

INITIAL RESULTS FROM THIN LAYER CHROMATOGRAPHY IN ASPHALT RESEARCH

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A method of thin layer chromatography with flame ionization detection was used for simultaneous fractionation of multiple samples of asphalt. It allowed chemical data to be accumulated more rapidly for correlation with physical behavior than previously established methods of separation. While it failed to establish a unique chemical profile for each asphalt source tested, it indicated relationships of composition with aging, slumping and asphalt-polymer compatibility. It was useful for observing the changes in asphalt shipments from suppliers and the changes occurring during aging. It is proposed as a screening and monitoring tool.

KEYWORDS

Aging, asphalt, asphalt-polymer, flame ionization detection, slumping, thin layer chromatography.

INTRODUCTION

The physical behavior of asphalt is governed by its chemical composition.¹ As researchers gain a better understanding of this relationship, workers within the industry will find it easier to select asphalts for desired characteristics. This paper discusses a method of thin layer chromatography for fractionating asphalt, and presents the initial results of ongoing work on physical properties correlation and asphalt fingerprinting.

Several pathways already exist for asphalt researchers who wish to explore chemical composition. There are procedures yielding anything from five fractions^{2,3} to three fractions.^{4,5} These methods all require precipitation and removal of the solid, high molecular weight asphaltenes from the remaining chemical groups. The other fractions are then separated in solvents, collected, reclaimed by solvent evaporation, and weighed. Such procedures have their advantages, but they are somewhat slow and tedious for building a large data base.

Thin layer chromatography with flame ionization detection (TLC-FID) is a way to simultaneously separate several asphalt samples into their component groups without preliminary precipitation of asphaltenes. The method has been in use for a few decades, or so, in the biomedical field, and has more recently been introduced to the petroleum and asphalt industries.

Very little literature is available on TLC-FID research with asphalts, except material which primarily discusses methods and techniques. Some of the literature may be helpful in initiating and optimizing a procedure.^(6,7,8)

This study separated asphalts into four fractions; these included saturated hydrocarbons (sat), aromatic hydrocarbons (arom), more polar aromatic hydrocarbons sometimes re-

ferred to as resins (polar), and asphaltenes (asph). Samples were obtained from approximately 18 different crude sources with multiple airblown grades in many cases. A few polymer-modified blends were also evaluated.

Initial accelerated weathering tests showed that longevity was related to initial polar aromatic content, asphaltene content, the sum of the polar and aromatic fractions, and the ratio of (arom + polar)/(sat + asph). Aged asphalts had large decreases in aromatic content, large increases in polar aromatic content and significant asphaltene increases. The modified asphalts changed less, overall, than the conventional materials.

Flow resistance of the asphalt samples used in the slump test did not directly correlate with composition. In the slump test, samples were vertically suspended for seven hours in an oven maintained at 71°C (160°F), and the distance of flow was measured. Although the results did not directly correlate, the non-slumping asphalts generally had lower values for the ration (arom + polar)/(sat + asph) than the slumping asphalts.

Initial blending of SBS copolymer with four asphalts indicated that increasing aromatic content was helpful for compatibility.

Chemical profiles established by this method were found to overlap in some cases. Some crude sources were similar and some identical asphalt grades differed when taken from different shipments. The method was useful for general asphalt comparisons and monitoring, but not for unquestionable identification of source.

EXPERIMENTAL

Equipment and Materials

Samples were analyzed on an Iatroscan TH-10 Mark IV TLC-FID Analyzer manufactured by Iatron Laboratories of Tokyo, Japan. It was interfaced with data reduction software through an A/D board installed in an Epson Equity III+ computer. Samples were digested in an ultrasonic bath. Samples were fractionated on Iatron's SIII Chromarods, consisting of quartz rods with sintered glass and silica. Accessories included a sample rack with slots for 10 rods and a special pair of tweezers for installing the rods. The samples were spotted onto the rods with a 2- μ l Hamilton No. 7102-N syringe in a Model No. 3200 Auto Spotter from SES (Heidelberg, West Germany). Spotted rods were solvent-developed in optically pure glass tanks (3.5cm x 3.5cm x 17cm) with ground glass covers. One wall of each tank was lined with a 15cm Whatman No. 40 filter paper disc. Developed rods were dried in a small vacuum oven with the venting valve connected to a nitrogen gas bottle. A glass desiccator was converted into a humidity chamber by placing a saturated

solution of sodium nitrite under the desiccator tray. The analyzer's burner was fed from a gas bottle of pure, zero grade hydrogen, and the drying oven was fed with medical grade nitrogen. All development solvents were HPLC grade. Asphalt aging was done in an Atlas Model Ci35w Xenon Arc Weatherometer.

