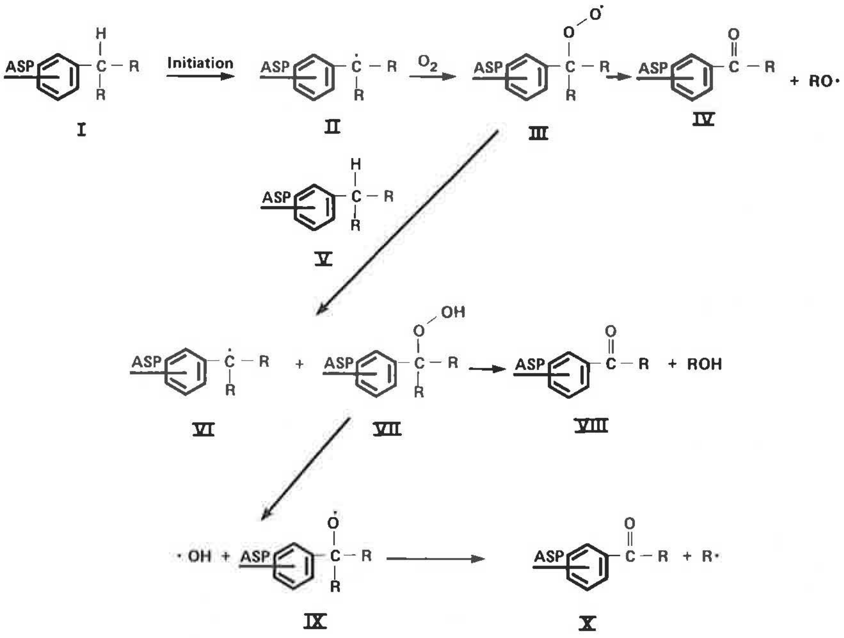


FIGURE 2 Suggested mechanism for the free-radical air oxidation of asphalt.

matics and asphaltenes (Table 4) showed the highest ketone formation on oxidation.

The formation of sulfoxides, the second most dominant oxidation product, has been shown to result from oxidation of organic sulfides that are part of complex asphalt molecules (57). These sulfides are highly reactive. Sulfoxides are formed in asphalt at a much higher rate than ketones and their formation often precedes significant ketone formation. This is probably because sulfides are hydroperoxide scavengers and are converted to sulfoxides by the scavenger reaction.

The significance of the polar oxygen-containing functional groups to physical properties will be discussed in detail in a later section of this paper. However, their influence on the hardening of the asphalt is apparent from the aging indexes (ratio of viscosity after oxidation to viscosity before oxidation) of the asphalts in Table 2, which range from 27 to 132. It is apparent that the relative amount of hardening is not directly related to the amount of oxidation when one asphalt source is compared with another. Note that the asphalts with the smallest and greatest aging indexes (Table 2) both showed about the same chemical reactivity with atmospheric oxygen. This is because all asphalts do not show the same sensitivity to the oxidation products formed. Asphalts from different sources have differing composition and thus their components interact differently with the oxidation products formed to increase viscosity. This varying sensitivity to oxidation products will be discussed later in more detail.

At this point it is instructional to consider the Rostler durability parameter with regard to the chemical information just presented. As previously stated, this parameter is the ratio of the quantity of nitrogen bases plus first acidaffins divided by the quantity of second acidaffins plus paraffins. The polar aromatic fraction, which should include the Rostler nitrogen bases and a good part of the first acidaffins, was shown to be the fraction most chemically reactive with oxygen after asphaltene separation. Also, the saturates and aromatics, which should account for much of the Rostler paraffin and second acidaffin fractions, were shown to be least reactive. Thus, it is understandable that a correlation was found between the Rostler durability parameter (ratio of most reactive to least reactive components as recognized by Rostler) and abrasion loss in the pellet abrasion test (5,6), which test is sensitive to asphalt hardening on oxidation. Although the ratio may indicate the amounts of components most reactive to oxygen (excluding the asphaltenes) relative to the amounts least reactive, it is not a precise measure of the compatibility of the sample, because the relative amounts of saturates and second acidaffins and the relative amounts of first acidaffins and nitrogen bases, whose sums make up the denominator and numerator of the ratio, are not specified.

Also, as previously mentioned, the asphaltenes, which have such a profound effect on asphalt compatibility and viscosity, are not considered in the ratio. These problems are compounded by differences in composition that may occur among similar generic-type fractions from different asphalts. Consider again the large differences in the effects of similar amounts of oxidation products (from chemical reactivity) on the hardening rate of two different asphalts, B 3036 and B 3051, shown in Table 2. Initial compatibility, rate of formation of oxidation products, and response of the system to the oxidation products produced are all interdependent variables and cannot be sufficiently defined by a single numerical value. The asphalt system is much too complex for this. It is the considered opinion of the author that although the Rostler parameter should show a general correlation with pavement performance, it is not sufficiently precise to be used as an accurate predictor and if used must be considered together with additional physiochemical data further defining the composition of the asphalt.

## MOLECULAR INTERACTIONS--A FUNDAMENTAL APPROACH TO CHEMICAL FACTORS AFFECTING ASPHALT DURABILITY

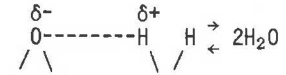
In this section of the paper a fundamental approach to asphalt chemical composition--physical property relationships--will be addressed. The approach draws heavily on past chemical data and information from component analyses but is based on more recent research that recognizes the fundamental chemical factors that affect asphalt properties. Parts of this section have been summarized previously (60). Because the physical properties of asphalt are controlled by the interactions of the molecules from which it is composed, an understanding of these interactions should provide the basis for understanding its physical behavior and thus its durability. It is not necessary (and would be virtually impossible) to know the exact structure of each molecule for a workable understanding. It should be sufficient to identify or characterize th various types of chemical or structural features of the asphalt molecules and how these interact with each other and their environment.

Many molecules of different composition will have similar features, or functionality, that will produce similar effects on physical properties. Functionality analysis has the advantage over component fractionation in that it can take into account the multiple functionality of asphalt molecules. Many asphalt molecules have several types of chemical functionality on the same molecule, often of diverse types, which frustrate chemical fractionation procedures because whole molecules must be moved into a given fraction. The molecular interaction approach taken here is primarily that of the author; however, many researchers, both past and present, have recognized the importance of chemical functionality on asphalt properties.

### Fundamentals of Molecular Interactions and Effects of Molecular Interactions on Flow Properties

Because the chemical and physical properties of an asphalt are the sum total of the composition and interactions of its individual molecules, it is instructive at this point to briefly review some fundamentals of molecular interactions. Molecules attract one another and interact through a variety of secondary bonds or association forces. These association forces are generally one to two orders of magnitude weaker than the covalent chemical bonding forces that hold the atoms together in the molecule. The association forces are significantly different from covalent bonding forces in that they form bonds that are generally reversible and are usually in dynamic equilibrium. That is, they "make" and "break" under forces induced by such factors as temperature and external stress, and thus they largely determine the physical properties of the composite material.

To illustrate the principles involved, the classic example of the hydrogen bonding of water molecules is considered. A simplified schematic of this bonding is as follows:



The electronegative oxygen atom reduces the electron density of the hydrogen atom by attracting its electron field, thus creating a dipole-dipole interaction involving the oxygen and hydrogen of two different water molecules. Additional dipole interactions produce a three-dimensional network of associated species. When water flows or is vaporized, the hydrogen bonds are the major association forces that must be overcome to allow the molecules to move with respect to one another and are the major forces controlling the properties of water. The formation and breakdown of molecular structure via association forces are extremely rapid. In liquids the average lifetime of a given arrangement of molecules, that is, a structural unit, may be as short as $10^{-13}$ sec and for water is estimated at $10^{-11}$ sec.

To further illustrate the great influence of the electronegative oxygen atom on physical properties, consider replacing the oxygen in water with sulfur to yield hydrogen sulfide, $H_2S$. Because sulfur is less electronegative than oxygen, the strength of the hydrogen bond is greatly reduced. As a result, hydrogen sulfide, even though a heavier molecule than water, is not a liquid but rather a gas at room temperature. Its boiling point is 162°C lower than that of water. The effects of intermolecular forces, as illustrated by the hydrogen bond, are basic to understanding the effects of chemical composition on asphalt properties because the intermolecular forces are the primary determinants of physical properties.

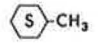
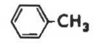
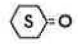
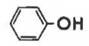
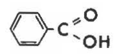
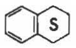
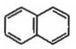
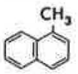
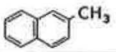
It should not be implied from the foregoing discussion that the hydrogen bond is the most important interaction force in asphalt. Many other reversible interaction forces are important in a material so chemically complex. These include a variety of dipole and induced dipole interactions. For simplicity in discussing molecular interactions in this paper, all molecular structural types in asphalt that exhibit these forces are considered as chemical functionality. These functionalities include, but are not limited to, the more classical chemical functional groups.

Nonpolar hydrocarbon components in asphalt such as those dominant in the saturate fraction exhibit only weak interaction forces, which accounts for the rather fluid character of this fraction. On the other hand, asphalt components containing highly condensed ring systems and chemical functional groups containing oxygen and nitrogen atoms may be highly polar or polarizable and thus interact strongly with each other. These strong interaction forces largely account for the fact that asphaltenes, even though they may not be significantly different in molecular weight than the saturates (61), are high melting solids.

To illustrate the potential applicability of molecular interaction theory and molecular structuring to the physical properties of asphalt, it is helpful to examine the effects of the chemical functionality of a series of model compounds on the physical properties of these compounds. A list of selected model compounds together with their structure, boiling point, and melting point are shown in Table 5. These chemical functionalities also represent important types found in asphalt and thus the reasoning developed may have direct application.

First, consider the series of compounds n-heptane through benzoic acid. All were chosen from the same molecular weight range to minimize the effects of this variable and are listed in order of increasing polarity or increasing tendency of the molecules to interact. As previously mentioned, molecular interaction forces must be overcome to allow vaporization; thus changes in boiling point reflect changes in the strength of the interaction forces between molecules. Note the continuously increasing boiling point with increasing polarity. The introduction of aromaticity in the molecule with toluene introduces mobile pi-electrons, which can be polarized, thus increasing its boiling point over methylcyclohexane. Introducing the ketone group with cyclohexanone adds a polar oxygen-containing functional group and significantly increases the boiling point over methylcyclohexane. Phenol has both aromaticity and a polar OH group that can form strong hydrogen bonds; thus it has an even higher boiling point. Finally, benzoic acid possesses a carboxylic acid functional

TABLE 5 Effects of Molecular Interactions and Molecular Structuring on the Physical Properties of Model Compounds

| Compound | Structure | Boiling Point, °C | Melting Point, °C |
|---|---|---|---|
| n-Heptane |  | 98.4 | —90.5 |
| Methycyclohexane |  | 100.3 | —126.4 |
| Toluene |  | 110.6 | —95 |
| Cyclohexanone |  | 156.7 | —45 (frz.) |
| Phenol |  | 182 | 41 |
| Benzoic Acid |  | 249 | 122 |
| Benzene |  | 80 | 5.5 |
| Hexahydronaphthalene |  | 205 | liquid |
| Tetrahydronaphthalene |  | 207.2 | —30 |
| Naphthalene |  | 217.9 | 80.2 |
| 1-Methylnaphthalene |  | 240 | —22 |
| 2-Methylnaphthalene |  | 245 | 35.1 |

group that forms strong hydrogen-bonded dimers. Note its extremely high boiling point.

Next consider the properties of the series hexahydronaphthalene through 2-methylnaphthalene in Table 5. As expected, the boiling point increases in a regular fashion with increasing aromaticity and the introduction of the methyl group; however, the melting point shows no such correspondence. Note also in Table 5 how introducing a methyl group on benzene to form the higher-boiling toluene greatly reduced the melting point. The melting point, which reflects the interaction forces between molecules when in an ordered or structured configuration, is greatly influenced by the geometry of the molecule. Interfering appendages on, or structural arrangements of, the molecules that do not allow them to fit together easily in the necessary geometric pattern for effective interaction greatly reduce the melting point. Thus, molecular shape dominates the low-temperature structuring properties.

It is instructive to consider the molecular interaction effects just described with regard to the flow properties of asphalts. The rather predictable effect of polar functionality on boiling point can be related to the effects of polar functionality in asphalt on its flow properties at higher temperatures in the Newtonian flow region. The polar interactions between molecules dominate in influencing the flow behavior, and the effects of molecular shape on geometry are minimized. This reasoning may explain why asphalts that have quite different flow properties at low temperatures look more alike at higher temperatures.

At lower temperatures, however, as the kinetic energy of the system is lowered, the asphalt molecules tend to associate or agglomerate into immobilized entities with a more or less ordered or structured spatial arrangement. Although this ordered arrangement is influenced by polar functionality, it is also greatly influenced (as was the melting point of pure compounds) by the geometry of the molecules. Thus, at low temperatures the effects of differences in chemical composition of asphalt play a more significant role in determining the complex low-temperature flow properties, for example, viscosity shear and temperature susceptibility.

Data obtained on asphalt-based systems will now be considered. To illustrate the effect of different types of molecular interactions on viscosity, consider data taken from an early paper by Griffen et al. (12) and abstracted as follows (to convert to viscosity in poise, multiply by 10):

| Fraction | Apparent Molecular Weight | Viscosity (Pa•sec), 25°C |
|---|---|---|
| Saturate | 500 | 10 |
| Aromatic | 500 | 1,000 |
| Resin | 500 | 100,000 |

Griffen separated asphalt into component fractions and then determined molecular weight versus viscosity profiles on the fractions. The foregoing data are taken for components of each fraction having the same molecular weight of 500.

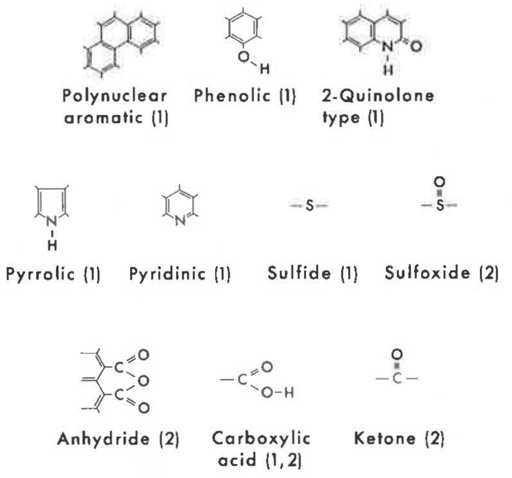
The saturates had a viscosity of only 10 Pa•sec. They do not contain polar chemical functionality and molecular interactions are weak. Molecular interactions of increased intensity are exhibited by the aromatic fraction the viscosity of which was 1,000 Pa•sec. Finally, the resins that contain polarizable condensed-ring systems and heteroatom functionality, and thus exhibit even more intense molecular interactions, had a viscosity of 100,000 Pa•sec. Because the molecular weights of each fraction were the same, the differences in viscosity resulted primarily from differences in the type and strength of molecular interactions. The association forces among asphalt molecules give asphalt many of the properties of high-molecular-weight polymers.

### Major Chemical Functional Group Types Affecting Asphalt Properties

As previously stated, asphalt molecules contain hydrocarbon structural constituents varying from saturated, paraffinlike chains to highly condensed and polarizable aromatic ring systems. From the previous discussion of model compounds, it is apparent that the relative amounts of the different structural or functional moieties of each molecule determine how molecules interact with each other. Those molecules that are most alike are most compatible and vice versa. In fact, as stated earlier, some asphalt components such as the saturates and asphaltenes are not mutually soluble when separated from the whole asphalt. It is the wide spectrum of molecular types in asphalt all interacting together that gives asphalt its unique properties and makes it appear as a homogeneous material. However, on a molecular level, asphalt is undoubtedly heterogeneous, and a delicate balance exists among strongly associated or agglomerated components and dispersing or solubilizing components. It is this delicate balance, or the lack of it, that affects the performance properties of asphalts. Incompatibility and poor performance generally follow when one component type unduly dominates at the expense of others.

As discussed previously, although asphalt molecules are composed primarily of hydrocarbon constituents, heteroatoms such as nitrogen, sulfur, and oxygen may also be present as part of the molecule. Heteroatom concentrations vary widely among asphalts. In many asphalts heteroatom concentrations are sufficient to average one or more heteroatoms for every asphalt molecule. Oxygen, nitrogen, and some forms of sulfur may introduce high polarity into the molecule, and although only a minor component, they can exhibit a controlling influence on the molecular interactions that control asphalt flow properties. Thus chemical functionality containing these atoms becomes a major consideration in understanding asphalt properties.

