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16. Abstract

Reliable analytical methods using gel permeation chromatography (GPC) and Fourier transform infrared (FT-IR) were developed to identify the changes that occur in asphalt due to oxidation, aging and solvent hardening. This represents a major breakthrough since the methods appear to accurately reflect the changes in composition and should permit the development of an accurate laboratory aging procedure. These methods have also led to the discovery that existing ASTM procedures for extraction and recovery of asphalt fail in three ways. Highly improved methods have been developed.

Numerous tank, hot-mix and roadway samples were collected and analyzed. The results demonstrate a dramatic increase in oxidation and aging with increased pavement voids. Thus, voids need to be as low as possible to slow oxidation and aging to the maximum extent. The increase in carbonyl compounds formed during aging correlated well with voids, viscosity and penetration. The results also indicate that TFOT and RTFOT aging tests do not reproduce the chemical changes which occur in the hot-mix process. A high pressure oxygen apparatus has been designed and constructed to study asphalt aging in the hot-mix process and on the roadway.

The results from this study clearly demonstrate that major progress has been made in correlating chemical and physical properties with performance. The analytical methods, extensive analytical results and numerous test sections established around the state will serve as an excellent platform for further work to relate properties to performance and to develop superior asphalts.

17. Key Words
Asphalt binders, gel permeation chromatography, infrared, asphalt oxidation and aging, asphalt extraction and recovery, hot-mix pavements, metals in asphalts

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DEVELOPMENT OF GEL PERMEATION CHROMATOGRAPHY, INFRARED, AND OTHER TESTS TO CHARACTERIZE ASPHALT CEMENTS AND CORRELATE WITH FIELD PERFORMANCE

VOLUME I

by

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METRIC (SI*) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
in	inches	2.54	millimetres	mm
ft	feet	0.3048	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
in²	square inches	645.2	millimetres squared	mm²
ft²	square feet	0.0929	metres squared	m²
yd²	square yards	0.836	metres squared	m²
mi²	square miles	2.59	kilometres squared	km²
ac	acres	0.395	hectares	ha

MASS (weight)

Symbol	When You Know	Multiply By	To Find	Symbol
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

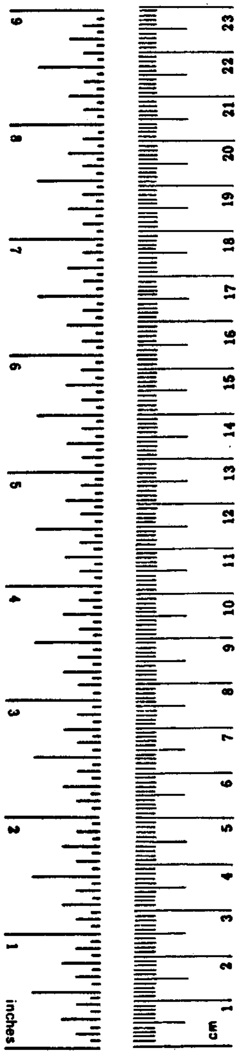
VOLUME

Symbol	When You Know	Multiply By	To Find	Symbol
fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	litres	L
ft³	cubic feet	0.0328	metres cubed	m³
yd³	cubic yards	0.0765	metres cubed	m³

NOTE: Volumes greater than 1000 L shall be shown in m³.

TEMPERATURE (exact)

Symbol	When You Know	Multiply By	To Find	Symbol
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C



APPROXIMATE CONVERSIONS TO SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
mm²	millimetres squared	0.0016	square inches	in²
m²	metres squared	10.764	square feet	ft²
km²	kilometres squared	0.39	square miles	mi²
ha	hectores (10 000 m²)	2.53	acres	ac

MASS (weight)

Symbol	When You Know	Multiply By	To Find	Symbol
g	grams	0.0353	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams (1 000 kg)	1.103	short tons	T

VOLUME

Symbol	When You Know	Multiply By	To Find	Symbol
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m³	metres cubed	35.315	cubic feet	ft³
m³	metres cubed	1.308	cubic yards	yd³

TEMPERATURE (exact)

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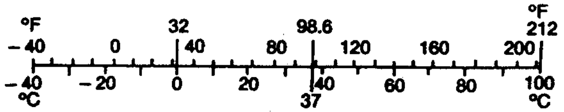

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* SI is the symbol for the International System of Measurements

SUMMARY

During this study, reliable analytical methods using gel permeation chromatography (GPC), Fourier transform-infrared spectrometry (FT-IR) and other techniques were developed to characterize asphalts. The GPC methods have proven invaluable in identifying the changes that occur in asphalt due to oxidation, aging and solvent hardening and in measuring the residual solvent left in asphalt extracted from cores. The FT-IR methods allow a quantitative measure of the production of carbonyl, sulfoxide and other oxidized species which are formed during aging. Based on many tank, roadway and hot-mix samples, the GPC and FT-IR analyses appear to accurately reflect the changes in asphalt composition that occur during aging. This represents a major breakthrough since the GPC and FT-IR methods developed in this study should permit the development of an accurate laboratory aging procedure and should greatly facilitate further work relating asphalt properties to performance.

A major portion of the work in this study has been to analyze and quantify the changes that occur during the hot-mix process and on the roadway. Numerous hot-mix and pavement samples from the Study 287 test sections and other roadways of varying ages around the state were collected and analyzed. In addition to GPC and FT-IR, other analyses including Corbett fractionation, Heithaus test, viscosity, penetration, aging tests and trace metals were performed on an extended number of asphalts. The results clearly demonstrate a dramatic increase in oxidation and aging with increased voids in the pavements. Thus, voids in asphalt pavements need to be carefully maintained as low as possible (without flushing and plastic flow) so as to slow oxidation and aging to the maximum extent. In general, the increase in carbonyl compounds formed on oxidation and aging were found to correlate well with pavement voids, viscosity and penetration. The high voids in the Study 287 test sections at Dickens and Dumas have caused extensive oxidation, hardening and aging. The GPC and FT-IR analyses appear to accurately reflect the changes that occur in asphalt composition during aging.

The results from the tank and hot-mix analyses indicate that the thin film

oven (TFOT) and rolling thin film oven (RTFOT) tests produce essentially the same aging at the times specified in the ASTM procedures with respect to viscosity, penetration, GPC and FT-IR. However, they do not represent the chemical changes which occur in the hot-mix process. Furthermore, they do not agree with one another at extended test times. A high pressure oxygen apparatus has been designed and constructed to study asphalt aging in the hot-mix process and on the roadway. Due to the time required to develop the GPC and FT-IR analytical methods to measure the changes that occur during aging, sufficient time was not available to conduct tests using the high pressure oxygen apparatus.

The GPC and FT-IR analytical methods developed in this study have also led to the discovery that the existing ASTM procedures for extraction and recovery of asphalt from cores generally fail in three ways: not all of the asphalt is extracted from the aggregate, solvent is frequently left in the recovered asphalt, and the solvent causes hardening of the asphalt. Because extraction and recovery are critical to this and all studies of recovered asphalt, a major digression was necessary. Improved methods were developed by making several modifications to the ASTM methods.

The results from this study clearly demonstrate that major progress has been made in correlating chemical and physical properties with performance. The analytical methods, extensive analytical results and numerous test sections established around the state will serve as an excellent platform for further work to relate properties to performance and to develop superior asphalts.

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IMPLEMENTATION

This study has produced numerous results which may be implemented. Current ASTM methods D1856 and D2172 for extraction and recovery of asphalts from cores have been shown to leave as much as 2% of the asphalt on the aggregate during extraction and to leave solvent in the asphalt, thereby lowering the viscosity by as much as 40%. Highly improved methods for extraction and recovery have been developed by making several modifications to the ASTM methods.

Analytical methods using gel permeation chromatography (GPC) and Fourier transform-infrared (FT-IR) analysis have been developed to monitor the oxidation which occurs through the hot mix plant and during aging on the roadway. These methods have been used along with the Study 287 and other test sections to:

1. Demonstrate the dramatic effect of voids on oxidation and aging,
2. Demonstrate that voids in asphalt pavements need to be as low as possible without flushing and plastic flow to slow oxidation and aging to the maximum extent,
3. Correlate asphalt aging as indicated by carbonyl formation to voids, viscosity and penetration, and
4. Show that the rolling thin film oven (RTFOT) and thin film oven (TFOT) tests produce the same results at the specified times and that neither reflect the aging and oxidation which occurs in the hot-mix process.

Based on the results from this study and others, voids in asphalt pavements have an overwhelming effect on the oxidation and aging that occurs and should be reduced and more carefully controlled. This should be immediately implemented across the state. The results from this study clearly demonstrate that major progress has been made in correlating asphalt chemical and physical properties with performance and that the analytical procedures and test sections have been established to serve as a platform for further work to relate physical and chemical tests and properties to pavement performance.

DISCLAIMER

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration or the Texas State Department of Highways and Public Transportation. This report does not constitute a standard, specification, or regulation.

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SECTION I

LITERATURE SURVEYS

The literature surveys that follow deal with three problem areas encountered in this study and presented in later sections of this report and with asphalt compatibility which is an important property affecting asphalt performance.

Work in Study 458 presented in Chapter IV-2 casts doubt on the adequacy of the commonly used oven tests to predict hot-mix plant aging. The first survey presented in Chapter I-1 examines the development and use of these tests and how they relate to hot-mix aging. The mechanism of aging is also investigated.

Work in Study 458 presented in Section III has firmly established that standard ASTM procedures for extraction and recovery fail in several ways, especially when properties of the recovered asphalt are to be examined. Extraction methods often do not remove all the asphalt from the aggregate, the asphalt hardens while in solution, and recovery procedures often leave solvent in the asphalt. In Chapter I-2, the development and use of various procedures is surveyed, and prior evidence in the literature that the procedures are inadequate is examined.

Results from the Dumas, Dickens and Lufkin test sections presented in Chapter IV-1 show the critical effect that air voids have on asphalt aging. Though this has been recognized for years, it continues to be a problem. Literature reports of studies on the effects of air voids are reviewed in Chapter I-3, and some history concerning the recognition of the problem is given.

Asphalt compatibility is an important property affecting asphalt performance, and it has not received as much attention as some other properties. The significance of compatibility and tests for measuring it are reviewed in Chapter I-4.

CHAPTER I-1

ASPHALT HOT-MIX AGING

Summary

During the hot-mix process asphalts undergo drastic chemical and physical changes as the result of oxidative aging. It is these properties after the hot-mix process which serve as the starting point for pavement performance. Consequently, predicting the hardening that takes place during the hot-mix process is vital for the development of better and longer lasting asphalt pavements.

Oven aging tests have evolved over a period of time and resulted in the thin film oven test (TFOT) and the rolling thin film oven test (RTFOT) for these assessments. They are based on reproducing the viscosity and penetration changes which occur in the batch hot-mix process and appear to work reasonably well for these two properties.

In addition to representing these limited physical changes, however, the laboratory tests should reproduce the hot-mix aging mechanisms in order to provide an accurate basis for predicting performance. In this regard the reaction kinetics, the effect of the aggregate surface, and diffusion likely play significant roles. Verification of the oven tests as being representative of the hot-mix processes from the point of view of chemical properties is questioned in the literature.

Introduction

Petroleum derived asphalts are very complex materials having elusive property-performance relationships. Asphalts are produced from the distillation residue of crude oil and consequently are a complex blend of hydrocarbon molecules representing a wide range of molecular sizes and chemical functional groups. Furthermore, the property changes of a given asphalt over time greatly increase the difficulty of understanding its behavior.

These changes, which occur during the processing and service life of asphalt pavements, are called aging or hardening. Aging results in an asphalt binder that no longer retains its original properties. The associated hardening of the asphalt results in an increase in viscosity and brittleness along with a decrease in ductility. While a certain amount of hardening relative to virgin properties is necessary for adequate strength, continued hardening in service reduces the useful life of the pavement.

A large amount of hardening takes place when the asphalt is mixed with the aggregate before being placed on the road (Hubbard and Gollomb, 1937, Traxler, 1961, - Discussion by Welborn and Weetman, Chipperfield and Welch, 1967, and Chipperfield et al., 1970). This mixing occurs at elevated temperatures usually between 275° and 350°F. Asphalt is not significantly affected if heated to the temperatures in mass (Hubbard and Gollomb, 1937), but when spread in thin films over the aggregate particles and mixed vigorously at high temperatures, definite chemical changes take place. The changes in the properties of the asphalt during mixing is attributed mainly to the reaction of the asphalt with atmospheric oxygen and the vaporization of lighter hydrocarbon asphalt components (Hubbard and Gollomb, 1937, Anderson et al., 1942, Griffin et al., 1955, and Vallerga et al., 1957).

The changes occurring during the hot-mix process reportedly have a large influence on the performance of the road once in service (Page et al., 1985) and since the beginning of asphalt pavements, the importance and difficulty of predicting asphalt performance after processing and during service have been appreciated (Welborn, 1984). A new or tank asphalt may have outstanding properties, but if their properties are destroyed during the hot-mix process, the asphalt becomes useless (Heithaus and Johnson, 1958).

The original properties of an asphalt do not give a good indication of how the asphalt will change during mixing or service (Santucci and Schmidt, 1966), and consequently, tests must be devised that predict the aging of asphalts. Such tests should be able to indicate the amount of hardening that takes place during mixing so that the asphalt properties can be known immediately after construction (Hveem et al.,1963). The tests should thus identify any poor quality asphalts, i. e., those that age severely during the hot-mix process (Welborn, 1984). Finally, the tests should satisfy certain conditions as specified by Lee (1968), such as the logical and realistic simulation of field conditions, the indication of actual changes that occur, good correlation between lab and field, simplicity and quickness of the methods, and acknowledgment and approval of the asphalt industry.

The remainder of this review focuses on the batch and drum hot-mix procedures, the development of the currently used tests for simulating these processes, a comparison of oven-test to hot-mix aging, a discussion of possible mechanisms and phenomena which govern hot-mix aging, and difficulties or complications in developing accurate hot-mix aging tests.

Hot-Mix Processes

The two major types of hot-mix plants used today are the batch or pugmill mixers and the drum dryer mixers. Batch mixing is the older of the two methods and is often referred to as the conventional method.

In the batch method, the mixing is done in a pugmill mixer having twin shafts equipped with paddles for mixing the ingredients into a homogenous mass. The asphalt and aggregates are heated to a temperature of 300^0 to 350^0F. The proper proportion of aggregates is first added to the pugmill and dry-mixed for a few seconds; then the asphalt is introduced and wet mixing occurs for approximately 30 seconds. The finished mix is then dumped into the bed of a waiting truck to be taken and placed on the road.

The drum method involves a continuous process. Aggregate that has been drained of moisture is added to a slightly tilted, revolving conveyer-mixer and is heated as it travels. The asphalt enters after approximately two-thirds of the length of the mixer and coats the aggregate. The product usually contains a small percentage of moisture (Granley and Olsen, 1973, and Chollar et al., 1989). This method reportedly results in less oxidation than batch methods (Chollar et al., 1989, Von Quintus and Kennedy, 1983, and Epps and Kari, 1983).

Several important differences exist between these two methods, resulting in slightly different chemical and physical properties in the asphalt mixes (Chollar et al., 1989, and Von Quintus and Kennedy, 1983). The principal advantages of drum mixers are that they are cheaper to operate and faster than their batch counterparts

(Chollar et al., 1989, Von Quintus and Kennedy, 1983, and Epps and Kari, 1983). Early drum mixers operated at lower temperatures than batch mixers. This resulted in less oxidation and a higher moisture content in drum mix products. Granley and Olsen reported (1973) that the higher moisture content helped to dissipate heat and aided subsequent roadway compaction. Later, it was discovered that the trapped moisture caused stripping problems and increased the rate of hardening of the asphalt once it was in service. The response was naturally to raise the temperature of the mixers to reduce the moisture content of the product. Thus, as reported by Von Quintus and Kennedy (1983) and Chollar, et al., (1989), today's drum mixers harden as much or more than present batch mixers and may result in higher air voids in the asphalt pavements.

History of Laboratory Hot-Mix Tests

Early tests for asphalt were designed to check the amount of mass that would be lost during the hot-mix process. This was important since some early heavy asphalts were "cut back" with lighter oils to give a lower viscosity. These light hydrocarbons left quickly during mixing and the product was very hard and had a short life. The early tests helped identify these asphalts and controlled large changes that occurred during the hot-mix process.

As discussed by Welborn (Welborn, 1984, and Lewis and Welborn, 1940), Dow in 1897 proposed two tests for analyzing asphalts. One test involved heating 20 grams of asphalt at 400°F for 30 hours. The residue was checked for any weight loss. The other test required that asphalt and sand be mixed together at 300°F and sampled before and after heating for an additional 30 minutes. The residue was extracted and recovered and the retained penetration was determined. These tests became the basis for asphalt tests that are still used today.

An ASTM Committee on Road and Paving Materials was formed to design appropriate test methods for asphalts (Welborn, 1984). By 1911 a test was adopted that had been developed by the Office of Public Roads and Rural Engineering of the Department of Agriculture. This test required that 20 grams of asphalt be placed in a shallow tin and heated at 325°F for 5 hours. The amount of volatilization and retained penetration were checked. This test was revised in 1916 to include a larger sample of 50 grams.

Shattuck (1940) developed a test where the actual conditions in the batch plant were simulated: 1880 grams of sand were heated to 400°F and mixed with 20 grams of asphalt heated to 300°F. The mixing took place in a small pugmill-type laboratory mixer for one minute. The mixture was then placed in a pan and heated at 350°F for 30 minutes. Extraction and recovery were performed after cooling the sample to room temperature. This test resulted in slightly more hardening than was present in actual hot-mix plants but provided a good indication of an asphalt's behavior under these severe conditions.

Lewis and Welborn (1940) designed a test consisting of shallow pans with asphalt 1/8 inch thick. These pans were placed on a rotating shelf in an oven that is maintained at 325°F for 5 hours. Tests were also performed at thicknesses of 1/8, 1/16 and 1/32 inch and at times of 5 and 7 hours. The penetration, ductility and softening point resulting from the hot-mix conditions were most closely duplicated by the test conducted at 325°F for 5 hours on the 1/8 inch films. This test is still widely used and referred to as the Thin Film Oven Test (TFOT).

The recognition that thinner films may be desired to simulate hot-mix aging led to the development of microfilm tests (Fink, 1958, and Traxler, 1967). Thinner films correspond better to actual pavement mixtures, harden faster, and lessen any diffusion effects that may be present in thicker films. The Microfilm Durability Test involves placing a 5 micron film on glass slides before subjecting the sample to aging in an oven (Griffin et al., 1955). This test was designed to simulate road aging, but has been correlated with hot mix as well as road aging (Heithaus and Johnson, 1958, and Simpson et al., 1959). Only small amounts of asphalt are aged with this method, and special devices for measuring viscosities were required.

Hveem, et al. (1963) designed the Rolling Thin Film Oven Test (RTFOT) to age large amounts of asphalt uniformly in thin films. This test uses 35 grams of asphalt in special rotating glass bottles in an oven maintained at 325°F. These bottles produce constantly renewed films of 5 to 10 micron thicknesses. Air is blown into the bottles to remove volatiles and promote oxidation. The RTFOT run for 75 minutes simulates the physical properties of hot-mix samples. The results from this test have been well correlated with TFOT, Shattuck-type tests, and plant mixes (Chipperfield et al., 1970, Hveem et al., 1963, Chollar et al., 1989, Epps and Kari, 1983, Schmidt, 1973, Schmidt, 1973, Button et al., 1983, Kim et al., 1984, and Thenoux et al., 1988).

Numerous variations have been made on the TFOT and RTFOT methods with many intended to simulate road aging as well. Vallerga et al. (1957) proposed tilting the oven used for the TFOT and provided an effect similar to that of the RTFOT. Schmidt and Santucci (1969) developed a rolling microfilm test in which benzene-dissolved asphalt was cast in bottles and aged in a manner similar to that used in the RTFOT. The modification of adding a circulating fan as suggested by Schmidt (1973) has been maintained. Schmidt (1973) has also used several modifications to the rolling microfilm test at various temperatures and rates of air circulation, as well as in the presence of aggregate, in an effort to simulate hot mix and road aging. Performing a TFOT procedure at various temperatures was suggested as a means of obtaining an indication of the sensitivity of asphalt aging to inconsistent plant conditions (Page et al., 1985).

Drum mixers may require slightly different laboratory simulations than batch mixers. The presence of a fair amount of moisture in some plants initiated the theory that something similar to steam distillation may be occurring in drum plants. A Small Steam Distillation (SSD) technique involving bubbling steam through an asphalt sample was found not to represent drum hot-mix plants (Chollar et al., 1989). Two other methods, Forced Air Distillation (FAD) and Revolving Forced Air Distillation (RFAD), were found to closely resemble drum mixes. These methods involve blowing air over asphalt samples and collecting the volatile matter removed. The FAD and RFAD are similar in operation to the TFOT and RTFOT methods, respectively, but the FAD method is performed at a temperature of 622°F. The FAD and RFAD tests are reportedly better than TFOT and RTFOT in representing the aging that takes place in drum mixers (Chollar, 1989).

Comparisons of Oven Test Aging to Hot-Mix Aging

The TFOT and RTFOT methods are still the most widely accepted and used techniques for simulating hot-mix aging. The tests are sometimes used to simulate the hot-mix stage while other methods, such as those using high pressure oxygen, are used to simulate the aging on the road (Lee, 1968, Lee, 1973, Edler et al., 1985). The TFOT results have been well-correlated with extracted hot-mix samples based mostly on viscosity and penetration data (Chipperfield et al., 1970, Page et al., 1985, Chollar et al., 1989, Epps and Kari, 1983, Lewis and Welborn, 1940, Button et al., 1983, Lee, 1973, Hveem et al., 1959, Bright and Reynolds, 1962, Sisko and Brunstrum, 1968, and Adam, 1988). The RTFOT results have also been shown to match extracted hot-mix samples (Chipperfield et al., 1967, Hveem et al., 1963, Chollar et al., 1989, Epps and Kari, 1983, Button et al., 1983, Kim et al., 1984, and Thenoux et al., 1988) as well as TFOT results (Schmidt, 1973, and Schmidt, 1973). The RTFOT is considered to be the better of the two methods. The RTFOT requires a shorter aging time, is easier to perform, and gives more precise results than the TFOT (Schmidt, 1973; discussion by Schmidt in Skog, 1967). This added precision is attributed to the fact that the RTFOT ages more uniformly than the TFOT (Chipperfield et al., 1970). Both methods are considered interchangeable, however, to predict hot-mix aging.

There are several properties and tools used for the verification of these tests. The most common method of evaluation is the comparison of the physical properties of the test samples and the extracted asphalt. These properties include the penetration and viscosity values at various temperatures, ductility, softening point, as well as various moduli determined from physical tests. The chemical compositions as determined by Corbett and Rostler fractions have also been used (Chipperfield et al., 1970, Thenoux et al., 1988, Brule et al., 1986). Chipperfield (1970) concludes that the chemical changes that occur in the hot mix are greater than those produced in the TFOT or RTFOT tests. Recently, more sophisticated tools have been used to evaluate the validity of hot-mix simulations. These include the use of Gel Permeation Chromatography (GPC) to provide a molecular size distribution of the asphalt molecules before and after the hot-mix and test procedures (Chollar et al., 1989, Edler et al., 1985, Sisko and Brunstrum, 1968, Jennings et al., 1982, Brule et al., 1986, and Glover et al., 1989). Chemical functional group analysis using infrared spectroscopy has also been used effectively for this purpose (Chollar et al., 1989, Glover et al., 1989, and Dickinson, 1980). These various methods do not necessarily support one another, however. For example, different infrared absorbances do not necessarily indicate different physical properties (Dickinson, 1980 - discussion by Plancher). An ideal test would duplicate the changes that occur in the hot-mix plant as detected by all of these techniques.

Mechanisms of Aging

In order to be truly indicative, a hot-mix aging test should approximate the mechanisms of the chemical and physical changes that actually occur in the plant. It is well-accepted that the oxidation reactions occurring in the plant are both reaction and diffusion controlled. The exact mechanisms of the oxidation reaction and the volatilization occurring during mixing are not presently agreed upon, and a clearer picture of the phenomena is needed.

The role of the aggregate in the aging process is debated. Some researchers claim that the type of aggregate does not affect the aging of asphalt (Chipperfield and Welch, 1967, and Bright and Reynolds, 1962). Others have concluded that the type of aggregate influences the amount of oxidation that takes place during the hot-mix process (Jennings et al., 1982, Nicholson, 1937, and Barbour et al., 1974). Some research indicates that the aggregate catalyzes the oxidation reaction (Vallerga et al., 1957, Jennings et al., 1982, and Petersen et al., 1974). The most probable explanation is that the aggregate affects the oxidation that takes place during the hot-mix process, but that road aging is not as affected (Santucci et al., 1981).

The oxidation reaction of the asphalt in the plant occurs almost instantaneously upon contact with the hot aggregate (Hubbard and Gollomb, 1937, Traxler, 1961 - discussion by Welborn and Nevitt, Jennings et al., 1982, and Culley, 1969). This fast reaction is reportedly sensitive to temperature changes (Hubbard and Gollomb, 1937, Page et al., 1985, Fink, 1958, Bright and Reynolds, 1962, Dickinson, 1980, and Halstead, 1985). Different oxidation reactions become more significant as their rates increase with an increase in temperature. The calculated increase in the oxidation reaction rates is more than can be accounted for by the increase in diffusion for a given temperature rise (Griffin et al., 1955).

The influence of diffusion becomes more prominent with longer mixing times (Hubbard and Gollomb, 1937, and Page et al., 1985). Diffusion rates are also greatly influenced by the film thickness of the asphalt on the aggregate particles (Hubbard and Gollomb, 1937, Page et al., 1985, Heithaus and Johnson, 1958, and Dickinson, 1980), as well as by increases in temperature (Traxler, 1961, Griffin et al., 1955, and Wurstner et al., 1960). The transfer of mass during the hot-mix process involves the diffusion of volatile components out and diffusion of atmospheric oxygen into the asphalt films. This behavior explains the fact that heating tests may produce weight gains. The oxygen gained during oxidation may more than offset the small amount of hydrocarbon volatiles that were removed.

The mechanisms of the chemical changes that occur during the hot-mix process are important to understand. From extensive literature evaluation (Hubbard and Gollomb, 1937, Traxler, 1961, Griffin et al., 1955, Vallerga et al., 1957, Page et al., 1985, Bright and Reynolds, 1962, Jennings, 1982, Dickinson, 1980, Nicholson, 1937, Barbour et al., 1974, Petersen, Barbour, and Dorrence, 1974, Santucci et al., 1981, and Culley, 1969), the most probable action taking place involves the following steps. First, oxygen on the hot aggregate surface reacts with the hot asphalt on contact and almost instantaneously. (This important role of the aggregate in the oxidation reaction may indicate that the presence of aggregate in a hot-mix simulation technique may be necessary, even though it leads to extraction and recovery problems, increased test time, and decreased control in consistency.) Secondly, naturally occurring components in asphalt may help to catalyze oxidation, especially in thin films and at high temperatures where oxygen may diffuse more easily into the asphalt. This behavior may be limited, though, since movement and orientation of large asphalt molecules may be slow. Finally, at longer mixing times, substantial volatilization in asphalts with light components may dominate the hardening. Hydrocarbon molecules diffusing out and leaving the asphalt layers could inhibit the introduction and diffusion of atmospheric oxygen into the asphalt. The importance of each of these factors will conceivably vary with different types of asphalt and different mixing methods and plants.

Difficulties in Developing Hot-Mix Aging Tests

The inherent variabilities in asphalt, its manufacture and processing, and its analysis make the development of a hot-mix simulation test very difficult. Different crude sources and refinery methods result in asphalts with very different chemical and physical properties. Also, the existence of several grades of asphalts makes the task of developing a universal test more formidable. The asphalt content and the gradation of a given mix design may also be important variables. As previously stated, different types of aggregate may catalyze the initial oxidation reaction differently. Finally, the complexity of asphalt composition makes any kind of complete chemical analysis hopeless and, furthermore, physical property changes are not uniquely related (at least to within experimental errors) to chemical changes. Consequently, monitoring exact changes due to hot mix or any other aging process is not possible, complicating process comparisons.

Of course, variability in plant operations, such as mixing time and temperature, and process type may have significant effect on the aging during the hot-mix process. Elevated plant temperatures are reported to adversely affect road aging (Page et al., 1985). Improper fuel-to-oxygen ratios can result in excess fuel being blown into the asphalt and lowering the viscosity (Chollar et al., 1989). Running with large excesses of air in the burner may result in a large amount of oxygen available for reaction with the asphalt. Since the TFOT and RTFOT were designed originally to simulate batch plant operations, it is not surprising that they do not match drum plant mixes as accurately (Heithaus and Johnson, 1958, Chollar et al., 1989, Lewis and Welborn, 1940, Thenoux et al., 1988, and Sandvig and Kofalt, 1968). Batch and drum processing methods evidently do not always produce equivalent asphalt mixes and may be a considerable source of error when comparing various hot mixes.

Another large source of error that is often overlooked involves the extraction and recovery techniques used to obtain asphalt samples from hot-mix and road cores. Dissolving the asphalt destroys any steric hardening that may have been present in the hot mix (Hubbard and Gollomb, 1937). Additionally, the extraction process itself may change the asphalt (Heithaus and Johnson, 1958, Lewis and Welborn, 1940, Schmidt and Santucci, 1969, and Sandvig and Kofalt, 1968). These changes may result from a loss of volatile materials when evaporating the solvent during recovery or from leaving highly polar material that may strongly affect physical properties on the aggregate. Actual chemical changes may occur when the asphalt is put in solution and may be dependent upon the solvent used.

Conclusions

Predicting the hardening that takes place during the hot-mix process is vital for the development of better and longer lasting asphalt pavements. The methods and theory behind present tests should be reviewed and ideas for new tests considered. Also, the analysis of the results of the existing TFOT and RTFOT should be reexamined. The measurement of physical properties alone in comparing the results of hot-mix tests may not give an indication of a different chemical composition that may exist in an asphalt (Chipperfield et al., 1970, Glover et al., 1989). A good hot-mix simulation will not only allow accurate predictions of hot-mix performance but will be the basis for developing other tests that can predict road aging.

CHAPTER I-2

ASPHALT EXTRACTION AND RECOVERY

Summary

To provide properties which are representative of the binder in situ properties, procedures must be effective in removing the binders from the aggregate without changing or aging the asphalts, and the solvents used for the extraction must be adequately removed from the asphalt binder so as not to distort the physical properties of the binder which are subsequently measured.

Commonly-used procedures for extraction and recovery use either room-temperature centrifuge or hot-reflux methods for extraction followed by either the Abson or Roto-vap procedures for solvent removal. The reflux method appears to be by far the most commonly used method in spite of the fact that the centrifuge method is recommended if asphalt properties are to be measured. A variety of solvents have been used in the asphalt extraction procedure, although trichlorethylene is the most commonly used and is that stipulated by the ASTM procedures. The addition of a more polar compound such as 10%-15% ethanol has been used in non-standard procedures to enhance a more complete extraction of the asphalt from the aggregate.

Problems have been reported with all aspects of the asphalt extraction and recovery process. First, the ASTM extraction procedures do not adequately remove all of the asphalt from the aggregate. Second, the solvent removal procedures do not adequately remove all of the solvent from the asphalt especially for hardened asphalts. Finally, contact of asphalt with solvent for extended times at elevated temperatures produces hardening of asphalt materials.

Introduction

The ultimate objective of asphalt pavement binder research is to relate documented pavement performance to the binder's composition and physical properties. To accomplish this, it is first necessary to reclaim asphalt from pavement samples. This is done by separating the asphalt from the aggregate by solvent extraction and then removing the solvent by distillation. Several methods for doing this exist and are in use presently. However, there is concern that none of these methods produces asphalts which are chemically and physically representative of the binder material in the pavement.

This review discusses the development of the extraction and recovery methods. It also examines the extent and probable sources of error in the methods; namely solvent aging, incomplete solvent removal, and incomplete extraction.

History of Methods

Extraction and recovery of asphalt has been practiced in some form since the turn of the century. In 1903, as discussed by Abson, (1933) Dow extracted with carbon disulfide (CS_2) and recovered using simple distillation. Bateman and Delp (1927) centrifuge extracted with CS_2 and removed the solvent by vacuum distillation. Soxhlet type reflux extractions using CS_2 were common in this early period. Several other methods were developed through 1930, but none gained lasting acceptance (Broome, 1949, and Abson, 1933).

Extraction Methods. Today centrifuge and reflux extraction methods (usually in the form of ASTM D-2172, methods A and B respectively) are used almost exclusively. Vacuum extraction (ASTM, 1981) and sonication methods (Plummer and Zimmerman, 1984, and Jennings et al., 1982) also have been used, but infrequently.

In 1921, the centrifuge extractor was developed (Broome, 1949) and was part of a proposed standard method in 1927 (Bateman and Delp, 1927). It was first adopted by ASTM in 1963 as D-2172A (ASTM, 1981). It still exists today and currently is the only ASTM approved method of extraction if the asphalt is to be recovered for further analysis.

The reflux extraction method was in existence prior to 1949. Broome (1949), in a British publication, notes that it is the preferred method of extraction in the U.S. but says that it has not been shown to give consistent results. Furthermore, the reflux extraction procedure, ASTM D-2172B, should not be used if the asphalt is to be recovered for property analysis; method B extractions have been known to induce asphalt hardening (ASTM, 1979).

Despite the warnings of ASTM, the reflux extraction method appears to be by far the more commonly used. Literature reports generally do not cite a specific method but of those that do, 12 used reflux extraction and only 3 centrifuge extraction. Two of the three cases of centrifuge use were studies comparing differences between method A and the normally used method B (Table I-2-1).