Sample Preparation

The asphalt was sampled by digging it out of the can with a warm micro spatula. Between samples, the spatula was cleaned by wiping it with a cotton cloth and burning it to a glowing red color in a bunsen burner flame. Sticky asphalts were preheated in a 150°C oven to a consistency at which some of the material could be twirled onto the end of a glass stirring rod. All samples, hard or soft, were placed in clean, preweighted 125-ml erlenmeyer flasks that had been fired in a 482°C furnace overnight. When sample weights of 2 ± 0.001 grams were achieved, 100mls of chloroform was added to each flask. They were closed with ground glass stoppers, and were agitated for one hour at room temperature in an ultrasonic bath.

When evaluating polymer-modified cap sheet asphalt, it was necessary to first determine the percent mineral matter in the top coating, so that the proper unfilled asphalt weight could be obtained. This was accomplished by removing about 5 grams of top coating with a hot scalpel, sonicating it in 100mls of chloroform for an hour, filtering the sample through a Whatman 934AH fiberglass disc in a gooch crucible with suction, and subtracting the dry mineral matter weight from the sample weight. To make filtration easier, the size of the top coating samples was reduced to give a weight of one gram of unfilled asphalt in 50mls of chloroform. The samples were sonicated for an hour, centrifuged for five minutes, and filtered.

The two percent solutions that have been described in this section were prepared only on the day in which they would be tested. The solvent exposure time, from sonication until rod spotting, was held to one-and-a-half to two hours on all samples for the sake of repeatability.

Chromatographic Development

Ten rods were installed in the sample rack with the supplied tweezers. The rod set was used through 40 test repetitions, at which time new rods were installed. While the asphalt samples digested in the chloroform, the rods were cleaned and activated with two blank scans in the analyzer, the first for 60 seconds per rod and the next for 30 seconds. The instrument conditions were set at 160ml/min. of hydrogen flow and 2,000ml/min. of air flow. Three tanks were prepared, each with 100mls of solvent, in the order in which they would be used.

- n-Heptane.
- 80 percent: 20 percent Toluene: Heptane.
- 95 percent: 5 percent Methylene Chloride: Methanol.

One wall of each tank was lined with filter paper and the air space in each was allowed to saturate for at least 45 minutes before using the tanks.

In the start-up procedure, it was difficult to put the same amount of solution on each rod by hand, and repeatability between rods suffered. So, the activated rods were spotted by using a 2- μ l syringe in an automatic spotter set to deliver

1- μ l of solution. The first nine of the rods received three asphalt solutions in triplicate, and the tenth rod always received a blank spotting of chloroform. The spotted rods were dried under nitrogen for three minutes in a 60°C oven and then conditioned at 65 percent relative humidity for ten minutes. This drying and humidifying step was repeated between each solvent bath.

The saturate fraction of the asphalts was developed to 9.5cm in the first bath, and then the rack was removed quickly to avoid overshooting the 10cm mark on the rods where the FID begins its scan. The rods were dried and humidified, and then developed to 5.5cm in the second bath. This placed the aromatic fraction in a position that did not overlap with the saturate and polar peaks on the chromatogram. After drying and humidifying again, the polar aromatic fraction was developed to 2.5cm in the third bath, and asphaltenes were left at the origin of the rods. After the final solvent was oven-dried, the sample rack was taken directly to the analyzer. The humidifying step, which was helpful for retention value of the rods in the solvents, was not needed here.