Much work has been done by the author and coworkers in identifying polar, strongly associating functional groups in asphalts, either naturally present or formed on oxidation, and in characterizing their association forces (9,14,52-56,59,62-69). Structural formulas of important chemical functionality in asphalts are shown in Figure 3. Nitrogen, which occurs in concentrations of 0.2 to 1 percent, is present in several forms from the slightly acidic pyrrole types to the more basic, strongly interacting pyridine types (69). The nitrogen types naturally occurring in asphalt are not known to be significantly altered by oxidation. Sulfur, in concentrations from about 1 to 5 percent, is present primarily as sulfides. Many of these sulfides are readily oxidized to polar sulfoxides by atmospheric oxygen during normal aging (57). Phenolics are also usually present. Naturally occurring carboxylic acids and 2-quinolone-type functionality, although occurring in relatively small amounts in asphalts, are highly polar and associate strongly (64). As discussed previously, asphalts are susceptible to oxidative aging by reaction with atmospheric oxygen, which is a major factor contributing to age hardening and embrittlement. The major oxygen-containing functional groups formed on oxidative aging are also included in Figure 3.



(1) Naturally occurring
(2) Formed on oxidative aging

**FIGURE 3** Chemical functionality in asphalt molecules normally present or formed on oxidative aging.

## Effects on Asphalt Performance of Polar Functional Groups Formed on Oxidation

Asphalts vary considerably in their susceptibility to the effects of deteriorating oxidation. If during aging the concentration of polar functional groups becomes sufficiently high to cause molecular immobilization through increased intermolecular interaction forces, that is, the asphalt molecules or micelles are not sufficiently mobile to flow past one another under the stress applied, fracturing or cracking of the asphalt will result.

Data in Figure 4 show a relationship between the amount of strongly interacting polar groups formed in a series of asphalts during controlled laboratory oxidative aging and the resistance to failure from cracking in roads in which these asphalts were used. The asphalts were from the California Zaca-Wigmore Experimental Road Test mentioned previously (4,9), in which construction variables were kept as constant as possible to evaluate the effect of asphalt composition (or source) on durability. In the laboratory studies (9), these asphalts were coated as thin films on inert fluorocarbon particles and were aged in a gas chromatographic (GC) column at 130°C for 24 hr by passing air through the column (59). (This procedure oxidizes the asphalt an amount equal to approximately 5 years or more in a road.) Following oxidative aging, a polar test compound, phenol, was passed through the GC column by using an inert gas carrier, and its interaction with the polar groups formed in the asphalt during oxidation was determined from the phenol retention time. As phenol passes through the column it is in equilibrium with the asphalt; those asphalts having a greater concentration of polar groups interact more strongly with the phenol functionality, giving a larger phenol interaction coefficient.

As seen from Figure 4, an excellent correlation was found between the asphalt polarity as measured by the phenol interaction coefficient and the service performance rating after 51 months of road service. Those asphalts that developed greater amounts of strongly interacting polar groups during aging failed sooner in the road. Figure 5 shows a similar correlation developed on 20 roofing asphalts the weatherability of which was determined by resistance to cracking when aged in a carbon arc Weather-Ometer. Thus, strong evidence exists relating the development of polar functional groups in asphalts on aging with asphalt failure from embrittlement and cracking.

## Effects of Polar Asphalt Components on Viscosity and Aging Characteristics

Data plotted in Figure 6 show the important influence of polar constituents (in this case, asphaltenes) on asphalt viscosity. In the study cited (14), four asphalts (all meeting the same specifications) were oxidatively aged in the laboratory both before and after a hydrated lime treatment (the lime with adsorbed asphalt components--about 4 percent of the asphalt--was separated from the asphalt during the treatment). The asphalts were aged by different methods to achieve different levels of oxidation. Following aging, both asphaltene content and viscosity were determined at 25°C. Each data point in the figure represents a separate level of oxidation. Although each asphalt had its own unique relationship, a good correlation existed for each asphalt between asphalt viscosity and asphaltene content. Several important points can be inferred from the data in Figure 6. First, the asphaltene fractions of the different asphalts are quite different from each

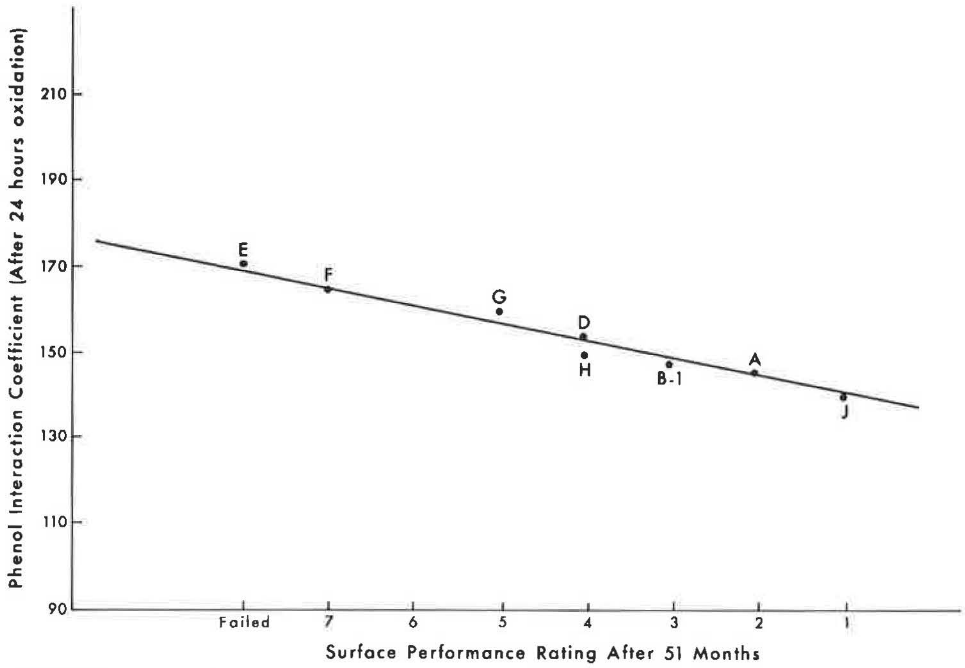


FIGURE 4 Relationship between phenol interaction coefficient and pavement surface performance rating.

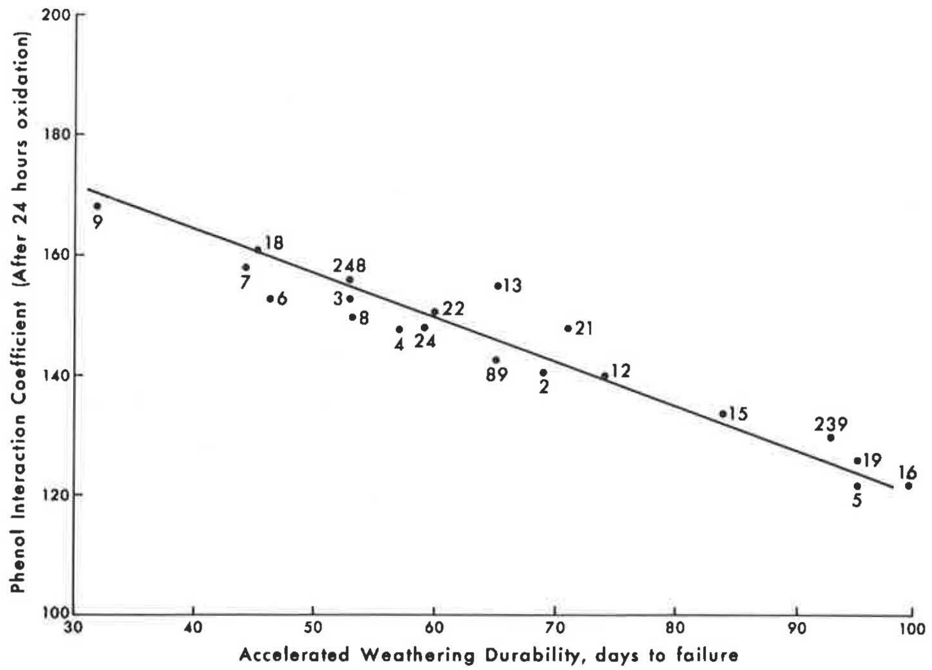


FIGURE 5 Relationship between phenol interaction coefficient and durability of 20 roofing asphalts.

other in composition or the petrolene fractions have widely different solubility power for the asphaltenes or both. This is a necessary condition in order for asphalts with widely varying asphaltene contents to have the same viscosity. Second, asphaltenes formed in asphalt on oxidative aging appear to have a predictable effect on viscosity increase.

The data in Table 6 give the effect of the lime treatment in reducing the hardening rate of the asphalts when subjected to a laboratory GC column oxidation procedure (14,59) during which the asphalts were supported as thin films on the surface of four different aggregates. Note that except for asphalt B-3602, lime treatment reduced the hardening index of the asphalts by more than 50 percent. Asphaltene formation on aging was also reduced by about 50 percent (14). Functional group analyses, however, showed that the oxidation reaction, as measured by the formation of ketones, was reduced by only about 10 percent by lime treatment. What was concluded was that lime removed carboxylic acids and other highly polar functionality that would have otherwise interacted with oxidation products to increase asphalt viscosity. Separate studies showed

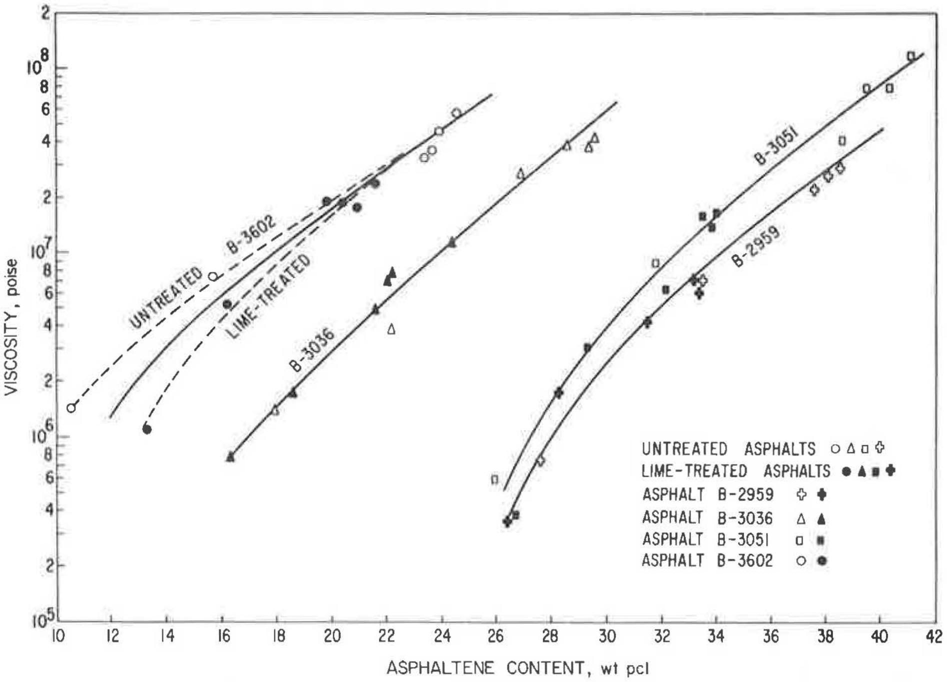


**FIGURE 6** Relationship between viscosity at 25°C and asphaltene content of untreated and lime-treated asphalts aged by different laboratory methods.

**TABLE 6** Reduction of Hardening Rate of Asphalt by Treatment with Hydrated Lime (*14*)

| Sample | Hardening Index[a] Untreated | Lime Treated | Reduction (%) |
|---|---|---|---|
| Asphalt[b] | | | |
| B-2959 | 37 | 17 | 54 |
| B-3036 | 27 | 10 | 63 |
| B-3051 | 132 | 35 | 73 |
| B-3602 | 29 | 18 | 39 |
| Aggregate[c] | | | |
| Quartzite | 57 | 22 | 61 |
| Hol limestone | 58 | 22 | 61 |
| Riverton limestone | 36 | 13 | 63 |
| Granite | 75 | 22 | 70 |

[a] Hardening index = viscosity after oxidative aging divided by viscosity before oxidative aging.
[b] Averaged for aggregates.
[c] Averaged for asphalts.

that the introduction of carboxylic acid functional groups into asphalt molecules greatly increased asphalt viscosity.

The reduction of asphalt viscosity by inactivating polar functionality was demonstrated (70) by adding 3 percent by weight hydrated lime to an asphalt (B-3051), leaving the lime in the asphalt, and measuring its viscosity versus time at 25°C. During the initial 24-hr period after lime addition, asphalt viscosity steadily decreased in a regular fashion from about 5 x $10^4$ Pa•sec (5 x $10^5$ to 1.5 x $10^5$ poise). This decrease was interpreted as the result of the adsorption of polar, strongly interacting groups on the lime surface, thus removing these viscosity-building components from the asphalt matrix. In some asphalt-aggregate systems, such phenomena might impart slow-setting or tenderness characteristics to a pavement mixture.

The flow properties and hardening rate of asphalt might also be significantly altered by manipulation of molecular interactions through chemical modification or the addition of modifiers that can interact with polar chemical functionality in the asphalt and alter its activity as suggested by the data on lime addition. The ability of surface-active materials such as antistripping agents (often amines) to alter asphalt viscosity, often to an extent not expected from simple additive effects, is familiar to many. Because antistripping agents have polar chemical functionality, they might be expected to affect the dispersibility of asphaltenelike components in asphalt by associating with polar functionality and thus altering association and micelle structure within the asphalt. The ability of high-molecular-weight amines to interfere with molecular structure buildup and subsequent viscosity increase in asphalt cutbacks during storage was reported as early as 1951 by Hoiberg (71).

The effects of antistripping additives on altering the flow properties and oxidative hardening rate of asphalts have recently been reported (72). It has been suggested by J.N. Dybalski of Akzo Chemie America that cationic asphalt additives augment the peptization of the asphaltene constituent in many asphalts and thus reduce the asphalt hardening rate as reported in a trade newsletter (73). According to the report, of 82 asphalts tested, 81 percent were benefitted by the additives with a minimum of 15 percent and a maximum of 65 percent reduction in hardening rate during the rolling thin-film oven test (ASTM D 2872-77). The hardening rate of a recycled pavement mixture during laboratory aging was also reduced severalfold by a high float emulsifying agent used to emulsify the recycling agent before recycling of the pavement mixture (74).

## Composition and Component Compatibility

Previous reference was made to the need for a good balance among asphalt components of differing polarity. Compatibility in asphalt deals with the mutual solubility of a variety of components with widely differing solubility and solvent powers. Earlier workers in the field considered compatibility in terms of the state of peptization of asphaltenes. Heithaus (42) stated that asphaltenes are the most polar and aromatic components in asphalt and are present in asphalts as rather concentrated solutions (10 to 40 percent). To obtain maximum solvency for the polar, strongly associating species in asphalts, the polarity of the solvent (maltenes, now preferably called petrolenes) must be matched to the materials to be dispersed (asphaltenes). For example, more polar asphaltenes require petrolenes with greater solvent power to effectively dissolve or disperse them.

A number of studies have addressed the dispersibility of asphaltenes and methods to measure dispersibility and compatibility (7,42,75-77). Altgelt and Harle (76) clearly demonstrated that selected asphaltenes from different sources had different effects on blend viscosity (different thickening power) when added to the same petrolene fraction. They further showed that petrolene fractions derived from asphalts of different sources had different solubility power for asphaltenes. To illustrate the principles they developed, consider what happens when a highly polar asphaltene fraction having a strong tendency to self-associate is added to a petrolene fraction having relatively poor solvent power for the asphaltenes. Intermolecular agglomeration will result, producing large, interacting, viscosity-building networks. Conversely, when an asphaltene fraction is added to a petrolene fraction having relatively high solvent power for the asphaltenes, molecular agglomerates are broken up or dispersed to form smaller associated species with less interassociation; thus the viscosity-building effect of the asphaltenes is reduced. It must be concluded that chemical composition becomes an important factor to be considered when asphalts (or crudes) are blended from different sources or when asphalt components are blended. The principles described help explain why viscosities of asphalt mixtures or blends often show irregularities when compared with the viscosities of the original asphalts.

It follows that asphalt compatibility can be improved or worsened by blending and that the initial properties of blended asphalts are not necessarily additive in determining blend properties. Compatibility considerations are also important with regard to the aging characteristics of asphalt because, as already described in detail, oxidative aging greatly alters the polarity of asphalt molecules and therefore their interactions. The discussion thus far implies that a better knowledge of the chemical functionality responsible for the strong interaction forces in asphalt, and the ability to manipulate these forces, has great practical value in altering the flow and thus the performance properties of asphalt. Application of compatibility principles to pavement recycling in which a recycling agent is added to restore useful properties should also greatly benefit this rapidly emerging practice.