Solvent Removal Methods. Typically, removal of solvent after extraction is performed by the Abson method or by rotary evaporation. These two methods share equal popularity. The literature shows six instances of rotary evaporation and eight of the Abson since the mid-1970's. Prior to that time, the Abson method dominated (Table I-2-1).

Abson (1933) presented his method which involves recovering benzene-extracted asphalt at 300°-325°F with the aid of bubbling CO_2. He tested seven asphalts ranging in penetration from 175 to 26. After mixing with benzene, they were recovered to within 3% of original penetrations. It was designated ASTM D-1856 and is still the recommended method.

Rotary evaporation methods became common in the mid-1970's. ASTM is considering a standard method for recovery using this apparatus. It consists of rotary evaporation in a 2000 ml flask at 280°F and 600 mm Hg vacuum with a nitrogen sweep of 600 ml/min. Testing of this method shows that it is not as precise as the Abson method (ASTM, 1988).

Choice of Solvent. Through the years, several solvents have been used for extracting asphalt. Initially, CS_2 was commonly used but was phased out due to its high volatility and flammability. Benzene became its primary replacement after Abson's method appeared. In the 1950's and 60's, chlorinated solvents became popular. The most common were trichloroethylene (TCE), 1,1,1-trichloroethane (TCEA), and methylene chloride. Abson and Burton (1960, and ASTM 1981) tested several of these and found TCE to be as effective as benzene. Addition of about 10% ethanol or methanol to benzene was shown to remove more asphalt from the aggregate (Traxler, 1967). This has become quite popular among many researchers.

Table I-2-1
Breakdown of Extraction/Recovery Methods Cited in Literature

Year	Solvent	Extraction Method	Solvent Removal Method
1933	Benzene	Not Applicable	Abson
1927	CS_2	Centrifuge	Vacuum Dist.
1949	Not Applicable		
1981	Not Applicable		
1984	THF	Sonication	Not Clear
1982	TCE, THF	B, Sonication	Roto-Vap
1979	Benz.,TCE	A	Not Applicable
1988	Not Applicable		
1960	TCE	Not Applicable	Abson
1967	Benzene/EtOH	B	Roto-Vap
1987-9	Not Applicable		
1936	Benzene	Not Clear	Simple Dist.
1969	Benz,Benz/EtOH, TCE, TCEA	Not Applicable	Roto-Vap
1963	TCE	Not Clear	Abson
1962	TCE	B	Abson
1984	TCE/EtOH	Not Applicable	Not Applicable
1978	TCE	B	Abson
1988	TCE	A,B	Abson, Roto-Vap
1982	TCE	A,B	Abson
1983	TCE	Not Applicable	Roto-Vap
1975	Benzene	B	Abson
1968	Not Clear	Montreal,Not Clear	Montreal, Abson
1968	Benzene	B	Abson
1982	Benzene	Not Clear	Not Clear
1977	Benz, Pyridine	Cold, Soxhlet	Roto-Vap
1974	Benz/EtOH	Not Clear	Not Clear
1966	Not Clear	Not Clear	Abson
1974	Benz/EtOH	B	Roto-Vap
1975	Benzene	Not Clear	Abson
1976	Benz, Pyridine	Cold, Soxhlet	Roto-Vap
1974	Benz, Benz/EtOH	Not Applicable	Roto-Vap
1942	Benzene	Not Applicable	Abson
1962	Benzene	B	Abson
1978	TCE	B	Abson
1968	Benzene	B	Abson
1967	CS_2	Soxhlet	Vacuum Dist.
1969	Benzene	A	Abson

Since benzene has been proven carcinogenic, its use has been phased out and TCE has been the primary replacement. There are rare occasions of the use of pyridine and THF for specialized extractions (Plummer and Zimmerman, 1984, and Jennings et al., 1982). The literature survey shows the use of benzene sixteen times, TCE twelve times, alcohol addition on four occasions, and other solvents five times.

Problems with Present Methods

There is strong evidence that the present extraction and recovery methods are either inadequate or are not being performed properly in the laboratories nationwide. AASHTO conducts interlaboratory proficiency tests periodically to determine the precision of the methods. They send identical pavement samples to 50-100 laboratories. The laboratories extract and recover the asphalt, perform various tests, and send the results to AASHTO. In a February 1989 report, the coefficients of variance on recovered viscosities were about 25%. In earlier years it has been as high as 42% (Anonymous, 1987, 1988, 1989).

In the extraction-recovery discussions, there seem to be three main areas where errors are likely to stem:

(1) The solvent has some hardening effect on the asphalt which increases with temperature and time of exposure.

(2) Solvent is often not completely removed from the asphalt during recovery. This results in viscosities which are lower than the true value.

(3) Asphalt is not completely removed from the aggregate. The strongly adsorbed material left on the aggregate has a significantly different composition than the bulk asphalt.

Solvent Aging. It has been known for a long time that asphalts do harden upon exposure to solvents. However, little is known about the causes or extent of solvent aging.

Abson (1933) dissolved a 156-penetration asphalt in benzene and let it sit at room temperature for different times. The penetration was down to 147 after 24 hours and 109 after 480 hours. For this reason, he advised that the extraction-recovery process should be completed within 8 hours. He did not study the effect of different solvents, concentration, or temperature. Bussow (1936) found that his asphalts did not age when the solvent-asphalt mixture was left in the dark. He suggested that the hardening is due to a photochemical reaction. There has been no other mention in the literature of this phenomenon.

Abson and Burton (1960) tested several chlorinated solvents and showed that some induced severe aging. The worst of these was CCl_4. An 89 penetration asphalt was dissolved in 4 volumes of CCl_4 at room temperature for 2 to 4 hours before recovering. The residue had a penetration of 56. TCEA also caused severe hardening.

Abu-Elgheit et al. (1969) studied effects of different solvents on an asphalt's 77^{0}F viscosity. After refluxing for 2 hours in 4 volumes of solvent, the viscosity hardening indices were 1.15 for benzene, 1.45 for benzene-ethanol, 1.9 for TCE and 2.0 for TCEA. Lottman et al. (1963) reported a 140^{0}F viscosity index of 1.4 for cold-extracted, Abson-recovered asphalt 16 hours after mixing with TCE. Bissett (1962) contradicted this when he reported no aging after 7 days in TCE at room temperature. Hagen et al. (1984) believe TCEA hardening may be due to nonvolatile components, such as p-dioxane, which are in the solvent and may remain in the asphalt after recovery.

One interesting problem that solvent aging can cause is demonstrated by Noureldin and Manke (1978). They experienced hardening after hot extraction in TCE and remedied it by reducing his recovery temperature to 311^{0}F and time to 6 minutes. It is likely that he did not correct the aging which occurred in the extraction step but corrected for it by leaving an amount of solvent which brought the penetration back to its original value.

Presently, the safest way to avoid the solvent aging problem is to use a cold extraction method, as ASTM suggests. Studies by Jennings et al. (1982) and Thenoux et al. (1988) suggest there are differences due to the use of different extraction methods.

Incomplete Solvent Removal. Although Abson showed that solvent can be completely removed using his method, many researchers have had problems accomplishing this. Often they do not even realize that there are problems due to residual solvent.

Lottman et al. (1963) modified his extraction-recovery procedure because he was experiencing excess hardening (most likely due to solvent aging). He replaced the CO_2 distribution coil with a smaller one. This lowered the hardening to 2% on test samples. However, when studying hot-mix samples he discovered lower than original viscosities, or "negative hardening" during the mix process. In the discussion of the paper, Rostler suggested that this probably was due to residual solvent in the sample.

A classic example of how incomplete solvent removal can ruin a massive research project is illustrated in a study of factors affecting asphalt in the extraction-recovery process by Carey and Paul (1982). The project's goals were to study the effect of time in TCE for aged and unaged asphalts, the effect of reduced asphalt concentration during recovery, intra- and inter-operator variations, the effect of solvent during primary distillation, and the effect of fines in aggregate mix on recovered asphalt properties. They performed recoveries after different lengths of time in TCE for 54 similar AC-30 and 54 artificially aged samples. Using a statistical package, ANOVA, they concluded that the time in a solvent directly affected viscosity. This had been shown by other researchers. None of the other variables were found to be statistically significant. However, 22 out of 54 AC-30 samples had lower viscosities after solvent aging and recovery. The aged samples (30,000 to 200,000 poise) softened 40 out of 54 times.

Carey and Paul (1982) noted this softening but gave no explanation for it. It is almost certain that residual solvent caused softening and added enough scatter to the data that the variables of interest had negligible effects in comparison. This probably masked most of the effect due to solvent aging also. This group's findings would have been much more valuable if they had shown that they could remove the solvent.

In 1983, the Pacific Coast Users Group tested the Abson, Roto-vap, and two other recovery methods. On four different asphalts having viscosities from 4,000 to 50,000 poise, they found that no method outperformed the others. The Abson method had the lowest reproducibility rating and failed to remove the solvent adequately from two of the four asphalts tested. Consequently, the residues' viscosities were about 75% of the original. The other methods caused excessive hardening on the other two asphalts tested. Hardening indices were as high as 1.5 (Davis, 1983).

Other authors have noticed or had data that indicated the presence of solvent removal problems. Roberts and Gotolski (1975), Sandvig and Kovalt (1968), and Gietz and Lamb (1968) have viscosities on recovered road samples that sometimes decrease with time on the road. This may actually occur, but it is probably due to an extraction-recovery problem. Noureldin and Manke (1978) also had his case of compensating solvent aging and incomplete solvent removal.

The problem of incomplete solvent removal is not as simple as it sounds. For one thing, solvent in asphalt is very difficult to detect. Usually an asphalt of known properties is mixed with solvent, recovered, and tested again. The deviations from original properties indicate the effectiveness of the recovery. Direct solvent analysis methods are rare. Petersen et al. (1982) mention using IR to detect solvent in asphalt. Bussow (1936) used odor and loss on heating as criterion for solvent concentration. Second, the mechanism of solvent evaporation may not be well understood. In a discussion of a paper by Hagen et al. (1984), Petersen says, "When dealing with low concentrations of solvents left in residues, boiling point is no longer a major factor and diffusion and molecular associations between asphalt and solvent become controlling factors for solvent removal."

Incomplete Extraction. It is evident that the per cent of total asphalt removed during extraction could also be significant in determining a method's effectiveness. As mentioned earlier, Traxler (1967) found that additional asphalt could be removed by adding 10% ethanol to benzene. Pyridine has also been used to extract additional asphalt (Plancher et al., 1977). Plancher and Petersen (Petersen et al., 1982, and Petersen, Ensley, and Barbour 1974) have published several papers which say that up to 4% but usually 2% of the asphalt remains on the aggregate after benzene or TCE extractions. The asphalt seems to be more strongly adsorbed in old cores than in laboratory mixes.

The strongly adsorbed material is also of a different nature than the bulk asphalt. Concentrations of carboxylic acids were 12-63 times higher, anhydrides 4-32 times higher, ketones 0.8-6.2, sulfoxides 1.1-3.6, and 2-quinoline types 3-10 times higher in the strongly adsorbed material (Petersen et al., 1982). Relative affinities of functionalities to the aggregate with respect to the bulk are carboxylic acids > dicarboxylic anhydrides > 2-quinoline types > sulfoxides > nitrogen groups > ketones. Ketones and sulfoxides can account for 90% of the polar compounds in the strongly adsorbed material. The amount of strongly adsorbed material is a strong function of the aggregate surface area and not as dependent on aggregate composition (Plancher et al., 1977). Apparently, no work has been done to determine the effect on physical properties of adding the strongly adsorbed material back to the bulk asphalt. It is not even clear whether the strongly adsorbed material should be considered part of the asphalt binder. Due to its strong interaction with the aggregate, it may play a stronger role as an aggregate substituent.

CHAPTER I-3

AIR VOIDS

Summary

Work during this study presented in Chapter IV-1 clearly demonstrates the extreme importance of percent voids in the aging of asphalt. What has been shown by the effect of voids on carbonyl formation has been known for many years from measurements of penetration and viscosity and by noting the short life of roads with high voids. The lack of implementation of this knowledge (two of the three Study 287 test section locations have uniformly high voids), when compared with its antiquity and its importance, is a matter of some interest. The work reviewed in this chapter demonstrates convincingly the high priority that should be given to assuring low voids.

Early Studies

Hubbard and Gollomb (1937) noted: "The cause of hardening of the asphalt within an asphalt pavement is primarily due to the contact of the relatively thin films with air or in other words oxidation. It is equally apparent that if the presence of air within the mixture is eliminated, little or no hardening should take place after construction." Comparing the changes in penetration of asphalt recovered from loose and compacted mixes exposed at both high and low temperature, they note the much greater hardening of the loose mix and recommend: "Compress all asphalt paving mixtures thoroughly so that they will be impermeable to air."

Also, Nicholson (1937) examined the properties of asphalt recovered from cores. The pavements varied in age from 3 to 36 months, but the percent voids had more effect than the age. Of 7 cores, one with 2% voids showed almost no aging, two at 4% and 5% showed moderate aging, and two at about 9% showed severe aging. One sample at 5% which at 36 months old was the oldest, showed severe aging.

In a particularly important paper, Heithaus and Johnson (1958) compared road aging of 3-year-old test sections laid in Illinois in 1952 and 1953. Viscosities at 77°F of extracted core material were compared to those of asphalts aged in the Microfilm durability test. In this test, asphalt is aged in a 5-micron film for 2 hours at 225°F. They found that voids had a major effect on road aging. In order to study the effect of voids, the aging rates of different asphalts were in effect normalized by calculating a ratio of road aging index to oven aging index. When this was plotted vs percent voids, virtually straight lines were obtained. The ratio was approximately one at 5.5% voids and had increased to two at 10% voids. Simpson et al. (1959) also noted much more rapid aging at higher voids in cores from the Zaca-Wigmore test sections.

Goode and Lufsey (1965) did a detailed study on the effect of voids, air permeability, asphalt content and aggregate gradation on oven aging of asphalt using molded test specimens. They found that for a given gradation, aging went up with voids and permeability went up with voids, particularly at high voids. They also found that aging increased as asphalt film thickness decreased. At fairly low voids, they found all gradations could be correlated with the ratio of voids to average film thickness. This factor, called the voids-bitumen index ratio, was suggested as a possible design parameter. In general this permits a range of air voids, depending on the aggregate. The tendency for lower hardening with higher asphalt content had been noted by Halstead (1963) relative to the Zaca-Wigmore test sections. McLeod (1967) noted the high voids that often result from road construction in late fall and the resulting poor service of these roads.

In the summer of 1966, the Alberta Department of Highways laid three test sections of 200-300 pen grade asphalts with a range of viscosities (Anderson and Shields, 1971). The point relative to the present study is that cores taken just after construction showed about 1% less asphalt and two to three times the voids indicated by the Marshall Design. Cores taken at 1, 2 and 3 years did not show hardening, but the results are highly suspect in every case. Recovered asphalt from cores after 1 year, and in some cases after 2 and 3 years, was of significantly lower viscosity at 140°F and higher penetration at 77°F than material from the fresh hot mix.

Studies of a number of test sections were conducted in Pennsylvania during the sixties and early seventies. This work was summarized by Gotolski et al. (1971) and Roberts and Gotolski (1975). The study included a variety of asphalts and aggregates. They point out the difficulty in correlating performance with air voids because of the variability in voids from point to point, and the steep variation across the road, as well as the effect of aggregate and gradation. Even so, they state the following: "Air voids are one, if not the greatest, factor affecting the rate of hardening of an asphalt pavement. The influence of the variable appears to be so pronounced that it completely overshadows the performance of asphalt type, aggregate type, traffic density and microclimate differences." One of their more interesting observations and conclusions is the following: "The pavements studied received better than average design and field control; yet these pavements were constructed with void contents as high as 13%. This underscores the need for more restrictive specifications and closer field control." They also noted that the asphalt sections with the lower air voids were constructed with asphalts having lower initial viscosities.

In 1966, FHWA personnel surveyed state highway department records to select roadways for an extensive study of the effect of chemical and physical properties on performance. Fifty three projects in nineteen states were selected. The results were reported by Vallerga and Halstead (1971). Because of the large number of uncontrolled variables, the correlations are not good and some conclusions seem contradictory, but one obvious observation is the rapid increase in viscosity of the recovered asphalt with air voids and the rapid decrease in ductility. The latter, measured at 60°F, showed a dramatic decrease over a narrow range of voids in the neighborhood of 2%. The ductility at 77°F showed a similar break around 4% voids.

Kemp (1973) reports correlations of laboratory tests with field hardening of asphalt in 24 test sections at 8 locations in California representing a variety of climates. A good correlation with the RMFC oven test viscosity at 77°F was found at both 30 and 50 months, but at 50 months, the best correlation was with percent original voids.

Lee (1973) reports results of an Iowa field test in which eight test sections were used to correlate an aging procedure, combining the TFOT and 1000 hours in an oxygen bomb, with physical and chemical parameters. There is much scattering of results, but the viscosity at 77°F of recovered material significantly increased with percent voids. They report no correlation with film thickness.

Recent Studies

Benson (1976) reports results of a Texas study of transverse cracking and asphalt hardening in nine test sections. Viscosity at 77°F, hardening index and penetration at 77°F all correlated significantly with transverse cracking. The best correlation, however, was with the final percent air voids which, of course, cross correlates with the other significant factors.

Anderson et al. (1976) report the performance of 20 test sections in Utah. The purpose was to correlate pavement stress with physical and chemical parameters as well as construction factors and use. They ran both controlled and uncontrolled sections. The former had two levels of air voids: 2.6% and 7.1%, and two asphalt sources and four pavement thickness-base-thickness combinations. In all cases the 7.1% voids showed significantly higher cracking after 5 years. Similarly, the penetration, viscosity and ductility changed much more slowly for the low void sections.

A Louisiana Study (Shah, 1978) was conducted to compare penetration and viscosity graded asphalts and, secondly, the effect of asphalt properties and pavement voids on hardening. They report no correlation with voids, but inspection of their data indicates this is not quite true. The two lowest voids show the least aging (this is average voids and not initial values) and all of the others have voids within too narrow a range to be significant.

Santucci et al. (1981) and Kemp and Predoehl (1981) report on the California Transportation Laboratory Test for 1974-1978. This test used briquettes rather than test sections. The test employed three HR-4000 California asphalts, two aggregates at three void levels: 3%-5%, 7%-9% and 10%-12%. Exposures were at four locations with different climates. In this test, climate proved to have the greatest effect, especially the desert site. Type of asphalt was quite significant with percent voids third. It is probable that the degree of aeration is much higher in these briquettes than in the roads, as the aging appears much more rapid at the lower voids levels than reported in the other studies above.

Kumar and Goetz (1977) report an interesting, but somewhat confusing, study of aging vs. permeability and film thickness. Laboratory compacted cores were prepared with graded and ungraded aggregate at varying asphalt content and compaction. The cores were aged by passing air through them at 140°F. The aging was measured periodically by a nondestructive creep test. "Changes in slope and intercept values of the creep curve (log strain vs. log time plots) resulting from progressive oxidation - - were utilized as a measure of asphalt hardening. - - The ratio of the slope (or intercept) of the creep curve after 'X' days of oxidation to the slope (or intercept) of the creep curve at no oxidation was utilized for evaluation. The ratio was designated as Durability Index (Slope or Intercept)." Correlations of this index were made vs. log film thickness, log voids, log permeability and log of the ratios of film thickness to permeability and film thickness to voids. For the single size mixtures, the best correlation was the ratio of film thickness to permeability and permeability alone. Film thickness over voids did not correlate well, even though there was shown to be a strong correlation between voids and permeability.

Surprisingly, for graded mixtures, everything correlated, which, as the authors admit, is not very logical. Based on microscopic studies, they decided the idea of film thickness is not applicable to graded mixtures, and so correlations were made only with permeability and voids. In view of this confusion, it may be more profitable to just look at the results of varying each factor. They found that those cores made with high compaction (low voids) aged less than those with less compaction. In studying the effect of asphalt content, the lowest content set had to be eliminated because of more aging during core compaction, but of the two remaining sets, aging was significantly higher in the one containing a lower percent asphalt. This is consistent with the result of Goode and Lufsey that voids and film thickness are primary factors in asphalt aging.

Dickinson (1980) reports results of an aging study in which aging of seal coats in several locations using seven asphalts was compared with their laboratory aging test. In addition, all asphalts were also laid at one location in a 1-inch surface course. Cores of these latter sections were taken at 3.8, 5.5 and 6.3 years. A considerable variation in compaction and voids content was found. Viscosity of extracted material at 45°C was used as the aging criterion. Though the variation in viscosity was not high, a significant correlation with both voids and results of the aging test was found. Once again, a surprising finding was how high the voids were where there had been less traffic compaction. After 6.3 years, the voids generally ranged from 8%-11% between the wheel tracks on the fast lane.

Kandhal and Koehler (1984) summarize the results of three Pennsylvania Road Tests. In 1962, four test sections were laid. All had fairly high voids which compacted with age, but one section had a significantly higher void content. It was first to crack and had the highest viscosity and lowest penetration and ductility after 10 years. A second group of six tests sections was laid in 1964. Again the voids were high, though all but one section rapidly compacted with age. This one test section showed the poorest performance and the highest viscosity and lowest ductility when evaluated in 1974. Void data were not given on the 1976 test sections.

Kim et al. (1984) compared laboratory compacted cores, which were made from asphalt and aggregate used in three road sections, and then aged in a pressure oxygen bomb, to cores recovered from the roads. The laboratory cores were made at two compaction levels. The resilient modulus was used as a measure of aging. Agreement between the bomb test and road aging was not good, but the aging of the road cores as measured by viscosity of the recovered material and the asphaltene content was in good agreement with the percent voids of the cores.

Page et al. (1985) combined data from a Florida test of hot-mix plant temperatures with the data of Goode and Lufsey (1965) and some data for cores recovered from 8-year-old pavements in Quebec. Goode and Lufsey's data indicated that the change of penetration with voids in their 12-day oven test varied as voids to a power. These expressions were then fitted to the 8-year-old data and compared with extropolated penetrations for the Florida roads. The fit was good except for one 345°F hot-mix section and one 300°F section. The first deviation was attributed to the high hot-mix temperature and the second to bad data. The Florida data were correlated to obtain an expression:

$$\log \eta_{77^\circ F} = 1.5624 + .3467 \log d + .4262 \log AV + .6463 \log \Delta\eta$$

where

d = age in days

AV = air voids

$\Delta\eta = \eta_{TFOT} - \eta_{orig}$ at 77°F

$r^2 = .705$

Another expression including hot-mix temperature was

$$\text{Pen} = \frac{134.74}{d^{0.1107}\ iAV^{0.2743} \left(\frac{T_{mix}}{325}\right)^{0.4614}}$$

where

d = age in days

iAV = initial air voids

T_{mix} = plant temperature

These expressions are for the 85-100-penetration grade asphalts as used in the Florida test sections.

One of the recommendations in this paper is particularly pertinent:

> "The air void content of asphalt concrete mixtures, as reported in the literature, often appears excessively high. In consideration of the results obtained in this investigation, it is recommended that more emphasis be placed on field compaction and mix design requirements to achieve initial air voids not in excess of six percent."

Welborn (1984) discussing the state of the art in relating physical properties to asphalt durability states, "The literature is replete with data showing the influence of air voids and asphalt content on asphalt aging in service and their effect on durability."

Davis (1985) in discussing the relation of asphalt rheological properties and the rheological properties of mixtures and pavements states: "The resistance of flow of asphalt pavements has an important bearing on their ability to resist the effects of oxidation and moisture. When the asphalt content of a compacted asphalt mixture reaches the point where the air voids are no longer connected, there is a marked reduction in the bearing capacity of the pavement. There is also a marked reduction in the effect of oxidation and moisture, since it is more difficult for water and air to reach the interface between aggregate and asphalt. If the bearing capacity of a pavement can be increased sufficiently to support traffic with reduced air voids, the subsequent improvement in resistance to oxidation and moisture can greatly increase the life expectancy of the pavement." In the conclusions he states, "The best approach to reducing problems with oxidation and moisture in asphalt pavements is a sufficient level of bearing capacity so that air voids can be kept below 3%."

The optimum void content depends on mix design, but it is obvious that more attention should be paid to field compaction and that the void content should be a major consideration in mix design.

CHAPTER I-4

ASPHALT COMPATIBILITY

Summary

The compatibility of a mixture of components refers to the ability of the various components to form a homogeneous and stable mixture. This property is almost certainly related to the durability and other performance characteristics of the asphalt. This has been recognized in literature reports of studies of asphalts which address the types of components which exists within asphalts and the ratios in which they are combined. However, an understanding of how to use this information to effectively explain and predict asphalt performance remains very limited, due to the complex nature of asphalt materials in both types and number of components.

Introduction

Asphalt from petroleum crude sources is a mixture of hydrocarbon compounds of varying polarity with smaller amounts of sulfur, nitrogen, oxygen and trace amounts of metals.

Two systems for describing asphalt in terms of its components are universally used. The first divides asphalt into asphaltenes and petrolenes or maltenes. The asphaltene fraction is solid, highly aromatic, polar, and of higher molecular weight. The petrolene/maltene fraction "solubilizes" the asphaltenes. The second system of nomenclature divides asphalt into oils, resins, and asphaltenes. In this system, the nonpolar oil fraction keeps the asphaltene fraction dispersed by the action of the intermediately polar resin fraction.

Compatibility is the property of asphalts which describes this internal phase relationship. Compatibility can be viewed as a measure of internal stability. This property is intricately related to the chemical composition of the asphalt and its various fractions. Several reviews on the subject of asphalt chemical composition (Petersen, 1982, Halstead, 1985, and Petersen, 1984) assert the importance of this property. Unfortunately, the chemical composition of asphalt differs from one source of crude to another and much about the chemical composition remains unknown. Asphalts which meet the same specifications often perform very differently in the field when used as pavement binders. Obviously, the existing specifications do not tell the whole story. Compatibility, as a property, is of particular interest when two asphalts are blended. The initial properties of the blended asphalts are not necessarily additive (Petersen, 1982).

Compatibility may be even more important when related to the phenomenon of aging. As asphalt ages, its chemical composition and structure undergo changes, thereby changing the original stability of the mixture. These changes are what determines how well the asphalt will perform, and it is assumed that the more that is known about the internal relationships and stability of components, the more the aging phenomena may be understood. The ultimate goal, of course, is the creation of better specifications and more accurate ways in which to predict field performance based upon original composition.

In the discussion which follows, the literature on fractionation procedures, solubility phenomena, and analysis of structure are reviewed. In addition, some of the tests devised for compatibility are discussed.

Fractionation Procedures

Many different fractionations or separations of asphalt have been published in the literature, some of which are referenced here (Rostler and Sternberg, 1949, Rostler and White, 1959, Corbett, 1969, Marcusson, 1916, Hoiberg and Garris, 1944, Traxler and Schweyer, 1953, Kleinschmidt, 1955, Jennings, 1985, Hubbard and Stanfield, 1948, Boduszynski et al., 1980, Hattingh, 1984, Mack, 1932, and Brule et al., 1986). The methods proposed for separation have been chemical, functional, physical or combinations of these three. Many researchers have attempted to correlate parameters obtained from the various fractionation procedures with pertinent physical properties (Halstead et al., 1966, White et al., 1970, Skog and Zube, 1966, Corbett, 1970, Girdler, 1965, Bransky et al., 1958, Traxler, 1960, and Davis and Petersen, 1967).

Perhaps the best known of these procedures is the Rostler-Sternberg fractionation (Rostler and Sternberg, 1949, and Rostler and White, 1959). This chemical separation method, based upon reactivity with sulfuric acid, was originally intended for use with petroleum oil extenders (Rostler and Sternberg, 1949). A brief description of the procedure follows. A sample of asphalt is dissolved in n-pentane and the precipitated asphaltenes (fraction A) are removed. The remaining solution is treated with 85% sulfuric acid which precipitates the most reactive compounds. The precipitate is labeled as fraction N because Rostler believed that the nitrogen bases were found here. This remaining solution is treated with 98% sulfuric acid to precipitate the A1 fraction (for first acidaffins). The solution is again treated, this time with fuming sulfuric acid containing 30% SO_3 to precipitate fraction A2 (for second acidaffins). The remaining unreactive fraction, the paraffins, is labeled P. Rostler and Sternberg (1949) describe the functions of the various fractions as they relate to the asphalt mixture. The asphaltene fraction is primarily responsible for asphalt viscosity and colloidal behavior due to its limited solubility in the remaining fractions. The nitrogen base fraction, a highly aromatic fraction, is responsible for dispersing the asphaltenes. The asphalts are solvated by the acidaffin fractions and gelled by the paraffins.

Several researchers have studied the relationships between the Rostler-Sternberg fractions and the physical properties of asphalt (Halstead, 1985, Halstead et al., 1966, White et al., 1970, and Skog and Zube, 1966). Halstead et al. (1966), in a continuation of the original work of Rostler and White (1959), investigated the relationship between the compositional parameter (N + A1)/(P + A2) and asphalt durability as measured by the pellet test. The parameter (N + A1)/(P + A2) represents the ratio of more to less chemically reactive components. For this study, asphalts were grouped by three penetration grades: 60-70, 85-100, and 120-150. The investigators derived a mathematical relationship for estimation of abrasion resistance from the composition parameter and viscosity at 77°F.

In another study White et al. (1970) attempted to quantify the compatibility and interchangeability of the Rostler-Sternberg fractional components. Four asphalts from different geographical regions were used. Each of the asphalts was separated into the five fractions and reblended in different proportions. When the asphaltene fraction was eliminated, all other components were compatible. With the asphaltene fraction present, compatibility depended mainly on the ratio of nitrogen bases to paraffins (N/P). The actual limiting value of N/P for compatibility depends on the individual asphalt. The conclusion reached was that the molecular weight of the asphaltene fraction and its content of nitrogen base type compounds accounted for the asphaltene effect on compatibility.

Skog and Zube (1966) applied the Rostler-Sternberg separation method in a study of asphalt durability. They investigated some of the findings of the original Rostler and White research. Rostler and White (1959) stated that in terms of durability, the N and A1 fractions undergo the greatest changes due to oxidation, while the A2 and P fractions change very little. Skog and Zube (1966) reached several conclusions. They found no relation between the asphalts in terms of change in A or A1 and A2 during mixing and service life. They also confirmed earlier results of Rostler and White which found a correlation between (N + A1)/(P +A2) of the original asphalt and abrasion loss. Skog and Zube found that this relation is not as good when viscosity is used at an equivalent test temperature. Further, there is no relation between (N + A1)/ (P + A2) and shear susceptibility; however A/N shows a relation.

A second well known fractionation method is that of Corbett (1969). Corbett separates asphalt into four generic fractions using solvent deasphalting, elution-adsorption chromatography, and densimetric characterization. This procedure uses n-heptane as the solvent for precipitating the asphaltene fraction (A). The portion of the asphalt that is soluble in n-heptane is separated by means of elution-adsorption chromatography on an alumina column. Solvents of increasing polarity are added to the column so that eluates of increasing polarity may be collected. The fractions recovered in order of increasing polarity are saturates, naphthene-aromatics, and polar-aromatics (fractions S, NA, and PA, respectively). The fractions collected are subsequently characterized by the densimetric method. The densimetric method involves a calculation which makes use of molecular weights and atomic hydrogen/carbon ratio. This method allows measurement of the degree of aromaticity and the degree of naphthenicity of the fractions. Corbett found that the amount of reduction of the asphalt by distillation and the crude source of the asphalt have pronounced effects on amount and composition of the individual fractions.

In a subsequent paper, Corbett (1970) was able to describe the characteristics of each fraction and the relationship of the fractional composition to physical properties. He reports that the S and NA fractions have relatively low viscosities and softening points as compared to the PA and A fractions. He describes asphalt as a system in which the S and NA fractions are the liquids acting as plasticizers for the solid PA and A fractions. The asphaltenes (A) function as solution thickeners. As regards physical properties, he concluded the following:

(1) The physical properties of each fraction are distinctly different.

(2) The fluidity of an asphalt is increased by the plasticizing effect of the S and NA fractions on the solid fractions.

(3) The combination of the S and NA or the NA and A fractions improves temperature susceptibility while the combination of the PA and A fractions reduces temperature susceptibility.

(4) Asphalt ductility depends mainly on the PA fraction.

(5) The flow resistance and softening point of an asphalt are increased by the combined S and A or the NA and A fractions and are decreased by the combined PA and A fractions.

(6) NA and A fractions acting together contribute to high asphalt viscosity relative to penetration.

(7) S and A acting together or the NA and A fractions acting together contribute to asphalt shear susceptibility, while the combined PA and A fractions lead to Newtonian flow.

(8) Asphalt properties depend both on individual effects and interactive effects from fractions.

Girdler (1965) used a modification of the Corbett procedure to study the asphaltene fraction in detail. Based upon the collective body of information available on asphaltenes, he sought to show that structural differences existed between the different asphaltenes which needed to be accounted for in the then current specifications. One of the most important results of this work was the establishment of n-heptane as the preferred solvent for the precipitation of asphaltenes. Progressively smaller amounts of material are precipitated as the number of carbons in the solvent is increased until about C_7, after which the amount remains relatively constant. He referred to this precipitated material as the "hard core" asphaltenes. These asphaltenes were studied by using various techniques including color intensity, molecular weight determination, elemental analysis, NMR spectroscopy, and IR spectroscopy. He found that the vanadium and nickel were located in these hard core asphaltenes. In addition, he supported the idea that most of the original nitrogen and sulfur occurs in the ring systems of the asphaltenes.

Part of the previously referenced work performed by Halstead (1985) involved a comparison of the relative merits of the Rostler-Sternberg and Corbett procedures. Both methods have been criticized for creating special terminology unfamiliar to many asphalt technologists. The Rostler-Sternberg procedure removes and chemically alters the fraction being separated, making it unavailable for further examination. The two methods also utilize different solvents for precipitation of the asphaltenes. For purposes of comparing the methods, the following similarities were noted. Components in the Corbett polar aromatics fraction are found in the Rostler-Sternberg nitrogen base fraction and possibly the first acidaffin fraction. The Corbett naphthene aromatics fraction is roughly comparable to the Rostler-Sternberg second acidaffin fraction with part of the first acidaffin fraction. The Corbett saturates fraction is similar to the Rostler-Sternberg paraffin fraction (Halstead, 1985).