Alternative solvent systems were available. This system was used after consulting the manufacturer's distributor and referring to M. Ranny's discussion⁹ on separating polar and non-polar components. Peak resolution was generally good with about 33 percent of the tests showing little or no peak overlap between the first three fractions, and about 67 percent of the tests showing 3-6 percent overlap between the third and fourth fractions. The percent composition for the various fractions showed no greater than a two point spread in triplicate runs in 81-90 percent of the tests.

TLC-FID Operation

The sample rack was placed in the frame inside the analyzer, and the rods were burned off with 160ml/min. of hydrogen and 2,000ml/min. of air in the flame for 35 seconds each. The computer printed a chromatogram with peak areas and estimated percentages of composition for the fractions on each rod.

Accelerated Weathering of Asphalts

Six conventional asphalts were selected for the first round to undergo accelerated weathering, and the other samples were saved until machine space would become available. Duplicate panels, of each asphalt, were prepared to a thickness of 0.64mm (.025 in.) by ASTM Method D 1669. The panels were installed in a Xenon arc machine with borosilicate glass filters and maintained at 71°C (160°F) with 0.35 W/m² irradiance. The panels were inspected weekly with a 5,000 volt spark generator using ASTM Method D 1670. The panels were removed when they achieved a level of 10 percent or more surface cracking failure.

Aged samples of cap sheet were obtained containing a blend of SBS copolymer with one of the AC-20 asphalts in the sample set. The modified cap sheet samples had been Xenon-aged at 60°C (140°F) with 0.35 W/m² irradiance, and had been removed from the weathering unit at 30 days, 60 days and 90 days. This cooler temperature kept the cap sheet samples from detaching and sliding away from the metal panel support, and may also have contributed somewhat to reducing the aging failure in the modified samples.

Slumping Tendency of Asphalts for Flashings

Twenty ASTM D 312 Type III grade and nine Type IV grade asphalts were tested for slumping tendency on a vertical incline in a warm oven. Sample sheets were pressed to a thickness of 1.5mm (0.060 in.) and duplicate 51 x 51mm (2 x 2 in.) squares were cut from each. The squares were then laid on a sheet of cardboard so that their bottom edges all aligned with a starting line labeled "0 mm." The squares were gently pressed against the board by hand so that they would stick. A staple was placed in each corner of the upper edge of the squares. The cardboard was suspended vertically in a 71°C oven, and the distance that the lower edge traveled over a seven-hour day was measured.

RESULTS

Asphalt Composition

A total of 84 samples were scanned in the TLC-FID analyzer. This included six samples of flux/AC grade (grade O in Figure 3), 73 mopping asphalts (grades 1-4), and five polymer-modified asphalts (grade 5). Nineteen out of the 73 mopping asphalts were repeat samples shipped six to nine months later than the first set. Since some of the suppliers did not name the crude sources of their materials, the test samples are listed by crude locality with a name in some cases and a region in others. Figure 10 contains the key to sample abbreviations used in this paper.

The samples came from about 18 different crude types or blends. Figure 1 shows the composition of fluxes from four distinct sources with a fifth sample that was a variation of the other Illinois flux. A typical progression of composition profile from grade 1 through 4 within a crude type is shown in Figure 2. Out of 18 sources, four were found whose profiles fell within the standard deviation of another source's profile. The standard deviations for the chemical fractions are shown by asphalt grade in Figure 3. The range of the deviations was from about 0.2-1.7 percent of fractional composition. On that basis, one of the California/Alaskan Type III asphalts was about the same as an Illinois Type III, and a Kansas Type IV resembled an Ohio Type IV. Out of 19 repeat samples, 13 were different from their corresponding sample in the earlier shipment. Some variations are shown in Figure 4.

Fractionations of the five polymer-modified asphalts did not isolate the polymer on the chromatogram, but showed the creation of distinct, new chemical profiles as a result of the polymer's presence (Figure 5). The modified blends were much lower in asphaltene content than the ASTM D 312 Type III and IV asphalts that were tested (Figure 6).

Asphalt-Polymer Compatibility

The asphalt fluxes and paving AC grades that blended successfully with the SBS copolymers had significantly higher aromatic content than Boscan AC-20 paving grade which did not blend well (Figure 1). Under a fluorescent microscope, the Boscan-polymer blend was seen to separate into black sections of asphalt and yellow sections of SBS copolymer instead of remaining together in a swirled network.