## Importance of Molecular Structuring to the Flow Properties of Asphalt

Molecular structuring in asphalts is probably one of the least understood physiochemical phenomena affecting physical properties. Unlike oxidative aging, which produces irreversible changes in asphalt composition, molecular structuring is a reversible phenomenon that can produce large changes in the flow properties of asphalt without altering the chemical composition of the asphalt molecules. Several factors account for its elusive nature and resistance to quantification. First, in asphalts at ambient temperatures, structuring is a slow process that may go on for days and even years; second, it is promoted by mineral aggregate surfaces (as in pavement mixtures) in an environment where it is difficult to measure its effects; and third, most normal asphalt recovery methods using solvents or heat or both destroy or reverse the structuring process. Yet molecular structuring is largely responsible for asphalt's unique physical properties. Without it, pavement mixtures would not set to produce a nontender pavement with the desired structural integrity, and too much structuring can produce pavements with poor low-temperature properties and high shear susceptibility.

Although the phenomenon of structuring in asphalt is as yet little understood, it was recognized and received considerable study by early investigators (71,78-84) and is often called steric hardening (82). It has been related to the thixotropic flow behavior commonly encountered in colloidal materials (79). The early literature is extremely revealing and might well be read carefully by present-day technologists, because little work has been done to build on or take advantage of the excellent past studies.

Traxler and coworkers characterized molecular structuring (which they also called age hardening, not to be confused with age hardening caused by oxidation) in a number of asphalts from a variety of sources and related it to the degree of complex flow (sensitivity of measured viscosity to shear rate) (78-81). Their experiments were carried out on bulk asphalt in the absence of significant oxidation. Selected data in Figure 7 and in Table 7 document this nonoxidative age hardening.

In Figure 7, selected data on three paving asphalts show different hardening rates as a function of asphalt source. Air-blown asphalts showed a greater rate of structure hardening than unblown asphalts as illustrated by the air-blown Venezuelan asphalt in Figure 7. Note also that for the air-blown asphalt, the log viscosity versus log time plot was not linear as with the unblown asphalts but the rate of change increased with time. Traxler and coworkers (78) devised an expression called the asphalt aging index to quantitatively measure reversible hardening from molecular structuring. This index is the slope of the log viscosity versus log time plot. Asphalt aging indexes for eight unblown asphalts from different sources are shown as follows (78):

| Asphalt | Asphalt Aging Index |
|---|---|
| Californian | 0.012 |
| Californian | 0.018 |
| Trinidad | 0.026 |
| Venezuelan | 0.037 |
| Midcontinent | 0.039 |
| Mexican | 0.051 |
| Venezuelan | 0.063 |
| Venezuelan | 0.071 |

The structuring phenomenon was found reversible and structured asphalt could be brought back to near its initial viscosity by heating to a temperature above its softening point or by continued mechanical working (80,84).

These early researchers found a correlation between the complex flow of asphalt (non-Newtonian behavior or viscosity lowering with increasing shear rates) and its tendency to exhibit molecular structuring. This is illustrated by data in Table 7,

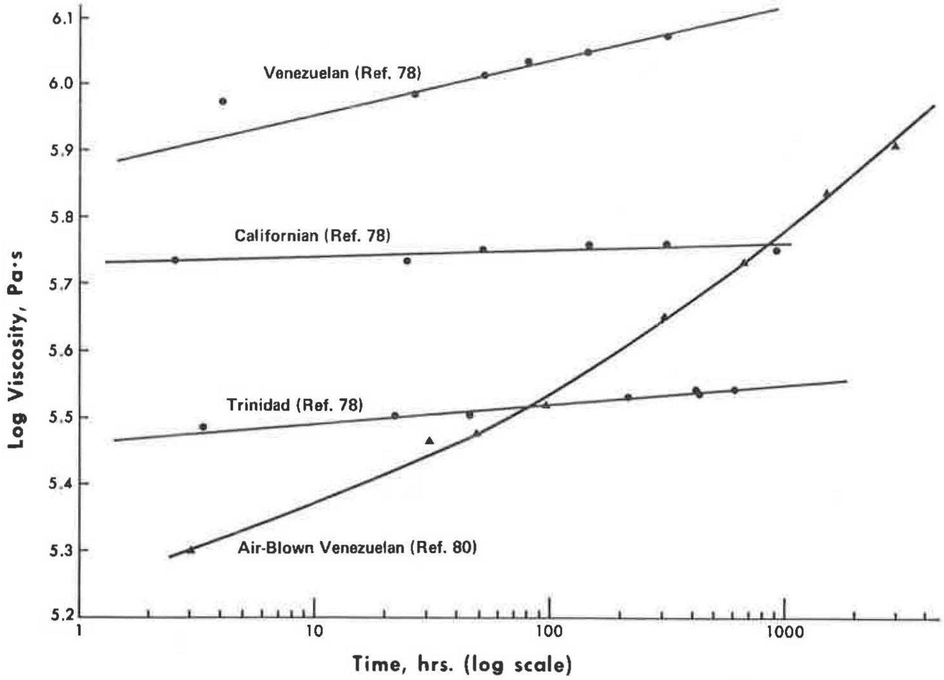


FIGURE 7 Hardening of asphalts from reversible molecular structuring at 25°C.

TABLE 7 Correlation Between Reversible Molecular Structuring and Degree of Complex Flow (*81*)

| Asphalt | Asphalt Aging Index[a] | Complex Flow[b] |
|---|---|---|
| Pressure-still | 0.017 | 1.0 |
| Air-blown Californian | 0.023 | 0.95 |
| Air-blown Midcontinent | 0.073 | 0.85 |
| Air-blown Northeast Texas | 0.183 | 0.50 |

[a] Slope of log-log plot of viscosity versus time in hours (nonoxidative hardening).

[b] Slope of log-log plot of shearing stress versus shear rate (measure of non-Newtonian flow).

which compare the complex flow (a value of 1 indicates Newtonian flow) for a series of asphalts with the asphalt aging index resulting from structural hardening. Those asphalts that showed more rapid structuring possessed the greatest degree of non-Newtonian flow behavior.

The relationship between complex flow and structural hardening has considerable potential significance with regard to hardening of pavement mixtures. It is known that as asphalts undergo oxidative aging, their flow behavior becomes more complex or non-Newtonian. Recently, the author and coworkers, while studying oxidation (58), found that two asphalts that had been previously oxidatively aged increased significantly in measured viscosity because of reversible molecular structuring after standing for 2 years; the increase was from 2.5 x $10^4$ to 1.2 x $10^5$ and 1.1 x $10^5$ to 3.0 x $10^6$ Pa•sec. The structural hardening was reversed on heating of the samples. The original unoxidized asphalt showed almost no increase from structural hardening (3.8 x $10^2$ to 4.2 x $10^2$ Pa•sec) on standing for the same length of time. This strongly suggests that the oxidation that takes place during the natural aging of asphalts in pavements significantly increases the rate of structural hardening and that oxidative and structural hardening may be synergistic.

A problem in the determination and quantification of structural hardening is that the structuring is destroyed during the solvent recovery of asphalts from aged pavements and therefore escapes detection during measurement of recovered asphalt properties. Thus, the tendency for an asphalt to harden from structuring, which may be a major contributor to loss of durability and pavement failure, is being virtually ignored in pavement performance considerations by present-day pavement technologists. Brown (82,83), who studied reversible molecular structuring (called by him "steric hardening"), in 1957, approximately two decades after the studies of Traxler and coworkers, noted that "this is not a new discovery, but has had relatively little emphasis." In the last two decades, not much has changed in this regard but the need is still there.

More recently, studies of molecular interactions of asphalts and of asphalt-aggregate interactions have been conducted at higher temperatures (above 130°C) by microcalorimetry (66,85,86). Reversible molecular interactions were shown to be present at temperatures as high as 250°C. Interactions at these high temperatures undoubtedly reflect the disassociation-association of the more stable micellar bodies in asphalt (87). Aggregate surfaces have been shown to promote molecular structuring and immobilization of asphalt molecules in the vicinity of the aggregate surface, which should have considerable effect on bond properties and thus properties of pavement mixtures (66,86,88). A relationship between molecular structuring and the setting characteristics of pavements was proposed by Hveem and coworkers (89) and a cohesiograph test was proposed to measure the setting property. A good correlation was found between the tendency for asphalts to form "tender-mix" pavements and their lack of molecular structuring when in contact with the surface of a standard Ottawa sand aggregate (86). Thus the phenomenon of molecular structuring is important not only to the bulk properties of asphalt but also to the asphalt-aggregate interaction. Both types of structuring will affect the performance and durability of asphalts in pavements. The common practice of evaluating asphalt performance in the absence of the aggregate with which it is to be used leaves unevaluated important criteria for pavement performance.

## SUMMARY AND CONCLUDING COMMENTS

Chemical composition is important in determining the physical properties and performance characteristics of asphalts. The interactions of polar or polarizable chemical functionality, either naturally present or formed on oxidative aging, play a major role in determining asphalt viscosity and related complex flow properties.

Two major factors affecting asphalt durability are (a) the compatibility of the interacting components of asphalt and (b) the resistance to changes resulting from oxidative aging. Both factors are a function of chemical composition, which can vary widely from one asphalt source to another because of inherent differences in crude sources or from processing and blending.

Historically, the study of asphalt chemical composition has been facilitated by the separation of asphalt into component fractions based on the polarity or adsorption characteristics or both of the molecular components present. The component fractions, sometimes called generic fractions, although useful in classifying and characterizing asphalts and to provide simplified mixtures for further study, are still complex mixtures the composition of which is a function of asphalt source. The component fractions are, however, sufficiently unique to identify their particular contribution to the complex flow properties of asphalt. A proper balance of component types is necessary for a durable asphalt.

Because asphalt occurs as a film exposed to atmospheric oxygen in pavements, it rapidly oxidizes in service with the formation of polar, strongly interacting, oxygen-containing chemical functional groups that greatly increase viscosity and alter complex flow properties. This hardening often leads to asphalt embrittlement and ultimately asphalt pavement failure. Not only does the susceptibility to oxidation vary from one asphalt to the other, but the effect of the oxidation products formed on physical properties also varies widely with asphalt source. The sensitivity of the asphalt to the chemical functionality produced on oxidation can be significantly reduced by removing or altering the polar chemical functionality initially present that would otherwise interact with the oxidation products to increase viscosity.

The identification and characterization of the chemical functional types normally present in asphalt or formed on oxidative aging that influence molecular interactions afford a fundamental approach to the chemical compositional factors that determine physical properties, which in turn governs the performance properties of both asphalts and asphalt-aggregate mixtures.

Asphalt physical properties are significantly altered not only by the oxidative formation of polar chemical functional groups but by reversible molecular structuring (also called steric hardening). This latter phenomenon is a slow process that appears to proceed concurrently and synergistically with oxidative aging during the lifetime of the pavement and may be a major factor contributing to asphalt pavement embrittlement in the later stages of pavement service life. Limited data indicate that the complex flow properties of asphalt and the tendency of asphalt to structure are directly related. This suggests possibilities for ways to evaluate this elusive property.

Because asphalt chemical composition can vary widely with asphalt source, and a variety of combinations of asphalt components with varying chemical structures in individual asphalts may produce asphalts that will provide satisfactory service, it seems unlikely to the author that satisfactory chemical composition specifications can be devised for asphalts. Such specifications would likely exclude from use many asphalts that would otherwise perform satisfactorily. Ideally, specifications should define the performance properties desired. Chemical information would be important in producing asphalts that meet the performance criteria.

Composition information is useful in helping to understand asphalt--what makes it behave as it does and what makes one asphalt behave differently from another. With given asphalt sources available, composition information can be used to improve the product through modification with additives, by blending, and so on, or to alter use design procedures to accommodate specific properties. Composition information can be used to match asphalt and aggregate, provide clues as to what modifications are necessary to make an asphalt-aggregate system more serviceable under a given environment, diagnose failures, and provide information needed in taking corrective measures.

As asphalts from new sources are utilized, and as processing and design procedures change, the use of more fundamental information, both chemical and physical, and particularly as related to long-term performance and durability, should provide for product improvement and reduce the number of early or unexpected failures of asphalt products.

It is hoped that this review will bring about a better understanding of the chemical compositional factors that control the properties of asphalt and will assist in providing direction to both research and application leading to improved asphalt products with better performance and durability.

## RESEARCH NEEDS

In the opinion of the author, future research effort on chemical factors that affect asphalt durability should include, as some of the most important, the following interrelated areas.

1. Development of techniques to measure and evaluate the effects of molecular structuring (in both neat asphalt and on the presence of aggregates) on the physical properties of pavements;
2. Determination of the relationships between molecular structuring and complex flow properties;
3. Identification and characterization of the chemical factors that cause and control molecular structuring, including the effects of oxidation;
4. Development and validation of methods that will predict changes in physical properties of asphalts in aged pavements because the properties of aged asphalts, not initial properties, determine the properties affecting durability;
5. Relation of the complex flow properties of asphalt (especially at low temperatures) with changes in chemical functionality resulting from oxidative aging and quantification of relationships between chemical functionality and changes in physical and performance-related properties;
6. Development of relationships between asphalt compatibility, composition, and changes in physical properties on oxidative aging; and
7. Examination of ways to improve asphalt component compatibility and durability by altering molecular interactions by such means as chemical modification, additives, component blending, and so on. This area should be highly rewarding in upgrading the performance of otherwise less durable asphalts.

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# Physical Properties as Related to Asphalt Durability: State of the Art

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ABSTRACT

Asphalt pavements were first constructed in the United States about 1876 with asphalt mined from a lake of native asphalt in Trinidad and fluxed with a petroleum residuum to make an asphalt cement of the desired consistency. As early as 1892, observers became aware that the durability of the asphalt pavements often depended on the asphalt cement in that it must be capable of cementing together the aggregate and it must be elastic and in no way brittle. Domestic asphalt became available around 1900. The engineers and chemists of the time realized that test methods were needed to measure the properties of asphalt and specifications were necessary to prevent the use of inferior or untried materials. Test and evaluation methods that have been used include the following: (a) oven volatilization in thick films, air blowing, and laboratory aging of mixes (tests for evaluating the aged asphalt included penetration, ductility, and softening point); (b) microfilm aging and microviscosity tests; and (c) field aging of pavements and penetration, ductility, and viscosity tests on the recovered asphalt. Of the various methods for testing and evaluating the durability of asphalts, only the thin-film and the rolling thin-film test methods have been adopted as standard by AASHTO and ASTM. Nearly all the states have adopted one of the methods as a means of measuring potential hardening of asphalt during hot-plant mixing. There is a real need for the development of a rational method to predict asphalt durability during service in pavements. The use of tensile and resilient tests should be investigated for this purpose.

The purpose of this paper is to prepare a state-of-the-art report on the use of physical properties of asphalt to evaluate asphalt durability. The literature shows that the first asphalt pavements in the United States were constructed during the 1870s. One of the earliest references concerning asphalt durability was in 1892. The report stated (1,p.25):

> The durability of asphalt pavements depends wholly on the suitability of the asphalt for the purpose. It must be of such a nature as to permanently and thoroughly cement together the sand and limestone powder forming the body of the pavement. It must be elastic, independent of the residuum oil required in making the paving cement and in no degree brittle.

The major source of asphalt available at that time was a native asphalt from a natural lake of asphalt in Trinidad. The asphalt occurs as a solid to semisolid material surface mined from the lake. Excess organic and inorganic material and water were removed and the asphalt was loaded and shipped to points of use. The asphalt was then softened to the desired consistency by adding a fluxing material, which was a residual petroleum product, remaining after the lighter distillate fractions and some heavier distillates had been removed. Early reports showed that the percentage of volatile material in the residuums ranged from 1.4 to 12.3 when the asphalt was heated to 400°F (204°C). Their use as fluxes often resulted in some asphalts that had high losses on heating and rapid and excessive hardening in service.

## EARLIEST TESTS

To determine the amount of loss and hardening, A.W. Dow in 1903 proposed two tests to measure the stability (resistance to hardening) of asphalt exposed to high mixing temperatures or during service in pavements (2).

### Dow Method 1

A 20-gm sample of asphalt was weighed into a glass retort in an air bath and heated to 400°F (204°C) for 30 hr. The loss in weight was determined and the consistency of the residue measured by the penetration machine, which had been developed by H.C. Bowen in 1888. One specification at that time required that the loss on heating should be less than 8 percent and the penetration of the residue more than 75 percent.