One of the oldest fractionation procedures is the Marcusson-Eickmann method (Marcusson, 1916). This method entails first dissolving the asphalt in high boiling petroleum ether. The insoluble portion is labeled asphaltenes and the remaining solution is treated with sulfuric acid. The portion that reacts and precipitates is removed and added to the asphaltene fraction. The remaining solution is labeled oils. Bransky et al. (1958) later used a modification of this procedure which defined three fractions: oils, resins, and asphaltenes. Their study showed the need to better relate asphalt composition to the prediction of asphalt performance. Hoiberg and Garris (1944) developed a fractionation method which separates asphalt into five fractions: hexane insolubles, hard resins, soft resins, oils, and waxes. The fractions are all recoverable; hence they may be studied individually. The separations are based upon solubility and molecular weight differences. Traxler and Schweyer (1953) developed a fractionation procedure intended as an improvement of the Hoiberg and Garris procedure. In this procedure the asphalt is dissolved in n-butanol first. The precipitated asphaltics are the first fraction removed. The n-butanol is removed from the remaining solution, acetone is added, then the resulting solution is chilled to -10°F. The precipitate is removed and labeled paraffins; the fraction remaining in solution is called the cyclics. In a later paper, Traxler (1960) relates the fractional compositional parameter "Coefficient of Dispersion" to a hardening index.

The last of what are considered the most common fractionation schemes is the Kleinschmidt procedure. This method (Kleinschmidt, 1955) uses solvent precipitation and chromatographic separation. The asphaltene fraction is precipitated with n-pentane. The remaining solution is concentrated and then adsorbed with Fuller's Earth. N-Pentane is then added to the column; the first eluate is the white oils fraction. Methylene chloride is next added to the column; the next eluate is the dark oils fraction. Methyl ethyl ketone is added to the column and the last eluate collected is the asphaltic resins fraction. A fifth fraction may be recovered from the residue in the column, but is usually combined with the asphaltic resin fraction.

A more recent method of separation using HP-GPC was discussed by Jennings (1985). This is a physical separation technique which divides asphalt primarily according to molecular size. The three divisions are LMS, MMS, and SMS (for large, medium, and small molecular size, respectively). The study suggests that cracking in asphalt is closely related to LMS, and that the appearance of a large LMS region indicates undesirable asphalt characteristics.

Other fractionation methods may be found in the literature, but are too numerous to detail here. These include Hubbard-Stanfield (1948), Boduszynski et al. (1980), Hattingh (1984), and Mack (1932). Brule et al. (1986) detail an "ultra fast GPC" method which they relate to a "colloidal instability index." Many more comparisons of the various fractionation methods may also be found in the literature, two of which are referenced here (Rostler and White, 1959, and Boduszynski, 1981). Rostler and White (1959) compare the Rostler-Sternberg procedure with the Marcusson-Eickmann, Hubbbard-Stanfield, Traxler-Schweyer, and Kleinschmidt procedures. Boduszynski (1981) compares his procedure with the classical Corbett procedure.

Solubility Phenomena

The focus of much of the recent compatibility literature (Altgelt and Harle, 1975, Mitchell and Speight (1973), Hagen et al., 1984, and Mertens, 1960), is on the solubility behavior of the asphalt "solution." The concept of asphalt as a solution is closely related to theories of asphalt structure, which will be discussed later.

Altgelt and Harle (1975) investigated the role of asphaltenes on asphalt viscosity by taking the approach that asphalt is a molecular solution rather than a suspension of small particles. They used three asphalts from different sources. The asphaltenes were separated from the parent asphalts, then subjected to analysis by GPC. Solutions were prepared of fractions and of whole asphaltenes in a variety of solvents. These solution viscosities were examined in terms of concentration, solvent power, and asphaltene molecular weight and structure. The separation yielded asphaltenes with molecular weights from less than 1,000 to greater than 20,000. The viscosity trends were explained in terms of intra- and inter-molecular aggregations. The tendency of the asphaltenes to aggregate was found to depend on the molecular weight, the particular solvent used, and the concentration. The highest molecular weight asphaltenes showed the highest viscosities due to the formation of complex extended molecular shapes. Intermolecular aggregation causes the intrinsic viscosity to increase with increasing concentration. This effect is most pronounced with the highest molecular weight asphaltenes. The asphaltene molecules aggregate more in the poorer solvents, thus causing the intrinsic viscosity to increase with decreasing solubility parameter. At low molecular weights, the solvent effect is very small; at high molecular weights it is quite pronounced.

Mitchell and Speight (1973) studied the ability of hydrocarbon solvents to dissolve Athabasca bitumen. The aim of this work was to find solvents that would precipitate the compounds containing metal and mineral contaminants, as these components are harmful to the cracking procedure. This study showed that normal hydrocarbons, branched hydrocarbons, and terminal olefins all caused the precipitation of varying amounts of asphaltenes. However, the cycloparaffins and the aromatics were found to be excellent solvents for the entire asphalt. The results were explained by postulating a micellar structure of asphalt. The center of the micelle consists of highly aromatic and polar asphaltene compounds. The more polar resins may also concentrate within the micelles; while the less polar resins and the nonpolar paraffins would be found outside the micellar region. The solvent power of most hydrocarbons is not high enough to prevent association among the polynuclear aromatic compounds, but it is strong enough to power them into the micelle structure. The solvents of high solvent power (larger solubility parameter δ) are strong enough to break up the intermolecular associations and penetrate the asphalt micelles. Solvents with δ_1 (as defined by Hildebrand and Scott) ≤ 4.2 will only be able to dissolve the low molecular weight asphaltenes (smaller asphaltene molecules).

Hagen et al. (1984) undertook a solubility parameter analysis of asphalts. The solubility parameters δ_r^2 and δ_V^2 were developed from the Hildebrand and Scott (1950) solubility parameter concept. The δ_r parameter is related to hydrogen bond interactions, while the δ_V parameter is related to nonpolar and dipole-dipole interactions. They presented the solubility profile of a substance as a plot of substance solubility versus (δ_r, δ_V) coordinates of the solvents. The solubility profile of a virgin asphalt is basically elliptical in shape with a high solubility region roughly covering the solubility domain of cyclic saturates and the naphthene aromatics. Upon mild oxidation, the profile expands to include the solubility domains of the acid derivatives and the phenolic derivatives. Upon exhaustive oxidation, the solubility profile is shifted as a whole toward the more polar solubility domains. These solubility profiles can be used to detect the presence of additives, to determine whether an asphalt has been cracked, and to predict oxidation products of aged asphalts.

Mertens (1960) devised a method for measuring the dispersibility of asphaltenes and was able to relate it to the solubility parameter. Since the durability had previously been related to the dispersibility, this work presented a way to estimate durability as well as relate it to a fundamental property of asphalt. The dispersibility of the least soluble asphalt was measured in a heptane-xylene solvent system. The procedure used is similar to the Oliensis Spot Test (1933). The solubility parameters δ_x and δ_H (defined by Hildebrand and Scott) along with the dispersibility (p_a) are used to calculate the critical solubility parameter (δ_c). This is the solubility parameter of the system at which flocculation of asphalt first occurs.

Analysis of Structure

The effects of solvents and solubilities are probably most important when studying asphaltenes, since they are defined as a solubility class. Historically, the asphaltene component of asphalt has been the subject of most studies. This is partly due to the large changes that this component undergoes during oxidation. Association of asphaltene molecules has a large influence on asphalt viscosity. Theories as to the macrostructure of asphalt have been proposed. Nellensteyn (1928) is first credited with the theory of a micellar structure. He proposed that asphalt had three components:

(1) The medium--composed of oils
(2) The lyophile part--protective bodies
(3) The lyophobe part--elementary carbon

The last two parts make up the dispersed phase or micelle. He referred to changes in the stability of the system as flocculative and peptizing reactions. The theory was based mainly on surface tension measurements of various solvents and the degree of solubility of asphalt in these solvents. Following Nellensteyn's work, Pfeiffer and Saal published data supporting the micelle structure (1938). Their conclusions were based on carbon/hydrogen ratios, molecular weight measurements, and other physical properties.

Much more sophisticated methods have been used to study asphalt structure. Yen et al. (1961) used X-ray diffraction to determine the aromaticity and crystallite parameters for several asphaltenes. The aromaticity values of some of the asphaltenes studied showed an inverse relationship with oxidation rate. In later work, Dickie and Yen (1967) studied the macrostructure of asphalt with X-ray diffraction and scattering, mass spectroscopy, GPC, and vapor pressure osmometry. Both of these studies supported the micelle structure of asphalt. They described asphaltenes as sheets of condensed aromatic systems. These sheets have a tendency to associate by stacking, to form clusters and micelles. The resins are less aromatic analogs of the asphaltenes. Speight (1971) also studied the structure of asphaltenes. He used proton magnetic resonance spectroscopy. Estimates of the aromatic structure indicate that the aromatic sheets vary from 6 rings to 14 rings (possibly more). Electrostatic association as well as chemical bonding are responsible for the high molecular weights measured.

In a review of the methods used to determine asphaltene structure, Speight and Moschopedis (1981) point out many problems. All of the methods used have serious shortcomings because the assumptions required to derive molecular formulae may not be valid. They point to conflicting data and particularly to widely conflicting reports of molecular weights. Of all the data studied, the X-ray diffraction results support the idea of asphaltenes existing as clusters in the micelle. However, some of the evidence of hydrogen bonding refutes this theory.

Compatibility Tests

A considerable amount of effort has been spent in attempts to devise accurate and practical tests for compatibility. To date, only the Oliensis Spot Test (1933) and the Heithaus Test (1960) have gained wide acceptance, although others have been proposed. The Oliensis test was first proposed in 1933 as a test to qualitatively determine the heterogeneity of asphalt. A sample of asphalt is dissolved in naphtha at a volume ratio of 5.1/1 and the solution is examined for residue. The test is based on the theory that as the heterogeneity of asphalt increases, the amount of residue should also increase. A drop of the solution is placed either on a glass slide or a piece of filter paper and examined after drying for the appearance of streaks or spots.

Oliensis (1936) updated the Spot Test to include a method for quantitatively determining the degree of heterogeneity of asphalt. The test solvent was changed from naphtha to a mixture of naphtha and xylene. The procedure was followed as before but the ratio of xylene/naphtha in the solvent was varied until the minimum proportion of xylene necessary to yield a negative spot was found. Oliensis also discusses several types of heterogeneous asphalts including cracked asphalts, refined asphalts accidentally subjected to higher than normal temperatures, and highly blown asphalts.

The Oliensis Spot Test eventually became accepted as an asphalt specification. This eventually led to problems because several asphalts that performed satisfactorily yielded positive spot tests. (In general, a positive spot test would indicate poor compatibility which means poor performance as a pavement binder.) Mallatt and Bransky (1956) called for the modification of the spot test so as not to reject crudes that give positive tests due to naturally occurring bodies. Most of the positive spot crudes were rejected due to excessive cracking or blowing at the refinery. It was discovered that most of the uncracked asphalts yielding positive spot tests were unusually high in sulfur content. The "oil fractions" of these asphalts are naphthenic and act as good solvents for the resins and asphaltenes (an indication of compatibility). When these asphalts are diluted with a paraffinic naphtha, the antisolvent or antidispersant action of the naphtha may cause a portion of the asphaltenes to precipitate. These investigators suggested replacing the xylene-naphtha mixture with 35% xylene in n-heptane.

In answer to the preceding and other criticisms of the spot test, Oliensis (1957) restated the purpose of the test and proposed it as a quality test. Oliensis stated that the original purpose of the test was not to distinguish between cracked and uncracked asphalts, but to determine the internal phase relationship of an asphalt. The test can reflect the degree of stability and the degree by which the stability has been impaired or may be impaired in the future. The test is a quality test, but should not be used as the sole test of quality.

Heithaus and Fink (1959) examined the Oliensis Spot Test and called for its replacement by more direct measures of quality such as those based on viscometric measurements. They demonstrated that the Oliensis Spot Test was not directly related to durability or asphalt quality. The test method evaluates only one point on the flocculation ratio versus reciprocal dilution ratio curve, which is not sufficient information to describe the stability of the system. Heithaus (1960) later proposed his own test for compatibility which used the entire flocculation ratio versus dilution ratio curve of an asphalt.

The Heithaus Test is based on the premise that in order to fully describe the colloidal system, information is needed about the solvency of the maltene fraction and about the solubility of the asphaltenes. Once these two pieces of information are known, the overall system can be adequately described. The test makes use of the straight line relationship between reciprocal dilution ratio and flocculation ratio. The flocculation ratio (FR) is defined as "the minimum proportion of aromatic in an aromatic/nonaromatic diluent mixture necessary to prevent precipitation of asphaltenes." The dilution ratio (X) is defined as the "ratio of total volume of diluent to volume of residue." In the testing procedure, toluene is the aromatic while n-heptane is the nonaromatic. The "peptizability of the asphaltenes" or p_a is closely related to the maximum value of FR (obtained from the plot), while the "peptizing power of the maltenes" or p_0 is related to FR_{max} and the minimum value of X. The two parameters are combined to give p, the state of peptization of the system. As the state of peptization increases, p increases.

In a study of peptization of asphalts (Venable et al., 1983), the values of Heithaus parameters correlated with properties of asphalts of known compatibility in extreme cases. However, the author concluded that useful application of the parameter will require more study. Skog and Zube (1966) studied the relationship of the Heithaus parameters to physical properties. The nature of changes in these parameters due to weathering was investigated. The results showed that there was no change or a varying amount of decrease in p_a, while p_0 was found to increase or decrease. When compared with physical properties, p values show a fair relation with viscosity of the durability test residue and p_a values show a good relation with the viscosity of the durability test residue. In addition, the p values show a good relation to the shear index of durability of the durability test residue (1966).

Plancher et al. (1979) have suggested another test to be used for asphalt compatibility. Their settling test seeks to quantify the compatibility of the asphalt components by upsetting their critical balance with hexane. The asphaltenes with longer settling times are more finely or better dispersed in the hexane-maltene phase. This implies a more compatible asphalt. This test also makes use of the correlation between durability and dispersibility discovered by Mertens (1960). It basically consists of mixing a sample of asphalt with n-hexane to cause precipitation of asphaltenes. The mixture is stirred until the asphaltenes are well dispersed and then transferred to a graduated cylinder so that the time it takes for the asphaltenes to settle can be measured with a stopwatch. The authors suggest using this test together with viscosity results both before and after aging.

SECTION II

ANALYTICAL METHODS

An important part of this study has been the development of analytical procedures and their use in asphalt characterization and evaluation. In this section, some new techniques for evaluating GPC analyses and some accurate procedures for infrared analysis are discussed. A pellet procedure was developed for obtaining very reproducible IR spectra, and this was used in much of the work. Later in the project a much faster, and essentially equivalent, internal reflections procedure was developed. This procedure was used in the hot-mix and solvent aging study.

A considerable amount of work was done on improving the Corbett procedure. It was discontinued when the seriousness of the problems was appreciated, but a better understanding of the sources of error was obtained. Also, the Heithaus procedure was used to measure the compatibility of asphalts used in the test section and hot-mix studies, and atomic absorption spectrophotometry was used to determine the trace metals' content of the test section asphalts as a possible indicator of aging and water susceptibility.

CHAPTER II-1

GEL PERMEATION CHROMATOGRAPHY (GPC) INFINITE DILUTION LMS

Summary

This chapter describes work to improve the use of percent Large Molecular Size (LMS) from GPC chromatograms as correlating parameters. The use of this parameter has a number of limitations, but the one addressed here is the effect of concentration. As percent, LMS is very concentration dependent; an infinite dilution value was determined such that this limiting value or the area under a segment of the percent LMS versus concentration curve could be used as parameters.

Introduction

GPC has been used routinely in every element of this study. Both the theory and practice have been discussed in the final report of a previous project, Glover et al. (1987) and in Glover et al. (1989), and using toluene as a carrier was presented in Donaldson et al. (1988). All the work of this current study was done with tetrahydrafuran (THF) as a solvent with a flow rate of 1 ml/min. Other operating parameters were as described by Glover et al. (1987), except that the 500 Å/50 Å column combinations were used exclusively with a refractive index detector. Injected volume was generally 100 μl, and asphalt concentration was 7%, except where noted.

Percent Large Molecular Size (LMS) first suggested by Jennings (1977) and Jennings et al. (1981, 1982), was adopted in this work and defined as the percent of the total chromatogram area (total area defined as the area between 20 and 35 minutes) that eluted between 20 and 25 minutes.

The definition of LMS as defined above is arbitrary and dependent upon operating variables such as asphalt concentration. In order to eliminate concentration as a variable and to obtain a more complete definition of LMS, an infinite dilution LMS has been defined yielding either two parameters (a zero concentration LMS and a slope of LMS versus concentration), or a single combined parameter (an area under the LMS vs concentration curve from 0 to 6% asphalt concentration).

Procedure

Thirty tank asphalts from the test sections and hot-mix aging studies, along with oven and hot-mix asphalts from the hot-mix aging study, were sampled at various dilutions (7, 6, 5, 4, 3, 2, 1, and 0.5 wt %). The asphalt samples were weighed into 20 ml glass scintillation vials and dissolved in tetrahydrafuran. They were sonicated for 30 minutes and filtered through a 0.45 micron filter. After filtering, the asphalt was transferred to glass sampling vials and loaded on the Automatic Sample Handler.

GPC chromatograms were obtained for each of the dilutions and the percent LMS was calculated and plotted versus concentration for four tank asphalts, as shown in Figures II-1-1 to II-1-4. The first three asphalts were used in the 1982-83 test sections, and the fourth is an asphalt from the hot-mix study. Note the reverse slope of the Diamond Shamrock. The slopes and intercepts are given in Tables II-1-1 to II-1-3. The percent LMS vs. concentration data are in Appendix A. The 7% and 0.5% data were omitted in calculating the values in Tables II-1-1 to II-1-3, because the 7% points were either below or on the curve, indicating nonlinear concentration effects were being encountered, and the .5% points were highly scattered.

Inspection of the data in Table II-1-1, suggests that asphalt provided by the same supplier may differ significantly in these LMS parameters. The MacMillan asphalt at Lufkin differs considerably from that at the other two locations. Also at Lufkin the Diamond Shamrock has a positive slope while the slope is negative at the other two locations. The chromatograms for the Diamond Shamrock at Lufkin and at Dumas at the 7 wt % concentration are shown in Figure II-1-5. These are both characteristic of Diamond Shamrock, but they are not the same asphalt. For the hot-mix asphalts in Table II-1-2, a difference in the Exxon delivered to the batch plant and the other 1987 Exxon is seen.

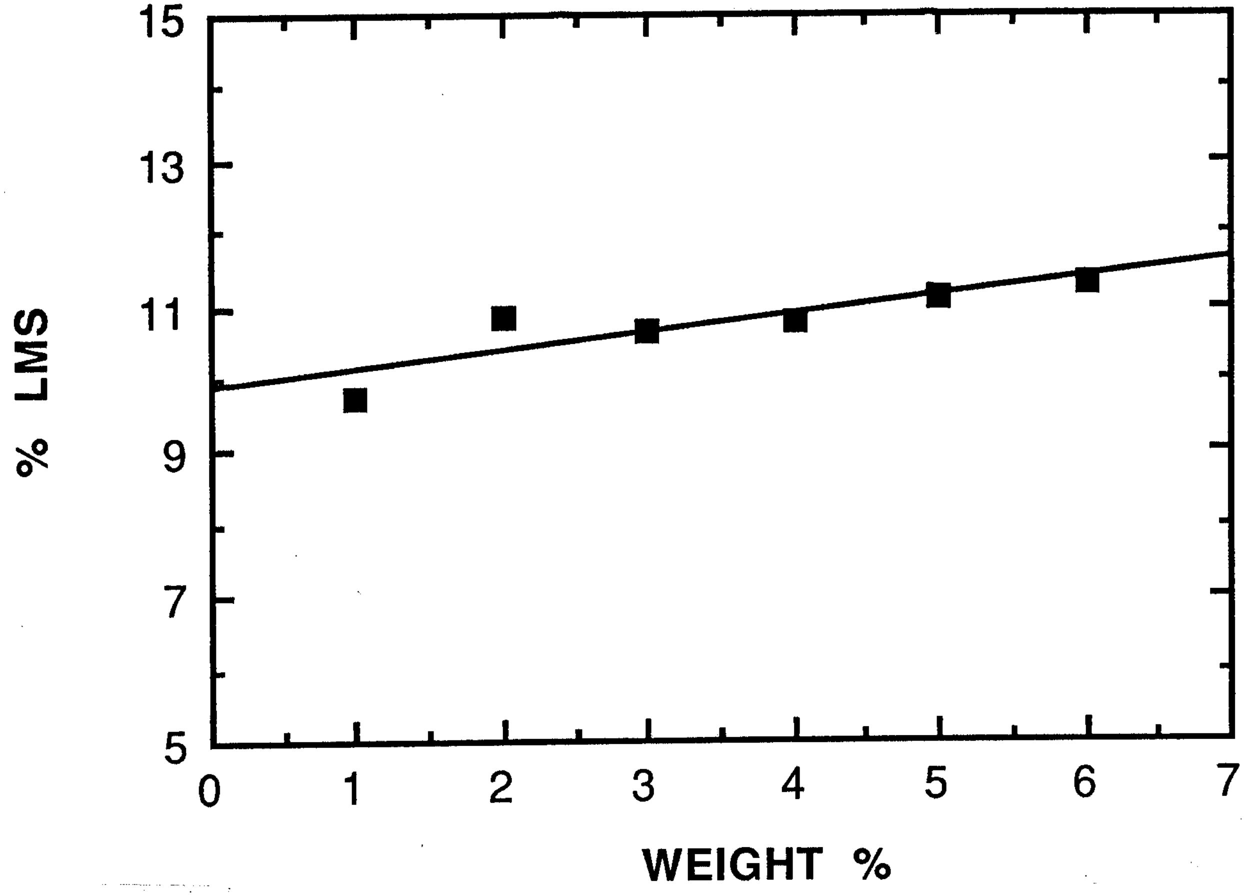

Figure II-1-1
Percent LMS Versus Concentration for Dumas Cosden AC-10

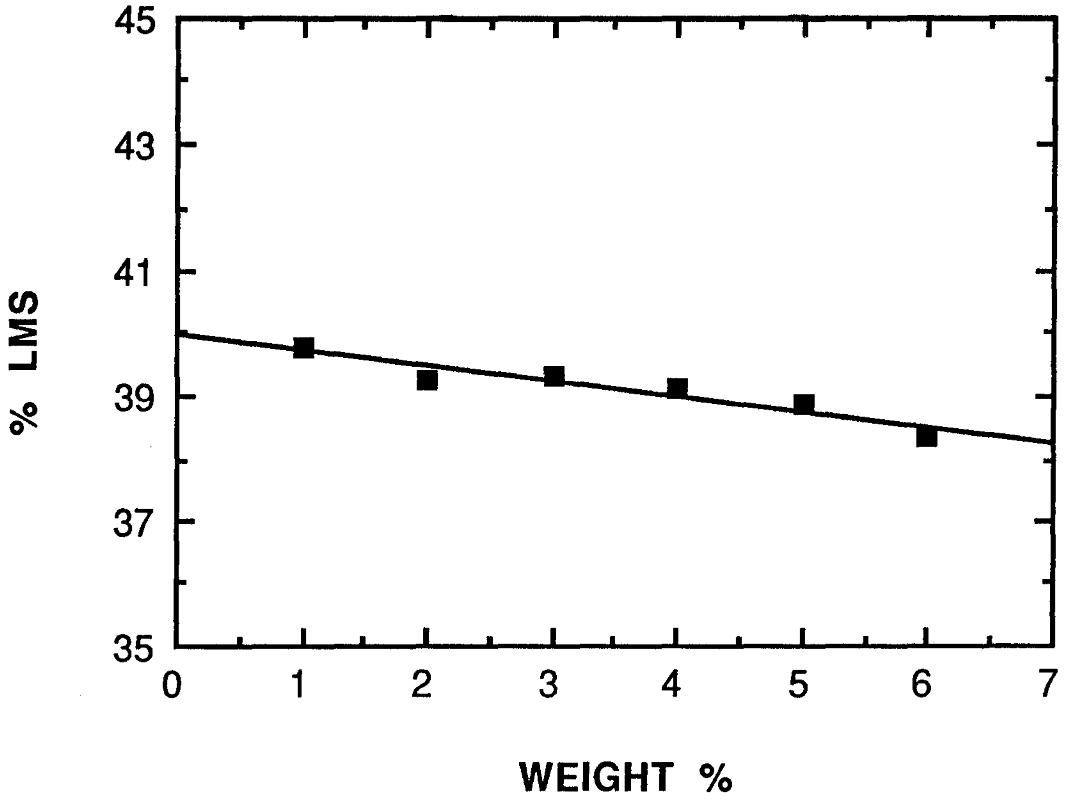

Figure II-1-2
Percent LMS Versus Concentration for Dickens Diamond Shamrock AC-10

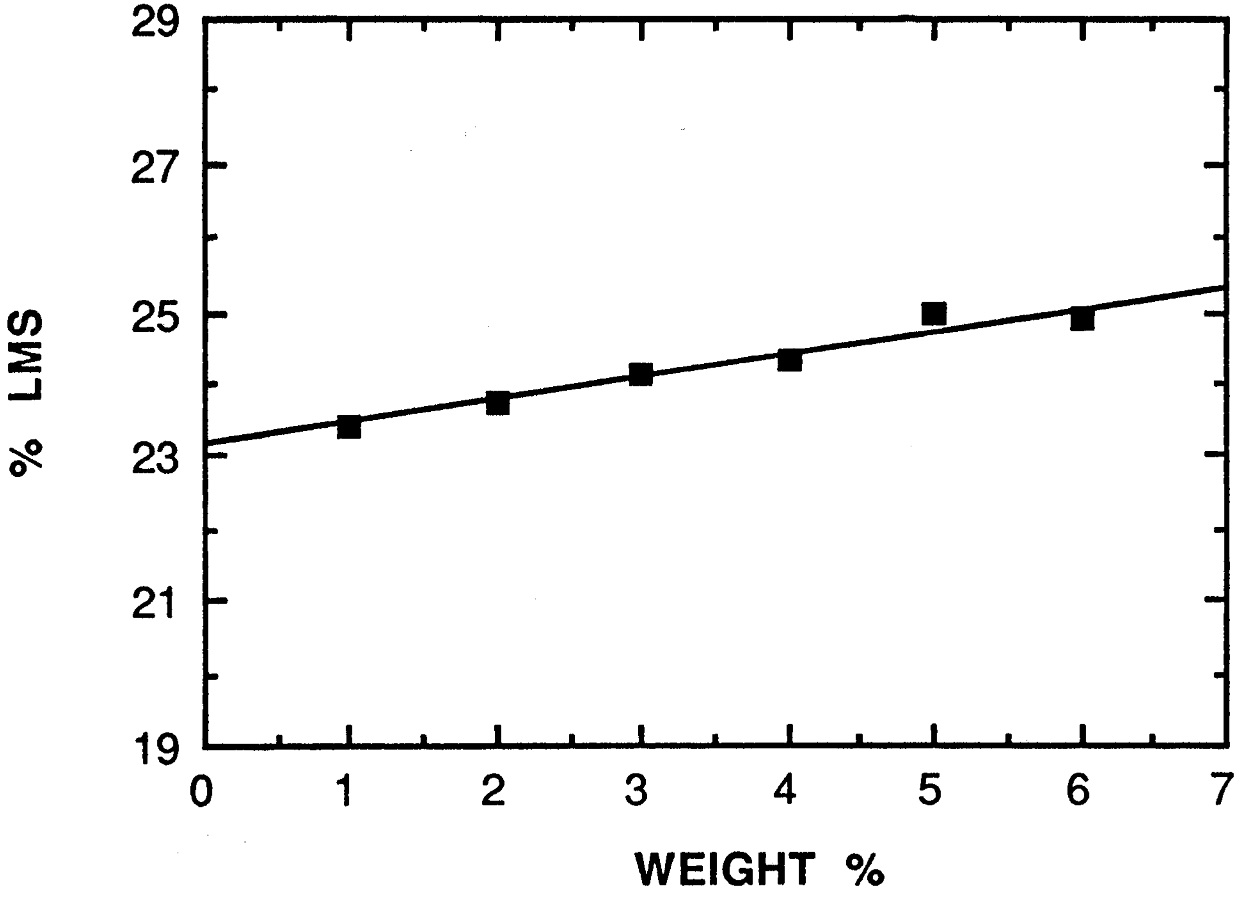

Figure II-1-3
Percent LMS Versus Concentration for Lufkin MacMillan AC-20

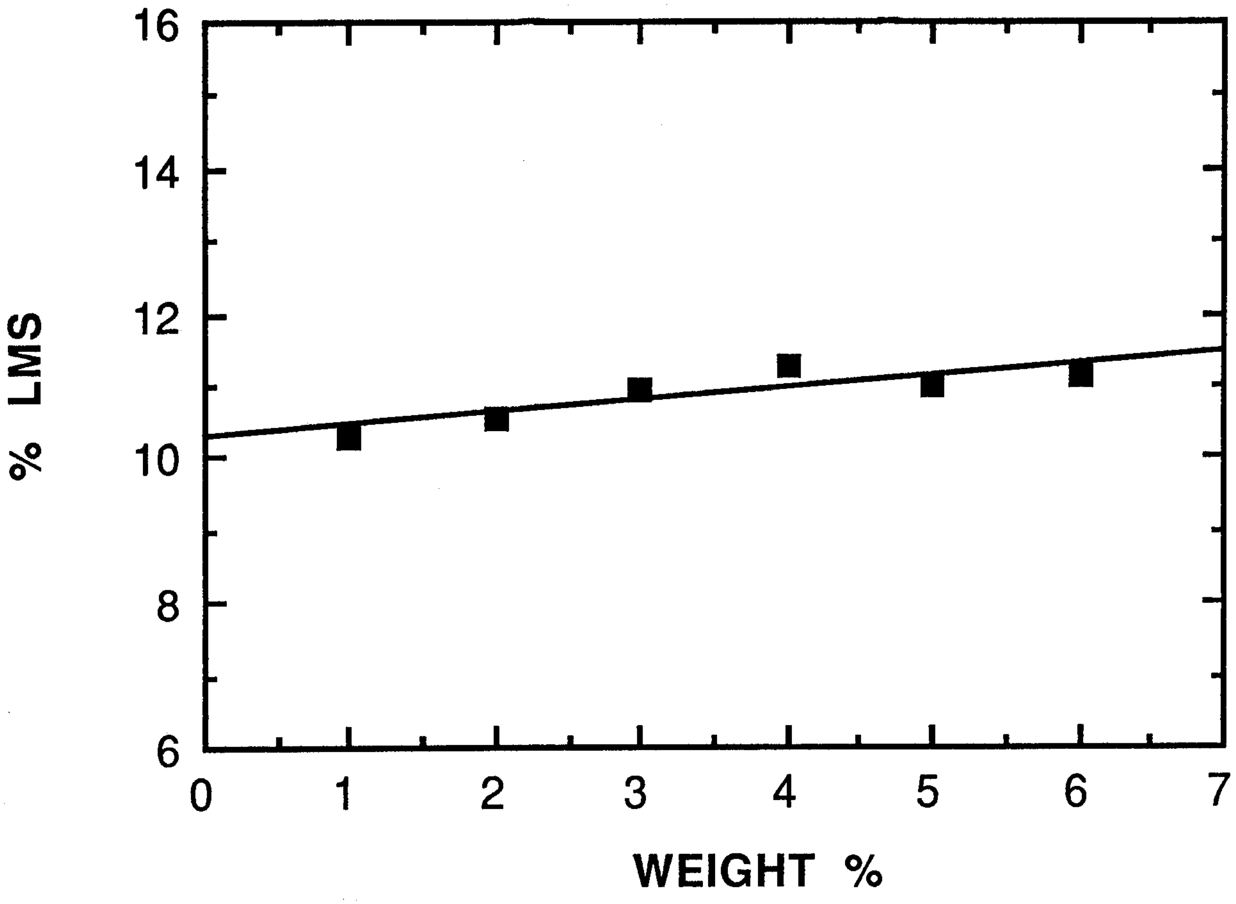

Figure II-1-4
Percent LMS Versus Concentration for 1989 Exxon AC-20

Table II-1-1

LMS Parameters for Test Section Tank Asphalts

Asphalt	Slope (% LMS vs Weight %)	Y Intercept (% LMS)
Dickens		
Cos AC-10	0.20	10.3
Cos AC-20	0.28	10.7
D.S. AC-10	-0.25	40.0
D.S. AC-20	-0.11	42.1
MacM AC-20	0.55	19.2
Dorch AC-20	0.70	14.8
EXX AC-20	0.23	11.8
Dumas		
Cos AC-10	0.25	9.9
Cos AC-20	0.21	10.7
D.S. AC-10	-0.12	41.5
D.S. AC-20	-0.22	40.4
MacM AC-10	0.45	14.5
Dorch AC-10	0.54	13.3
EXX AC-10	0.23	9.3
Lufkin		
Cos AC-20	0.30	10.4
D.S. AC-20	0.21	32.6
TEX AC-20	0.32	13.7
MacM AC-20	0.32	23.2
Dorch AC-20	0.54	12.9
EXX AC-20	0.12	10.2

Diamond Shamrock (D.S.)	MacMillan (MacM)	Exxon (EXX)
Dorchester (Dorch)	Cosden (Cos)	Texaco (TEX)