Asphalt Durability

The six aged conventional asphalts experienced large reductions in aromatic content, large increases in polar aromatic

content, and significant increases in asphaltene content (Figure 7). Initial asphaltene content and polar aromatic content were related to longevity in accelerated weathering with correlation coefficients of -0.77 and $+0.75$, respectively (Figure 8). The sum of the aromatic and the polar aromatic fractions and the ratio of $(\text{arom} + \text{polar})/(\text{sat} + \text{asph})$ both related to longevity with a coefficient of 0.84 (Figure 9). The aged modified asphalts showed smaller decreases in aromatic content than the conventional asphalt. They also took longer periods of time to attain comparable levels of increase in the polar and asphaltene fractions. The difference in test temperature probably made some contribution to this.

Slumping Tendency

A total of 31 samples were tested for slumping tendency at 71°C (160°F). There was no apparent correlation between the distance of flow and any fraction or ratio. However, when comparing asphalts, only on the basis of whether they slumped or not, the data showed a trend with the ratio of $(\text{arom} + \text{polar})/(\text{sat} + \text{asph})$. All the Type IV asphalts passed the slump test, remaining stable on the cardboard support without movement. Six out of nine of these had ratios below 1.4. Ten Type III asphalts passed, eight of which had ratios below 1.4. Twelve Type III asphalts slumped and failed. Ten of these had ratios from 1.4-2.2.

DISCUSSION

Asphalt Composition

The TLC-FID method was successful at distinguishing most of the crude sources. The results obtained on changes in composition during airblowing were in agreement with previous findings;¹⁰ that the saturate fraction changes very little, that aromatics are lost and that polar aromatics and asphaltenes increase. The method also pointed to variations between single source shipments of the same blowing grade, and showed how polymers affect asphalt composition. I. Corbett's paper on asphalt composition links variation between batches with the cutpoint of the petroleum residuum during distillation.¹¹ This probably contributes to the overlap of chemical profiles obtained when fractionating different sources of asphalt. Another point to consider is the possibility of incomplete separation of chemical groups by this method, and the possible need to further subdivide the polar aromatic fraction¹⁰ which gave the most variable results. TLC-FID test precision is connected with the variations in the production and handling of the sample rods. The rods are not physically identical and have different chemical retention values. They cannot be sample-spotted exactly the same way each time. Peak resolution is also a contributor to precision and may be related to the ratio of the asphalt's chemical components,¹⁰ so that some asphalts or blends produce greater variations than others. It is wise to make no less than three test runs of each asphalt when establishing a chemical profile. This guideline helped achieve standard deviations of 0.2-1.7 percent, but it limits the operator to three triplicate evaluations per sample frame. The operator can increase the number of evaluations per work shift by adding an extra sample rack and using the same solvent baths.

Asphalt-Polymer Compatibility

Work in this area has been limited as yet; but the method showed that the polymer-compatible asphalts were higher in aromatic content than the incompatible sample. Work done in Europe¹² indicates that aromaticity is important for compatibility, and that it must have the proper balance with asphaltene content for the particular loading of polymer. The samples analyzed by TLC-FID all had the same polymer loading, and the Boscan material, which was incompatible, had the lowest ratios of arom / asph and (arom + polar) / asph.

Asphalt Durability

Only a small portion of the fractionated asphalts have been aged so far. Consequently, the curves relating longevity to composition are somewhat sparsely populated. They seem, however, to support earlier work¹⁰ which has linked durability to initial aromatic and resin content, which act respectively as the dispersing medium and the stabilizing agent for asphaltenes.¹ The ratio of (arom + polar)/(sat + asph) has been linked to resistance to hardening by oxidation and volatilization.¹³ The polar and the asphaltene fraction both seem to exert an influence on aging as well. The curves in the results section show an Illinois Type IV asphalt that weathered better than expected for the chemical relationships just described. Additional weathering work may label that data point on the curves as an outlier or may point to other relationships that have been overlooked.