### Dow Method 2

A portion of a sand-asphalt mix, in the proportions to be used on the job, was heated in an oven at 300°F (149°C) for 30 min. The asphalt was then extracted from portions of the aged and unaged mixes with carbon disulfide and recovered by distillation. The change in asphalt consistency from heating or aging the mix was determined by the penetrometer. There was no evidence found that Method 2 was used in specifications, but it gave some indication of the relative durability of asphalts supplied at that time. The interesting fact is that the overall procedures developed by Dow before 1900 are similar to extraction and asphalt recovery test methods used today.

The early use of asphalt in pavements was essentially a matter of rule-of-thumb practices. Some mixes resulted in excellent pavements and some were partial or total failures. The chemists and engineers soon realized that specification requirements for asphalts, mixtures, and construction practices were essential to high quality and durability. Thus, during the early 1900s numerous laboratory-accelerated aging tests were used or proposed to assure more uniform and more durable asphalt pavements. The test conditions for heating varied from 212 to 400°F (100 to 204°C) and the time of heating varied from 30 min to 30 hr. The loss in weight and penetration of the residues were usually determined to measure the effect of aging.

### Office of Public Roads and Rural Engineering Method

In 1911 the Office of Public Roads and Rural Engineering of the Department of Agriculture published Bulletin 38, Methods for the Examination of Bituminous Road Materials. Its objective was to present a description of methods used by the Office for the examination of bituminous road materials and in such a form that "with a little practice and proper equipment such examinations may be made by any intelligent person. The various tests have, therefore, been described rather more in detail than would be necessary if they were intended for the use of chemists only, and the illustrations of practically all of the apparatus required have been included." For the record, the authors of the methods were Prevost Hubbard, chemical engineer, and Charles S. Reeve, chemist. Bulletin 38 was revised to show improvements in methods and was published as Bulletin 314 in 1915 (3).

### ASTM Methods

In 1903 an ASTM Committee on Road and Paving Materials was formed to develop test methods and specifications for highway materials. Test methods for volatilization, penetration, and bitumen were developed by the Office of Public Roads and were adopted by ASTM in 1911. In the volatilization test a 20-gm sample was heated for 5 hr at 325°F (163°C) in a tin box 6 cm (2.4 in.) in diameter and 2 cm (0.8 in.) deep. The loss in weight was determined and the consistency of the residue was an optional requirement of that time. To provide a greater depth of sample the method was revised to use a 50-gm sample and a tin box 5.5 cm (2.2 in.) in diameter and 3.5 cm (1.4 in.) deep.

For the asphalt cements produced at that time the adoption of the volatilization and penetration tests provided some degree of control of excessive changes during plant mixing that might be reflected in more durable asphalts. The adoption of the method for bitumen was intended to provide a means for identifying Trinidad asphalt by observing the amount and color of the insoluble ash.

### Specifications

The early specifications were concerned with only a few sources of asphalt, and requirements often were used just to identify or restrict the use of materials from new sources. With the increase in the use of asphalt in highway construction and with the introduction of asphalts from new unproven sources and refining methods, specifications in force could not be depended on to restrict the use of unsatisfactory materials. Standard specifications that were believed to adequately control the quality and serviceability of the early asphalts were subject to considerable questioning. The consumer was confronted with the problem of revising or adding new requirements, often based on limited data, or developing new methods that would assure improved asphalt durability.

During the 1920s the following three national specifications for asphalt cements were published:

1. Federal specifications, adopted in 1925;
2. AASHTO specifications, adopted in 1924, revised in 1926; and
3. ASTM, specifications, adopted in 1922 to 1926, withdrawn in 1939, and reissued in 1947.

Some of the general requirements of asphalt that were related to use or performance were as follows:

1. The federal specifications stipulated that only those asphalts that had been demonstrated by service tests as satisfactory for the intended use would be accepted. The specifications also indicated the type and location of construction and the relative amount of traffic for each of the grades.
2. The AASHTO specifications indicated that the use of each grade depended on the type of road, climate, and traffic.
3. ASTM suggested the type of construction for which each grade would be used.

With minor exceptions the requirements for physical and chemical properties were essentially the same for the three national specifications. The specification tests included:

- Penetration [77°F (25°C)],
- Flash point [°F (°C)],
- Ductility [77°F (25°C)], 5 cm per min,
- Loss at 325°F (163°C), percent,
- Penetration of residue, percent of original,
- Bitumen, solubility in $CS_2$,
- Bitumen, solubility in $CCL_4$.

The federal specifications included requirements for specific gravity, 77°/77°F (25°/25°C) and softening point, °F (°C).

The only requirements in the three specifications that might be indicative of durability were the percentage of loss on heating and penetration of the residue. However, based on a survey of asphalt production in the United States in 1935 the results of percentage of loss and of original penetration were of little value to predict the resistance to change in heating during plant mixing or during service in the pavement.

## STATE OF THE ART IN ASPHALT DURABILITY

The primary objective of this paper is to develop a state-of-the-art report of the use of physical methods to evaluate asphalt durability. The scope of the paper will be limited to test methods and properties of asphalt that are directly or indirectly related to durability and will essentially disregard the influence of aggregates and mix properties, construction practices, environment, and quality assurance. For example, the literature is replete with data showing the influence of air void and asphalt content on asphalt aging in service and their effect on durability.

During the 1930s the then Highway Research Board organized a committee to investigate the relation of asphalt properties to pavement durability. One of the objectives was to acquire information on which to base the need for more rational specifications that were related to pavement performance. To define the problem, the committee collected and studied information on the causes of failures and the reasons for good service behavior. A summary of 91 replies to a questionnaire brought out these facts:

1. Failure or unsatisfactory performance from the use of poor-quality asphalt occurred in all sections of the country.
2. Cracked asphalts appeared to be more troublesome than uncracked asphalts. (Cracked asphalts were produced from petroleum by high-temperature and high-pressure refining methods.)
3. Among the asphalt cements used, the harder grades appeared to be the chief source of unsatisfactory pavement performance.
4. Age hardening and increased brittleness of the asphalts were found to be the changes that most frequently produced the most unfavorable performance.
5. Cracking and raveling appeared to be the principal types of distress attributed to poor-quality asphalts.

The HRB activity as well as the general concern that more information was needed to develop performance-type specifications prompted an accelerated research and development program. Beginning in the 1930s a large number of studies were initiated to develop methods to measure or predict the durability of asphalt cements. One of the most important breakthroughs was the development of a method by Gene Abson in 1933 for recovering the asphalt from mixtures immediately after plant mixing or after periods of extended service in the pavement. Since its development, the recovery test has been used extensively in studies to determine change in asphalts and to relate the changes to asphalt durability. In the following part of this paper the information on a number of research studies or investigations that were conducted to develop physical tests to measure and evaluate durability characteristics of asphalt cements will be summarized.

Numerous attempts were made during the period between the 1900s and the 1980s to devise or develop test methods or procedures that would measure and predict asphalt durability. A review of the literature shows that the studies could be classified as follows.

### Laboratory-Accelerated Tests and Evaluation Methods

In these studies asphalt aging was determined by oven volatilization, by air blowing at high temperatures, or by aging asphalt mixtures and testing the recovered asphalt. In most cases the effects of the aging procedures were evaluated by penetration and ductility. In some instances the changes in asphalt were measured by physical tests on compacted mix specimens. Table 1 gives the data reported, the investigator, the test, and the evaluation method used. The time and temperature of the various tests varied appreciably. Most of the evaluation methods compare the rate of change in properties.

Of the tests listed in Table 1 only the 1/8-in. thin-film oven (TFO) test has been adopted as a standard method for evaluating asphalt durability, particularly from the standpoint of hardening during hot-plant mixing. Extensive studies were made to select the test and specifications before its adoption. Some of the studies using mixtures and recovered asphalt were found to be too complex for routine control.

### Laboratory Microfilm Tests and Evaluation Methods

**TABLE 1 Laboratory Accelerated Test and Evaluation Methods to Determine Asphalt Durability**

| Date | Investigator | Test Method | Evaluation Method |
|---|---|---|---|
| 1903 | Dow *(2)* | 30 hr, 400°F | Change in weight penetration of residue |
| 1903 | Dow *(2)* | Mixture aged for 30 min, 300°F | Recovered asphalt, change in penetration |
| 1937 | Nicholson *(4)* | Air blowing, 15 min 425°F | Penetration, ductility |
| 1937 | Rashig and Doyle *(5)* | Air blowing, 15 min, 400°F | Change in penetration |
| 1937 | Hubbard and Gollumb *(6)* | Mixture, time, and temperature varied | Recovered asphalt, change in penetration |
| 1939 | Lang and Thomas *(7)* | Mixture, oven aging, outdoor exposure | Change in mix properties, abrasion, strength, etc. |
| 1940 | Shattuck *(8)* | Mixture, oven aging 30 min, 325°F | Recovered asphalt, penetration, ductility, soft point |
| 1940 | Lewis and Welborn *(9)* | 1/8-in. film oven test 5 hr, 325°F (TFOT) | Change in weight, penetration, ductility |
| 1946 | Lewis and Halstead *(10)* | 1/8-in. film oven test, 5 hr, 325°F (TFOT) | Change in weight, penetration, ductility |
| 1952 | Pauls and Welborn *(11)* | Mixture, oven aging, 325°F (TFOT) | Compressive strength, recovered asphalt, TFOT residues |

Note: t°F = (t°C ÷ 0.55) + 32. TFOT = thin-film oven test.

During the development of tests to measure and predict durability there was considerable concern with testing the asphalts in relatively thick films such as those used in the TFO test and air-blowing tests listed in Table 1. Thus, beginning in the 1950s several studies were made to develop testing apparatus and to age and test asphalts in microfilm thicknesses.

Several modifications of the microfilm test are shown in Table 2. In general the studies have indicated that the microfilm tests can be used to measure and predict hardening of asphalts under laboratory and field conditions.

**TABLE 2 Laboratory Microfilm and Evaluation Methods to Determine Asphalt Durability**

| Date | Investigator | Test Method | Evaluation Method |
|---|---|---|---|
| 1955 | Griffin et al. *(12)* | Shell microfilm test, 5-micron film, 2 hr, 225°F | Viscosity before and after aging, aging index |
| 1958 | Heithaus and Johnson *(13)* | Road tests, laboratory aging, microfilm test | Recovered asphalts, microfilm aging index |
| 1961 | Traxler *(14)* | TFOT and microfilm, 15-micron film, 2 hr, 225°F | Microviscosity at 77°F compared |
| 1961 | Halstead and Zenewitz *(15)* | TFOT and 15-micron film, 2 hr, 225°F | Microviscosity at 77°F compared |
| 1963 | Hveem et al. *(16)* | Shell microfilm test, modified; 20-micron film, 24 hr at 210°F | Microviscosity at 77°F before and after aging |
| 1963 | Hveem et al. *(17)* | RTFOT and TFOT | Viscosities of RTFOT, TFOT, and recovered asphalts compared |
| 1969 | Schmidt and Santucci *(18)* | RTFOT, 20-micron film, 210°F | Microviscosity of residue |
| 1981 | Kemp and Predoehl *(19)* | Tilt-oven durability test, 168 hr, 235°F | Penetration, 77°F, ductility, 77°F |

Note: t°F = (t°C ÷ 0.55) + 32. TFOT = thin-film oven test, RTFOT = rolling thin-film oven test.

In line with the effort to develop a test that would age asphalts in a film thinner than that in the 1/8-in. TFO test, California developed a rolling thin-film oven (RTFO) test. The test procedure involves heating a 35-gm (±0.5-gm) sample of asphalt at 325°F (163°C) in a special bottle that rotates, causing the asphalt to flow and expose a new surface during rotation. Tests have shown that the hardening effects are comparable to the hardening in the TFO test. The RTFO test has been incorporated into the California specifications and has been adopted by ASTM as a standard.

There have been several modifications of the RTFO test using the thin-film bottle. Some studies have been made to give a thinner film of asphalt in the bottle by first dissolving a specified amount of asphalt in benzene or other solvents, coating the inside of the bottle, and evaporating the solvent during rotation of the bottle. The microfilm is then exposed in the oven at 210°F (99°C) for 48 hr and the change in consistency is measured by viscosity.

More recently, the RTFO test has been modified to heat the bottle with the oven slightly tilted to prevent asphalt build-up. Studies indicate that the tilt-oven asphalt durability test could be used to predict asphalt hardening in hot climates.

Studies by Traxler (14), and by Halstead and Zenewitz (15) compared the aging in 15-micron (0.0006-in.) films heated for 2 hr at 225°F (107°C) with aging by the TFO test. Traxler concluded that for six asphalts, the hardening in a 15-micron film for 2 hr at 225°F (107°C) and the hardening measured by viscosity at 77°F (25°C) on the residue from the TFO test were of the same order.

Halstead and Zenewitz also reported on the hardening measured by an aging index for the 15-micron film and for the residue from the TFO test. All viscosities were determined by a sliding plate viscometer, which is a standard ASTM method, at 77°F (25°C) at a shear rate of 0.05 per sec. For low aging indexes (low hardening rate), there was no significant difference in the results of the two tests. As the resistance to hardening decreased, the increase in aging index for the microfilm residue increased much more rapidly than for the TFO test residue. The authors showed that there was a straight-line correlation between the aging index of the TFO test residue and the percentage of original penetration.

## Field Test and Evaluation Methods to Determine Asphalt Durability

Another source of information for evaluating the durability of asphalt is the correlation of pavement condition with physical properties of the recovered asphalt. The development of the Abson method for recovering asphalt from paving mixtures prompted many of the studies.

Table 3 presents the source of information, the number of pavements or test sections included in each study, and critical properties of the recovered asphalt for most of the studies reported from 1937 to 1975.

The literature search shows that early asphalt pavement construction often used asphalts in the 40 to 60 penetration range. The initial asphalt hardness together with the hardening during hot-plant mixing and in service probably contributed to the cracking problems shown in Table 3.

In 1979 an NCHRP study, Relationship of Asphalt Cement Properties to Pavement Durability (31), concluded that the hardness of asphalt in the pavement is the one property most closely associated with pavement performance and depends on

1. The initial consistency of the asphalt,
2. The susceptibility of the asphalt to hardening during plant mixing, and
3. The rate of hardening of the asphalt in the pavement.

To develop a performance-related specification for asphalt pavement construction, the durability factor of the asphalt must be considered.

TABLE 3 Field Test and Evaluation Methods To Determine Asphalt Durability

| | | | | Recovered Asphalt | |
|---|---|---|---|---|---|
| Date | Investigator | No. and Location of Pavement | Condition | Penetration at 77°F | Ductility at 77°F |
| 1937 | Radar *(20)* | 8, Michigan | Good | 34 | 15 |
| | | | Poor | 13 | 3.2 |
| 1937 | Powers *(21)* | 12, Arizona | Good | 10+ | 10+ |
| | | | Cracked | 10− | 10− |
| 1937 | Rashig and Doyle *(5)* | 30, various states | Good | 25+ | 15+ |
| | | | Poor | 25− | 15− |
| 1937 | Hubbard and Gollumb *(6)* | 19, five states | Sound | 30+ | − |
| | | | Prone to crack | 30− | − |
| | | | Cracked | 20− | − |
| 1939 | Miller et al. *(22)* | 40, various cities | Sound | 25+ | 24+ |
| | | | Prone to crack | 18-25 | 4-24 |
| | | | Cracked | 18− | 4− |
| 1940 | Shattuck *(8)* | 33, Michigan | Very good | 20+ | 50+ |
| | | | Good | 20+ | 25+ |
| | | | Cracked | 20− | 25− |
| 1959 | Parr and Serafin *(23)* | 6 sections, Michigan | No difference in performance after 4 years | | |
| 1967 | Serafin et al. *(24)* | Same as above | No difference in performance after 12 years | | |
| 1959 | Simpson et al. *(25)* | 20 sections, Zaca Wigmore, California | Fatigue cracking | Low[a] | Low |
| 1971 | Vallerga and Halstead *(26)* | 53, 19 states | Variable distress | Variable | Variable |
| 1975 | Zenewitz and Welborn *(27)* | 54, 19 states | Variable distress | Variable | Variable |
| 1967 | Chipperfield and Welch *(28)* | 8 asphalts, France; 8 asphalts, Germany; 124 test sections each | No difference in performance | | |
| 1970 | Chipperfield et al. *(29)* | Same as above | No significant difference in pavement performance attributed to asphalt | | |
| 1968 | Cisco and Brunstrum *(30)* | 12, 12 states | Some pavements cracked | Increase in complex modulus | |

[a] Low viscosity.

## SUMMARY

This development of the state of the art of physical properties as related to asphalt durability shows that there has been great concern with asphalt durability almost since the beginning of asphalt pavement construction. The engineers and chemists have searched for test methods that would predict asphalt durability with a high probability of correlation with pavement performance. They usually were aware that an evaluation method for asphalt durability per se can be negated by external variables resulting from mixture design, including asphalt grade and aggregate type, construction practices, environment, traffic, and quality assurance.