Table II-1-2

LMS Parameters for Hot-Mix Tank Asphalts

Hot-Mix Study Asphalts	Slope (% LMS vs Weight %)	Y Intercept (% LMS)
1987 Exxon Tank	0.42	11.7
1987 Exxon AC-20 Batch	0.16	9.3
1988 Exxon AC-20	0.09	9.8
1989 Exxon AC-20	0.16	10.3
1989 Cosden AC-10	0.12	9.7
1989 Cosden AC-20	0.12	23.3
1989 Ampet AC-20	0.25	13.5
1989 Texaco AC-20	1.04	13.4
Coastal AC-20	0.88	13.7
Texas Gulf	0.37	13.8

Table II-1-3

LMS Parameters for Hot-Mix and Oven Test Asphalts

Asphalt	Slope (% LMS vs Weight %)	Y Intercept (% LMS)
1988 Exxon AC-20		
14.5 hr TFO	0.06	14.4
5 hr TFO	0.28	11.2
Hot Mix	0.18	14.4
1987 Exxon AC-20 Batch		
14.5 hr TFO	0.22	13.3
5 hr TFO	0.36	9.9
Hot Mix	0.23	14.1
1987 Exxon AC-20 Drum		
14.5 hr TFO	0.35	15.4
5 hr TFO	0.32	12.7
Hot Mix	0.13	17.0
Texas Gulf AC-20		
14.5 hr TFO	0.41	18.6
5 hr TFO	0.43	15.5
Hot Mix	0.61	14.9
1989 Texaco AC-20		
14.5 hr TFO	0.76	18.4
5 hr TFO	0.64	16.5
Hot Mix	1.01	15.4
1989 Ampet AC-20		
14.5 hr TFO	0.52	17.5
5 hr TFO	0.43	14.4
Hot Mix	0.15	17.9

Table II-1-3 (Cont'd)

LMS Parameters for Hot-Mix and Oven Test Asphalts

Asphalt	Slope (% LMS vs Weight %)	Y Intercept (% LMS)
1989 Cosden AC-10		
14.5 hr TFO	0.36	15.1
5 hr TFO	0.34	11.7
Hot Mix	0.08	18.2
1989 Cosden AC-20		
14.5 hr TFO	0.31	30.8
5 hr TFO	0.32	27.8
Hot Mix	0.34	26.6
1987 Coastal AC-20		
14.5 hr TFO	0.58	21.9
5 hr TFO	0.40	19.3
Hot Mix	0.13	23.7

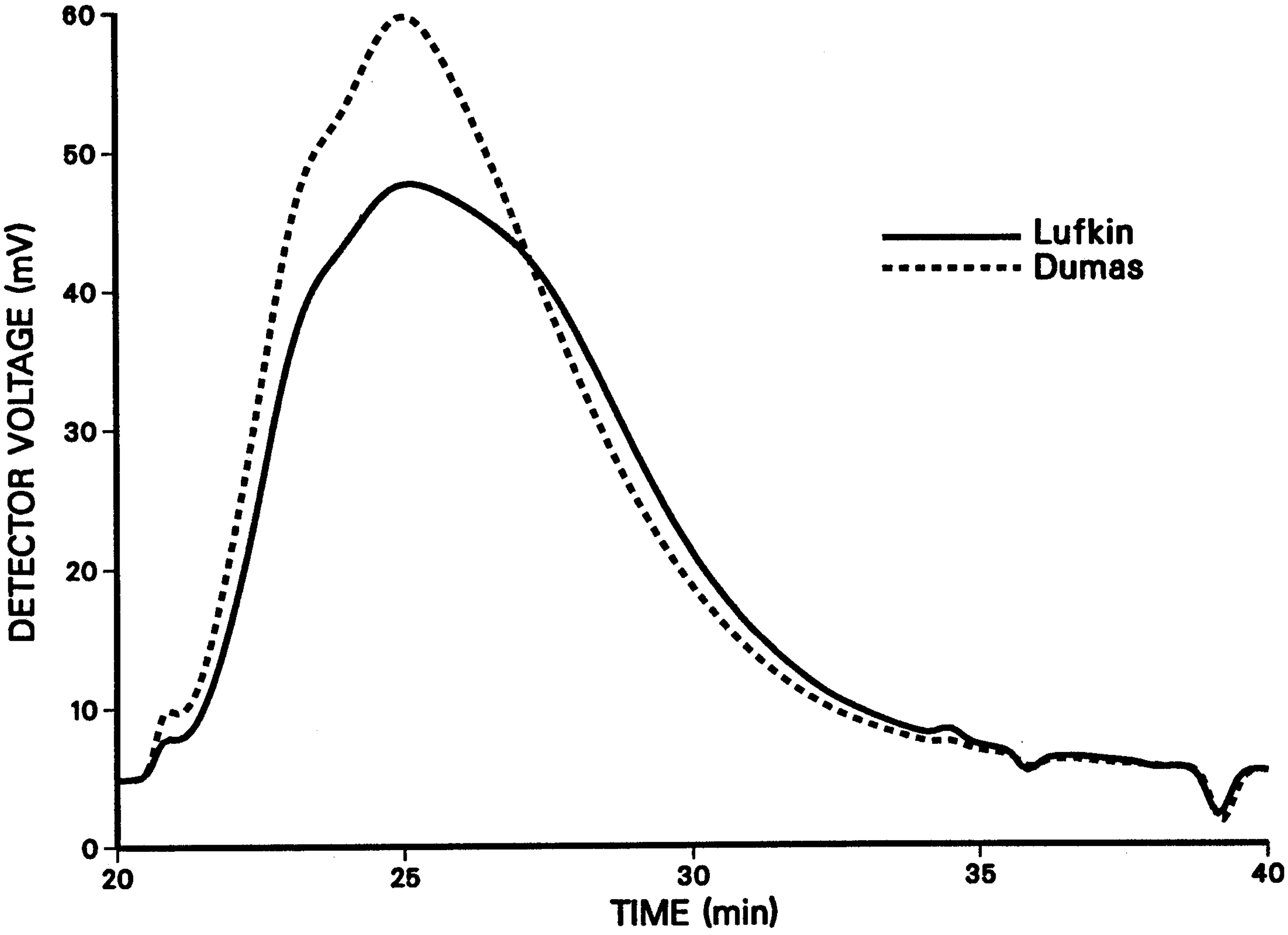

Figure II-1-5
A Comparison of GPC Chromatograms for the Lufkin and Dumas Diamond Shamrock Asphalts

CHAPTER II-2

A POTASSIUM BROMIDE PELLET PROCEDURE FOR THE ANALYSIS OF ASPHALTS USING FT-IR

Summary

In this chapter the development of a very accurate KBr pellet procedure for asphalt analysis is discussed. Its advantages over solution methods are freedom from solvent interferences and a strong signal. Perhaps the key feature of the procedure is very careful pellet preparation, including freezing of the asphalt so that it can be ground and thoroughly mixed with the KBr.

Introduction

Infrared (IR) analysis of asphalt continues to challenge asphalt chemists because of the complex nature and adhesive properties of asphalt which makes sample preparation difficult. In general, the infrared spectra of substances are fairly easily determined if the sample is a gas, a liquid, or a solid. But in this case, the asphalt sample is a material which is soft and sticky at room temperature and causes some problems in the course of sample preparation for infrared analysis.

Most researchers such as Petersen (1986) and Curtis et al. (1987) have determined the spectra of asphalt samples in solution. This method uses solvent to dissolve asphalt and then the obtained solution is analyzed by IR. Since all solvents absorb strongly in at least several regions of the infrared spectrum, it is necessary to use more than one solvent to be able to get a complete spectrum of the asphalt sample. The most commonly used solvents in the solution method are carbon tetrachloride (CCl_4) and carbon disulfide (CS_2).

Unfortunately, this method has several problems. First, it is difficult and time-consuming to prepare all the solutions at the same concentration because solvents tend to evaporate from the cell continuously during the course of analysis.

A second problem is solvent compensation. If a double-beam infrared spectrophotometer is used for analysis, solvent compensation is performed by placing the asphalt solution in the sample beam and the solvent blank in the reference beam. When matched liquid cells are used, the concentration of solvent will always be higher in the reference cell than in the sample cell. Thus, unequal absorption by solvent in the two cells complicates solvent compensation. When a single-beam infrared spectrophotometer is used, solvent compensation is further complicated by the difficulties inherent in quantitatively replacing the solution in the cell. Solvent evaporation causes drying of the sample and deposition of asphalt film inside the cell. Flushing the cell in place does not quantitatively exchange the solution; demounting, cleaning, and refilling the cell does not easily provide a solution of exactly the same pathlength.

A third difficulty is the weak absorption bands and the consequent low signal-to-noise ratio of the asphalt spectrum remaining after subtracting the solvent background. Increasing the asphalt absorption to improve this ratio can be achieved either by increasing its concentration in the solution or by increasing the cell pathlength. Increasing the concentration, however, is limited by the necessity for a homogeneous solution. Increasing the pathlength is limited by the necessity of keeping the solvent absorption within the range of Beer's law so as to achieve quantitative solvent subtraction. Solvents such as carbon tetrachloride and carbon disulfide have some very strong absorption bands which reach detector saturation in very thin cells. Hence, multiple analyses with different solvents which have strong absorption bands at different frequencies are necessary to obtain a complete picture of the asphalt spectrum.

In this section an alternative procedure using asphalt-KBr pellets is presented. The reproducibility of infrared absorption spectra for this method is shown.

Experimental Apparatus and Procedures

Materials and Apparatus. The instrument used in this study for IR analyses was a Nicolet 60SX Fourier transform-infrared (FT-IR) single beam spectrometer. Potassium bromide was IR grade obtained from Fisher Scientific.

Pellet Preparation. Dry KBr powder was prepared for each batch of pellets. The KBr was oven-dried for 2 hours or more at 300°C to complete dryness, as verified by the absence of water IR absorption bands near 3710 and 1630 cm^{-1} in a pure KBr pellet. The dry KBr powder was stored in a desiccator until use.

Asphalt samples to be analyzed were collected and stored in a freezer (-20°C) for at least 2 hours prior to use. This cold storage was necessary to obtain a grindable and otherwise workable asphalt material which could be mixed with KBr powder to make pellets for IR analyses. Each asphalt sample was stored in its own closed container to avoid collecting moisture.

The asphalt-KBr mixture was prepared by accurately weighing the KBr and asphalt onto a sheet of aluminum foil: 0.975 g of dry KBr powder and 0.025 g of asphalt were weighed to obtain a total mixture of 1.000 g. All amounts were adjusted to within 0.2 mg of the desired weight and weighed with a precision of 0.1 mg. The asphalt was weighed as quickly as possible to keep it at a low temperature, thereby maintaining its workability. The mixture was quantitatively transferred to a mortar and ground from 20 to 30 minutes with a pestle to obtain a homogeneous mixture.

The amount of this asphalt-KBr mixture needed for one pellet was accurately weighed and placed between two highly polished stainless steel dies inside a pellet press where it was compressed at 25,000 psi for one minute to make a small pellet approximately 0.5 inch in diameter. Prepared pellets were stored in a desiccator to prevent moisture absorption by the KBr. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons.

Analyses were made of both the blank and asphalt-KBr pellets. Prior to analysis, the instrument sample compartment was purged with nitrogen for at least 20 minutes. The blank KBr pellet spectrum was subtracted from the asphalt-KBr spectrum to correct for moisture absorption by the KBr pellet. All baselines were adjusted to have zero absorption at 600, 1800, and 4000 cm^{-1}.

Results and Discussion

Spectra Reproducibility. Figure II-2-1 is an overlay of three spectra for the entire IR region obtained for a Coastal AC-20 asphalt. The high degree of reproducibility obtained for these three pellets is shown in increasingly more detail

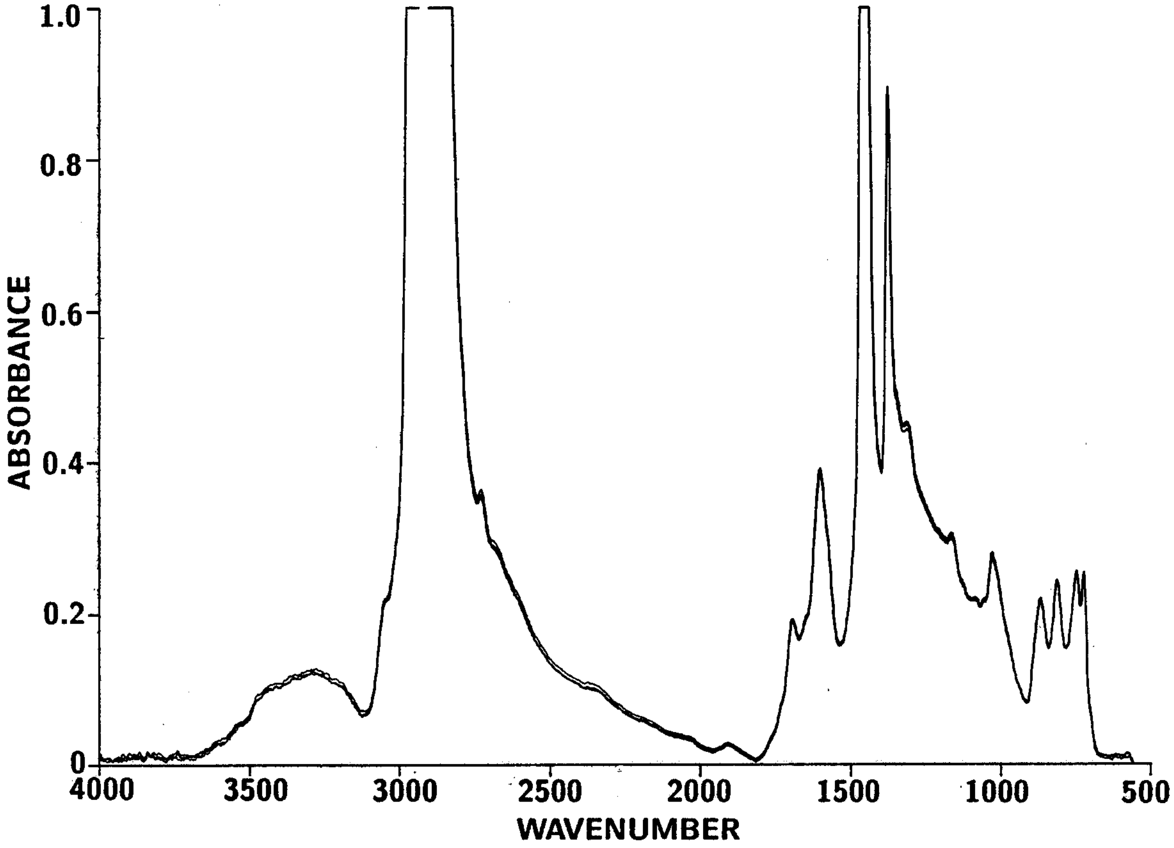

Figure II-2-1
Reproducibility of Three Asphalt FT-IR Analyses Over the Range from 600 to 4000 cm^{-1} Using 300 mg Pellets

for the 600-1800 cm^{-1} region in Figure II-2-2 and for the carbonyl region in Figure II-2-3. Very accurate reproducibility is possible by the pellet technique because of the weighing precision and the minimal background compensation of the KBr. In Figure II-2-1 the small spectra differences in the hydrogen bonding region between about 3600 cm^{-1} and 3200 cm^{-1} may be attributed to the instrument's small signal to noise ratio and lack of complete removal of moisture by the nitrogen purge. The carbonyl (1675-1750 cm^{-1}) and sulfoxide (950-1050 cm^{-1}) regions, of particular importance to asphalt aging, show excellent reproducibility.

Pellet Thickness. Potassium bromide's lack of IR absorption allows a wide range of pellet thickness, thereby providing a convenient means of adjusting the level of sample absorption. Weak absorption bands can be increased to good signal-to-noise ratios by using thick pellets; strong absorption bands can be kept within Beer's law by using thin pellets. By contrast, adjustments to the asphalt concentration in the KBr mixture are limited. Too low a concentration jeopardizes homogeneity; too high a concentration produces an unworkable mixture. The concentration of 2.5 weight percent used in this study was chosen to optimize workability. The effect of pellet pathlength can be seen in Figure II-2-4, which shows an essentially linear change in absorption between 300 and 500 mg pellets made from Coastal AC-20.

FT-IR Studies of Asphalts Using KBr Pellets. A highly reproducible infrared analysis for asphalts is of value for a number of composition comparisons. This method was used exclusively in the Texas test sections study described in Chapter IV-1 of this report. It is compared to a later developed internal reflection procedure in the next chapter. The pellet method was also used in some initial work on the hot-mix aging study given in Chapter IV-2.

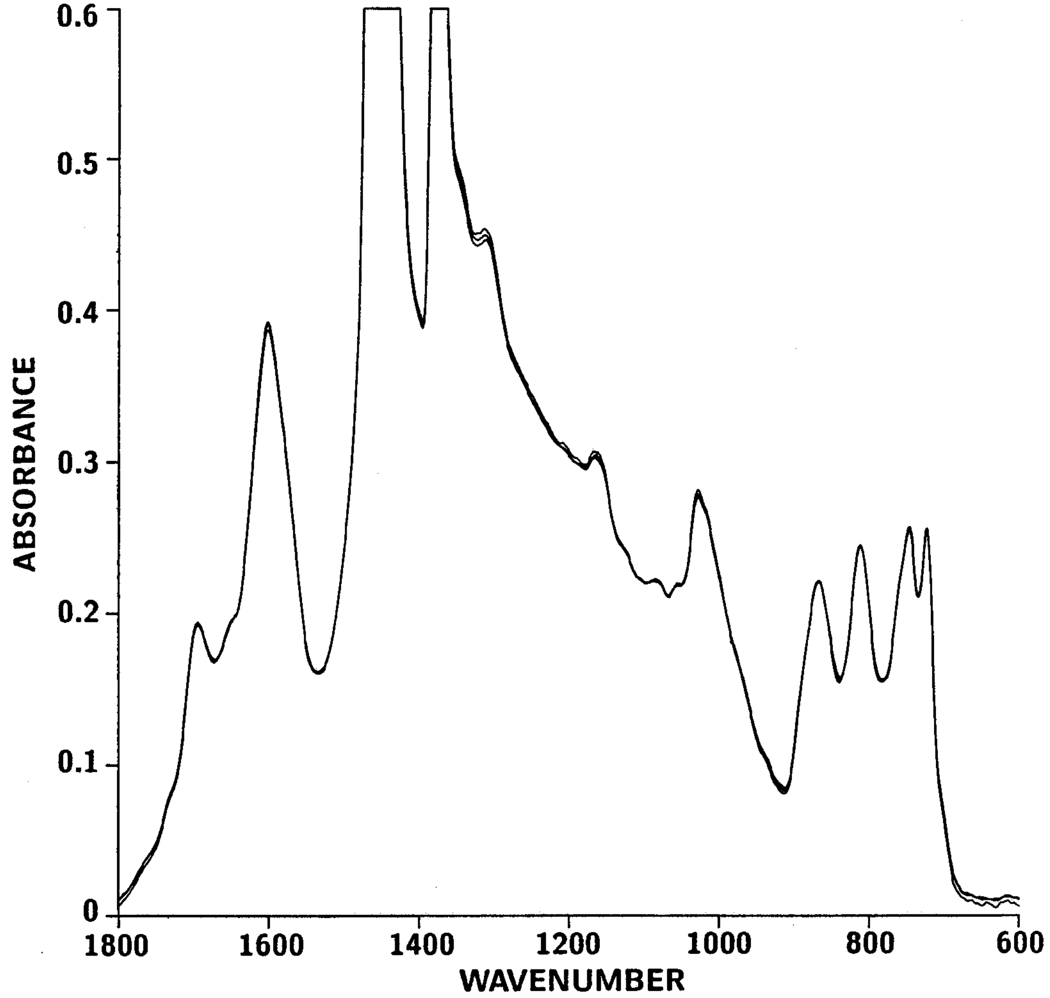

Figure II-2-2
Reproducibility of Three Asphalt FT-IR Analyses Over the Range from 600 to 1800 cm^{-1} Using 300 mg Pellets

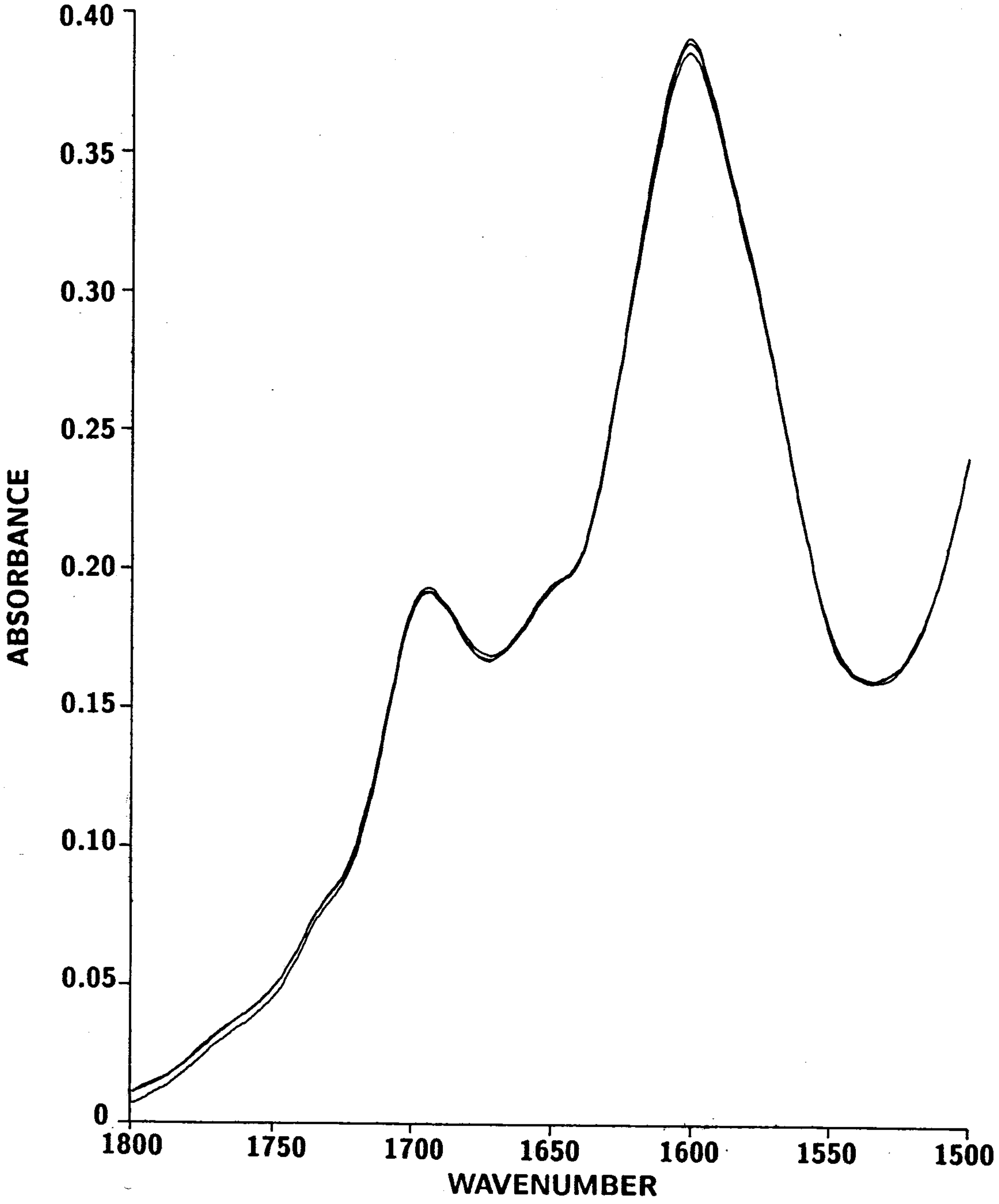

Figure II-2-3
Reproducibility of Three Asphalt FT-IR Analyses Over the Range from 1500 to 1800 cm^{-1} Using 300 mg Pellets

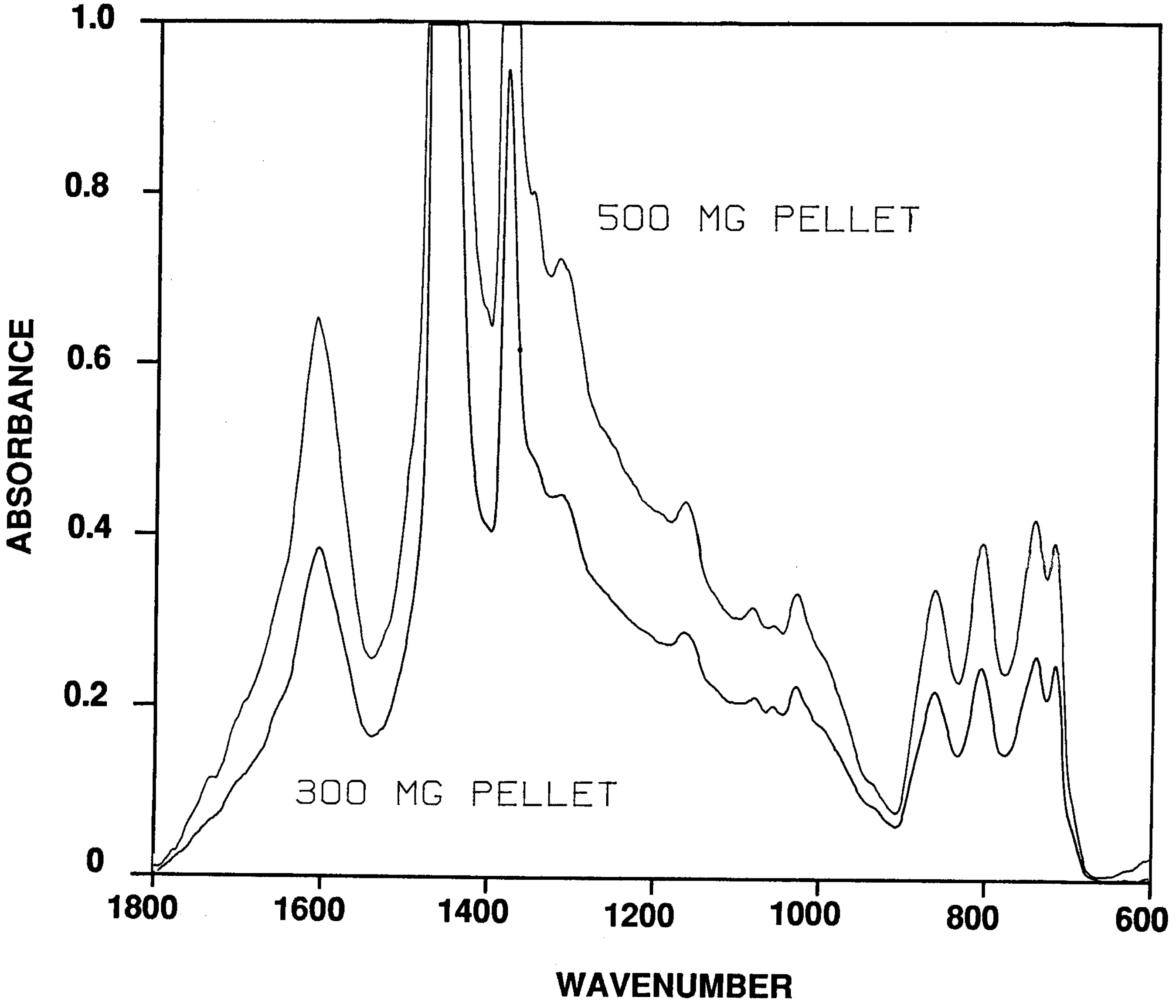

Figure II-2-4
Comparison of FT-IR Spectra for 300 and 500 mg Pellets
Over the Range from 600 to 1800 cm^{-1}

CHAPTER II-3

ATTENUATED TOTAL REFLECTANCE METHOD FOR THE ANALYSIS OF ASPHALTS USING FT-IR

Summary

The KBr pellet procedure discussed in Chapter II-2 is slow. To speed this work, the attenuated total reflection method (ATR) was investigated. Even though the signal strength is only about 10% that of the pellet procedure, comparable results were obtained with the instrument used in this work. There is some variation in the spectrum with wave length because of the change in path length with wave length, but that has little effect on its usefulness.

Introduction

The attenuated total reflection (ATR) or internal reflection method of analysis is a fast and accurate method of obtaining infrared spectra of viscous samples such as asphalt. In this method, the infrared beam is directed into a prism made of material with a high refractive index, such as Zinc Selenide, Germanium, or Silver Chloride. The beam passes into and through the prism and is reflected back to the detector at the sample interface surface, as shown in Figure II-3-1. The reflected beam intensity is affected by absorption into the sample (a function of frequency), and only small reflectivity losses occur at the entrance and exit surfaces.

The reflected beam actually penetrates into the sample to a specific depth. This depth is a function of the infrared wavelength, the refractive indices of the prism and the sample, and the angle of reflection and is approximately one-tenth of the wavelength for most of the normal infrared range. This phenomenon provides measurements that are independent of sample thickness for thicknesses greater than the few microns of the penetration depth. It is imperative, however, that there be good contact between the sample and the reflecting surface so that the absorbance in the penetration depth is affected only by the sample. The reflection spectra

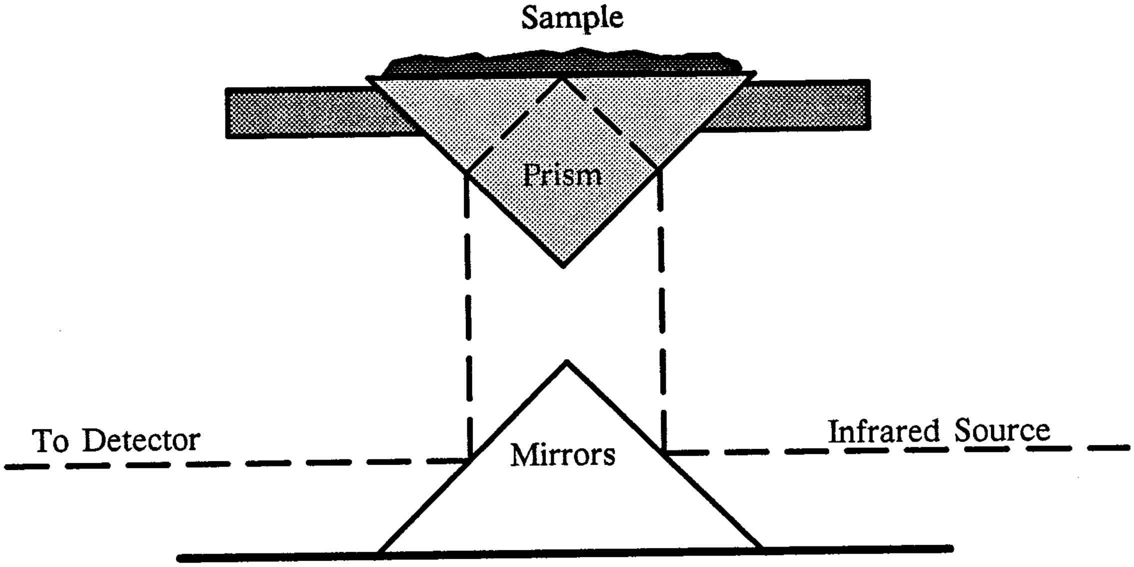

Figure II-3-1
Attenuated Total Reflection Sampling Apparatus

obtained using the attenuated total reflection very closely resembles transmission spectra.

The ATR method is especially valuable for the analysis of asphalt. Less than a gram of sample is needed in order to obtain a good spectrum. The absorbances of the weaker bands in asphalt are very small compared to other methods, but the spectrum can be clarified if a good nitrogen purge and background subtraction are used and the machine is tuned properly. No normalization or baseline manipulation is needed in order to obtain a complete and clear spectrum over the range from 4000 to 650 wavenumbers. The range from about 1000 to 650 may exhibit a slightly larger relative absorbance than the rest of the spectrum due to the longer wavelengths of the radiation corresponding to a slightly larger penetration depth (still only a few microns).

Sample Preparation

The single reflection ATR prism (ZnSe) obtained from Harrick Scientific was first cleaned with methylene chloride and a small lint-free tissue. Methylene chloride was chosen due to the good asphalt solubility and its volatility. The FT-IR detects even tiny amounts of solvent on the prism surface, so a small heating gun (e.g., a hair dryer) is used to blow warm air over the prism surface to remove the last traces of the solvent. This cleaning process takes approximately 2 minutes. A background spectrum is then taken using the prism. The asphalt sample is heated to its softening point, mixed thoroughly, and using a teflon coated spatula (the prism is easily scratched), a small amount of asphalt is spread on the reflective surface of the prism. To ensure good contact between the asphalt and the prism surface, the prism (which is removable from the mirror assembly that remains in the infrared sample chamber) is then placed in an oven for about 1 minute to allow the asphalt to remelt smoothly onto the prism interface. The sample is then ready for analysis. With a good background subtraction and swift nitrogen purge, this method results in an excellent and reproducible spectrum in less than 30 minutes.

Comparison of KBr and ATR

In Chapter 2 of this section, a Potassium Bromide pellet method is discussed for the analysis of asphalt samples. This method yields good strong spectra over a large range.

The ATR technique has several advantages over KBr pellet technique, however. The sample preparation for the ATR procedure is negligible compared to that used to obtain a KBr pellet and thus takes only a fraction of the time. If not done properly, the KBr spectrum may have a significant amount of water that has been absorbed by the highly hygroscopic KBr from the atmosphere, while this is not a problem with the neat sample used on the ATR prism. The spectrum obtained using the KBr method is often corrected for baseline shifts, while there is usually no need for such corrections on ATR spectra.