The composition data from the aged asphalts seem to support earlier conclusions¹⁰ that aromatics are converted to asphaltenes during weathering. But, it also appears that some aromatics are distributed to the polar fraction as well. The TLC-FID data show that SBS polymer-modified asphalts begin with higher aromatic and lower asphaltene content than conventional asphalts, giving them a head start on durability. The data from the aged modified asphalts show that they resist compositional change more than the conventional materials. The differences seen between the two polymers indicate that TLC-FID may be useful for comparing the effect of different polymers on durability.

Slumping Tendency

While the numerical measurements of slumping tendency did not correlate well with composition, slumping asphalts tended to have higher values for the ratio of (arom + polar) / (sat + asph) than the non-slumping asphalts. This implies that the chemical relationship which contributed to durability may work adversely for flow resistance. Data taken by Knowles et al¹⁰ links the aging-resistant combination of aromatic and polar content with temperature susceptibility. Temperature susceptibility allows cracks formed during aging to heal. This ability could contribute to asphalt flow on a vertical incline.

CONCLUSIONS

Asphalt fractionations can be performed by the TLC-FID method with standard deviations of 0.2–1.7 percent of composition when samples are run in triplicate. The number of simultaneous evaluations can be multiplied by adding additional racks to the solvent baths.

TLC-FID is a useful tool for the study of aging and of the effect of polymer addition on asphalts. Initial results indi-

cate a correlation between longevity and the polar fraction, the asphaltene fraction, the sum of the aromatic and polar fractions, and the ratio of (arom + polar) / (sat + asph). Initial results indicate that SBS polymer compatibility is related to the ratio of aromatics to asphaltenes. TLC-FID may also be useful in the study of relationships of other physical properties, such as flow resistance to asphalt composition. Initial results indicate that higher values of (arom + polar) / (sat + asph) contribute to slumping tendency.

TLC-FID is a useful tool for comparing different asphalts, monitoring changes during airblowing and aging, and observing variations between shipments. Additional work is needed in correlating composition with physical properties, in creating chemical standards for comparing results between different laboratories, and in deciding the usefulness of the method in industry specifications.

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Sample	% Sat	% Arom	% Polar	% Asphalt
CALANS FLUX	13.5	43.8	26.9	15.9
ILL A AC-20	6.7	37.4	36.8	19.1
ILL B AC-20	6.6	39.4	33.7	20.3
ANS FLUX	15.3	51.2	22.3	11.2
BOSCAN AC-20	8.8	32.1	37.9	21.2

Figure 1 Composition of fluxes and paving asphalt cements.

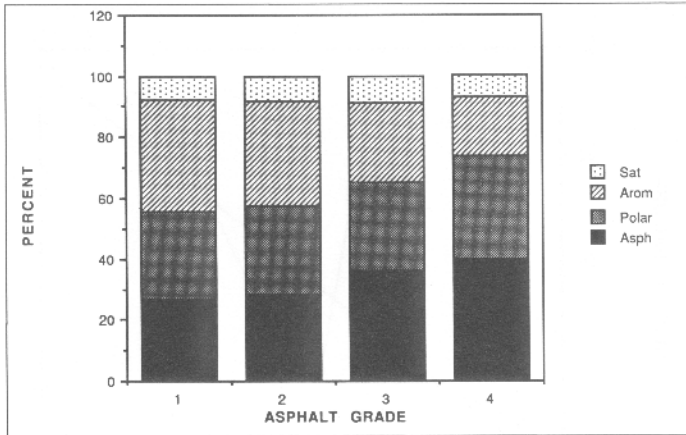


Figure 2 Composition of asphalts blown from Alabama crude.