More than 40 years ago the TFO test and later the RTFO test were developed and subsequently adopted by AASHTO, ASTM, and almost all state highway departments and other governmental agencies as specification tests. The significance section of the AASHTO and ASTM standards states, "This method indicates approximate change in properties of asphalt during conventional hot-mixing at about 302 degrees F. (150 degrees C) as indicated by viscosity, penetration or ductility measurements. It yields a residue which approximates the asphalt condition as incorporated in the pavement. If the mixing temperature differs appreciably from the 302 degrees F level, more or less effect on properties will occur."

The TFO tests have served to screen out or predict the behavior of those asphalts that showed excessive change in physical properties when subjected to the high temperatures encountered in hot-plant mix construction. Although the tests predict the properties of the asphalt at the time of construction, they do not provide adequate information on change in properties during service in the pavement. In order to develop performance-related specifications for asphalt pavement, such information is essential. To accomplish this, the following approaches should be investigated:

1. Evaluation of the present TFO tests to determine whether modifications are necessary to conform with current asphalts and construction practices,
2. Investigation of current or new methods that can be used to predict long-term durability of asphalts in pavements, and
3. Investigation of the use of tensile strength and resilient-modulus properties of asphalt paving mixtures to predict asphalt durability during long-term exposure in pavements.

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# Significant Studies on Asphalt Durability: California Experience

**GLENN R. KEMP and GEORGE B. SHERMAN**

ABSTRACT

Some of the key durability studies conducted by the California Department of Transportation since the late 1930s, the conclusions reached, and how the results have been implemented in asphalt specifications are reviewed. A description is given of a recent study in which carefully prepared laboratory briquettes of three divergent types of asphalt and absorptive nonabsorptive aggregates were used. The mixes were compacted using three different void contents and weathered in the field in four different climatic areas. New asphalt tests and specification requirements that will be used in obtaining asphalt for test roads in hot desert areas are described. A summary of the major findings from these studies is also included.

## PREVIOUS ASPHALT DURABILITY STUDIES

Durability studies were under way in the late 1930s. Using the criterion that asphalts hardened under field conditions at the slowest rate were the most durable, an attempt was made to evaluate asphalt products available in California (1). This required new and different test methods because the specifications then in use did not separate hardening during construction operations from the natural rate of hardening during the service life of the pavement under traffic. A test investigated during this early period was the asphalt classification by the Benson method of thin-film studies on microscope slides (2). This study led to the belief that thin films were essential for a durability determination. However, the Benson test did not lend itself well to specification purposes.

In 1939 Lang and Thomas of Minnesota (3) published their durability work using mixes of Ottawa sand and asphalt. They explored three methods of testing these samples:

1. Elongation of a test briquette,
2. Destruction by impact, and
3. An abrasion method that tumbled the briquettes in the Devel testing machine.

From these studies, an abrasion test evolved--the shot abrasion test--that used Ottawa sand and 2 percent asphalt mixtures prepared at 230°F and compacted into the lids of 3-oz ointment tins. The compacted specimens were cured under drying lamps in a special weathering machine in which the temperature was maintained at 140°F. The briquettes were then abraded by a stream of free-falling shot dropped from a prescribed height. The weight loss due to abrasion was determined after various cycles of weathering.

The testing program proved two valuable points: major hardening differences were found between asphalts manufactured from various crude sources and the initial consistency of the asphalt was a major factor in the resistance to abrasion (4). The result of this work showed the durability advantage to be gained by use of the softest practical asphalt consistent with mix stability.

### First Field Test Program

In 1954 and 1955 an experimental project was constructed on a major highway. It was called the Zaca-Wigmore Experimental Test Road and involved field tests of 10 different asphalts, including Arkansas Smackover Asphalt. The test results (5) clearly showed that asphalts manufactured from different sources and by different methods of production can affect the durability under equivalent conditions of traffic and climate. Performance differences between sections constructed in 1955 and 1956 showed that construction differences or foundation conditions or both could also affect asphalt durability.

### Implementation of the Road Test Results

The results of these studies led to new, tighter specifications. The Thin-Film Oven (TFO) test replaced the older loss-on-heating test for estimating asphalt durability. To control temperature susceptibility, the specifications included requirements for penetration at 77°F, penetration ratio, and viscosity at 275°F. After deliberations with city, county, asphalt producers, contractors, and materials engineers from the Pacific Coast states, new asphalt specifications were adopted called the Uniform Pacific Coast Asphalt Specifications.

Because abrasion indicated the difference in performance due to consistency of the asphalt as well as its composition, further research was carried out to determine whether the viscosity change during construction operations could be predicted by laboratory tests before construction. This research (6,7) resulted in the development of the Rolling Thin-Film Oven (RTFO) test (6). This test consists of placing the asphalt into cylindrical bottles and aging the asphalt in an oven at 325°F. The asphalt is rolled and aged for 75 min. The increase in viscosity at 140°F after aging approximates that obtained during the construction process. The actual field increase will vary, however, dependent on the aggregate temperature, time of mixing, and such other variables as time held in storage silos. In spite of these difficulties, the properties of the asphalt after the RTFO test more closely defined the properties of the asphalt in the pavement immediately after construction. This led to the concept of preparing a specification based on the viscosity after the RTFO test.

### Aged-Residue Viscosity-Graded Paving Asphalt Specifications

New specifications were developed to approximate the viscosity of the asphalt as it is placed in the roadway rather than as shipped by the refiner. The test simulates the condition of the asphalt in the pavement during and shortly after construction.

The aged-residue grading system was made possible by the RTFO test, which was a major improvement over the conventional TFO test because the testing time was reduced from 5 hr to 75 min, the amount of asphalt available after the test was more than doubled, and the precision was greatly improved. Multilaboratory precision for the viscosity at 140°F (coefficient of variation) was reduced to 4.2 percent, considerably less than the 11.6 percent for the TFO test. The aged-residue viscosity-graded specifications were adopted on the Pacific Coast in 1973 and by ASTM in 1975.

## LONG-TERM DURABILITY STUDIES

The aged-residue grading system separated out the hardening of asphalt due to construction operations from that occurring in the pavement on long-term aging. The California Department of Transportation (Caltrans) then focused its attention on long-term durability studies. The first approach was to evaluate various tests to define asphalt durability followed by field tests. The results were somewhat inconclusive, however, because of the large number of variables inherent in field test programs. However, this program did show that oxidation is one of the most important detrimental reactions affecting asphalt durability (8).

In order to control or eliminate variabilities encountered in normal construction, it was decided to conduct a series of field weathering projects on carefully prepared laboratory-fabricated test specimens. The research plan was as follows (9).

### Objective

The objective was to determine the relationship between asphalt properties, degree of compaction (voids), aggregate porosity, and weathering under various field climatic conditions using laboratory-prepared test specimens.

### Materials

Asphalt materials included three AR-4000 grade asphalts prepared from three crude sources representing high-, moderate, and low-temperature susceptibility. Two aggregate sources were used, one nonabsorptive and the other a porous, absorptive aggregate.

### Mix Design

The asphalt concrete prepared from the foregoing materials conformed to California type B, 3/4-in. medium grading specifications. The optimum percentage of asphalt, as determined by stability tests, was used with each type of aggregate.

### Fabrication of Test Briquettes

The test specimens were compacted to three void ranges: 3 to 5 percent, 7 to 9 percent, and 10 to 12 percent.

### Laboratory Weathering

The California tilt-oven durability test was used in the laboratory to simulate field weathering of the asphalts used in the briquette study.

### Field Weathering

The laboratory-prepared test briquettes were exposed to the weather in four climatic conditions:

1. High mountain climate with mild dry summers and severe and wet snowy winters; average yearly temperature of 41.6°F; precipitation, 19.7 in.;
2. Coastal climate with mild humid summers and mild wet winters; average yearly temperature of 52.1°F; precipitation, 31.7 in.;
3. Interior valley climate with hot summers and cold wet winters; average daily temperature of 63°F; precipitation, 14.2 in.; and
4. Low desert climate with mild to warm winters and very hot dry summers; average daily temperature of 73°F, precipitation, 5.4 in.

Complete sets of test specimens were weathered at each location for 1, 2, and 4 years.

In the hot, low desert test site, the results from the briquette studies were compared with those from a previous field test project, the Calipatria Test Road. Results from the latter indicate that briquette weathering per unit of time is slightly more severe than actual road weathering conditions in the hot Indio Desert climate. These results indicate that 24 months of briquette weathering is approximately equal to 32 months of road weathering.

High average air temperature (thermal oxidation) is the most significant factor affecting the rate and amount of asphalt hardening. Viscosity at 140°F versus time is shown in Figure 1 and viscosity at 77°F versus time in Figure 2. Void content also contributes to the rate of oxidation. The effect of voids is similar among all asphalts; higher percentages of voids are the most detrimental (see Figure 3). Aggregate porosity also has a significant effect in hot climatic regions (Figure 4).

It appears that the California tilt-oven asphalt durability test could be used to predict asphalt hardening resulting from a 2-year exposure at the hot Indio site. Further, the test could be used to prepare hot-climate asphalt specifications to control field hardening in hot climatic areas.

In addition to improved hot-climate asphalt, it is believed that the following factors will improve asphalt durability:

1. Adherence to compaction specifications to reduce voids;
2. The selective use of asphalts that are most suited to the quality of aggregate available;
3. Avoidance of use of absórptive aggregate, if possible, in hot climates;
4. Use of the softest grade of asphalt consistent with mix curing and stability constraints; and
5. Insulation of the pavement with a cover such as a reflective chip seal, especially in hot climates.

## IMPLEMENTATION OF ASPHALT DURABILITY STUDY

Caltrans will include additional requirements for an AR-4000 grade of asphalt on experimental projects in low desert environments starting in 1984. The additional requirements are given in Table 1. These include penetration at 77°F, viscosity at 140°F, and

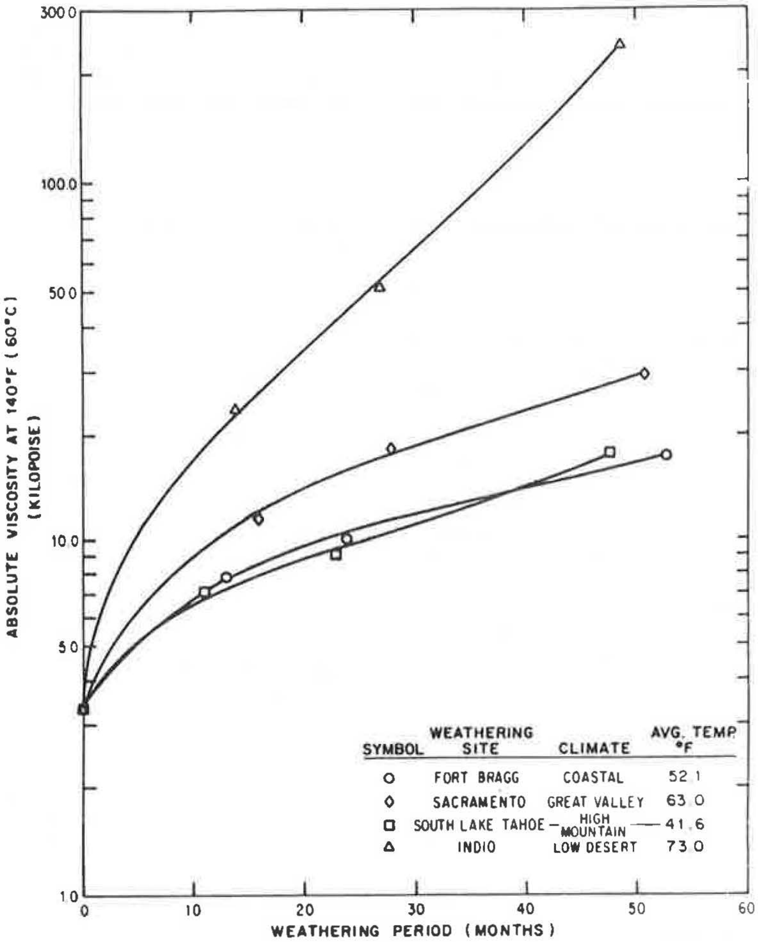

FIGURE 1 Effect of climate on hardening: combined asphalts, aggregates, and voids at 140°F.

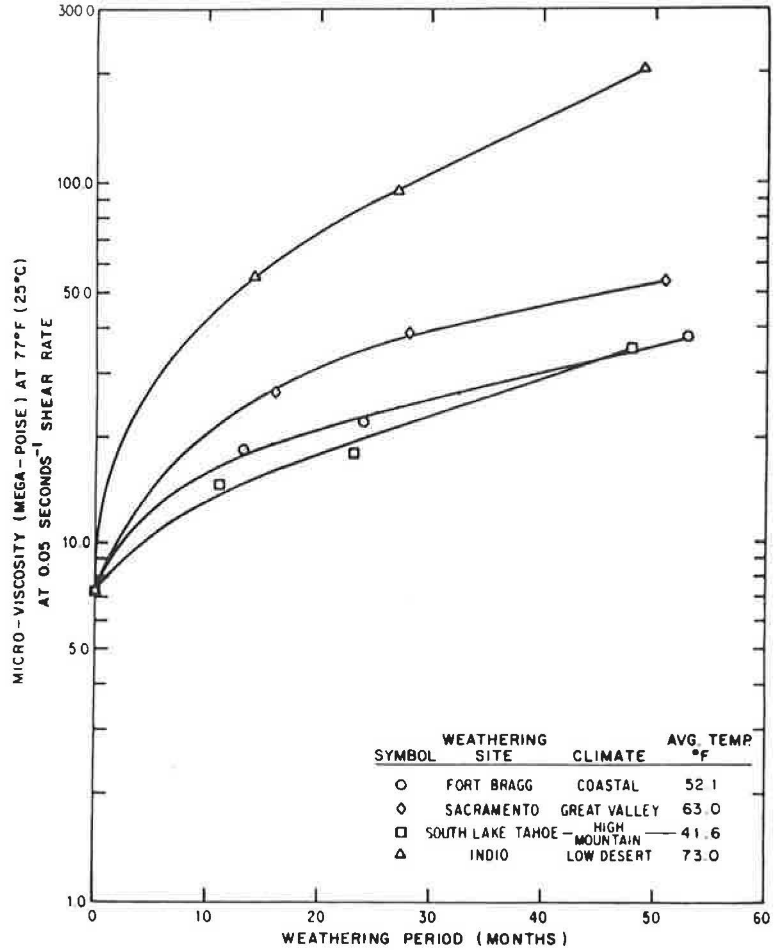

FIGURE 2 Effect of climate on hardening: combined asphalts, aggregates, and voids at 77°F.

ductility after aging in the California tilt-oven durability test.

The California tilt-oven durability test (California test method 374) ages the asphalt for 168 hr (7 days) at a temperature of 232°F. The temperature susceptibility of the aged asphalt is determined by the penetration test at 77°F and asphalt viscosity at 140°F. Temperature susceptibility is important to minimize thermal cracking and rutting of pavements. The penetration-ductility requirements are important durability requirements. The penetration of 77°F indicates the hardness of the material, whereas the ductility test is a measure of asphalt elongation or extension at the break. The ductility requirement prevents separation of asphalt components on aging.

These experimental test sections will be studied to determine the predictive capability of the California tilt-oven durability test on asphalts exposed to severe low desert environments.