A possible source of concern associated with the ATR method may be its weak absorbance signals. The KBr technique discussed in Chapter 2 of this section has over 10 times the infrared absorbance found in ATR spectra. The low absorbance may be a problem in machines that do not have good background subtraction or for which the purge is inadequate. An increased number of scans will help to reduce the random noise error to produce a cleaner spectrum. Figure II-3-2 and II-3-3 show the good reproducibility of three different spectra taken of the same asphalt. The spectra obtained using the two methods are similar and show the same important characteristics, as shown in Figures II-3-4 through II-3-6. Recall that the magnitudes of the absorbances differ by more than a factor of 10 and have been adjusted for this overlay. The spectra differ due to the fact that the KBr pellet will have a constant pathlength, while the pathlength into the sample on the prism becomes larger with increasing wavelength. This accounts for the lifting of the ATR spectrum above that obtained from the KBr pellet, especially at the lower wavenumbers. This is of no practical significance, however, for comparing asphalts to each other or for assessing the aging of asphalts, so long as the same technique is used throughout.

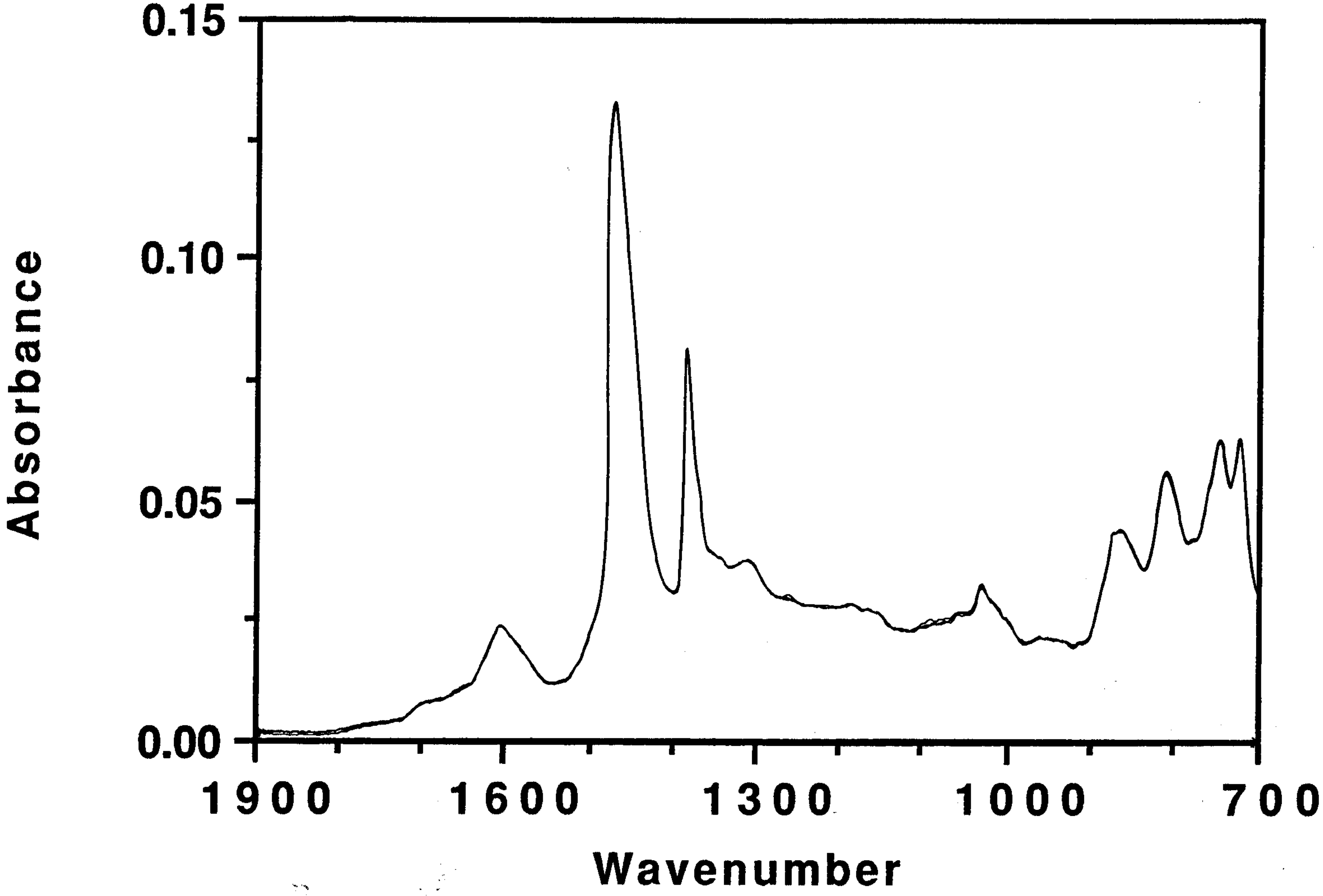

Figure II-3-2
ATR Reproducibility for 1987 Exxon AC-20 (Drum) Hot-mix

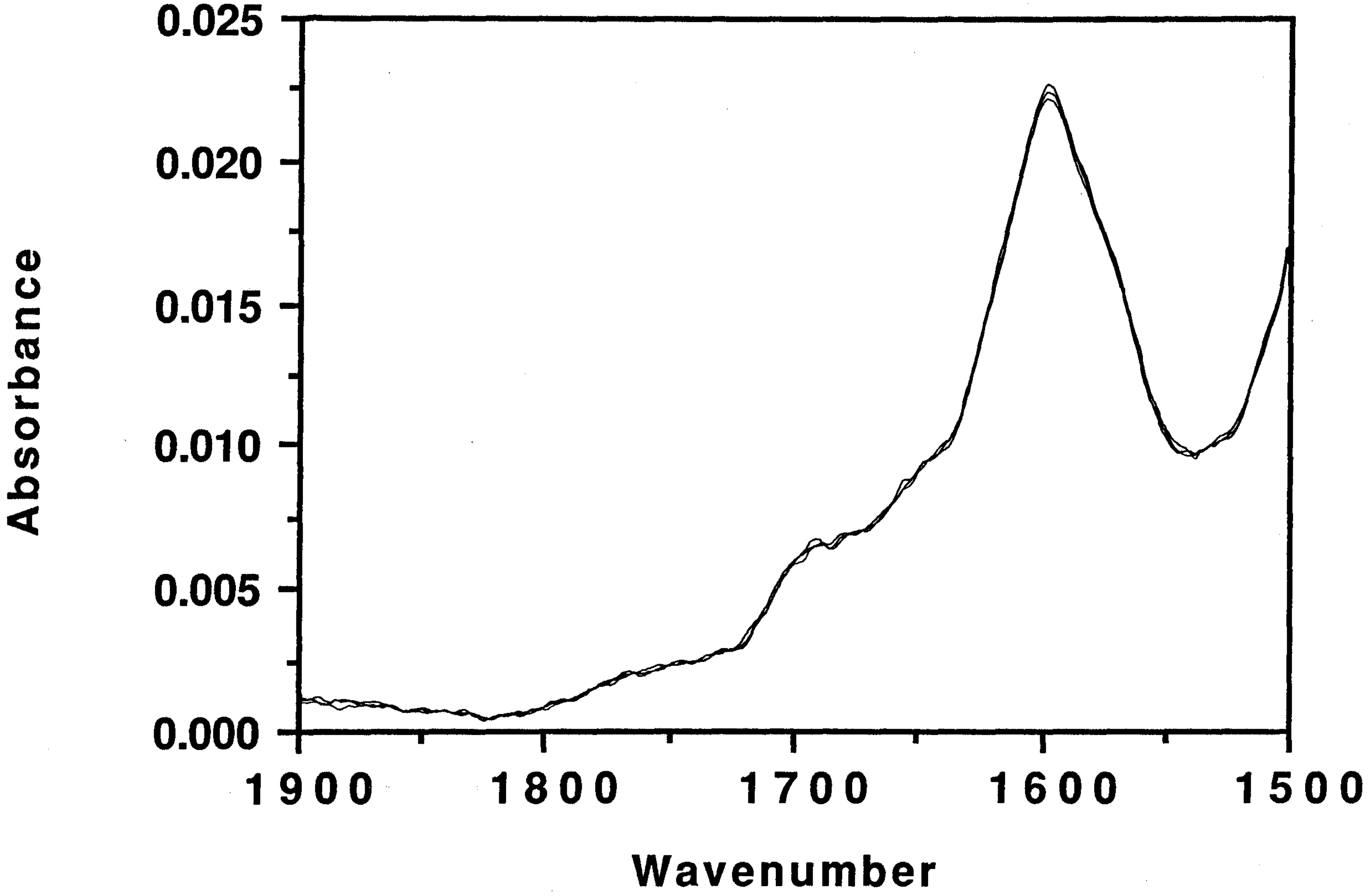

Figure II-3-3
ATR Reproducibility in the Carbonyl Region for
1987 Exxon AC-20 (Drum) Hot-mix

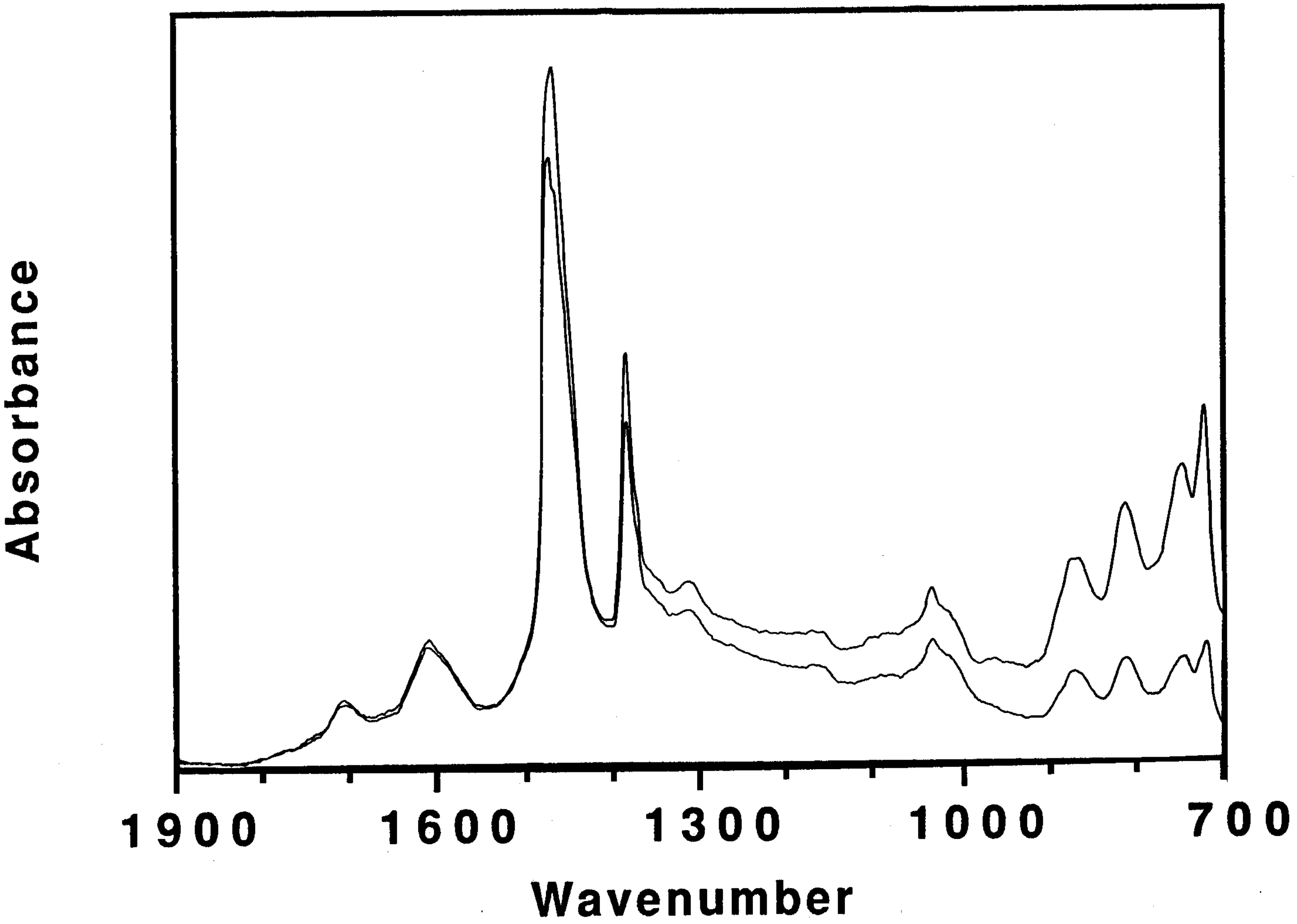

Figure II-3-4
Comparison of ATR and KBr Pellet Procedures - Lufkin MacMillan 1987 Core

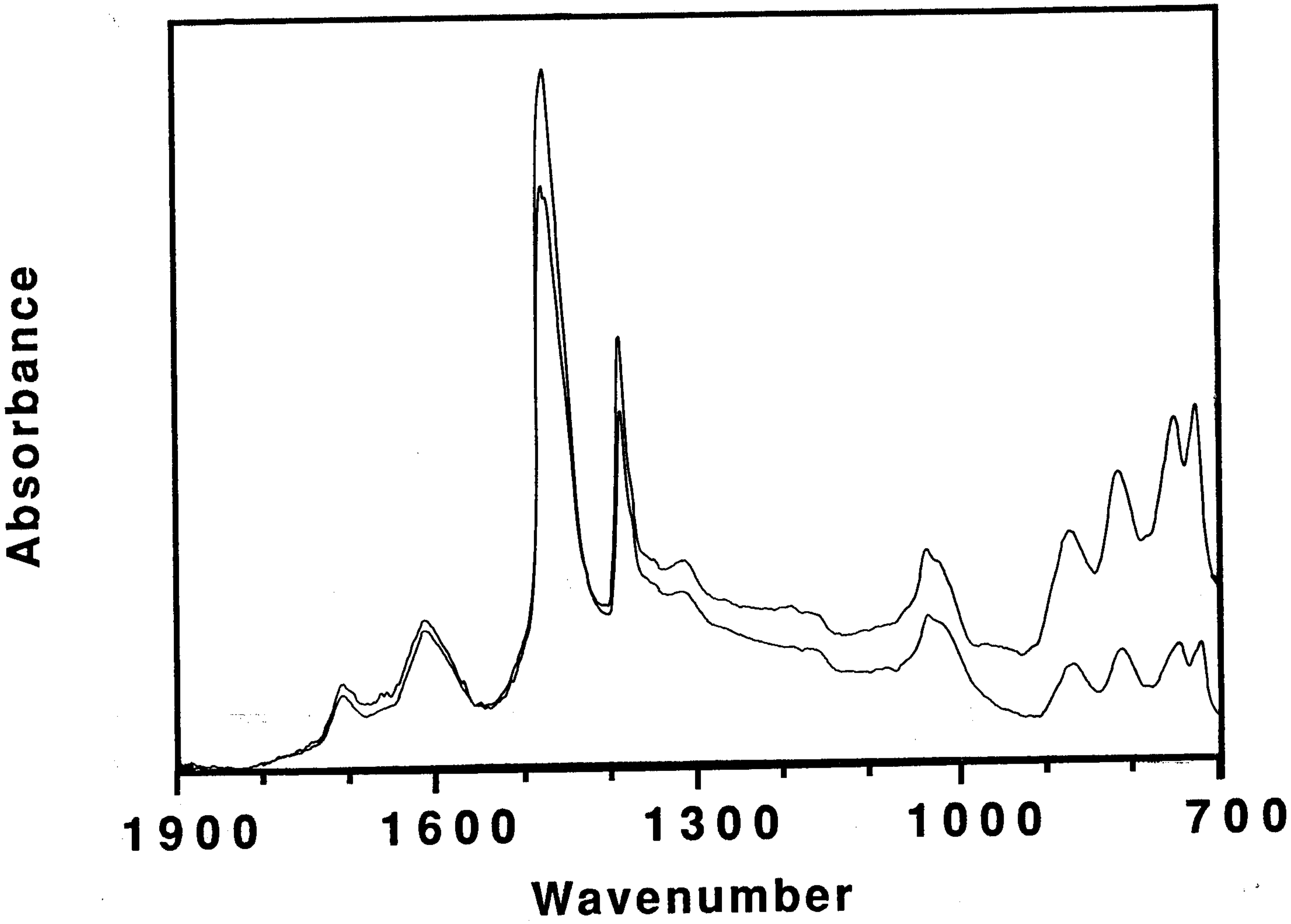

Figure II-3-5
Comparison of ATR and KBr Pellet Procedures - Lufkin Texaco 1987 Core

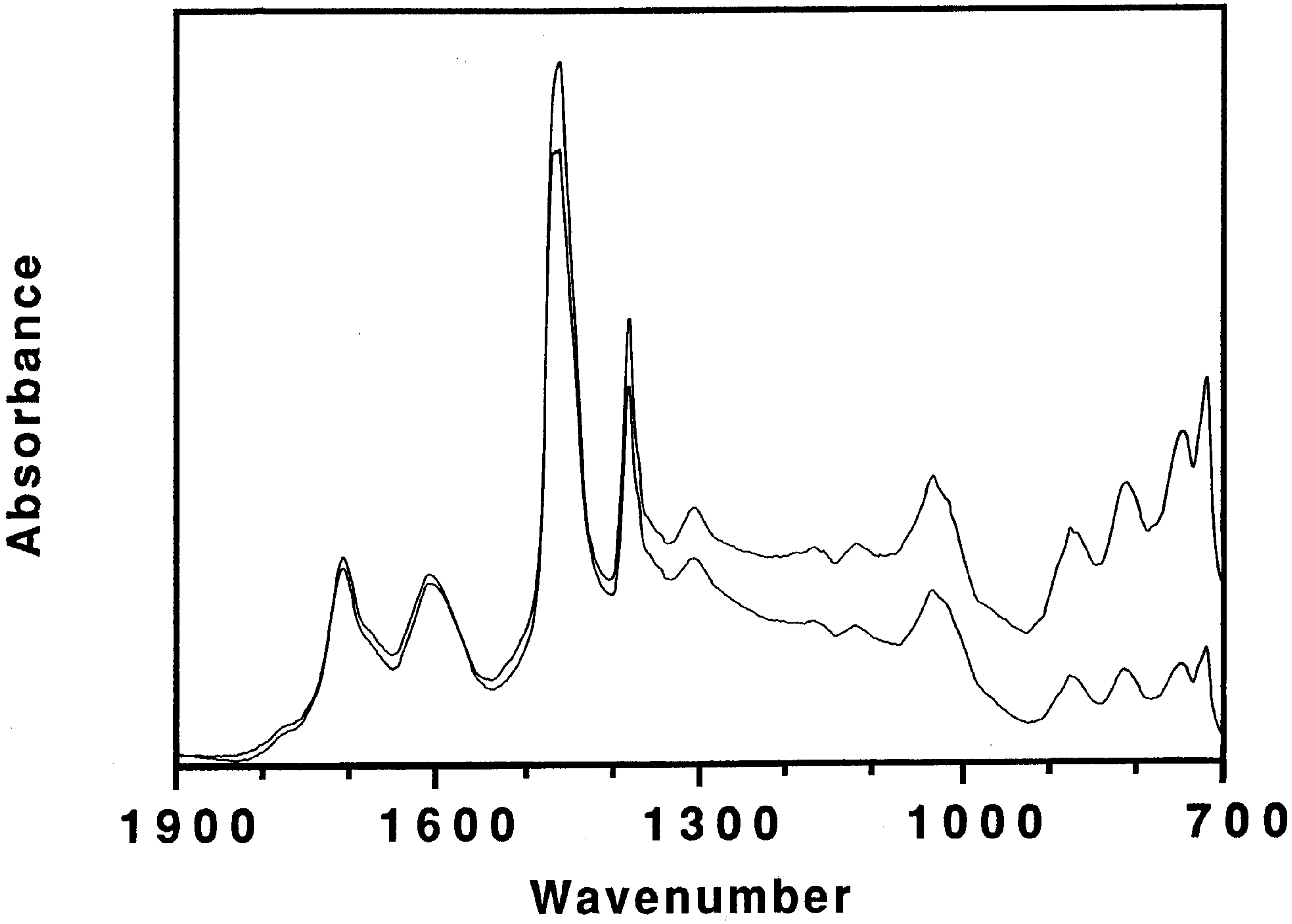

Figure II-3-6
Comparison of ATR and KBr Pellet Procedures - Dickens Exxon 1987 Core

CHAPTER II-4

STUDIES OF THE CORBETT FRACTIONATION PROCEDURE

Summary

This chapter describes an attempt to improve the Corbett fractionation procedure by eliminating column fingering and getting better cut points. A reverse flow column improved the flow characteristics, but the limited data do not prove better results. Procedures are described for more closely identifying the boundaries between fractions.

Introduction

This study involves the examination of ASTM D 4124-82: "Standard Test Method for Separation of Asphalt Into Four Fractions." This method has been used successfully to estimate four broad chemical group concentrations as defined in the procedure. For an estimate of the size of these fractions, this method is sufficient. However, for more quantitative accuracy, some method modifications were examined.

The Corbett procedure is dependent on many parameters which are difficult to control. Results of interlab comparisons demonstrate how operator-dependent and inconsistent the results can be. Packing density and uniformity, solvent flow rate, and cut points are operator-dependent and all have influence on the results.

Evaluation of the Standard Procedures

In the initial testing, it was observed that the petrolene solution was channelling throughout the alumina. This appeared as a fingering effect as the darker polar aromatics protruded unevenly into the region of lighter naphthene aromatics. The "fingers" extended as much as 16 inches as the polar aromatics fraction descended. This caused a large zone of polar and naphthene aromatics overlap and eliminated a well-defined cut point. The cause of this was the primary problem addressed in this study.

An additional step was initiated into the procedure to closely monitor these crucial cut points. To quantitatively determine the frontal breakthrough, a series of 10 small aliquots were taken at 30-second intervals, around and including the usual cut points, and weight percentages were measured for each set. When the small aliquots were analyzed, it became clear where the cut point occurred as the trailing fraction was always less than 0.20% by weight, and when the new fraction appeared, the weight percent increased rapidly (Fig. II-4-1). Aliquot dry weights were added to the appropriate fractions: for example, aliquot dry weights from weight percents less than 0.20% were added to the trailing fraction and those from higher than 0.20% were added to the emerging fraction. When this additional step was initiated, the cut points became more consistent.

Reverse Flow Column

The fingering phenomenon was first considered to be a function of improper column packing technique and the nature of the solvents used. The packing method stabilized through operator experience and subsequently was discounted as a major fingering influence.

The second cause considered was that of solvent properties and progression. It was noted that each subsequent solvent used has a greater density than the previous one, which would promote the channelling effect in a gravitational column. Because heavier solvents would move more quickly through the alumina bed, channelling would occur and would be observed as a fingering effect. Due to the progressive increase in density of the solvents used in this method, gravitational flow is a serious disadvantage. The increase in solvent density would be beneficial if the flow direction were reversed. A column was designed and constructed to separate the petrolene solution with flow from bottom to top, hereafter referred to as "reverse".

Solvents were introduced onto the column from a 1000 ml separatory funnel mounted 12 in. above the top of the bed and travelled to the flowmeter through

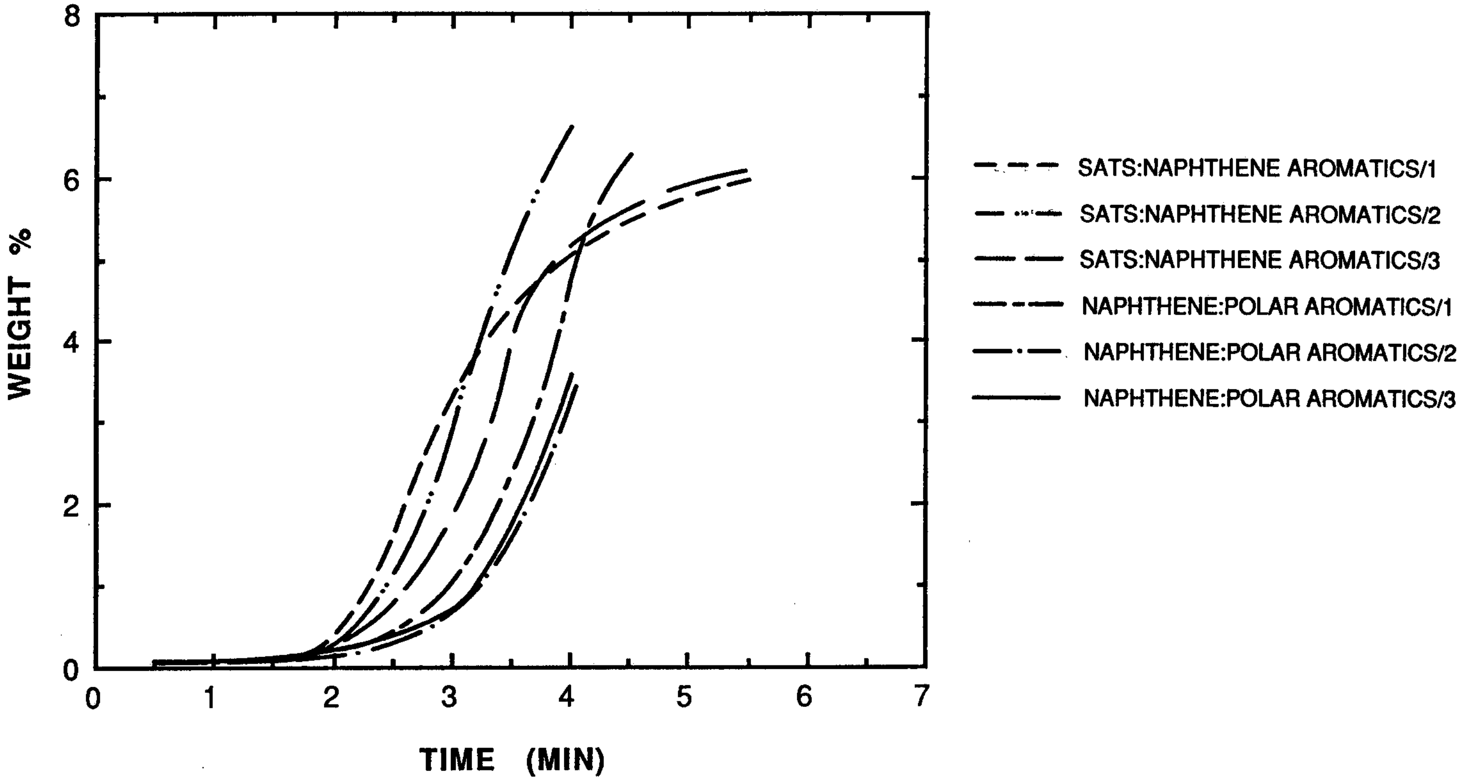

Figure II-4-1
Variation in Concentration at Corbett Fraction Cut Points

5 ft. of 1/8 in. Teflon tubing. Sample introduction was achieved using a 100 ml glass syringe connected via a three-way valve between the flowmeter and column. The sample was poured, and beaker rinsed with heptane, into the syringe. The valve connected the syringe to the column and the petrolene solution was slowly transferred to the column by depressing the plunger. The syringe was rinsed three times using the valve to allow clean heptane to be drawn into the barrel by gently pulling on the plunger then forcing the rinse onto the column after readjusting the valve.

Sample removal from the column was achieved by keeping a slight positive pressure of nitrogen on top of the bed and allowing the effluent to flow out through 1/8 in. Teflon tubing into 600 ml Griffin beakers.

Comparisons with Several Asphalts

Five asphalts representing five manufacturers and two viscosity grades were separated using both the ASTM and reverse methods. The Diamond Shamrock AC-20 asphalt is extremely unusual, and these methods do not adequately separate this sample. This specific manufacturer's asphalt is worthy of further chemical characterization studies, but in this study the Diamond Shamrock AC-20 sample will not be used in method comparisons.

The reverse column method inhibited channelling and the naphthene to polar aromatics cut point ascended as a flat ring in all samples analyzed. When the initial analyses were performed on the Ampet AC-10, this cut point was fingering up to 16 inches, however when the Exxon AC-20 was analyzed, the cut point descended as compactly as it ascended in the reverse column. The MacMillan AC-10 did not result in fingering at this cut point, whereas the Cosden AC-20 behaved very much like the Ampet AC-10. This inconsistency would suggest the fingering or channelling trend to be a function of the asphalt characteristics and not solely due to the method or solvents used.

Results are shown in Tables II-4-1 and II-4-2. Despite the notable reduction in channelling with some asphalts in reverse flow, significant improvement in reproducibility did not result. Problems are still present in determining the

Table II-4-1

Reproducibility of ASTM D 4124-82 (gravitational flow)

Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes	Total
AMPET AC-10				
9.61	43.30	31.57	13.45	97.93
8.82	39.52	34.83	14.59	97.76
9.26	41.30	32.56	14.78	97.90
8.96	38.60	33.17	16.49	97.22
8.74	38.20	37.12	13.84	97.90
9.39	37.47	36.80	14.21	97.87
9.13±0.34	39.73±2.19	34.34±2.29	14.56±1.06	97.76±0.27
COSDEN AC-20				
12.37	35.36	38.16	13.24	99.13
11.69	34.11	39.94	12.45	98.19
11.97	35.21	39.03	11.97	98.18
12.01±0.34	34.89±0.68	39.04±0.89	12.55±0.64	98.50±0.55
EXXON AC-20				
9.10	39.39	42.22	7.99	98.70
9.46	39.59	41.95	7.46	98.46
9.12	38.56	43.40	8.23	99.31
9.23±0.20	39.18±0.55	42.52±0.77	7.89±0.39	98.82±0.44
MACMILLAN AC-10				
10.48	42.09	32.59	12.08	97.24
10.24	42.82	32.52	12.94	98.52
10.07	42.79	33.54	12.63	99.03
10.26±0.21	42.57±0.41	32.88±0.57	12.55±0.44	98.26±0.92

Table II-4-2

Reproducibility of a Modified ASTM D 4124-82 Method (reverse flow)

Saturates	Naphthene Aromatics	Polar Aromatics	Asphaltenes	Total
AMPET AC-10				
9.32	38.45	35.21	14.33	97.31
9.59	38.03	35.40	14.08	97.10
9.75	38.97	35.38	14.78	98.88
9.55±0.22	38.48±0.47	35.33±0.10	14.40±0.35	97.76±0.97
COSDEN AC-20				
12.29	35.36	39.68	12.62	99.95
11.69	33.43	41.18	13.15	99.45
11.98	35.48	38.88	12.48	98.82
11.99±0.30	34.76±1.15	39.91±1.17	12.75±0.35	99.41±0.57
EXXON AC-20				
8.05	40.06	41.23	7.91	97.25
8.20	38.86	42.92	7.79	97.77
8.40	37.60	43.63	8.12	97.75
8.22±0.18	38.84±1.23	42.59±1.23	7.94±0.17	97.59±0.29
MACMILLAN AC-10				
10.05	41.89	33.55	12.00	97.49
10.27	43.00	32.88	12.65	98.80
10.07	43.65	32.78	12.45	98.95
10.13±0.12	42.85±0.89	33.07±0.42	12.37±0.33	98.41±0.80

naphthene aromatic, polar aromatic cut point, as shown by the poorer standard deviations in these two fractions.

There are several likely sources of error. One is incomplete recovery from the column, another, as noted, is poor cut point identification even with the improvements described. It is known that some polar aromatic material is left on the column because continual solvent flow eventually recovers some more. Even so when the total recovery is low, it does not correlate with low polar aromatics. The total loss is actually higher than indicated because GPC analysis of the fractions shows solvent residue in some. This, of course, introduces error into the fractional analysis as well as the total recovery.

Fraction Recombination

Following the Corbett Fractionations, the fraction sets were recombined in two ways to further test the procedure using GPC analysis. The first recombination was achieved by weighing each fraction of the set into the same vial in proportion to their recovered percentages and dissolving in THF to a 7% concentration. The resulting chromatogram was labelled "recombined." The second set of chromatograms termed "reconstructed" were obtained by summing the datafiles of each fraction run individually. Each fraction was dissolved in THF at a concentration equal to 7% by weight times its weight fraction in the original asphalt as indicated by the Corbett analysis. The resulting chromatograms are compared in Fig. II-4-2 and II-4-3 and in Appendix A.

The agreement is not always very good, and apart from error in analysis, there are several other sources of error. First, of course, lost material would not be comparable to the remaining material, but two other factors are involved. It is now known that significant asphalt hardening occurs when in contact with solvents for extended times, as in the Corbett analysis, and this is probably why the recombined asphalts show greater LMS regions than the original asphalt.