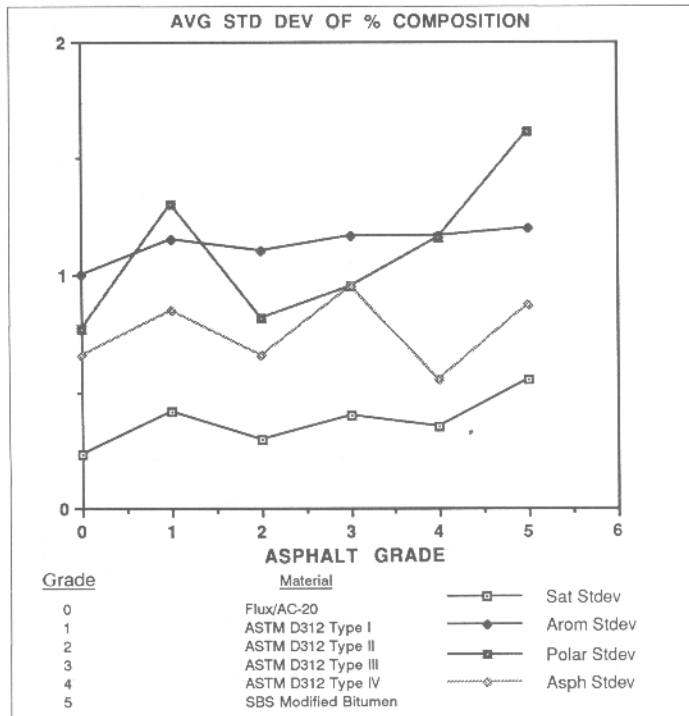


Figure 3 Test precision vs. asphalt grade.

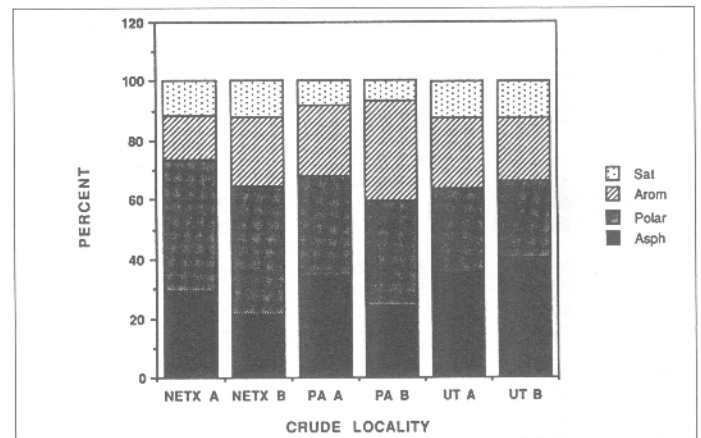
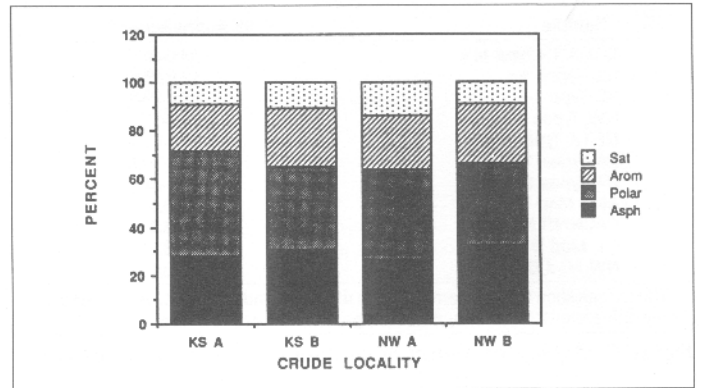


Figure 4 Variations between Type III batches.

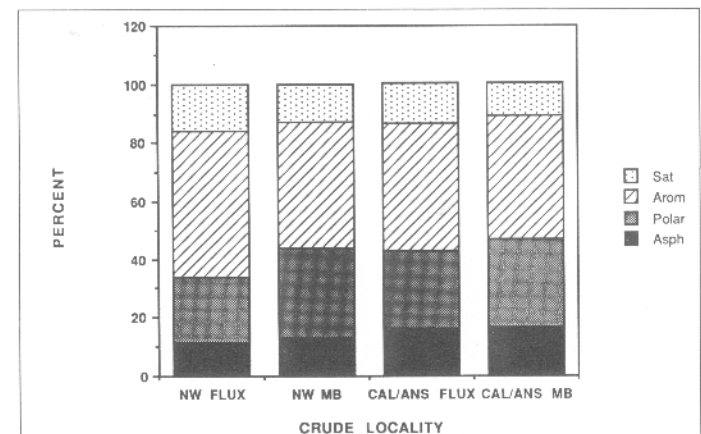
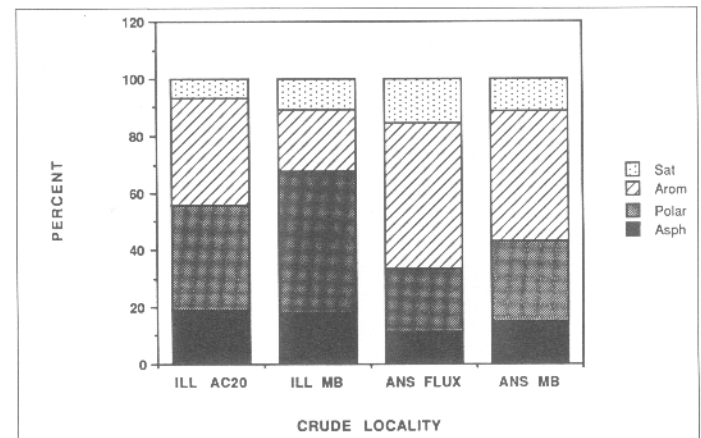