## SUMMARY

The major findings are as follows:

1. Thin asphalt films are essential for durability determinations;
2. Initial consistency of the asphalt is a major factor in resistance to abrasion and shows the durability advantage to be gained by using the softest practical asphalt grade consistent with stability;
3. Different sources and methods of manufacture can affect asphalt durability under equivalent conditions of traffic and climate;
4. Construction differences or foundation conditions or both can also affect asphalt durability;
5. Construction operations have an effect on the properties of the asphalt in the pavement after construction;
6. The RTFO test is useful for predicting the viscosity of the asphalt in the pavement during and shortly after construction;
7. The aged-residue viscosity-grading system is useful because it separates the hardening due to construction operations from long-term aging of the asphalt in a pavement structure;
8. Studies of cores have indicated that thermal oxidation is one of the most detrimental factors affecting asphalt durability;
9. Air temperature (thermal oxidation) is an important factor affecting the rate and amount of asphalt hardening;
10. The more voids, the more detrimental the effect on the asphalt;
11. Aggregate porosity is particularly important in hot climates;
12. It appears that the California tilt-oven durability test can be used to predict asphalt hardening in hot climatic areas;
13. Adherence to compaction specification requirements to reduce voids will reduce the rate of asphalt hardening;
14. Use of absorbent aggregates should be avoided whenever possible in hot climatic areas;

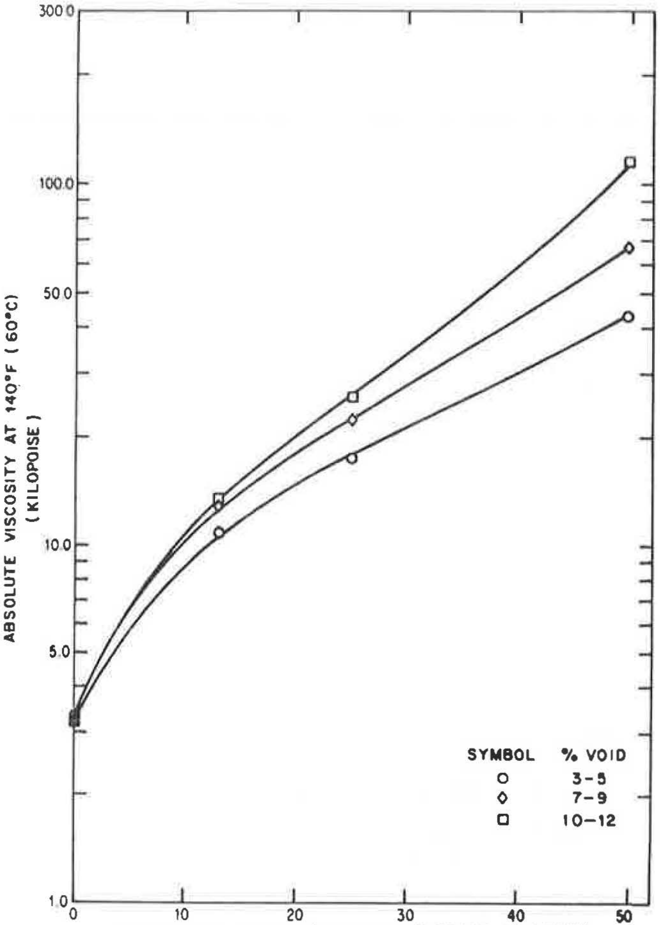

FIGURE 3 Effect of voids on hardening: combined sites, aggregate, and asphalts.

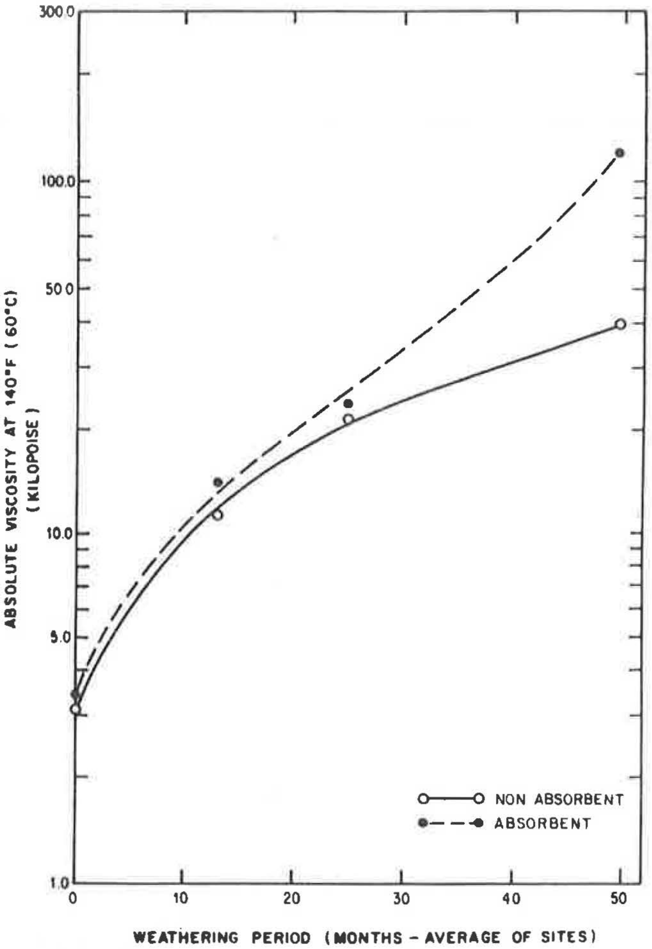

FIGURE 4 Effect of aggregates on hardening: combined sites, voids, and asphalts.

TABLE 1 Additional Specifications for AR-4000 Grade Asphalt

| Test on Residue[a] | AASHTO Test Method | Minimum | Maximum |
|---|---|---|---|
| Penetration at 77°F | T49 | 15 | |
| Absolute viscosity at 140°F (kpoise) | T202 | – | 100 |
| Ductility at 77°F, 5 cm/min (cm) | T51 | 20 | – |

[a] From the California tilt-oven durability test.

15. In high-temperature climates an insulating layer, such as a reflective chip seal, may be desirable; and

16. A new set of requirements for durability has been added to the AR-4000 grade asphalts for use in desert environments; these are now under field study.

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# Significant Studies on Asphalt Durability: Pennsylvania Experience

**PRITHVI S. KANDHAL and WILLIAM C. KOEHLER**

## ABSTRACT

Because a widely accepted laboratory durability test for asphalt does not exist, many agencies including the Pennsylvania Department of Transportation (DOT) have resorted to controlled field experiments to evaluate and characterize those physical properties of the asphalt binder that are associated with aging and their relationship to pavement performance. Three asphalt durability projects undertaken by the Pennsylvania DOT are summarized in this paper: 1961-1962 test pavements, 1964 test pavements, and 1976 test pavements. The study was limited to the evaluation of dense-graded asphaltic concrete wearing courses in which a different asphalt source or type was used. Except for the 1961-1962 test pavements, the only significant variable was the asphalt type. Mix composition and construction techniques were held reasonably constant. After construction, periodical core samples were obtained from these pavements to determine the percentage of air voids and the rheological properties of the aged asphalts. It has been observed that aging of the pavements results in progressively lower penetration and higher viscosity, which exhibit a hyperbolic function with time. However, the accompanying decrease in low-temperature ductility after the penetration falls below 30, and the rate of gain in shear susceptibility relative to increase in viscosity at 77°F, have been found to be important factors that affect the pavement performance. Lower ductility values were associated with a higher incidence of load-associated longitudinal cracking. High stiffness modulus of the asphalt cement at low temperatures and a 20,000-sec loading time contributed to nonload-associated transverse cracking.

Durability of asphaltic concrete has been of considerable interest to the industry ever since asphalt paving became a common practice. A durable asphaltic pavement should be able to support traffic-induced stresses and strains as well as adverse effects of climatic conditions during its service life. Although the durability of asphaltic pavement is affected by other factors such as aggregate characteristics, mix design, and construction practices, most durability studies in the past have been confined to analyzing the properties of aging asphaltic binder as it is this main constituent that contributes to the cohesiveness and adhesiveness of the mixture and thereby affects pavement performance.

Because a widely accepted laboratory durability test for asphalt does not exist, many agencies [including the Pennsylvania Department of Transportation (DOT)] have resorted to controlled field experiments to evaluate and characterize those physical properties of the asphalt binder that are associated with aging and their relationship to pavement performance. Unlike many states that have limited sources of asphalt crudes, Pennsylvania, because of its geographical location, receives paving asphalts manufactured from a wide variety of crude sources such as mid-continent, South America, and the Middle East. Since the 1973 Arab oil embargo, blending of various crudes has also increased significantly. These factors have made the task of evaluating asphalt durability rather complex.

Although many asphalt durability projects have been undertaken by the Pennsylvania DOT since 1960, three projects have been studied in more detail. An attempt has been made to summarize these projects in this paper. More details such as mix composition, construction data, and periodical evaluation data can be obtained from the cited references.

## 1961-1962 TEST PAVEMENTS (1)

Two pavements were completed in October 1961 in Lycoming and Beaver counties, and two were constructed during June 1962 in Washington and Lebanon counties. These four test pavements were asphaltic concrete overlays, consisting of 2-in. binder and 1-in. wearing course, placed on 9-in. portland cement concrete pavements. This study was limited to the evaluation of dense-graded Pennsylvania type ID-2 bituminous wearing course surfaces, each containing a different type of asphalt. Slag aggregate was used in Beaver and Washington counties, whereas limestone aggregate was used in Lycoming and Lebanon counties. All mixtures were designed according to the Marshall method. Physical and chemical properties of the four asphalts used are given in Table 1.

**TABLE 1 Asphalt Properties (1961-1962 pavements)**

| Property | Beaver 1 | Lycoming 2 | Washington 3 | Lebanon 4 |
|---|---|---|---|---|
| Penetration at 77°F, 100 g, 5 sec | 96 | 69 | 76 | 76 |
| Viscosity at 140°F, poises | 2,570 | 4,024 | 3,163 | 3,000 |
| Ductility at 60°F, 5 cm/min, cm | 150+ | 150+ | 150+ | 150+ |
| Ductility at 39.2°F, 5 cm/min, cm | 12.5 | 8.0 | 5.9 | 7.8 |
| Softening point, R & B, °F | 118.0 | 122.0 | 123.2 | 126.4 |
| Flash point, °F | 510 | 505 | 580 | 585 |
| Thin film oven test | | | | |
| Percent loss by weight | 0.135 | 0.368 | 0.040 | 0.060 |
| Percent retained penetration | 58.4 | 57.8 | 59.1 | 61.2 |
| Rostler analysis | | | | |
| Asphaltenes | 26.3 | 26.4 | 19.3 | 22.2 |
| Nitrogen bases | 29.9 | 35.4 | 23.1 | 26.4 |
| First acidaffins | 14.0 | 9.5 | 5.9 | 8.4 |
| Second acidaffins | 22.7 | 20.2 | 38.4 | 31.2 |
| Paraffins | 7.1 | 8.5 | 13.3 | 11.8 |
| Properties of asphalt after mixing in pugmill | | | | |
| Penetration at 77°F, 100 g, 5 sec | 60 | 47 | 67 | 56 |
| Viscosity at 140°F, poises | 7,273 | 15,158 | 3,800 | 5,100 |
| Ductility at 60°F, 5 cm/min, cm | 39 | 19 | 24 | 45 |
| Ductility at 39.2°F, 5 cm/min, cm | 5.3 | 4.2 | 4.7 | 5.4 |

The construction methods used on these four paving jobs were basically similar. The initial or breakdown roller was a 12-ton steel-wheel roller. This was followed by a pneumatic-tire roller with 90-psi contact pressure, and a steel-wheel finishing roller of 10-ton capacity. The average mix temperature was 295°F. The temperatures at the pavers varied from 260° to 290°F with an average temperature of 270°F.

The average daily traffic at the time of construction on these test pavements in Beaver, Lycoming, Washington, and Lebanon counties was 3,850, 6,600, 2,850, and 6,000 vehicles, respectively.

Since construction of the test pavements, periodical core samples were obtained to determine the percentage of air voids in the pavements and the rheological properties of the aged asphalts including ductility at 60°F at 5 cm/min. The pavements were studied for more than 10 years.

### Pavement Air Voids

The decreasing trend of the air voids with time under traffic is shown in Figure 1. All pavements had relatively high air voids when constructed; however, after 10 years all pavements except the Washington county pavement attained air voids of 5 to 6.5 percent. The Washington pavement still had more than 10 percent air voids, which caused excessive asphalt hardening in this test pavement.

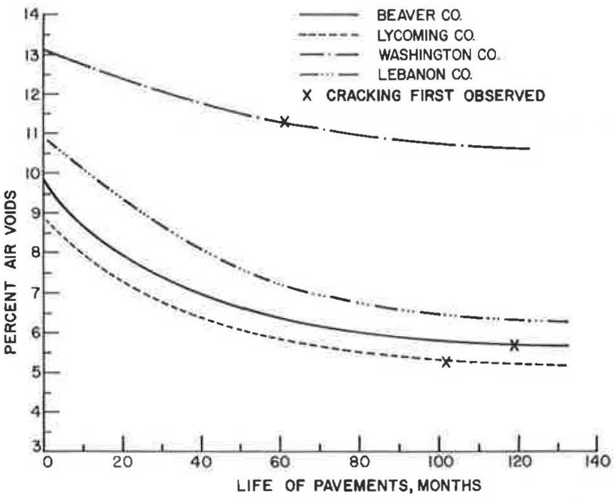

**FIGURE 1** Percentage of air voids versus time in months, 1961-1962 pavements.

### Penetration at 77°F

The decreasing trend of penetration with time is shown in Figure 2. Maximum drop in penetration occurred in Washington pavement due to higher air voids. The Beaver pavement had the highest penetration after 10 years.

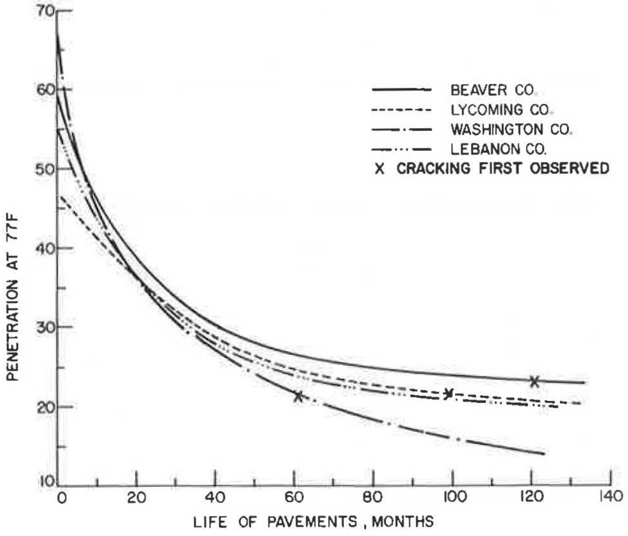

**FIGURE 2** Penetration versus time in months, 1961-1962 pavements.

### Viscosity at 140°F

Figure 3 shows the increase in viscosity at 140°F with time. The Washington pavement had the least viscosity at the time of construction, but after 10 years, it had the highest viscosity due to excessive air voids.

### Ductility at 60°F

Ductility of the recovered asphalts was determined at 60°F at 5 cm/min. The decreasing trend of ductility with time in Beaver, Lycoming, Washington, and Lebanon pavements is shown in Figure 4.

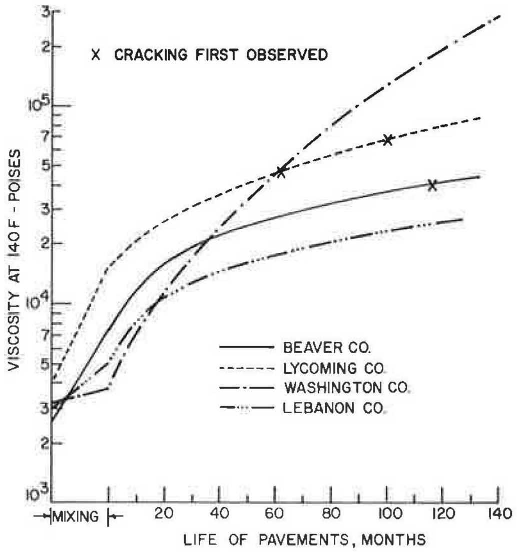

FIGURE 3 Viscosity at 140°F versus time in months, 1961-1962 pavements.

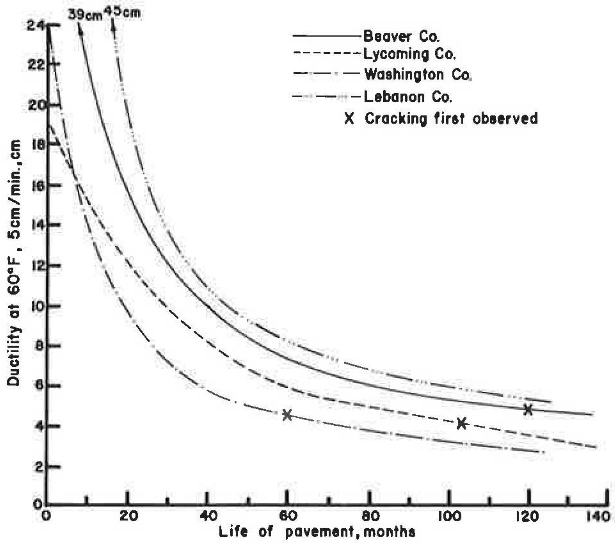

FIGURE 4 Ductility at 60°F versus time in months, 1961-1962 pavements.