The recombined asphalts usually have smaller LMS regions than the original asphalt in spite of solvent hardening. This is probably explained by the GPC results described earlier in this section which show a variation of LMS with asphalt

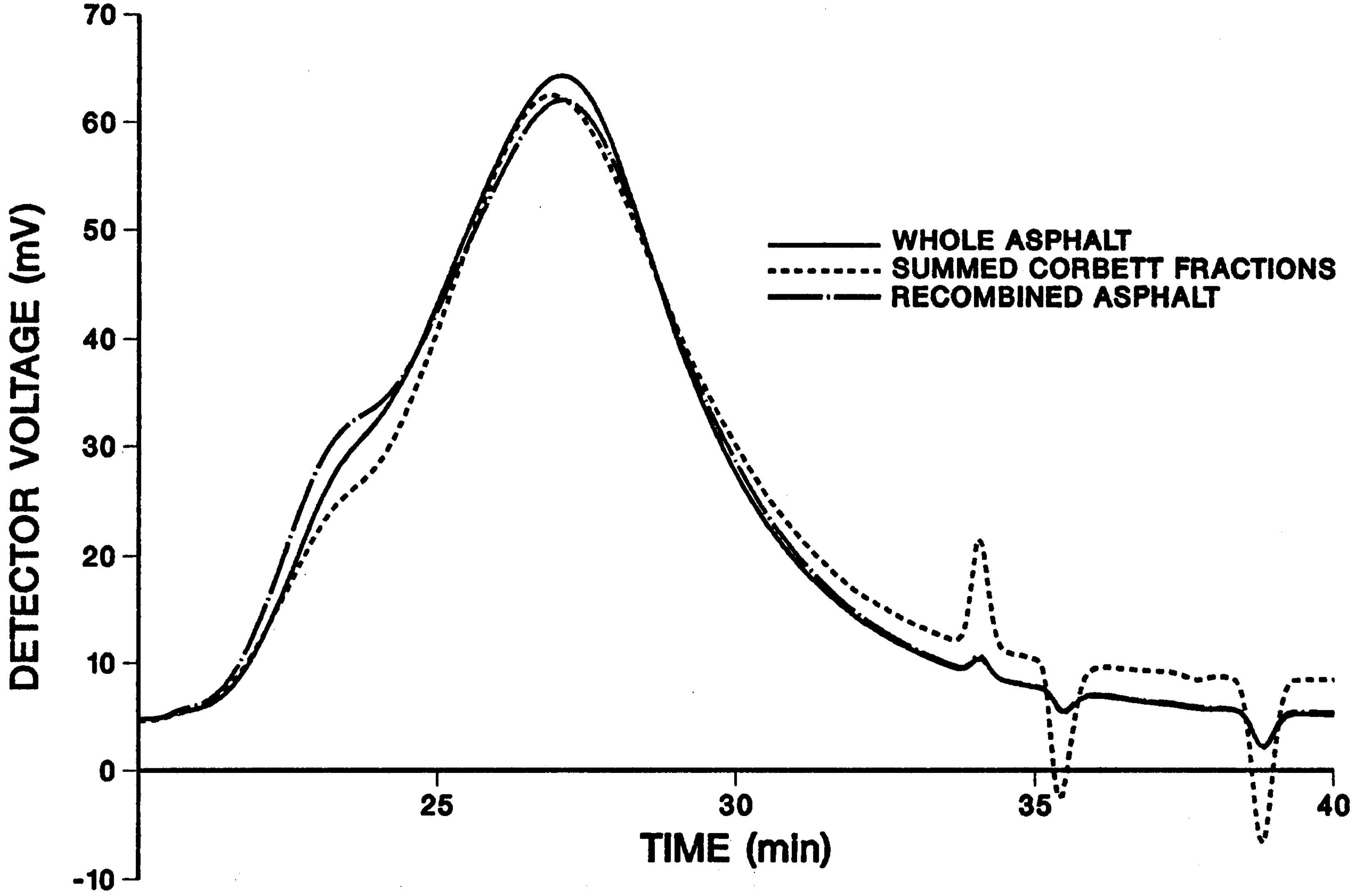

Figure II-4-2
Comparison of GPC Chromatograms for Whole Asphalt and
Those Derived from Corbett Fractions (Downflow) - MacMillan AC-10

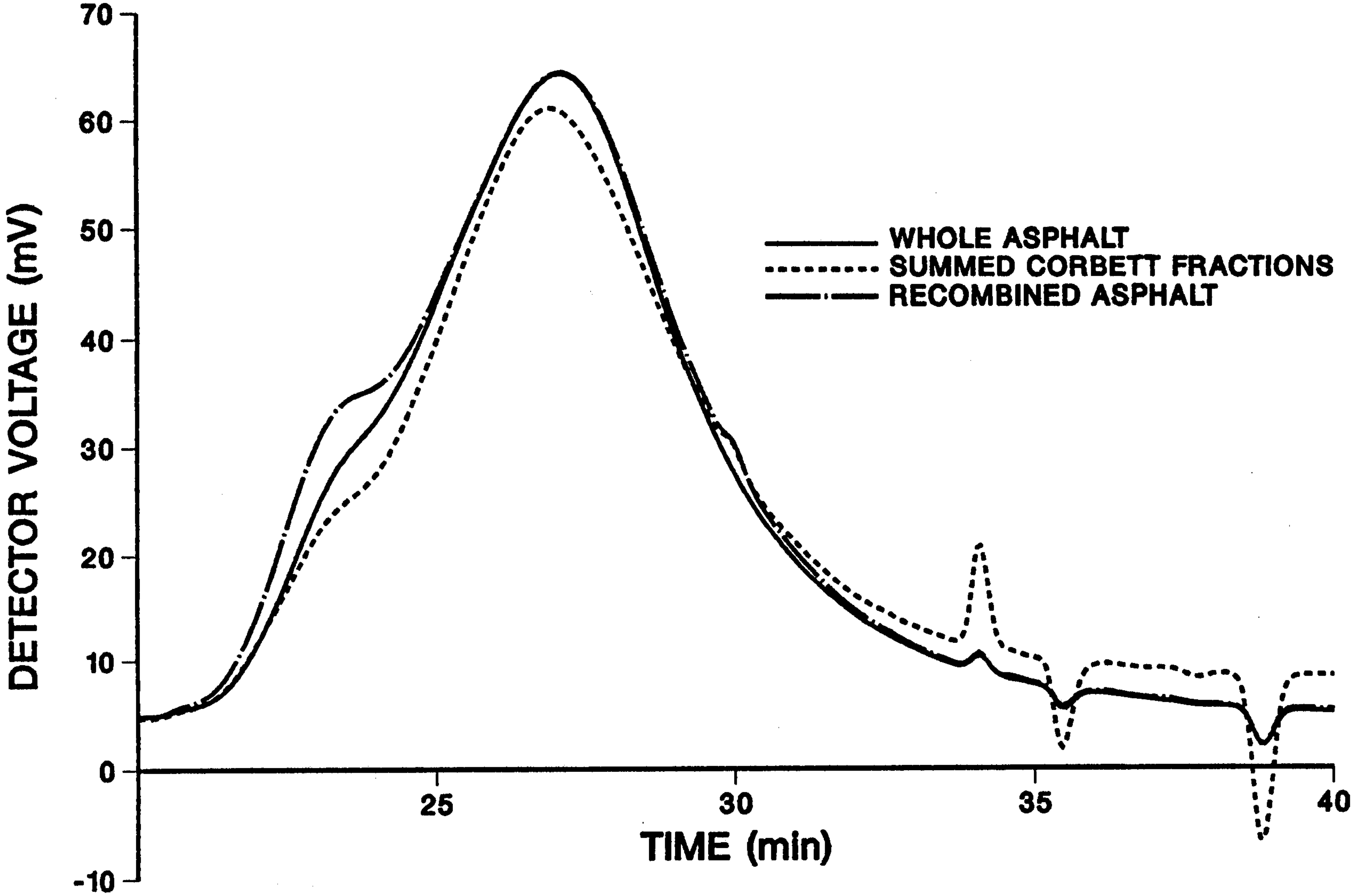

Figure II-4-3
Comparison of GPC Chromatograms of Whole Asphalt and Those Derived from Corbett Fractions (Upflow) - MacMillan AC-10

concentrations. The reconstructed chromatograms were made with each fraction at the same concentration as it would have been in a whole asphalt but in the absence of the other fractions and therefore at a lower total concentration and probably resulting in a smaller LMS.

Because of the difficulties encountered and because the problems of solvent hardening and solvent removal also impact the much more important tasks of extracting and recovering asphalt, the Corbett work was suspended.

CHAPTER II-5

HEITHAUS TESTS

Summary

The procedure suggested by Heithaus (1960) for measuring asphalt compatibilities was applied in this study to the tank asphalts from the Dumas, Dickens and Lufkin test sections and from the hot-mix study. In the procedure, asphalts dissolved in toluene are titrated to precipitation with heptane. Several distinctive differences between the asphalts were observed and, in fact, in some cases the asphalts made by the same supplier, but used at different locations, gave different parameters, suggesting that the asphalts were not entirely the same after all. Preliminary studies using the Heithaus procedure but with other asphalt/solvent/nonsolvent systems were investigated as an alternative way of characterizing compatibility.

Introduction

The amount of heptane required to initiate precipitation as a function of the starting asphalt concentration is an indication of the compatibility of the various components within the asphalt. Adding the nonpolar heptane to the toluene/asphalt mixture provides a less polar environment for the very polar asphaltenes. To the extent that the maltenes of the asphalt, together with the toluene, are not able to hold the asphaltenes in solution as normal heptane is added, the compatibility of the maltenes with the asphaltene is assumed to be less. Accordingly, then, a series of Heithaus measurements for different asphalt/toluene concentrations can be used to characterize an asphalt with respect to compatibility.

Standard Procedure and Results

For each asphalt to be studied, a total of 16 analyses at 4 different asphalt to toluene ratios were made. The first set of four analyses was done in a cursory fashion so that the titration range with normal heptane could be determined. The other three sets of four analyses were done carefully to provide a total of 12 data points at 4 compositions.

Each series of four analyses was done using the following procedure. The asphalt was first melted and blended well to assure uniformity of the asphalt used for each of the four samples. Then the amount of asphalt desired was weighed into each of four Erlenmeyer flasks, followed by the addition of toluene. The asphalt weights and toluene used for each flask are indicated in Table II-5-1. The asphalt in each flask was then dissolved in the toluene by heating on a hot plate set at 160°F. After the asphalt was in solution, the amount of evaporated toluene was determined by weight, replaced, and the sample cooled to room temperature while stirring with a magnetic stirrer. After cooling, the sample was titrated to a flocculation endpoint with normal heptane. The flocculation (asphaltenes precipitation) was detected using a 100X microscope.

Table II-5-1

Starting Asphalt/Toluene Amounts for the Heithaus Titrations

Flask	Asphalt Wt. (g)	Toluene Vol. (ml)
1	4.0 ± .5	2.0 ± .1
2	4.0 ± .5	4.0 ± .1
3	2.0 ± .5	4.0 ± .1
4	2.0 ± .5	14.0 ± .1

Each sample analysis gave a titration endpoint from which was calculated two indices of compatibility

$$FR = \frac{\text{Volume of Toluene (ml)}}{\text{Total Volume (ml) of (toluene + n-heptane titrant)}}$$

$$1/X = \frac{\text{Asphalt Wt. (g)}}{\text{Total Volume (ml) of (toluene + n-heptane titrant)}}$$

and the values are shown in Figures II-5-1 to II-5-4. For each asphalt as the flocculation ratio decreased, the value of 1/X increased, essentially linearly, and a straight line linear regression was determined, which is also shown in Figures II-5-1 to II-5-4. From this line two parameters were obtained, FR_{max} and $1/X_{min}$, which are taken as measures of the compatibility of the components in an asphalt. A listing of the results can be found in Table II-5-2 and II-5-3. As in the GPC studies, we see that Lufkin MacMillan is not the same asphalt as the Dumas and Dickens MacMillan. Raw data are given in Appendix A.

Alternative Procedure and Results

The Heithaus test measures the quantity of heptane required to precipitate asphaltenes from asphalt/toluene solution. Thus it measures the tendency of a non-polar solvent to cause asphaltene separation. Other measures of compatibility are possible. For instance one could measure the precipitation by a polar solvent of asphalt in a cosolvent.

Some preliminary work along this line is reported here. Both toluene and TCE were used as cosolvents and various alcohols as the antisolvent. Samples were otherwise made as shown in Table II-5-1.

Results for Cosden AC-20 with toluene as the solvent and ethanol, propanol and butanol as titrants are shown in Figure II-5-5; with methanol as titrant, precipitation was almost immediate and it appeared that methanol, not asphalt, was separating. Results with TCE as solvent and methanol, ethanol, propanol and butanol as titrants are shown in Figures II-5-6. Complete data are given in Appendix A.

In general the results did not correlate linearly, and in most cases the slope is positive rather than negative as for the standard Heithaus. Furthermore, the end points were difficult to detect, and it is suspected that often it was solvent rather than an asphalt fraction that was separating. For this to be productive, better solvent combinations must be found.

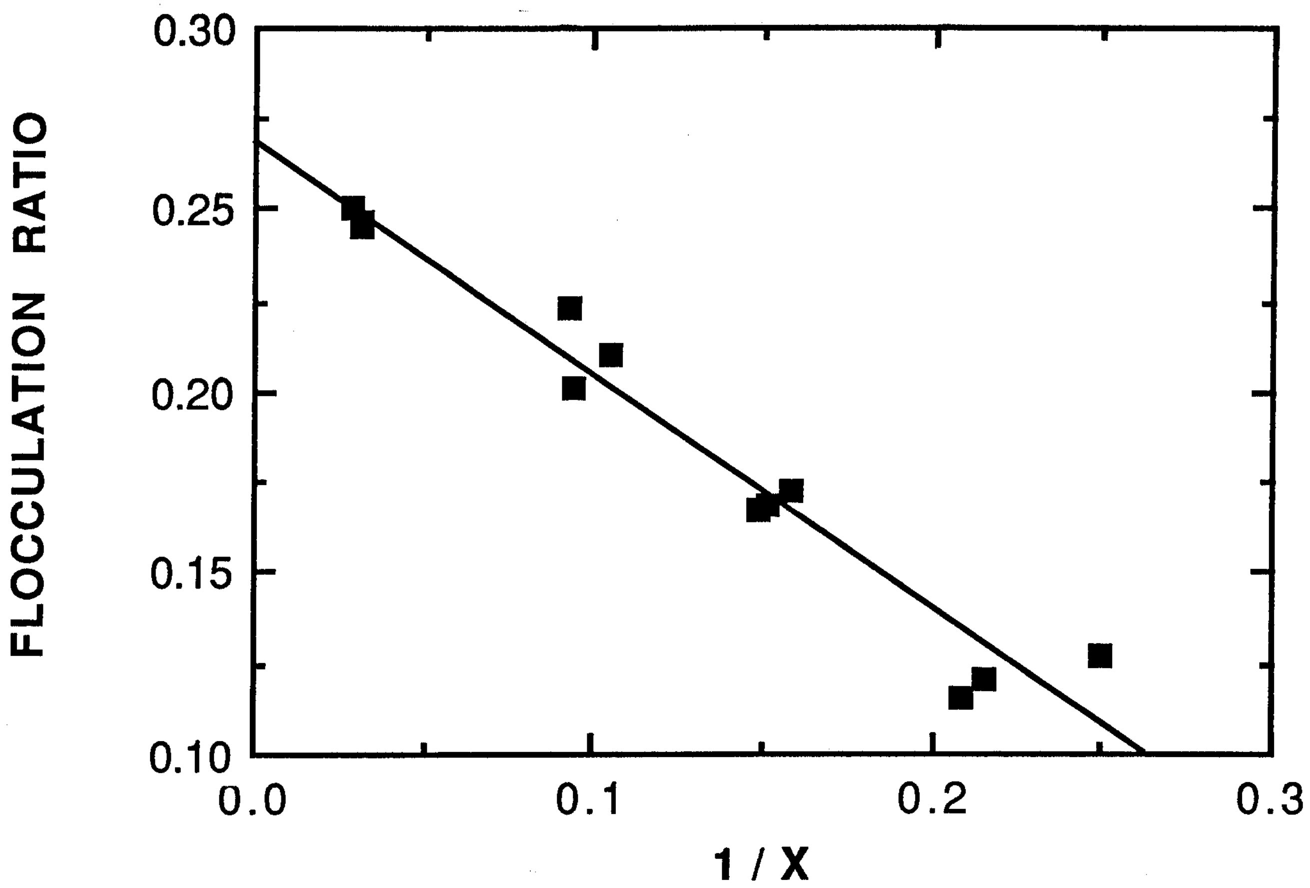

Figure II-5-1
Heithaus Results with Lufkin Texaco AC-20

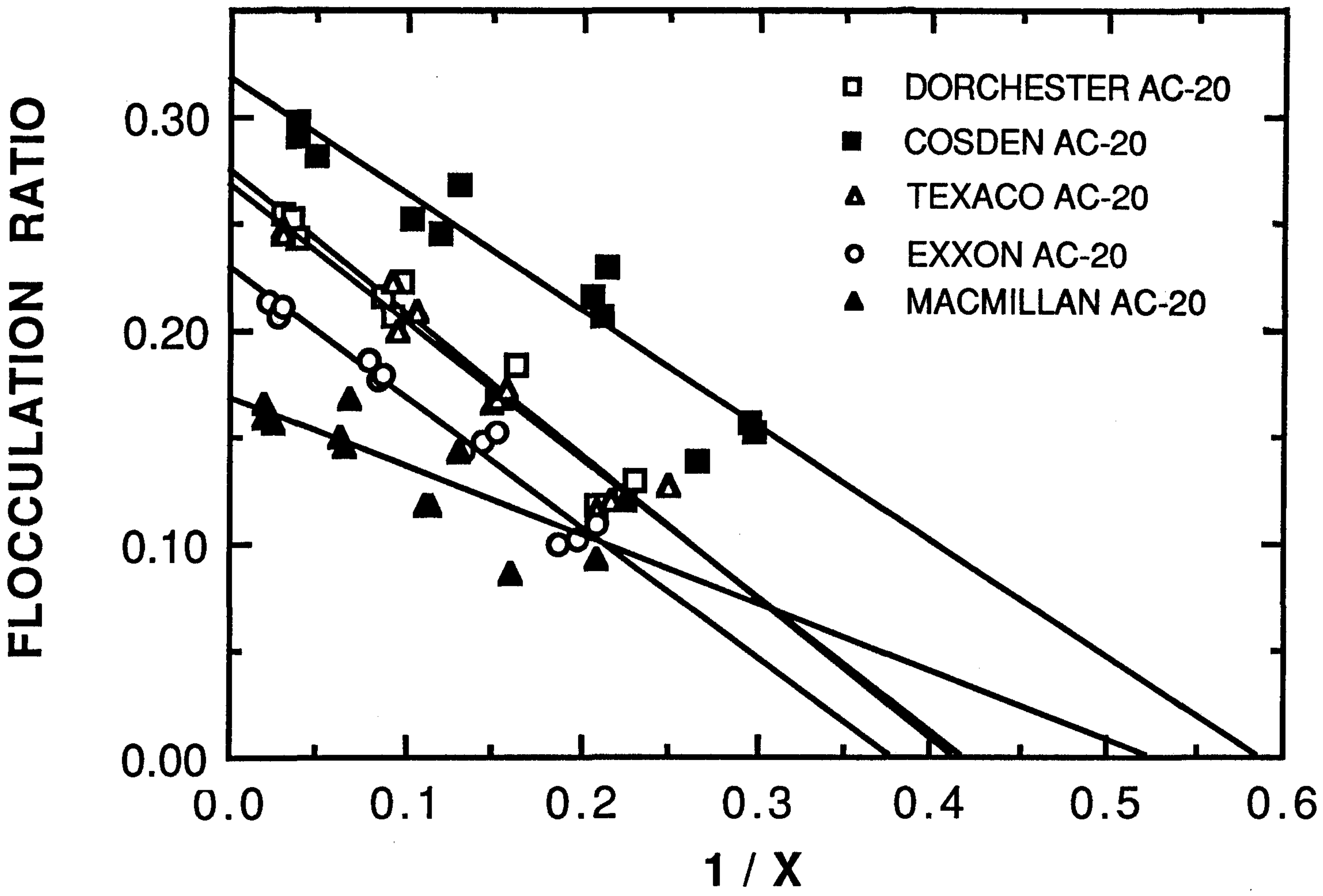

Figure II-5-2
Heithaus Results for All Lufkin Tank Asphalts

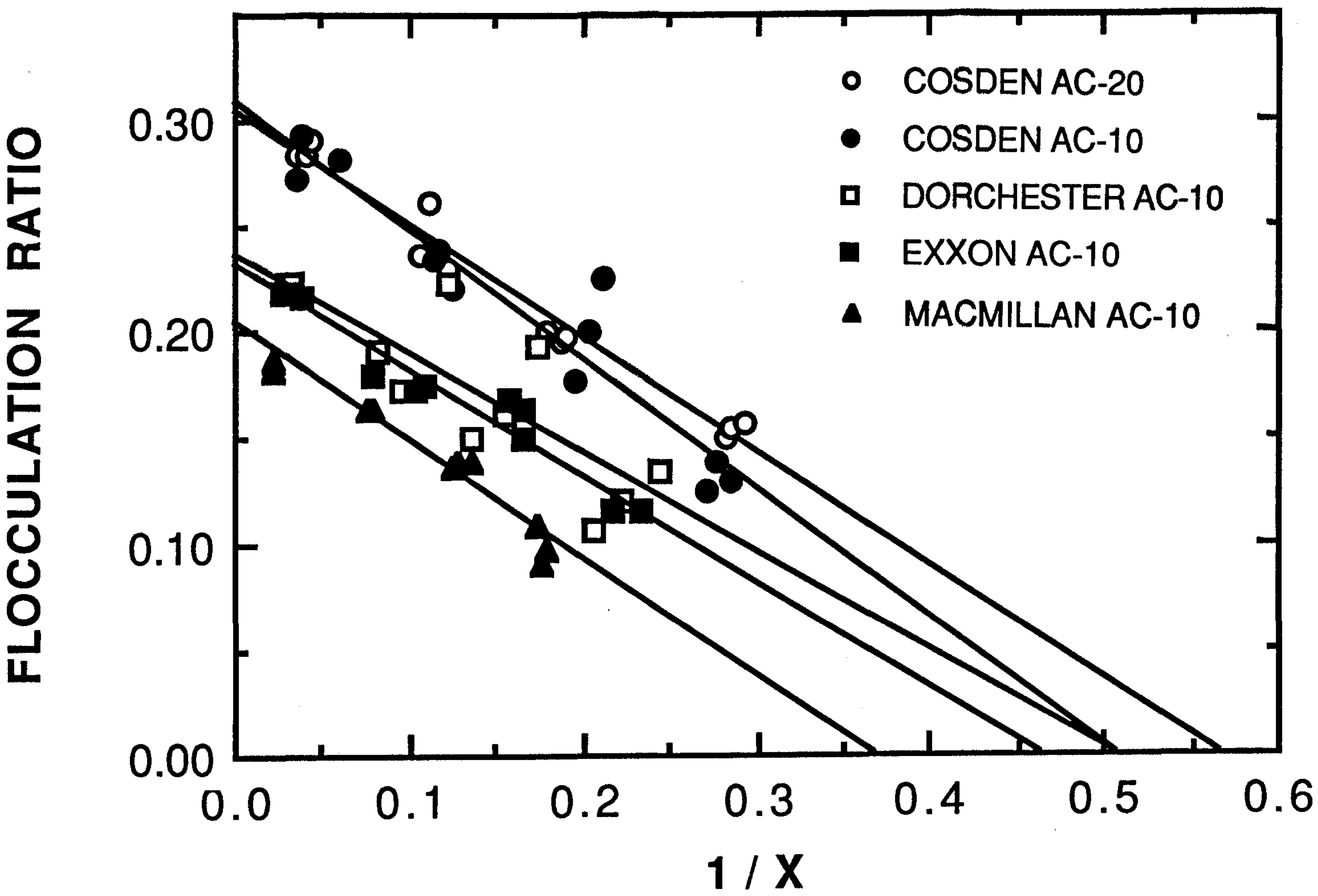

Figure II-5-3
Heithaus Results for All Dumas Tank Asphalts

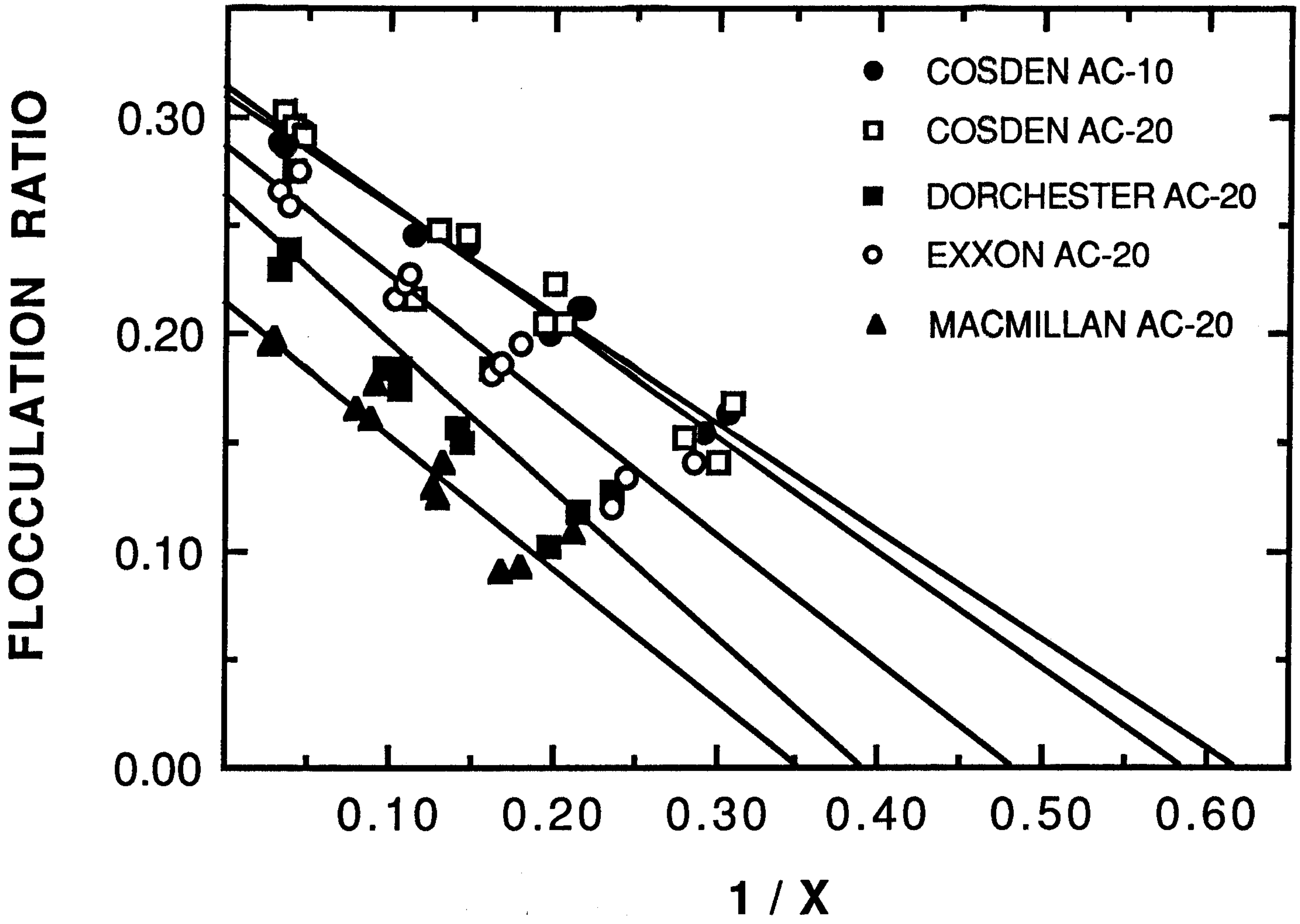

Figure II-5-4
Heithaus Results for All Dickens Tank Asphalts

Table II-5-2

1982-1983 Asphalt Heithaus Parameters for Test Section Asphalts

Core Site	Producer	AC#	FR_{max}	$1/X_{min}$
Dickens	Cosden	10	.310	.616
Dickens	Cosden	20	.314	.587
Dickens	Dorchester	20	.263	.387
Dickens	Exxon	20	.287	.482
Dickens	MacMillan	20	.214	.353
Dumas	Cosden	10	.310	.507
Dumas	Cosden	20	.305	.566
Dumas	Dorchester	10	.236	.508
Dumas	Exxon	10	.232	.467
Dumas	MacMillan	10	.204	.368
Lufkin	Cosden	20	.317	.584
Lufkin	Dorchester	20	.274	.413
Lufkin	Exxon	20	.229	.377
Lufkin	MacMillan	20	.168	.522
Lufkin	Texaco	20	.269	.418

Table II-5-3

1987-1989 Hot-Mix Study Tank Samples Heithaus Parameters

Producer	AC#	FR_{max}	$1/X_{min}$
1987 Coastal	20	.288	.489
1987 Exxon Batch	20	.214	.423
1987 Exxon Drum	20	.230	.406
1988 Exxon	20	.214	.404
1989 Ampet	20	.191	.373
1989 Cosden	10	.312	.568
1989 Cosden	20	.154	.310
1989 Exxon	20	.194	.380
1989 Texaco	20	.258	.422
1989 Texas Gulf	20	.323	.636

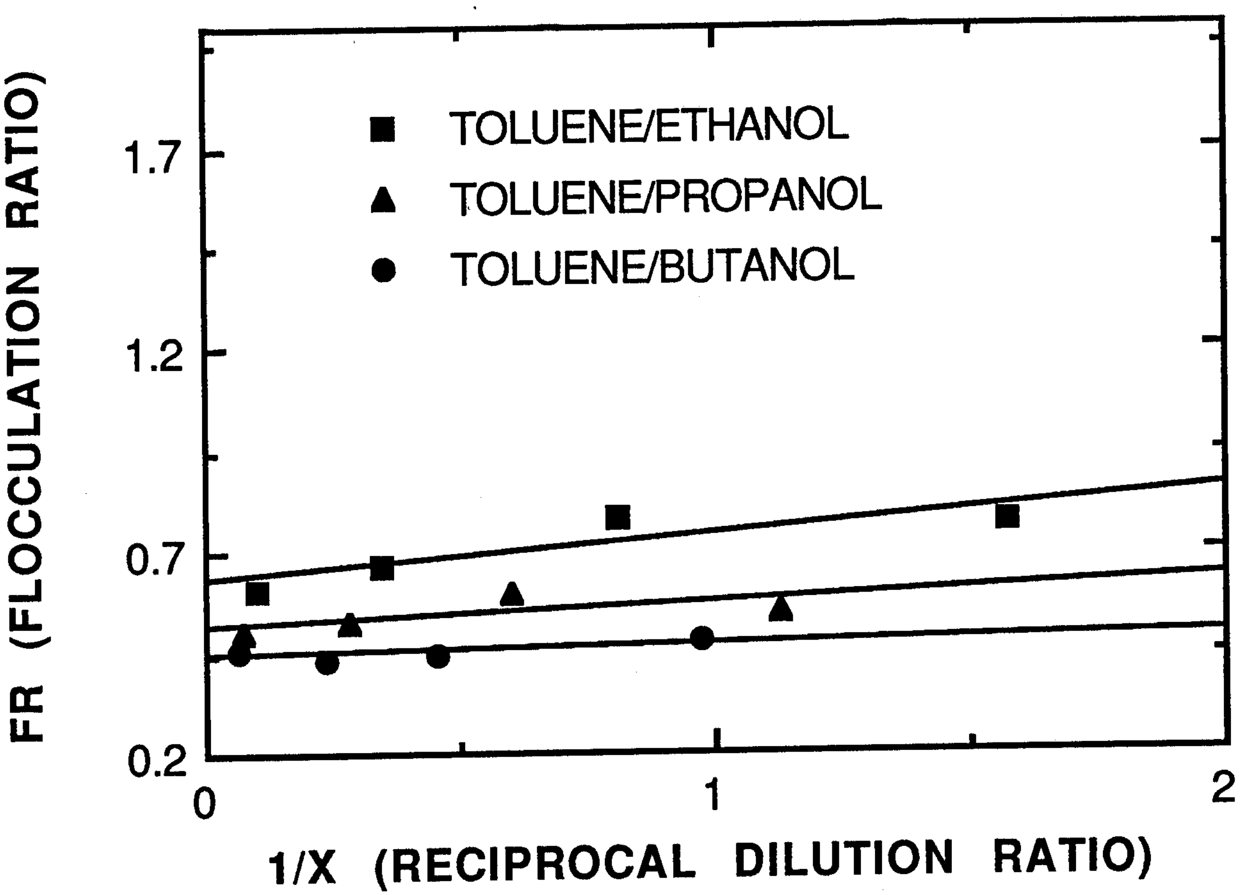

Figure II-5-5
Modified Heithaus Test Using Toluene and Alcohols - Cosden AC-20

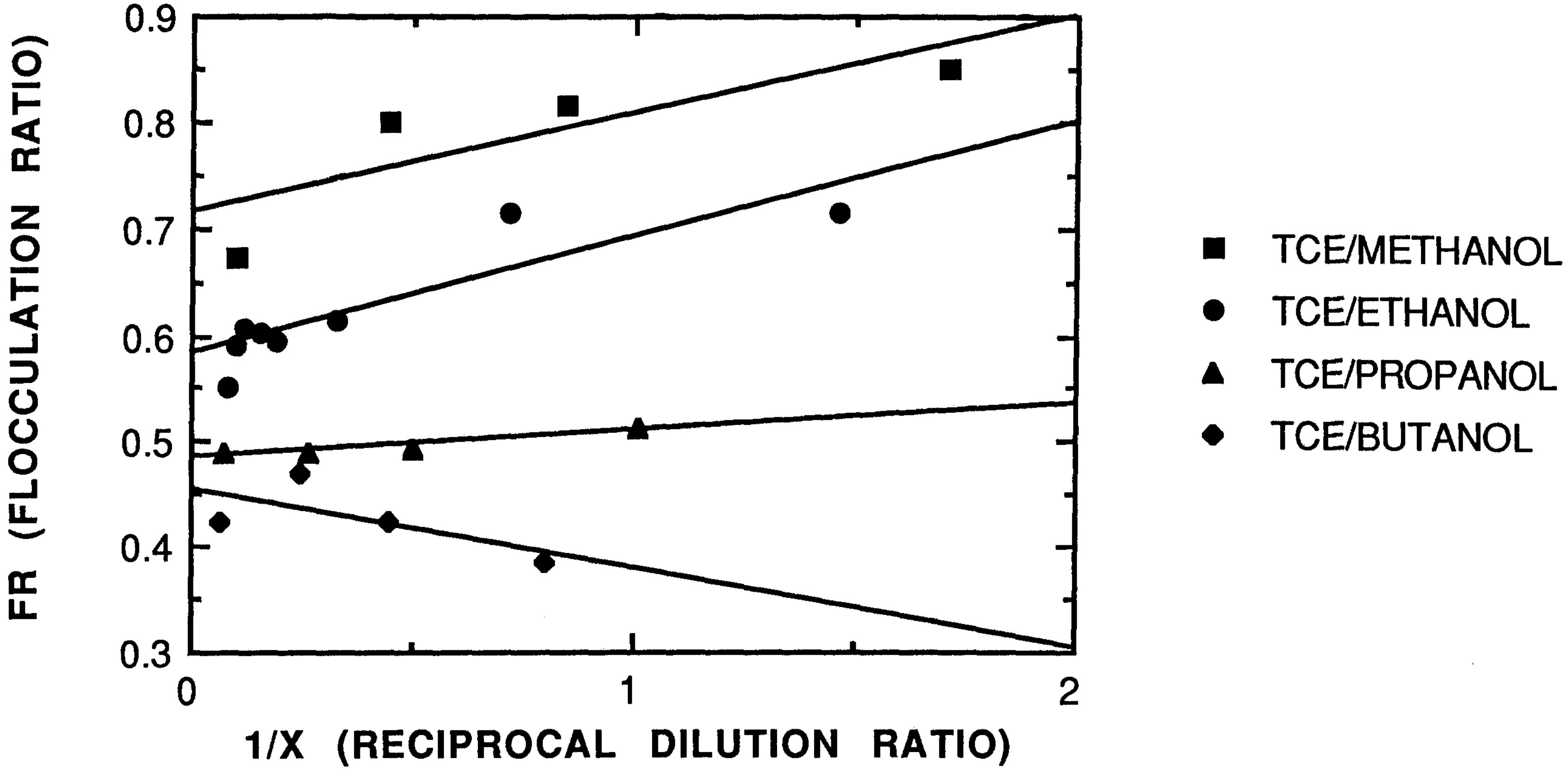

Figure II-5-6
Modified Heithaus Test Using Trichloroethylene and Alcohols - Cosden AC-20

CHAPTER II-6

TRACE METALS' ANALYSIS BY ATOMIC ABSORPTION

Summary

The technique of atomic absorption spectrophotometry has been developed and applied in this study to the analysis of asphalts. This analysis technique provided trace metals' analysis for sodium, potassium, iron, nickel, and vanadium. Some differences between asphalts were observed and may indicate differences in properties such as water and aging susceptibility.