Figure 5 Modified vs. base asphalt composition.

Sample	% Asphaltenes*
CAL/ANS Type III's	24.6-37.5
ILL Types 1-4	21.6-27.6
KS Type 1-4	23.4-34.8
NW Types 3-4	22.7-32.3
NETX Types 1-4	24.3-32.4
PA Types 1-4	24.2-34.5
UT Types 3-4	35.6-41.1
ANS Mod Bit	15.0
CAL/ANS Mod Bit	16.8
ILL Mod Bit	18.2
NW Mod Bit	13.1

*The ranges shown below correspond to minimum and maximum values obtained from the entire locality sample set, regardless of asphalt type.

Figure 6 Asphaltene content of modified and conventional asphalt.

		Conventional	SBS Poly 1	SBS Poly 2
Sat:	30 days	-0.2 to -3.2	—	-1.3
	40 days	-0.1 to -2.2	—	—
	60 days	—	-2.8	-1.4
	90 days	—	-2.1	-1.4
Arom:	30 days	-11.3 to -16.7	—	-5.7
	40 days	-11.9 to -16.7	—	—
	60 days	—	-5.3	-6.2
	90 days	—	-5.3	-9.9
Polar:	30 days	6.5 to 10.4	—	4.1
	40 days	5.7 to 13.9	—	—
	60 days	—	11.2	5.9
	90 days	—	10.6	6.2
Asph:	30 days	4.0 to 8.8	—	4.1
	40 days	1.8 to 6.3	—	—
	60 days	—	1.4	2.6
	90 days	—	0.8	6.3

*A range of composition change is given for multiple sample testing.

Figure 7 Changes in composition* with asphalt aging.

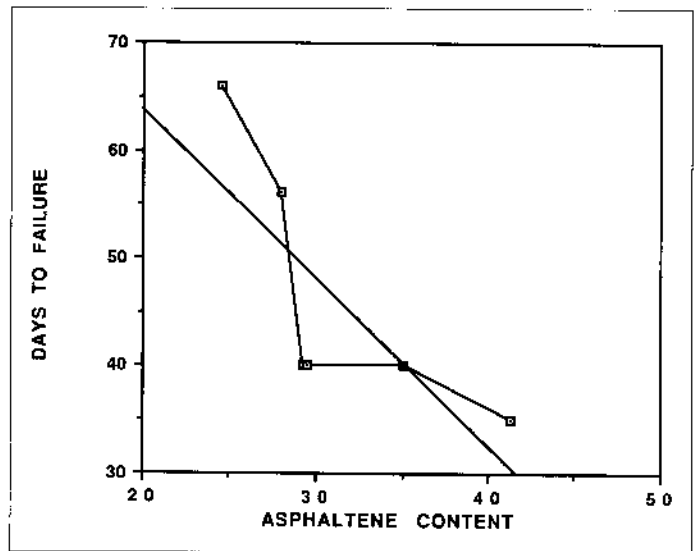
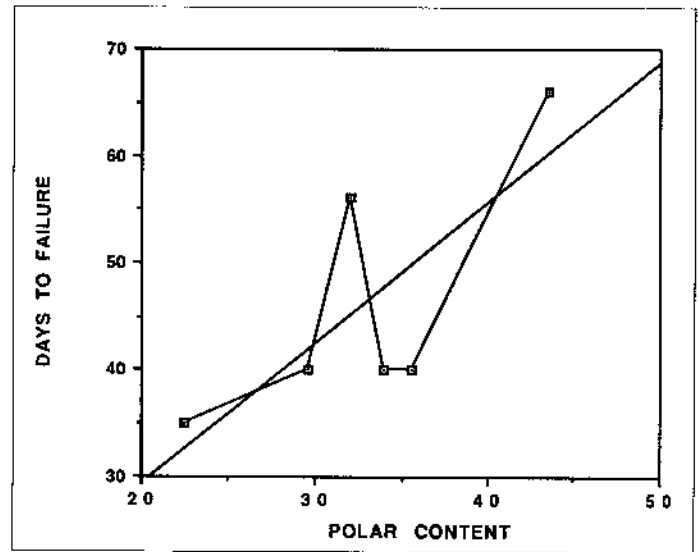