### Pavement Performance in Relation to Rheological Properties

When constructed in October 1961 and June 1962 and visually inspected during November 1963, all four test pavements appeared satisfactory. Pavement condition surveys have been conducted annually. Visual evaluation included riding quality, loss of fines, raveling, and cracking. After 10 years' service, the Lebanon pavement was rated the best followed by Beaver, Lycoming, and Washington pavements. The Washington pavement developed extensive cracking covering the entire riding surface after eight years in service. This pavement had to be resurfaced early. The ranking orders of pavement performance, percentage of air voids, penetration at 77°F, viscosity at 140°F, and ductility at 60°F, are given in Table 2. Pavements in Beaver, Lycoming, Washington, and Lebanon counties have been numbered 1, 2, 3, and 4, respectively.

It appears from the ranking orders that the asphalt ductility value obtained at 60°F is a good indicator of the pavement performance. Also, the viscosity at 140°F conforms to the pavement performance rankings; however, later studies have not always confirmed this relationship. It was noted that the pavement condition was satisfactory when ductility at 60°F was maintained above 10 cm. Load-associated cracking began to develop when the ductility value fell in the approximate range of 3 to 5 cm.

TABLE 2 Ranking Orders (1961-1962 pavements)

| Pavement Performance | Pavement Air Voids | Pentration at 77°F | Viscosity at 140°F | Ductility at 60°F, 5 cm/min |
|---|---|---|---|---|
| 3 (poorest) | 3 (highest) | 3 (lowest) | 3 (highest) | 3 (lowest) |
| 2 | 4 | 4 | 2 | 2 |
| 1 | 1 | 2 | 1 | 1 |
| 4 (best) | 2 (lowest) | 1 (highest) | 4 (lowest) | 4 (highest) |

It was observed that the aging of the pavement results in progressively lower penetration and higher viscosity; however, an accompanying decrease in low temperature ductility is an important factor. After the penetration of asphalt drops below 30 due to hardening, the pavements containing asphalt with low ductilities are likely to show poorer service than pavements containing asphalts of the same penetration but with high ductilities. At lower temperatures, the ductility values are lower, more reproducible, and better-defined than ductility values are at higher temperatures such as 77°F.

## 1964 TEST PAVEMENTS

Six test pavements, 3.67 miles long, are located in Clinton County on Legislative Route 219 (US-220) between Mill Hall and Beech Creek, Pennsylvania. The original pavement consisted of 8-in. reinforced concrete 18 to 20 ft wide. This pavement was resurfaced with 2 in. Pennsylvania type ID-2 binder and 1-in. wearing course during October 1964. This study was limited to the evaluation of six experimental sections of the dense-graded wearing course, each containing a different type asphalt. Average daily traffic on this road at the time of construction was 4,200 vehicles.

Properties of the six asphalts used in the project are given in Table 3. Excellent control was maintained throughout the entire project to ensure uniform construction of these six test pavements (2). In this closely controlled research project, the only significant variable was the asphalt type.

Since construction of these pavements, periodical core samples were obtained to determine the percentage of air voids in the pavements and rheological properties of the aged asphalt (3). The last core sampling was done in March 1974, 113 months after construction.

### Test Data

Air voids data are shown in Figure 5. The recovered aged asphalt was tested for viscosity at 77°F (Figure 6) and 140°F (Figure 7). Shear susceptibility (or shear index) values were also determined for the six asphalt cements after increasing periods of aging. The value used in this study is the tangent of the angle of log shear rate versus log viscosity determined with the microviscometer. The relationship between shear susceptibility and viscosity at 77°F is shown in Figure 8. Aging indexes based on viscosity at 77°F (0.05 per sec shear rate) before and after aging, were also determined.

TABLE 3 Asphalt Properties (1964 pavements)

| Property | Asphalt Type 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| A. Original asphalts | | | | | | |
| Viscosity at 39.2°F at 0.05 per sec, poises | $1.19 \times 10^9$ | $2.65 \times 10^8$ | $4.22 \times 10^7$ | $9.50 \times 10^7$ | $1.68 \times 10^8$ | $2.57 \times 10^8$ |
| Viscosity at 77°F at 0.05 per sec, poises | $3.05 \times 10^6$ | $1.06 \times 10^6$ | $4.83 \times 10^5$ | $9.15 \times 10^5$ | $1.32 \times 10^6$ | $1.85 \times 10^6$ |
| Viscosity at 115°F at 0.05 per sec, poises | $2.09 \times 10^4$ | $1.54 \times 10^4$ | $1.15 \times 10^4$ | $1.15 \times 10^4$ | $2.19 \times 10^4$ | $2.80 \times 10^4$ |
| Viscosity at 140°F, poises | 1,613 | 1,544 | 1,447 | 966 | 2,220 | 2,649 |
| Viscosity at 275°F, centistokes | 340 | 343 | 475 | 318 | 509 | 557 |
| Penetration at 39.2°F, 200 g, 5 sec | 9 | 11 | 28 | 19 | 15 | 12 |
| Penetration at 77°F, 100 g, 5 sec | 62 | 92 | 149 | 114 | 94 | 80 |
| Ductility at 39.2°F, 1 cm/min, cm | 14.0 | 53.3 | 101.0 | 23.5 | 68.3 | 21.9 |
| B. After pugmill mixing | | | | | | |
| Penetration at 77°F, 100 g, 5 sec | 36 | 69 | 98 | 66 | 69 | 60 |
| Viscosity at 140°F, poises | 3,645 | 2,505 | 2,971 | 2,078 | 3,463 | 4,770 |
| Viscosity at 77°F, 0.05 per sec, poises | $1.01 \times 10^7$ | $2.01 \times 10^6$ | $1.21 \times 10^6$ | $3.02 \times 10^6$ | $2.77 \times 10^6$ | $3.52 \times 10^6$ |
| Ductility at 39.2°F, 1 cm/min, cm | 4.1 | 11.9 | 42.2 | 7.5 | 24.3 | 7.3 |

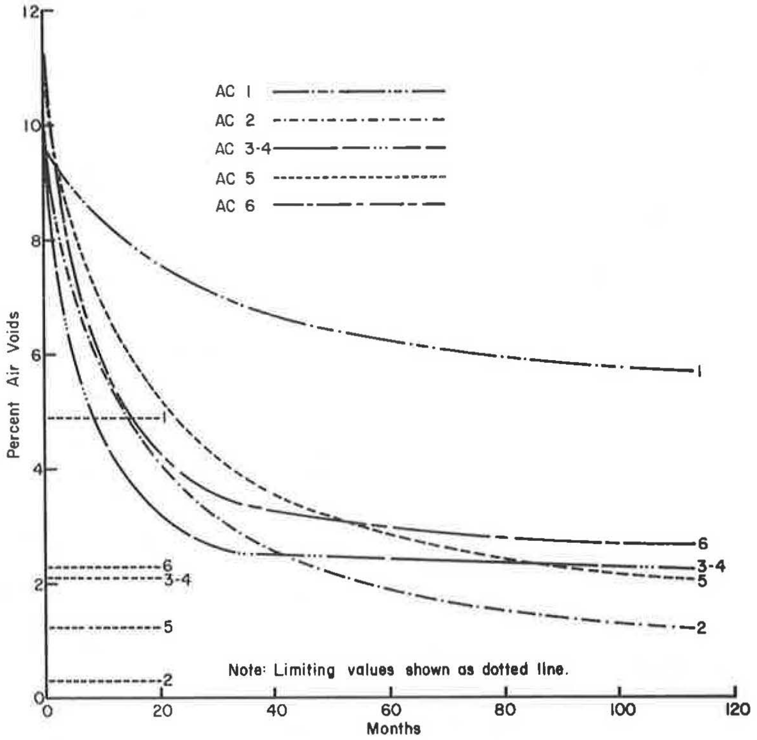

FIGURE 5 Percentage of air voids versus time in months, 1964 pavements.

## Pavement Performance

No differences in texture or color tones were observed between the asphalts when the pavements were visually inspected just after construction and after one year of service. Visual evaluation during April 1967 (after 30 months of service) indicated that the entire road surface was good with the exception of the Asphalt 1 section, which showed some raveling. Although initial air voids in the six pavements when constructed were within the permissible range of Marshall design and control criteria, Asphalt 1 offered maximum resistance to compaction under traffic as will be discussed later.

The rating method suggested by Olson et al. (4) was used as a guideline to accomplish the visual pavement condition survey for evaluating the effects of asphalt aging. Visual evaluation included riding quality, raveling, spalling, loss of matrix, rutting, cracking (transverse, longitudinal, and alligator except reflection cracking), and surface texture. A team of five engineers evaluated these sections during 1971 (after 80 months of service) (2,5,6). The last performance evaluation was conducted in 1974 (after 113 months of service) by eight evaluators (3). The pavement performance ratings are given in Table 4 in ranking order. An ideal pavement according to this performance evaluation would rate 72.

## Conclusions

The following conclusions were drawn from this study (3):

1. Changes in percentage of air voids and asphalt properties, such as viscosity and shear susceptibility, were found to follow the hyperbolic model suggested by Brown et al. (7) and Lee (8). If the changing asphalt properties are determined during the early life of the pavement (2 or 3 years),

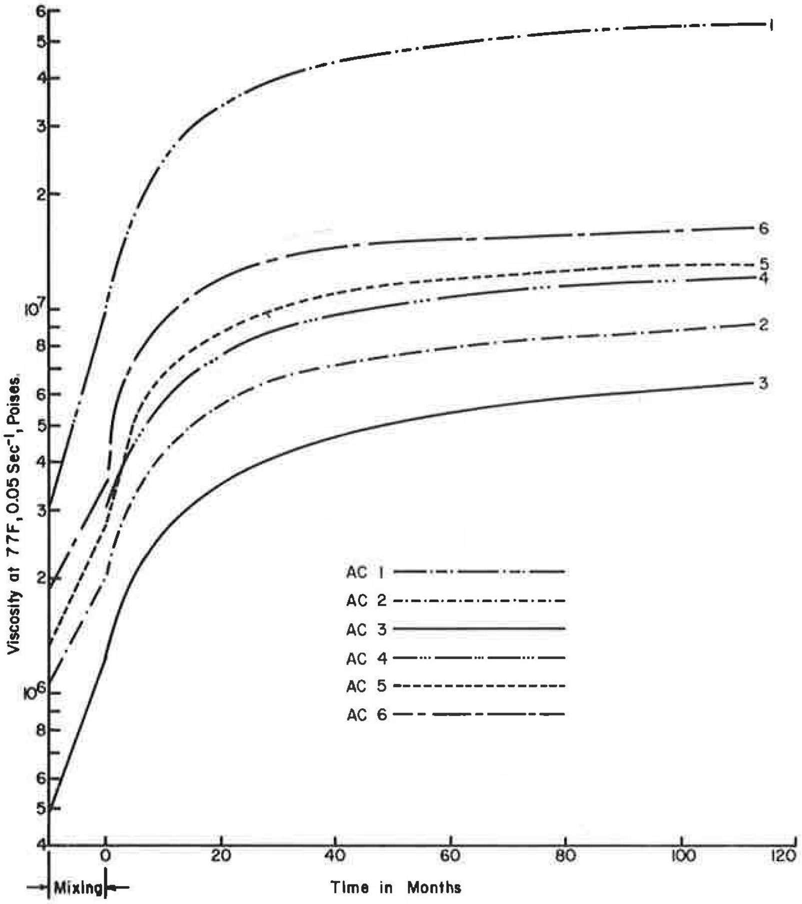

FIGURE 6 Viscosity at 77°F versus time, 1964 pavements.

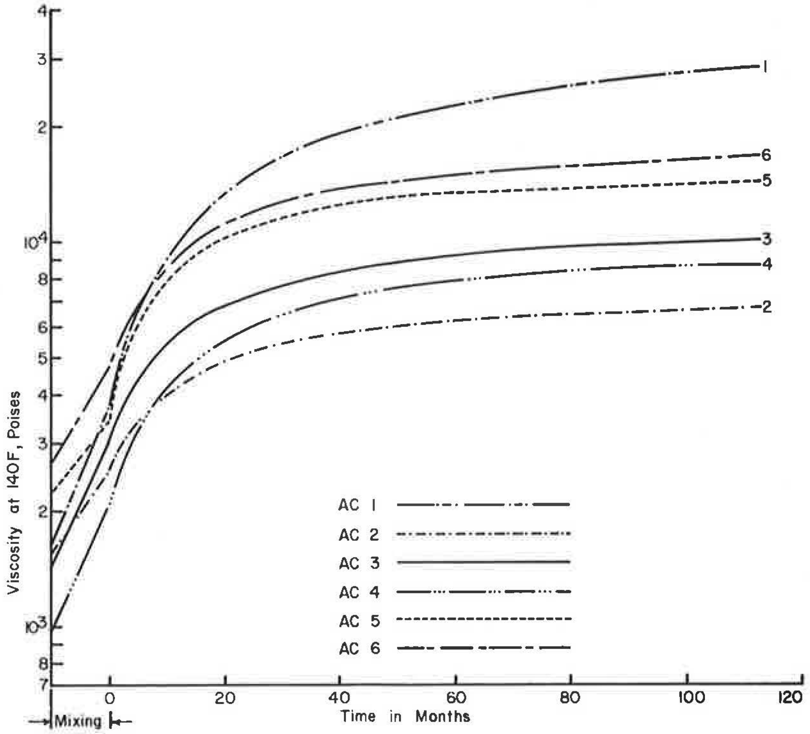

FIGURE 7 Viscosity at 140°F versus time, 1964 pavements.

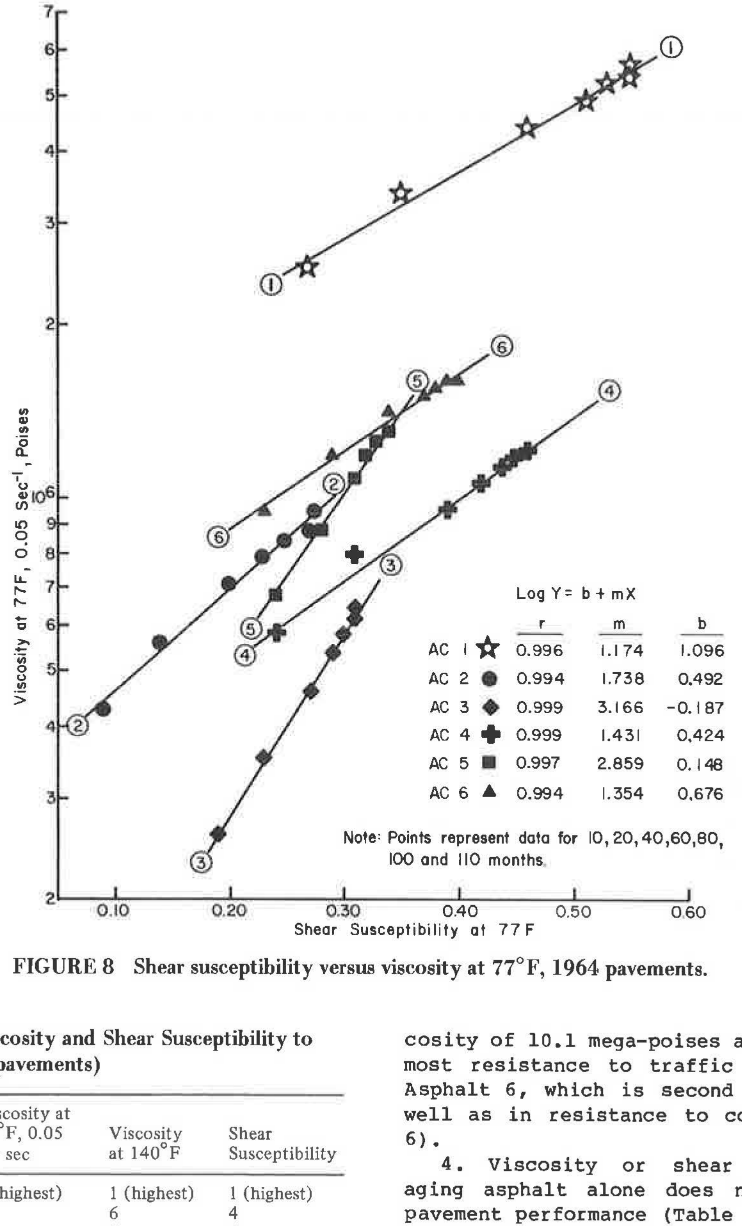

FIGURE 8 Shear susceptibility versus viscosity at 77°F, 1964 pavements.

TABLE 4 Relationship of Viscosity and Shear Susceptibility to Pavement Performance (1964 pavements)

| Test Pavement | Performance Rating (113 months) | Viscosity at 77°F, 0.05 per sec | Viscosity at 140°F | Shear Susceptibility |
|---|---|---|---|---|
| 1 (poorest) | 51.1 | 1 (highest) | 1 (highest) | 1 (highest) |
| 6 | 59.8 | 6 | 6 | 4 |
| 4 | 60.1 | 5 | 5 | 6 |
| 2 | 60.4 | 4 | 3 | 5 |
| 5 | 61.2 | 2 | 4 | 3 |
| 3 (best) | 61.5 | 3 (lowest) | 2 (lowest) | 2 (lowest) |

the changes to be experienced over later years can possibly be calculated from this relationship without waiting out the time.