Introduction

There is no standard method for the analysis of asphalts, a petroleum byproduct, by atomic absorption spectrophotometry. There are three sample preparation methods presently being employed for the determination of metals in petroleum products by atomic absorption spectrophotometry (AAS):

1. Dilution of the sample in an organic solvent,
2. Ashing of the sample and dissolution with an appropriate acid, or
3. Acid digestion.

Each method of sample treatment has advantages and disadvantages and the choice depends on the aims of the analysis, the nature of the sample, and elements being analyzed.

The chemical form of the matrix in petroleum is largely unknown and for several metals, the absorbance varies considerably according to the nature of the metal bonding. Due to strong matrix interferences, AAS should not be used for the determination of vanadium and nickel (two important metals in question), in petroleum samples dissolved in organic solvents, but only as a means of studying matrix effects. Therefore, the procedure to be used requires total matrix destruction which converts the elements to a common form.

Ashing and acid digestion are lengthier procedures than simple dilution, but give total metal contents which represent the sum of particulate and soluble metal. It was decided to proceed with an ashing method similar to the one proposed by Milner, et al., (1952) and referenced by Hofstader, et al., (1975) and the Varian Technical Bulletin.

Procedure. Virgin asphalt samples, in 3-4 gm aliquots were weighed in fused silica crucibles to 0.1 mg on a Precisa 120A balance. Concentrated sulfuric acid was weighed into each crucible in slight excess of the sample weight. The crucibles were covered and remained at ambient temperature overnight.

The sulfated asphalts were placed uncovered on a Corning PC35 hot plate at a low initial temperature setting. The temperature was slowly increased throughout the day to digest the sample and drive off the acid. The crucibles were left at high temperature on the hot plate overnight.

The crucibles were placed in a Lindberg 51848 furnace under airflow with covers slightly ajar. (The furnace was inside a fume hood due to heavy smoking as the samples ashed.) The initial temperature setting of 150°C was held for 30 minutes. At half-hour intervals the setting was increased 25°C until 450°C was reached. (Due to the open furnace door and airflow, the 450°C setting was tested to give an actual temperature of approximately 540°C.) The samples were heated at this temperature overnight.

To each ashed sample, one ml of concentrated hydrochloric acid was added. The crucibles were covered and heated at low temperature on the hot plate for 10-20 minutes until the solutions were clear yellow with no visible residue. After cooling, the solutions were filtered using Whatman 1 paper into 25 ml volumetric flasks. The crucibles and covers were rinsed with distilled, deionized (DD) water into the filter. The filter was further rinsed using 5 ml each of 10,000 ppm A1 (as an ionization inhibitor for vanadium) and 5,000 ppm Cs (as an ionization inhibitor for potassium.) The flask was filled to the mark with DD water and the solution was transferred to a 100 ml nalgene bottle. This solution was used to test for Co and K and for lower concentrations of Ni, Fe, and V.

A second dilution was made from this initial volume by transferring 5 ml of sample to a clean 25 ml volumetric flask. To this was added 4 ml of 10,000 ppm A1 and the flask was filled with DD water. This solution was transferred to another 100 ml nalgene bottle. This volume was used for higher concentrations of Ni, Fe, and V.

To test for sodium, which utilizes a very low calibration curve, a third dilution of sample was made. From the second dilution, 5 ml of sample was transferred to a clean 25 ml volumetric flask. To this was added 5 ml of 10,000 ppm K as an ionization inhibitor. Distilled, deionized water was added to the mark and the three sample dilutions were ready for analysis.

Analysis was performed on a Varian Spectr AA-30 atomic absorption spectrophotometer analyzer using the manufacturers recommendations for all parameters with the exception of a higher acetylene flow rate (7.00 liters per minute) for the Vanadium test.

Discussion. Six metals were analyzed in twenty tank asphalts representing three of the Study 287 test sites, five suppliers, and two viscosities. These metals included sodium, potassium, cobalt, iron, nickel and vanadium. All asphalts contained only trace amounts of cobalt; therefore this metal is not included in the following discussion or concentration tables. Results are given in Tables II-6-1 through II-6-5, expressed in parts per million (ppm).

The greatest concentration range was found in the sodium analysis. Most asphalts contained less than 50 ppm; however one sample, Dickens MacMillan AC-20, contained over 500 ppm sodium. The MacMillan asphalts reported exceptionally higher sodium concentrations at all sites which could indicate caustic washing in the refining process. This group of asphalts may result in poorer performance if the presence of this metal promotes water susceptibility.

The very low concentration range of potassium, 0.5 to 3.5 ppm, suggests that this metal will have negligible effect on asphalt performance. All AC-10 samples exhibited less than 2.0 ppm and most AC-20 samples contained greater than 2.0 ppm. The only asphalt containing greater than 3.0 ppm was the Dickens MacMillan AC-20 (3.5 ppm) which indicates the strong relationship of asphaltic sodium and potassium.

Table II-6-1

Sodium Analyses of the Test Section Virgin Asphalts *

		Cosden	Dorchester	D. Sham.	Exxon	MacMillan
Dumas:						
	AC-10	—	—	49.1	26.1	—
		27.6	37.4	34.0	27.8	85.6
		15.3	26.6	34.1	27.6	83.9
	AC-20	29.0	—	—	—	—
		23.0	—	50.6	—	—
		17.4	—	40.6	—	—
Dickens:						
	AC-10	—	29.0	—	—	—
		25.1	29.6	29.7	—	—
		20.5	31.0	24.9	—	—
		—	35.1	—	—	—
	AC-20	—	—	27.1	—	—
		21.3	—	24.1	65.4	527
		18.2	—	30.6	67.9	483
		—	—	27.2	—	—
Lufkin:						
	AC-10	—	54.9	—	—	—
		—	56.7	—	—	—
		—	62.0	—	—	—
		—	75.9	—	—	—
	AC-20	—	—	51.0	—	—
		32.6	—	51.1	—	—
		15.3	—	45.6	33.5	260
		17.9	—	57.6	24.9	219
		—	—	51.6	—	—

---

* All values are parts per million (ppm).

Table II-6-2

Potassium Analyses of the Test Section Virgin Asphalts *

		Cosden	Dorchester	D. Sham.	Exxon	MacMillan
Dumas:						
	AC-10	1.80	2.71	1.96	1.20	1.51
		1.65	0.863	1.97	1.36	1.56
	AC-20	2.31	—	—	—	—
		2.08	—	2.32	—	—
		2.62	—	2.34	—	—
Dickens:						
	AC-10	—	0.609	—	—	—
		1.45	0.516	1.98	—	—
		1.59	1.07	1.93	—	—
		—	1.19	—	—	—
	AC-20	2.22	—	2.09	1.81	3.82
		2.83	—	2.38	6.06	3.27
Lufkin:						
	AC-10	—	1.42	—	—	—
		—	1.47	—	—	—
		—	1.57	—	—	—
		—	2.41	—	—	—
	AC-20	2.98	—	1.81	—	—
		1.84	—	1.83	1.65	2.44
		1.69	—	1.75	1.57	2.02

* All values are parts per million (ppm).

Table II-6-3

Iron Analyses of the Test Section Virgin Asphalts *

		Cosden	Dorchester	D. Sham.	Exxon	MacMillan
Dumas:						
	AC-10	—	—	—	3.85	—
		97.0	26.2	127	40.4	32.7
		88.6	15.9	141	44.9	33.1
	AC-20	73.7	—	—	—	—
		84.1	—	142	—	—
		79.9	—	154	—	—
Dickens:						
	AC-10	—	13.2	—	—	—
		74.0	12.6	164	—	—
		83.0	16.1	191	—	—
		—	16.4	—	—	—
	AC-20	83.3	—	213	36.5	39.6
		84.9	—	193	55.8	45.3
Lufkin:						
	AC-10	—	26.6	—	—	—
		—	30.7	—	—	—
		—	26.6	—	—	—
	AC-20	104	—	122	—	—
		144	—	157	67.1	144
		114	—	152	82.9	118

* All values are parts per million (ppm).

Table II-6-4

Nickel Analyses of the Test Section Virgin Asphalts *

		Cosden	Dorchester	D. Sham.	Exxon	MacMillan
Dumas:						
	AC-10	32.8	23.2	18.7	35.3	11.1
		36.1	23.7	21.2	40.7	7.79
	AC-20	39.7	_	_	_	_
		37.2	_	14.2	_	_
		38.7	_	17.1	_	_
Dickens:						
	AC-10	_	20.6	_	_	_
		36.9	20.2	17.3	_	_
		35.2	20.2	19.9	_	_
		_	21.8	_	_	_
	AC-20	37.0	_	22.7	52.3	11.8
		39.4	_	17.7	49.5	10.4
Lufkin:						
	AC-10	_	47.9	_	_	_
		_	47.8	_	_	_
		_	46.8	_	_	_
		_	55.5	_	_	_
	AC-20	37.3	_	25.6	_	_
		35.4	_	24.1	37.7	21.8
		36.0	_	25.4	40.6	18.1

* All values are parts per million (ppm).

Table II-6-5

Vanadium Analyses of the Test Section Virgin Asphalts *

		Cosden	Dorchester	D. Sham.	Exxon	MacMillan
Dumas:						
	AC-10	76.2	40.6	17.9	105	11.1
		84.3	41.4	17.9	122	10.8
	AC-20	84.4	—	—	—	—
		88.1	—	19.5	—	—
		92.4	—	20.7	—	—
Dickens:						
	AC-10	—	33.2	—	—	—
		85.5	32.1	18.0	—	—
		86.5	31.5	18.6	—	—
		—	33.7	—	—	—
	AC-20	85.8	—	22.7	90.3	16.1
		86.4	—	20.6	106	11.5
Lufkin:						
	AC-10	—	168	—	—	—
		—	167	—	—	—
		—	167	—	—	—
		—	218	—	—	—
	AC-20	85.7	—	39.7	—	—
		81.1	—	40.9	110	36.4
		85.8	—	40.2	114	35.6

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* All values are parts per million (ppm).

Significant concentration range, 20 to over 200 ppm, was also exhibited by the iron analysis. The Dickens site again provided the sample with the highest concentration, Diamond Shamrock AC-20. Higher iron contents, greater than 100 ppm, were found in the Diamond Shamrock samples at all test sites indicating the metal's source as the crude or the refining process. It is also noted, however, at the Lufkin site, most of the AC-20 samples also contained greater than 100 ppm iron, suggesting some site influence on concentration. Higher concentration of iron is believed to prevent water susceptibility, suggesting that asphalts which are high in iron and low in sodium would be the least susceptible to problems initiated by water.

Nickel and vanadium in asphalts are well known to be closely related. In this analysis, the nickel ranged from 10 to over 50 ppm, and vanadium from 10 to over 200 ppm. The maximum concentrations of both metals were found in the Lufkin Dorchester AC-20 asphalt, and the minimum amounts were found in Dumas MacMillan AC-10. It should be noted, as with the iron results, that there is a marked trend of similar concentrations based on the supplier indicating these metals originated in the crude or were introduced during the refining process.

Based on total metal concentrations, this analysis has identified those asphalts which should be the most water susceptible, Dickens MacMillan AC-20, and the least, Dickens Diamond Shamrock AC-20, as influenced by sodium, potassium and iron. The highest total nickel and vanadium values found in the Lufkin Dorchester AC-20 asphalt could indicate poorer aging performance due to the metals' influence on oxidation.

SECTION III

EXTRACTION AND RECOVERY OF ASPHALT FROM AGGREGATE

The work reported in this section is something of a digression from the original objectives of this study, but it was necessary for the achievement of the study goals and represents some of the most important work in this report even though the work is not entirely complete. In order to study the performance of asphalt in hot mixes and roads, it is necessary to extract and recover these asphalts. As there are standard ASTM methods for doing this, serious problems were not anticipated.

Partly because of the powerful tools available for this study, particularly GPC and FT-IR, it was found that the extraction and recovery procedures were inadequate in nearly every respect when the recovered asphalt is to be studied relative to its physical and chemical properties. It was found that extraction often left several percent of hard-to-remove material on the aggregate, that recovery often left solvent in the asphalt, and that solvent hardening occurred during extraction and recovery.

A detailed analysis of solvent recovery has been made, and the parameters necessary to assure solvent removal have been established and are reported. A considerable study is underway relative to solvent hardening, and preliminary results are reported. A detailed study has not been made of extraction, but it has been found that addition of ethanol to TCE considerably improves removal of asphalt from the aggregate. The actual procedures used are discussed in the hot-mix and road aging studies in Section IV.

CHAPTER III-1

SOLVENT REMOVAL FROM ASPHALT

Summary

The volatiles' loss from virgin or unaged tank asphalts can produce 7% to 10% hardening of the original asphalt viscosity. Rolling thin film, oven-aged asphalts do not exhibit this hardening, apparently due to the loss of volatiles during the aging. The same asphalts show hardening of from 10% to 40% (including that due to volatiles' loss) upon contact with TCE and subsequent solvent removal. Short times and moderate temperatures produce little additional hardening; extended times at elevated temperatures (such as during reflux solvent extraction) can produce significant hardening.

Experiments were also conducted on the Abson and Roto-vap solvent removal methods for the purpose of evaluating their effectiveness in removing solvents. The Abson method, taken to its standard recovery time, can leave enough solvent to produce significant softening, especially for hardened asphalts such as those obtained from aged pavement cores. Increasing the temperature of the solvent removal and the recovery time can reduce this residual solvent concentration, although the above-mentioned solvent hardening effects must be considered. The Roto-vap method appears to be less consistent and less reproducible than the Abson method but may have some advantages for solvent removal.

A complicating factor in hot-mix and pavement core recoveries appears to be the possibility of fuel contamination from the hot-mix plant. Evidence of such contamination was found in some drum hot mixes, but the extent and significance of this possible contamination has yet to be determined.

Introduction

To obtain asphalt properties which are representative of the binder in situ properties, procedures must be effective in removing the binders from the aggregate without changing or aging the asphalts, and the solvents used for the extraction must be adequately removed from the asphalt binder so as not to distort the physical properties of the binder which are subsequently measured. Problems have been reported with all aspects of the asphalt extraction and recovery process, including incomplete asphalt extraction, solvent hardening of the extracted material, loss of volatiles during recovery, and incomplete solvent removal. The present effort focuses on incomplete solvent removal, which seems a simple problem but which has flawed many studies involving extracted asphalt. Typical residual concentrations of solvent can distort significantly asphalt physical properties. Background for this work is given in Section I, Chapter 2. Complete data for this chapter are found in Appendix B.

Experimental Procedures

The objective of this study was to determine the effectiveness of the existing recovery methods, examine the procedures' responses to changes in process variables, and establish new conditions which would guarantee complete solvent removal. Our strategy was to first find a method of directly analyzing solvent concentrations in asphalts. TCE was chosen because of its common usage. Then, recoveries were performed, using the Abson and Roto-vap methods, at various temperatures and on a wide range of asphalt viscosities. An in situ sampling method was developed so that samples could be taken at several different times during a recovery. The viscosities of solvent-contaminated asphalts were compared to their original viscosities to show the effect of solvent.

TCE Analysis by GPC. The residual concentration of TCE during solvent removal can be measured easily by gel permeation chromatography (GPC). TCE elutes as a single peak with no interference from other low-molecular size materials in the sample. This was discovered during an earlier study of extracted pavements. A distinct low molecular size peak appeared on the chromatograms. No such peak had been seen on tank or oven-aged samples.

The GPC analyses were performed on an IBM model LC-9533 HPLC. A 100 μl sample (7 wt % asphalt in THF) was injected into the carrier solvent (tetrahydrofuran, THF) flowing at 1 ml/min through two Polymer Laboratories columns in series containing PL gel material of 500 Å (column 1) and 50 Å (column 2) pore sizes. The details are as described in Section II, Chapter 1 and by Glover et al. (1987).

Standard blends of TCE in THF were made for calibration of the solvent analysis. Dilutions in THF equivalent to those which occur in GPC analysis of 5, 2, 1, 0.5, 0.1, and 0.05 weight percent TCE in asphalt were analyzed by GPC, the relative peak areas related linearly to the TCE concentrations with a coefficient of variance of 0.997. Analyses of TCE in asphalt samples were performed similarly. Solvent concentrations were determined using the calibration. In this study, residual solvent concentrations in recovered asphalt ranged from 0 to 2.5%.

Solvent Removal Methods. As earlier mentioned, the literature shows that while the Abson recovery method is recommended by ASTM, the Roto-vap method also is used widely. Both were tested in this study and a brief discussion of these methods follows.

Abson Method (D-1856)

The Abson method removes solvent by distillation with the aid of a CO_2 purge. About 150 ml of a concentrated asphalt/solvent solution, containing roughly 50 g of asphalt, are charged to a 250 ml widemouth round-bottom flask. The flask is electrically heated. The liquid boils and is condensed and collected in a receiving flask. The CO_2 flow is set at 100 ml/min once the temperature reaches 275°F. When the temperature is 315°F, the flow is raised to 900 ml/min. The temperature is then maintained between 320°F and 330°F for 10 minutes. If the asphalt is expected to have penetration of less than 30, the distillation should be continued for another 10 to 12 minutes (ASTM, 1979).

Instructions set forth in ASTM D-1856 were adhered to strictly. The CO_2 flow was accurately metered using a Gilmont R-012 flow meter. A variac and heating mantle supplied heat to the flask of asphalt and solvent. Temperature control was found to be difficult from the beginning. Due to a lag in the response of the asphalt temperatures to heater action, significant excursions outside the specified limits were difficult to avoid. Consequently, an analysis of the heater system with respect to temperature control was performed to obtain the sequence of heater settings which would give good control at 320°, 340°, or 380°F, as required. Manual control of the variac using these setting profiles made temperature control easier and more accurate.

Sampling

In order to facilitate this study, an in situ sampling technique was devised. First, it was thought that the asphalt could be drawn into a 1-ml disposable pipette during the recovery. The asphalt would then solidify and could be stored until time for GPC sample preparation. However, the asphalt had to be melted and drained into a scintillation vial. During this process, solvent was apparently lost. Consequently, this method yielded solvent concentrations that were low and imprecise. To remedy this, 8-inch pieces of 1/8-inch I.D. Nalgene autoclavable tubing were substituted for the glass pipettes. After sampling, these tubes were cut lengthwise at room temperature to allow easy removal of the asphalt for GPC sample preparation. This method's precision seems to be better than any alternative.

Roto-Vap Method

The Roto-vap method uses a rotary evaporator to mix the solution and a vacuum and vent gas to vaporize and sweep away solvent. It has a distinct advantage over the Abson method in that there is no need to primarily distill the solution down to 150 ml before proceeding with the recovery. Large volumes of solution can be handled in this apparatus. During this study, recoveries were run on mixtures of 100 ml TCE and 50 g of asphalt in order to save time and solvent.

There is no formally approved Roto-vap recovery procedure available. A tentative ASTM (1988) method and another used by the Pacific Coast User's Group (Davis, 1983) appear identical and well-studied, though. These methods formed the basis for the procedure used in this study.

Initially, the oil bath is heated to 280°F. A 1000 ml round bottom flask containing 150 ml of concentrated solution is attached to the Roto-vap. CO_2 is metered at 500 ml/min through a tube that touches the solution's surface. The flask rotates at 45 rpm in the oil bath. When the bulk of the solvent has been distilled, a 600 mm Hg vacuum is applied and the CO_2 flow is raised to 600 ml/min. These conditions are held for 15 minutes (ASTM, 1988). In an alternate method studied, no vacuum is applied, but the CO_2 flow is raised to 900 ml/min.

Asphalt sampling was similar to that in the Abson method. The 1000 ml flask was modified with the addition of a 24/40 ground glass fitting at approximately 45^0 from the flask's neck. The connection was closed with a ground glass cap. During the recovery, the flask rotation was stopped, the cap removed, the Nalgene sample tube inserted into the hole and the sample pulled using a pipetter. Immediately afterwards, the cap was replaced and rotation resumed. This process took approximately 20 seconds to perform when there was no vacuum and about 35 seconds if vacuum was used.

Asphalt Viscosity. Asphalt viscosities were measured according to ASTM D-2171. They were run at 140^0F in Cannon-Manning Viscometers. All samples were melted and mixed well before viscosity measurement. This is critical, as it was found that asphalt tends to stratify during cooling. Samples taken near the top while cool and hard tended to have much higher TCE concentrations because of this.

FT-IR Analysis. A Nicolet Fourier Transform Infrared Spectrometer was used to analyze the functional chemistry of samples. Some of the hot mixes left a mysterious oily film on the flask sides after recovery. This was run on the FT-IR because of the small sample size required. An attenuated total reflectance method worked well (Fahrenfort, 1961). The samples were applied as thin films onto a special fine selenide prism.

Materials

The asphalts used in this study were derived mainly from locally sampled Exxon AC-20. For the studies of the effect of viscosity and temperature on the time for solvent removal, hardened asphalt was produced. Two 300 g samples of asphalt having viscosities of 20,000 and 300,000 poise were produced by bubbling oxygen into 450^0F asphalt for from 3 to 8 hours. In these experiments, both the recovered asphalt and solvent were reused in subsequent runs without significant effects on properties. Recovery data were also taken on several extracted hot mixes.

Results and Discussion

Extraction and Solvent Removal Effects on Viscosity. Figure III-1-1 tracks the viscosity relative to initial viscosity (the hardening index) of asphalt (plus residual solvent) during solvent removal processes for three situations. The tank (AC-20) and oven-aged (rolling thin film oven test - RTFOT) asphalts were well dissolved in TCE at room temperature and with solvent removal initiated within 1 hour. The refluxed sample was approximately a 25 weight percent mixture of tank asphalt (AC-20) in TCE which was refluxed for 4 hours at 200°F before initiating solvent removal. This reflux procedure simulated the conditions of hot extraction methods such as ASTM D-2172, Method B.

These data show several artifacts of the extraction and recovery procedures on asphalt viscosity. The first factor is the considerable softening of asphalt by even small amounts of residual solvent. Even 0.5% residual solvent can produce viscosities 30% low. Second are the different degrees of residual hardening upon reaching zero-solvent concentration for different asphalts and situations. The tank asphalts typically harden 5% to 10% above their original values. This most likely results from loss of volatile components that are lost during recovery. The RTFOT samples return to their original viscosities because their volatiles were removed in the oven-aging test. Asphalts exposed to hot reflux (simulating a reflux extraction procedure) may exhibit a 20% to 30% viscosity increase, indicating significant solvent hardening beyond that attributable to volatiles lost.

Figure III-1-2 shows that the solvent hardening phenomenon also occurs at room temperature for extended exposure times. A series of Roto-vap solvent removals (asphalt recoveries) were conducted for mixtures of 7 weight percent asphalt in TCE. Before recovery, however, the mixtures were allowed to incubate at room temperature for the times indicated in Figure III-1-2. For short room-temperature incubation times, hardening due to volatiles' loss and solvent aging in the hot-recovery Roto-vap method is from 14%-18%. For extended times, hardening is in excess of 40%. For comparison, a recovery under vacuum at a reduced solution temperature (approximately 100°F) and with short room-temperature exposure produced about 10% hardening, close to that due to volatiles' loss only.

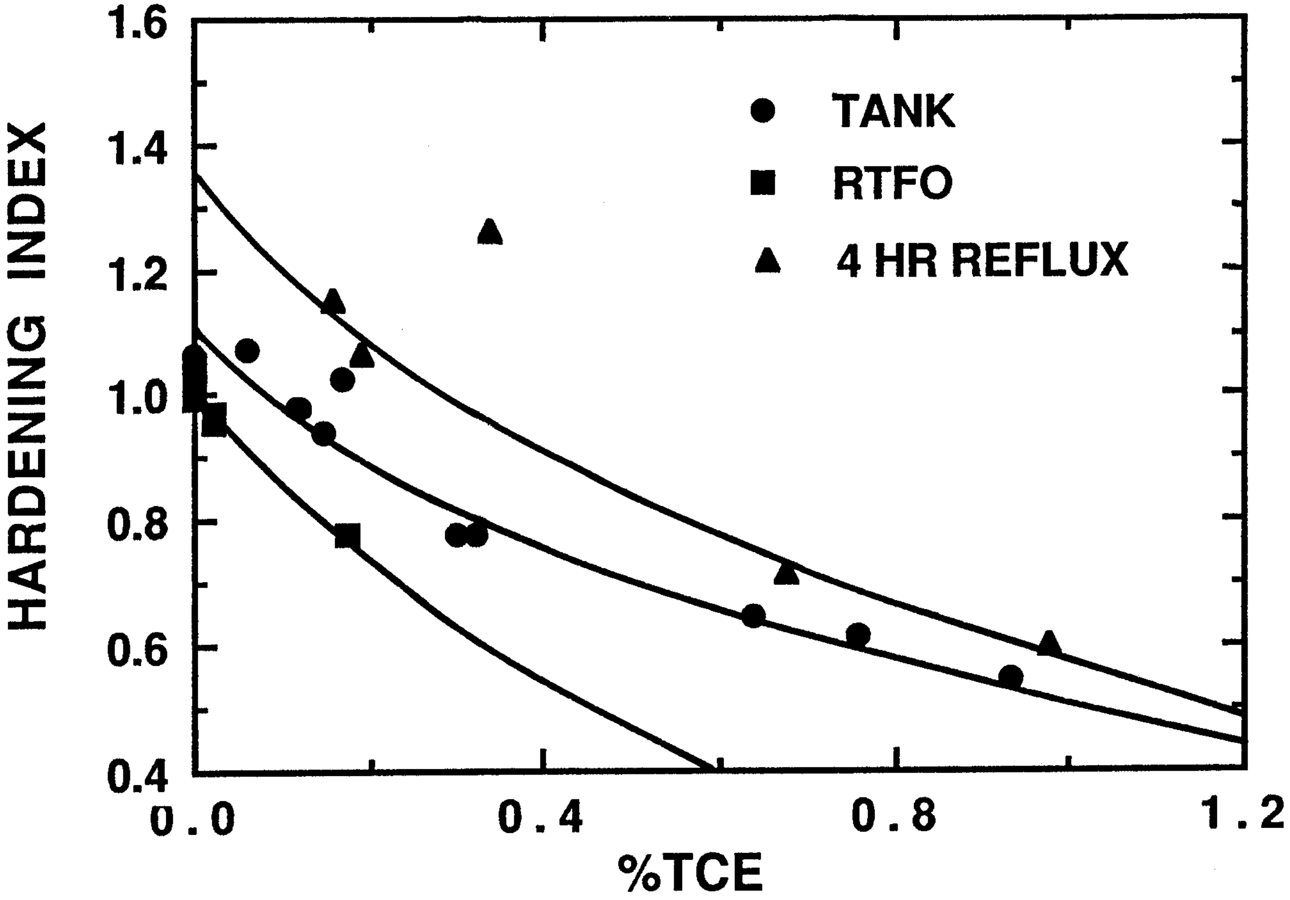


Figure III-1-1
Removal of Solvent and Resulting Changes in Asphalt Viscosity. The Tank and Oven-aged Asphalts were Dissolved in Solvent and Immediately Recovered with no Incubation Time in the Solvent

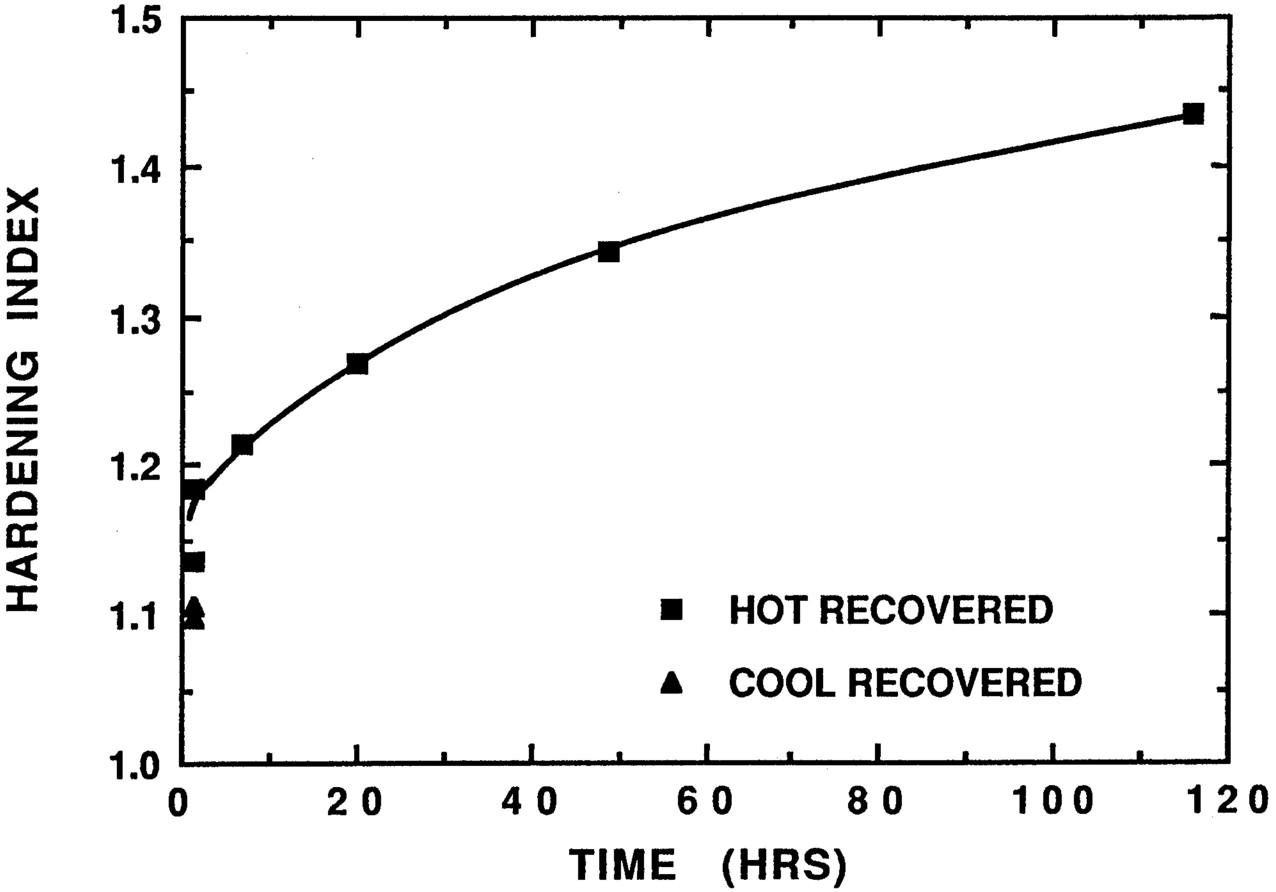


Figure III-1-2
Hardening of Asphalt in Solvent at Room Temperature for Extended Periods of Time Prior to Hot Recovery. Also Shown is the Aging During a Cool Recovery Process with Short Incubation Time

Abson Solvent Removal Method. Several recoveries at strict Abson conditions consistently resulted in significant TCE presence after the 10 minutes required by the method. The experiments also showed the reproducibility of the Abson recovery and sampling methods used (Figure III-1-3). Approximately 0.2% TCE remains in the asphalt after the Abson time on recoveries of 2000 poise asphalt. From Figure III-1-1, this equates to about a 5% decrease in viscosity (below initial value) on a sample that would show an increase of about 7% (due to volatiles' loss) at 0% solvent. If the recovery procedure is calibrated using tank asphalts and with no TCE analysis technique, inadequate operating parameters are established because tank asphalts show no viscosity decrease even though their residual TCE levels are at about .1% to .2%.