Figure 8 Longevity vs. composition (accelerated weathering).

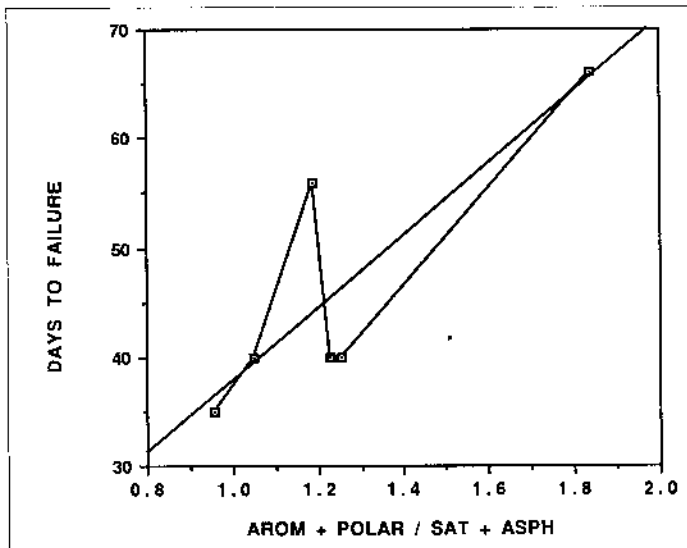
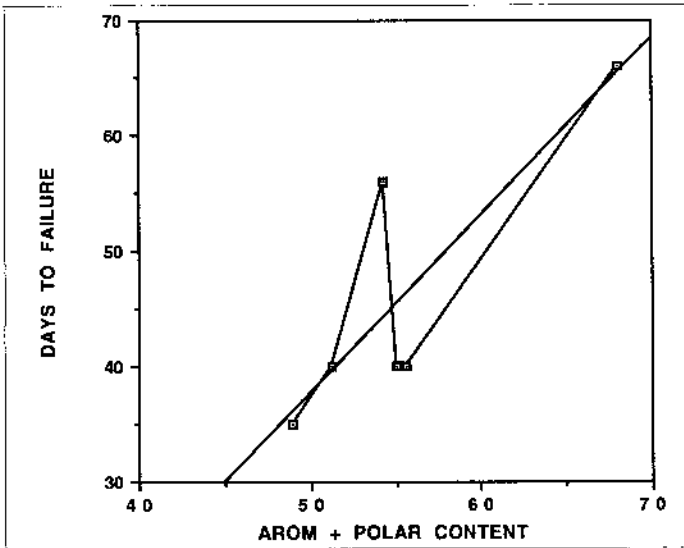


Figure 9 Longevity vs. composition (accelerated weathering).

AC-20	Paving Asphalt Cement (2000 P Viscosity @ 140°F)
ANS	Alaskan North Slope
Boscan	Boscan Venezuelan AC-20
CAL	California
ILL A AC-20	Illinois Blend "A" AC-20
ILL B AC-20	Illinois Blend "B" AC-20
KS	Kansas
MB	Modified Bitumen
NW	Northwest
NETX	Northeast Texas
PA	Pennsylvania
UT	Utah

Figure 10 Key to sample abbreviations.