2. Pavement performance is affected significantly by the extent of air voids in a pavement. The rate of hardening of asphalts is reduced considerably if the pavements can compact under traffic during the first 1.5 to 2 years, so as to have air voids of less than 5 percent.

3. Following optimum compaction during construction, the apparent viscosity at 77°F (after pugmill mixing) appears to control the capability of the pavements to compact further under traffic at ambient temperatures, all other factors affecting the compaction being the same. The percentage of air voids should, therefore, be considered a secondary control factor because it is affected by other primary parameters including the apparent viscosity at 77°F after mixing. Asphalt 1, with the highest viscosity of 10.1 mega-poises after mixing, offered the most resistance to traffic compaction, followed by Asphalt 6, which is second highest in viscosity as well as in resistance to compaction (Figures 5 and 6).

4. Viscosity or shear susceptibility of the aging asphalt alone does not necessarily indicate pavement performance (Table 4). The rate of gain in shear susceptibility relative to increase in viscosity at 77°F (indicated by slope m in Figure 8 and Table 5) appears to be one of the major factors affecting pavement performance. Relatively lower gain in shear susceptibility with the corresponding increase in viscosity is associated with better pavement performance in this study.

5. Asphalt ductility values, determined at 39.2°F before and after pugmill mixing and at 60°F after 113 months in service, appear to be consistent

TABLE 5 Relationship of Slope m (from Figure 8) to Pavement Performance

| Test Pavement | Performance Rating (113 months) | Slope m (Figure 8) |
|---|---|---|
| 1 (poorest) | 51.1 | 1.174 |
| 6 | 59.8 | 1.354 |
| 4 | 60.1 | 1.431 |
| 2 | 60.4 | 1.738 |
| 5 | 61.2 | 2.859 |
| 3 (best) | 61.5 | 3.166 |

with pavement performance (Table 6). Higher ductility values are associated with better pavement performance. It is possible that the ductility test results obtained at lower temperatures reflect indirectly the viscosity-shear susceptibility relationship at these temperatures.

**TABLE 6 Ductility Data (1964 pavements)**

| Asphalt Type | Pavement Performance Rating | Ductility in cm: 39.2°F, 1 cm/min, Original | After Mixing | 60°F, 5 cm/min, After 113 Months |
|---|---|---|---|---|
| 1 (poorest) | 51.1 | 14 | 4.1 | 0 |
| 6 | 59.8 | 21.9 | 7.3 | 8 |
| 4 | 60.1 | 23.5 | 7.5 | 7 |
| 2 | 60.4 | 53.3 | 11.9 | 19 |
| 5 | 61.2 | 68.3 | 24.3 | 19 |
| 3 (best) | 61.5 | 101.0 | 42.2 | 49 |

It should be mentioned that a subsequent study (9) of 20 AC-20 asphalt cements determined a fair correlation between the shear susceptibility and ductility at 60°F of thin-film oven (TFO) residues.

## 1976 TEST PAVEMENTS

This project is located in Elk County (north-central Pennsylvania) on traffic Route 219 just north of Wilcox. Six test pavements, each approximately 2,000 ft long, were constructed in September 1976 using AC-20 asphalt cements from different sources. The research project consisted of 1.5-in. dense graded asphalt concrete resurfacing of the existing structurally sound flexible pavement. Average daily traffic on this two-lane, 20-ft-wide highway was 3,700 vehicles at the time of construction (10). The mix composition and compaction levels were held reasonably constant on all test pavements. The only significant variable is the asphalt type or source.

AC-20 asphalt cements were supplied by five refineries. Asphalts T-1 and T-5 came from the same refinery. Table 7 gives the crude sources, methods of refining, and chemical compositions of the six asphalt cements. The properties of original asphalt cements sampled from the tankers at the bituminous concrete plant are given in Table 8. Asphalt was also recovered from cores taken just after construction; the recovered asphalt properties are given in Table 9.

The most recent cores were obtained in November 1982 (about 6 years after construction) for Abson recovery. The preliminary data on recovered asphalts are given in Table 10.

### Pavement Performance

Periodical performance evaluation of these test pavements has been conducted by a team of 8 to 10 evaluators. The last inspection was made in October 1982. Performance ratings were determined (on a scale of one to ten) by evaluating four factors: loss of fines (matrix), raveling (loss of aggregate 0.25-in. and larger), transverse cracking, and longitudinal cracking. Results of this pavement condition survey and performance ratings are given in Table 11. An ideal pavement according to this performance evaluation would rate 40.

The 1976-1977 winter following the construction of these test pavements was very severe in Pennsylvania. Visual observation of the pavements after that winter revealed that two test pavements (T-1 and T-5) had developed extensive low temperature-associated transverse cracking. The critical temperature data obtained by a nearby thermocouple installation are given by Kandhal (10). Low ambient

**TABLE 7 Crude Sources, Methods of Refining and Chemical Compositions (1976 pavements)**

| Asphalt Type | Crude Sources (%) | Method of Refining | Rostler Analysis[a], %: A | N | $A_1$ | $A_2$ | P | $(A_1+N)/(A_2+P)$ |
|---|---|---|---|---|---|---|---|---|
| T-1 | 49 Sahara, 21 W. Texas, 21 Montana, and 9 Kansas | Vacuum Distillation and propane deasphalting | 8.1 | 9.0 | 39.9 | 30.9 | 12.1 | 1.14 |
| T-2 | 66-2/3 Texas Mid-Continent and 33-1/3 Arabian | Steam Distillation | 22.4 | 17.4 | 24.4 | 24.4 | 11.3 | 1.17 |
| T-3 | 85 Light Arabian and 15 Bachaquero | Vacuum Distillation | 17.0 | 23.2 | 18.8 | 31.0 | 10.0 | 1.02 |
| T-4 | 75 W. Texas Sour and 25 Texas and Louisiana Sour | Vacuum Distillation | 19.4 | 23.1 | 17.0 | 27.7 | 12.8 | 0.99 |
| T-5 | 49 Sahara, 21 W. Texas, 21 Montana, and 9 Kansas | Vacuum Distillation and propane deasphalting | 15.9 | 28.7 | 18.2 | 27.7 | 9.4 | 1.26 |
| T-6 | Blend of Heavy Venezuelan and Middle East Crude | Vacuum Distillation | 10.4 | 25.8 | 19.1 | 25.3 | 19.3 | 1.01 |

[a] A = asphaltense, N = nitrogen bases, $A_1$ = first acidaffins, $A_2$ = second acidaffins, and P = paraffins.

**TABLE 8 Properties of Original AC-20 Asphalt Cements (1976 pavements)**

| Test | Asphalt Type: T-1 | T-2 | T-3 | T-4 | T-5 | T-6 |
|---|---|---|---|---|---|---|
| Penetration at 39.2°F, 100 g, 5 sec | 2.0 | 7.4 | 6.2 | 6.7 | 3.4 | 7.5 |
| Penetration at 60°F, 100 g, 5 sec | 11.2 | 25.0 | 24.5 | 23.0 | 16.0 | 29.0 |
| Penetration at 77°F, 100 g, 5 sec | 42 | 64 | 72 | 65 | 54 | 80 |
| Viscosity at 140°F, poises | 2,710 | 2,284 | 1,764 | 1,705 | 1,759 | 1,982 |
| Viscosity at 275°F, centistokes | 420 | 402 | 393 | 355 | 356 | 406 |
| Softening point (R and B), °F | 123 | 122 | 120 | 122 | 124 | 121 |
| PI (pen/pen) | -2.77 | -0.71 | -1.51 | -1.05 | -2.23 | -1.29 |
| PVN | -1.04 | -0.70 | -0.61 | -0.86 | -1.03 | -0.45 |
| TFO Residue | | | | | | |
| Penetration at 77°F, 100 g, 5 sec | 26 | 38 | 45 | 38 | 37 | 44 |
| Viscosity at 140°F, poises | 5,501 | 6,835 | 3,982 | 4,694 | 3,248 | 5,721 |
| Viscosity at 275°F, centistokes | 563 | 569 | 556 | 527 | 464 | 575 |
| Ductility at 39.2°F, 1 cm/min, cm | 3.5 | 3.5 | 4.6 | 5.2 | 8.6 | 12.4 |
| Ductility at 60°F, 5 cm/min, cm | 11.6 | 7.0 | 95.2 | 12.8 | 90.6 | 33.0 |

**TABLE 9 Properties of Recovered AC-20 Asphalt Cements Just After Construction (1976 pavements)**

| Test | Asphalt Type<br>T-1 | T-2 | T-3 | T-4 | T-5 | T-6 |
|---|---|---|---|---|---|---|
| Penetration at 39.2°F, 100 g, 5 sec | 1.5 | 4.5 | 4.5 | 4.0 | 2.0 | 5.8 |
| Penetration at 60°F, 100 g, 5 sec | 7 | 17 | 16 | 13 | 9 | 20 |
| Penetration at 77°F, 100 g, 5 sec | 24 | 40 | 43 | 34 | 29 | 49 |
| Viscosity at 140°F, poises | 5,525 | 5,729 | 3,789 | 3,829 | 4,019 | 4,611 |
| Viscosity at 275°F, centistokes | 565 | 569 | 526 | 487 | 488 | 576 |
| Softening point (R and B), °F | 134 | 128 | 129 | 128 | 130 | 129 |
| Ductility at 39.2°F, 1 cm/min, cm | 0.2 | 4.6 | 13.9 | 5.9 | 0.6 | 14.9 |
| Ductility at 60°F, 5 cm/min, cm | 8.3 | 7.2 | 48.5 | 10.0 | 15.5 | 34.0 |
| Ductility at 77°F, 5 cm/min, cm | 150+ | 80 | 150+ | 150+ | 150+ | 150+ |
| PI (pen/pen) | -2.24 | -0.80 | -0.99 | -0.65 | -2.03 | -0.64 |
| PVN | -1.13 | -0.68 | -0.72 | -1.03 | -1.16 | -0.47 |

**TABLE 10 Properties of Recovered Asphalts After Six Years (1976 pavements)**

| Test | Asphalt Type<br>T-1 | T-2 | T-3 | T-4 | T-5 | T-6 |
|---|---|---|---|---|---|---|
| Penetration at 77°F, 100 g, 5 sec | 15 | 26 | 35 | 25 | 22 | 35 |
| Viscosity at 140°F, poises | 13,339 | 20,556 | 7,422 | 14,418 | 6,495 | 11,263 |
| Viscosity at 275°F, centistokes | 815 | 858 | 721 | 781 | 583 | 815 |
| Ductility at 60°F, 5 cm/min, cm | 1.2 | 4.5 | 14.0 | 5.0 | 4.0 | 11.2 |

**TABLE 11 Pavement Performance Evaluation (1976 pavements)**

| Observations | Asphalt Type<br>T-1 | T-2 | T-3 | T-4 | T-5 | T-6 |
|---|---|---|---|---|---|---|
| Loss of fines (matrix) | Slight to moderate | Slight | Slight | Slight | Slight | None to slight |
| Raveling (loss of particle .25-inch or larger) | Moderate | Slight | None to slight | Slight | Slight to moderate | Slight |
| Transverse cracking | Very severe | Slight | None | Slight to moderate | Very severe | Slight to moderate |
| Longitudinal cracking | Very severe[a] | Moderate | None to slight | Slight to moderate | Severe[a] | Slight |
| Overall rating number | 18.4 | 29.4 | 36.2 | 30.5 | 20.8 | 31.7 |

[a] Mostly block-cracking resulting from low temperature shrinkage.

temperatures prevailed again at the experimental site during the second (1977-1978) and the third (1978-1979) winters. The temperature data are given by Kandhal (11). A periodical crack survey during this period indicated that test pavements T-1 and T-5 were developing more cracks and the existing cracks appeared to widen after each successive winter (11). Test pavements T-2, T-3, T-4, and T-6 had not developed any significant transverse or longitudinal cracking during the first 3 years. Since then, pavements T-2, T-4, and T-6 have gradually developed cracking to different degrees as indicated in Table 11. Pavement T-3 is rated the best with no transverse cracking and minimal longitudinal cracking.

## Conclusions

Evaluation of these pavements is continuing. However, the following conclusions have been drawn from the data obtained to date:

1. Both direct measurements (11) and indirect methods (10) indicate that the stiffness modulus of the asphaltic concrete is a good indicator of potential low temperature cracking. Asphalts T-1 and T-5, which developed such cracking prematurely, had higher stiffness moduli at low temperatures compared to the remaining four asphalts. Limiting asphaltic concrete stiffness modulus criteria of $10^6$ psi at the lowest pavement temperature for a loading time of 20,000 seconds to minimize low temperature cracking was verified on this project.

2. A maximum permissible stiffness modulus of 275 $kg/cm^2$ for original asphalt cement (at minimum pavement design temperature and 20,000 seconds loading time) was selected to develop AC-20 asphalt cement specifications for cold regions of Pennsylvania to minimize low temperature cracking.

3. Comparison of preliminary data on recovered asphalts after 6 years in service (Table 10) and pavement performance ratings (Table 11) indicates the following: (a) viscosity of the aging asphalt alone does not necessarily correlate with the pavement performance. Temperature-susceptible asphalts T-1 and T-5, although poor performers, do not exhibit comparatively higher viscosities at 140°F; (b) penetration at 77°F of the aging asphalt indicates a general trend: lower penetration associated with poor performance and vice versa. However, it appears to become insensitive and does not discern the relative performance rankings when the value drops below 30 (for example, asphalts T-2, T-3, and T-4); (c) asphalt ductility values, determined at 60°F after 6 years in service, appear to be consistent with the pavement performance. Higher ductility values are associated with better pavement performance, especially the resistance to load-associated longitudinal cracking.

## SUMMARY

Three asphalt durability projects undertaken by the Pennsylvania Department of Transportation in 1961-1962, 1964, and 1976 are discussed briefly in this paper. Aging of the pavements results in progressively lower penetration and higher viscosity, which are a hyperbolic function of time and approach a definite limit with time. However, it has been demonstrated that the accompanying decrease in low-temperature ductility is an important factor. After the penetration of asphalt drops below 30 due to hardening, the pavements containing asphalt with low ductilities are likely to show poorer service than pavements containing asphalts of relatively the same penetration but with high ductilities.

Due to its empirical nature, it is not clearly understood what fundamental property is being measured by the ductility test although a fair correlation has been indicated between the ductility and shear susceptibility of TFO residues at 60°F. The 1964 test pavements showed that the rate of gain in shear susceptibility relative to increase in viscosity at 77°F was an important factor affecting the pavement performance.

Lower ductility values were associated with higher incidence of load-associated longitudinal cracking. High stiffness modulus of the asphalt cement at low temperatures and a 20,000-second loading time contributed to nonload-associated transverse cracking.

Because the asphalt cements from different sources age differently in service after the pugmill mixing, it appears that the tests on TFO residue are not completely reliable to predict the long-term asphalt durability. There is an urgent need to develop an accelerated laboratory aging procedure for asphalt cements that can closely simulate the hardening that takes place in the pavement under certain climatic conditions. The asphalts thus aged can then be tested for the desired durability parameters such as retained ductility at 60°F, and stiffness modulus at low temperatures.

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# Discussion

## Richard L. Davis*

The authors are to be congratulated on a fine, informative paper. In their Figures 2, 3, and 4 they show the relation between penetration, viscosity, and ductility values and time to first cracking observed. While although many factors can contribute to the cracking of pavements, these figures appear to confirm my experience that pavements begin to crack when a certain viscosity or stiffness is reached. The ductility test could serve as a viscometer if stress levels were recorded.

First cracking is usually observed in cooler weather when the viscosity of the asphalt is higher. I look on all three of these methods as attempts to estimate a critical viscosity at which cracking would occur even though this may not have been the intent of the authors. Because all these test methods are run at higher temperatures than the temperatures at which first cracking takes place, there is extrapolation involved.

Extrapolation widens the precision limits on a test method, and this appears to be true in Figures 2, 3, and 4. The greatest variation is shown at 140°F with less at 77° and 60°F. It would have been interesting to have measurements of viscosity at temperatures approaching the lowest that the pavement reached and to have compared these with first cracking.

In viewing Figures 2, 3, and 4, I could not help but wonder if there is any significant difference in the values for penetration, ductility, and viscosity. When one considers the effect on precision of extrapolation, there may not be any real difference in these values. Confidence limits would be helpful in deciding the significance of the observed variation.

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