Recovery temperature and asphalt viscosity noticeably affect the Abson methods' ability to remove TCE. Figures III-1-4, -5 and -6 show the TCE concentration profiles for recoveries of 2000, 20,000, and 200,000 poise asphalts respectively, each at 325°, 340°, and 380°F. Figures III-1-7, -8, and -9 are the same data at 325°, 340°, and 380°F, respectively, for each asphalt grade. These show, without fail, that removal is achieved sooner for lower viscosity material or for higher temperature. The poor removal at high viscosities at 325°F illustrates the need to modify the existing conditions. The 20,000 poise material's degree of softening due to residual solvent is nearly 30% at completion of the prescribed method.

It is reasonable that changes in recovery temperature and asphalt viscosity should affect the method's performance. As the solvent is removed, the solution behaves like a pure molten asphalt. The high viscosities of these materials lower the mobility of the solvent, due to increased diffusion resistance. This resistance slows the solvent in reaching the liquid-vapor interface where evaporation occurs. So, while equilibrium may be maintained at the asphalt surface, significant quantities of solvent remain in the bulk asphalt, its removal rate limited by diffusion. Furthermore, higher viscosity asphalts have lower diffusion rates, resulting in increased difficulty in removing solvent. Also, the higher asphalt viscosities reduce the mixing effectiveness of the CO_2 purge.

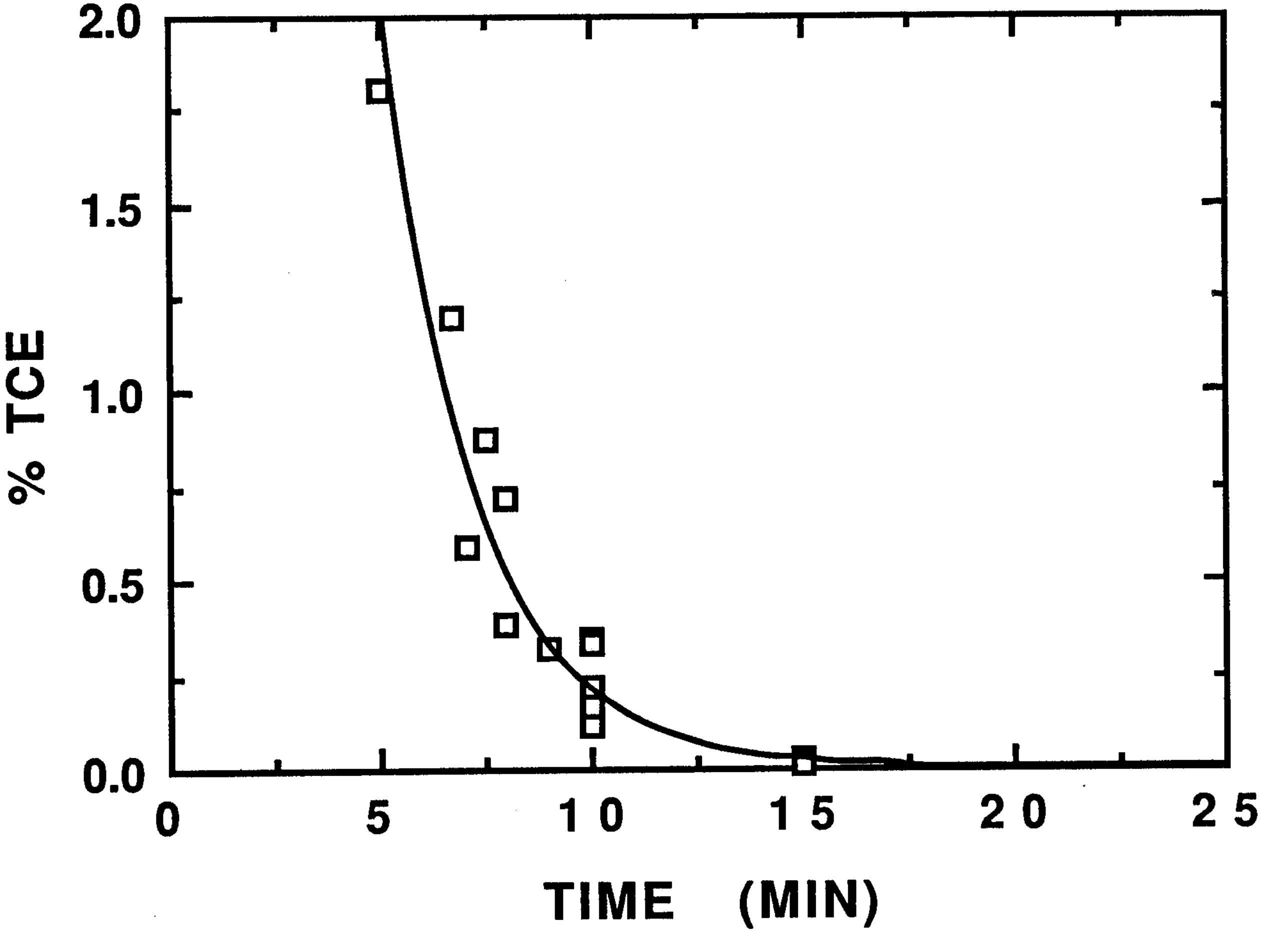


Figure III-1-3
Residual Solvent Concentration Versus Abson Recovery Time
for a Tank (AC-20 Asphalt

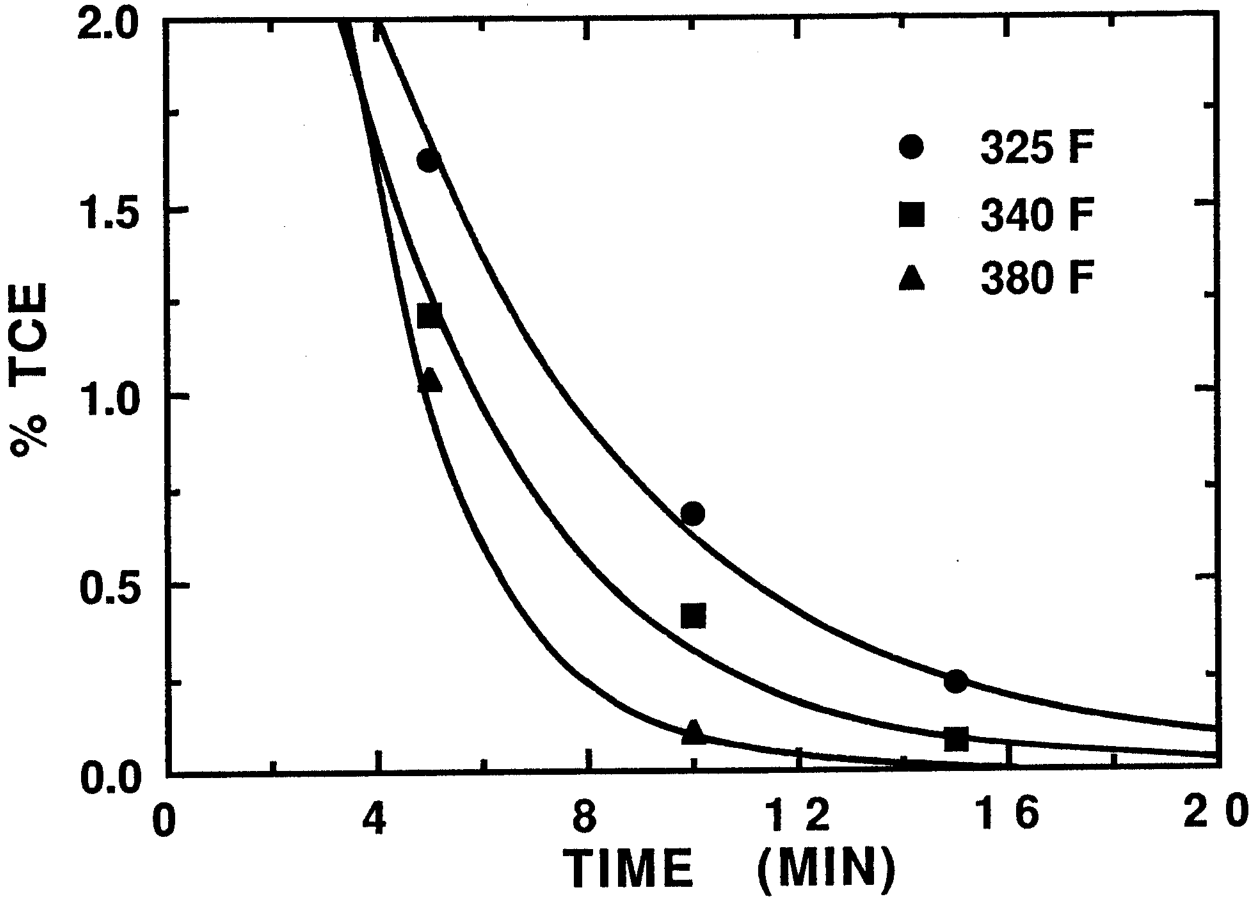


Figure III-1-4
Residual Solvent Concentrations Versus Abson Recovery Time
at Three Temperatures for a Tank (AC-20) Asphalt

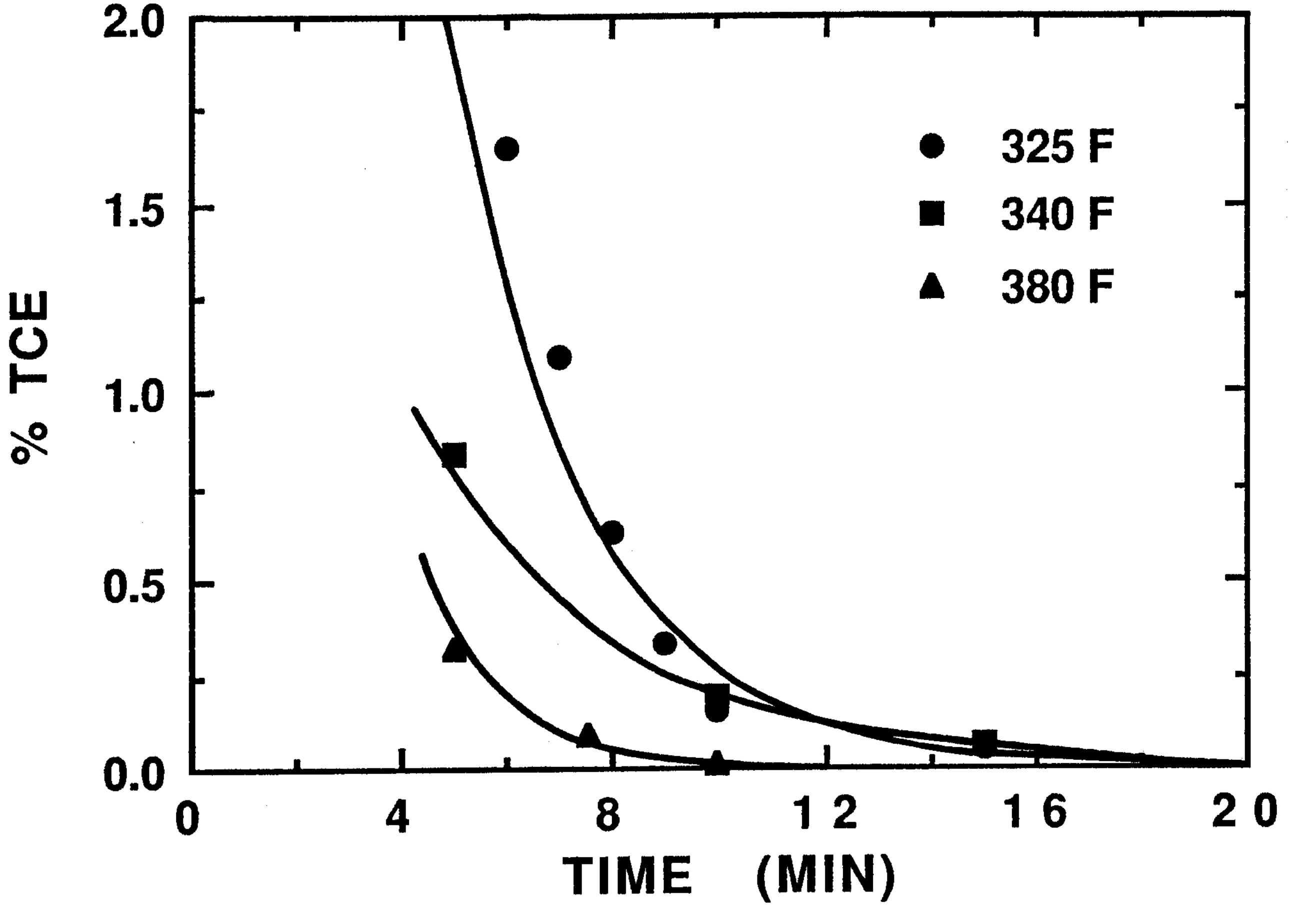


Figure III-1-5
Residual Solvent Concentrations Versus Abson Recovery Time
at Three Temperatures for a 20,000 Poise Asphalt

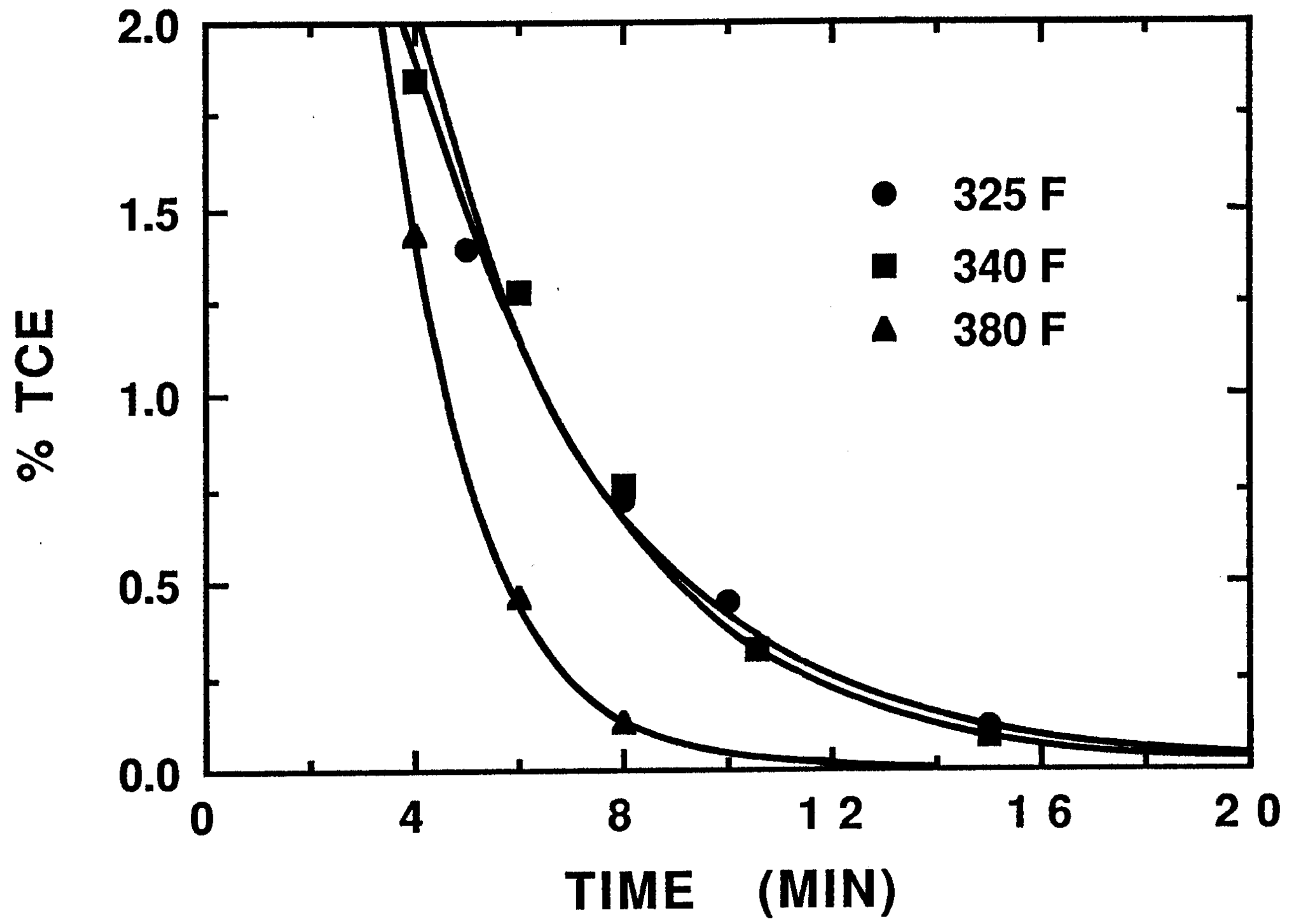


Figure III-1-6
Residual Solvent Concentrations Versus Abson Recovery Time
at Three Temperatures for a 200,000 Poise Asphalt

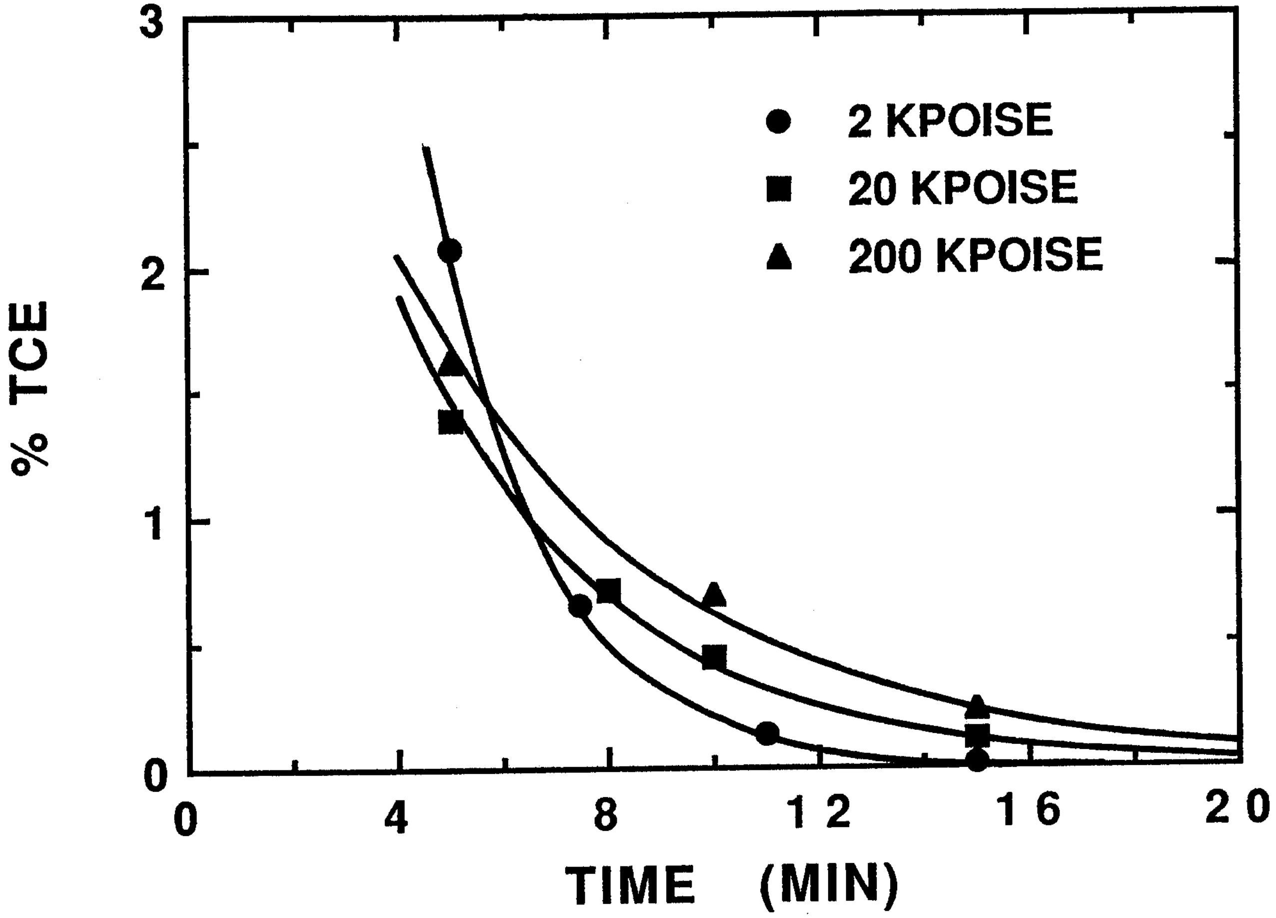


Figure III-1-7
Residual Solvent Concentrations Versus Abson Recovery Time
for Three Asphalt Viscosities at 325°F

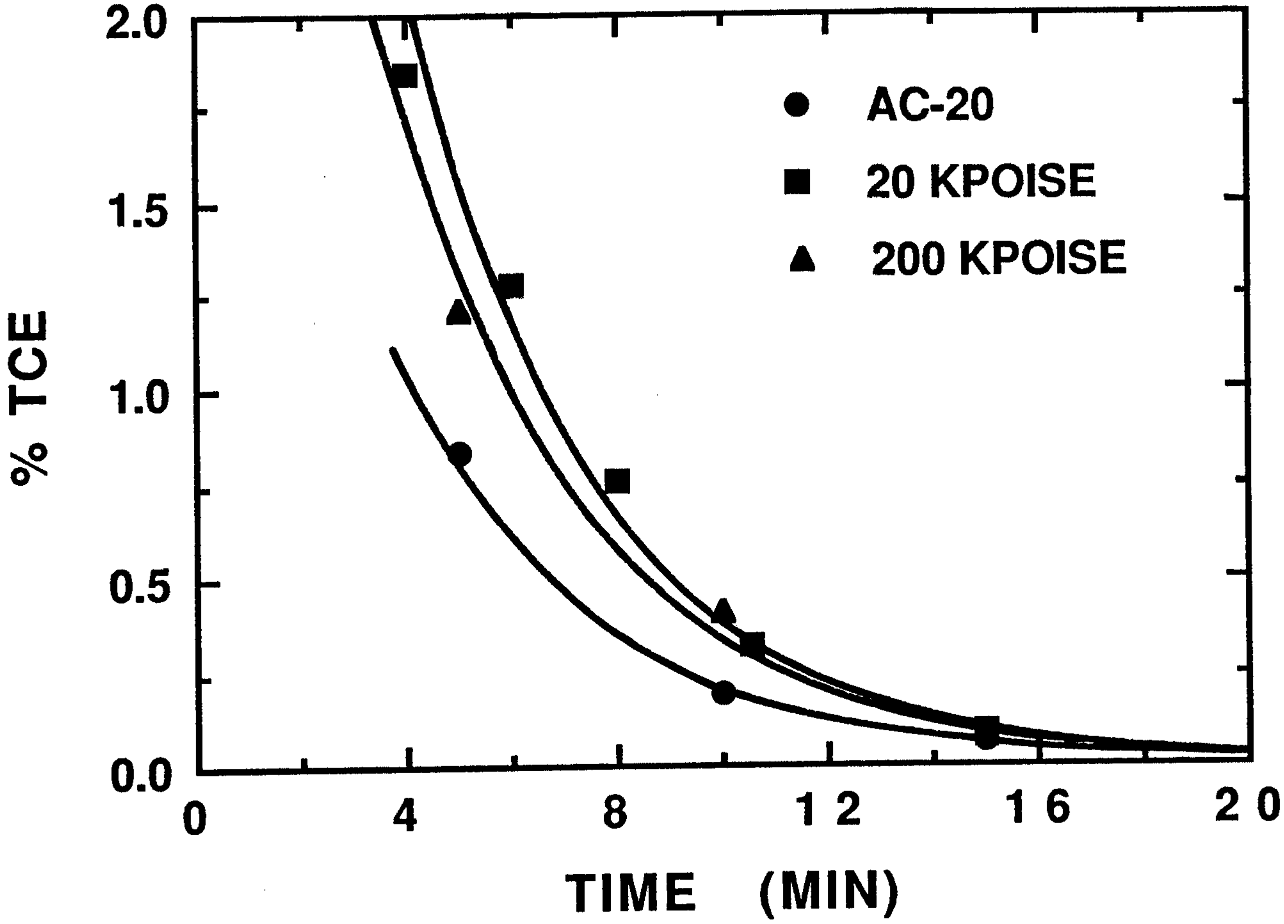


Figure III-1-8
Residual Solvent Concentrations Versus Abson Recovery Time
for Three Asphalt Viscosities at 340°F

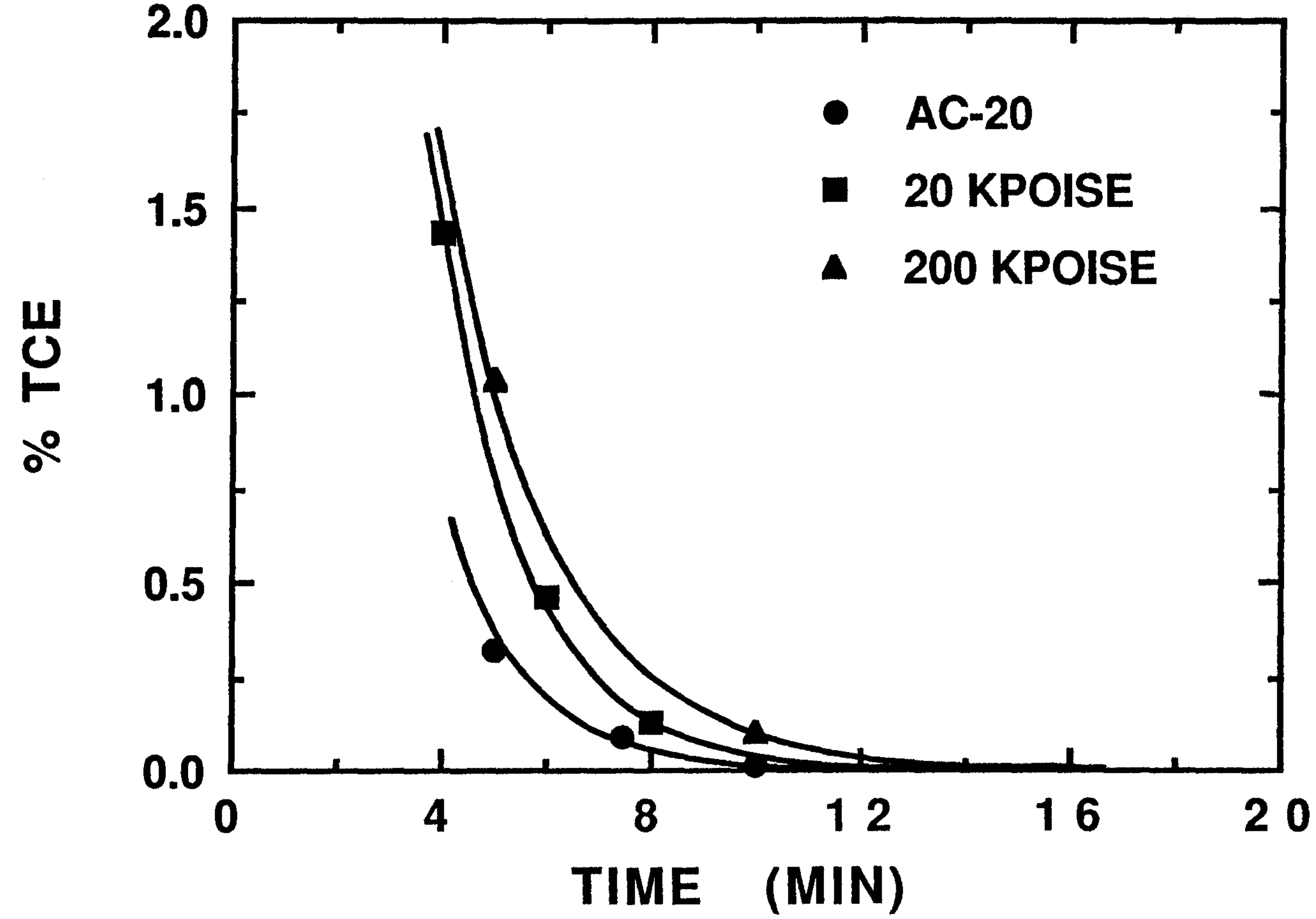


Figure III-1-9
Residual Solvent Concentrations Versus Abson Recovery Time
for Three Asphalt Viscosities at 380°F

Roto-Vap Solvent Removal Method. Figures III-1-10, -11, and -12 show Roto-vap method residual solvent profiles for the AC-20, 20,000 poise, and 200,000 poise materials, respectively, at three removal temperatures. Zero time is that of the last observed drop from the solvent condenser. Unless otherwise indicated, the Roto-vap method used was that without vacuum, i.e., with a CO_2 purge only. The profiles show pronounced temperature dependence, but surprisingly, no discernable viscosity dependence. Also, the use of a gas purge alone seems to be as effective as that with a vacuum at 280°F (Figure III-1-11 and 12). In most cases, the 280°F recoveries, vacuum or gas purged, left significant solvent residues after the method's suggested time of 15 minutes past the last sign of condensation. However, the 325°F and 350°F runs showed complete removal after 15 minutes.

Reproducibility of the Roto-vap method appears to be less than that of the Abson method. Two separate recoveries of 20 kilopoise asphalt at 325°F gave drastically different solvent removal profiles, one having complete removal in less that 2 minutes. This is possibly due to the difficulty in determining when the last sign of condensate disappears, though other factors are likely to contribute.

The use of vacuum during the initial recovery seems to reduce solvent hardening. Two AC-20 recoveries were performed using a high vacuum so that the boiling temperature was less than 100°F. Two others were run using no vacuum, and boiling points were about 200°F. Figure III-1-2 shows the vacuum-recovered asphalts hardened about 10% which is barely above the hardening that is typically due to volatiles' loss. The hot-recovered samples hardened about 16%.

Hot-Mix Recoveries and Volatiles' Loss. Several extracted hot mixes were recovered (Abson method) and found to behave somewhat differently from tank or oven-aged material. Figure III-1-13 shows a solvent removal comparison between diesel-fired and gas-fired plants. Hot mixes from batch and natural gas-fired plants showed normal solvent removal behavior when conducted at 320°F. However, diesel-fired drum plant mixes, even though recovered at 340°F, contained significant levels of material, eluting where TCE does on the GPC, which remained after 30 minutes.

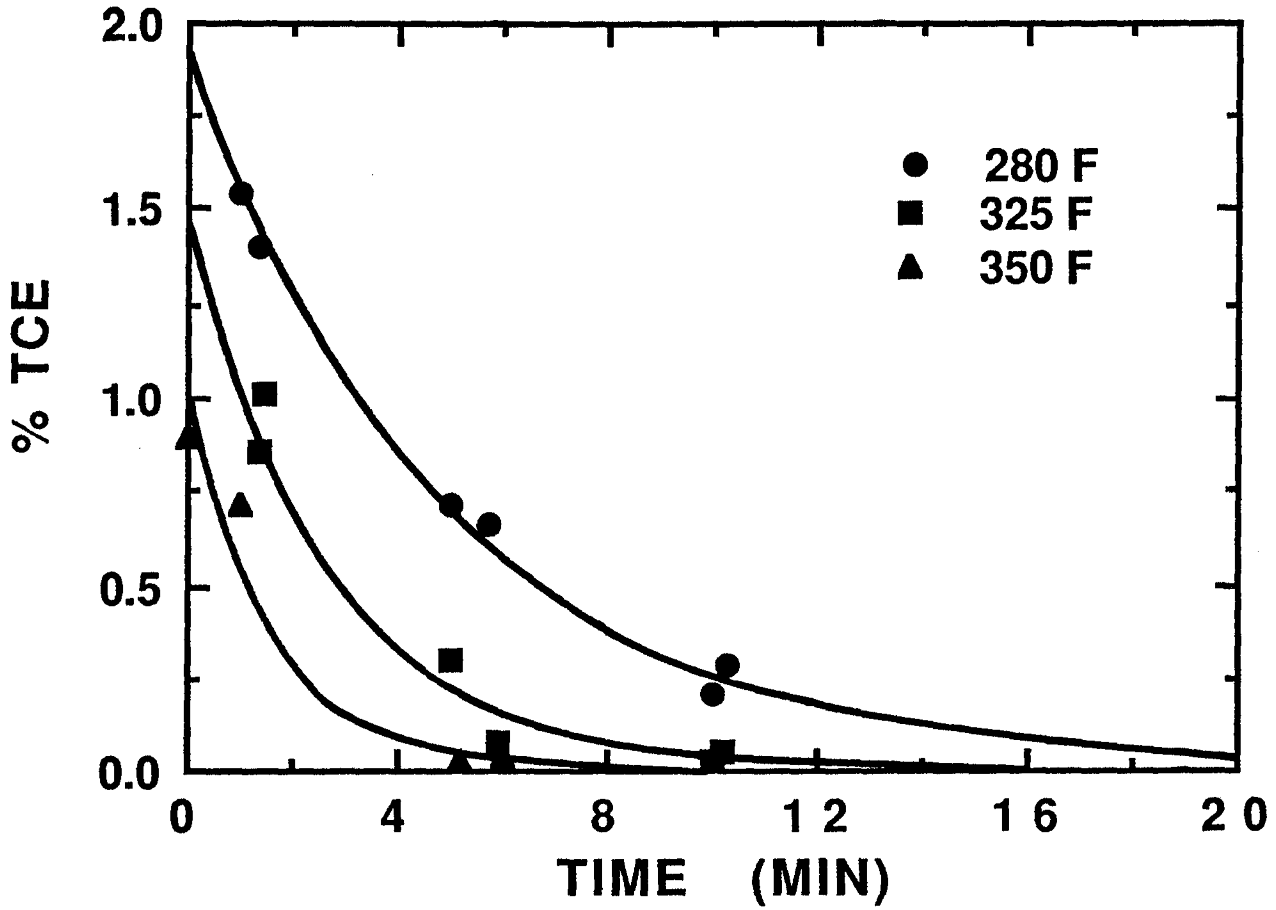


Figure III-1-10
Residual Solvent Concentrations Versus Roto-vap Recovery Time
at Three Temperatures for an AC-20 Asphalt

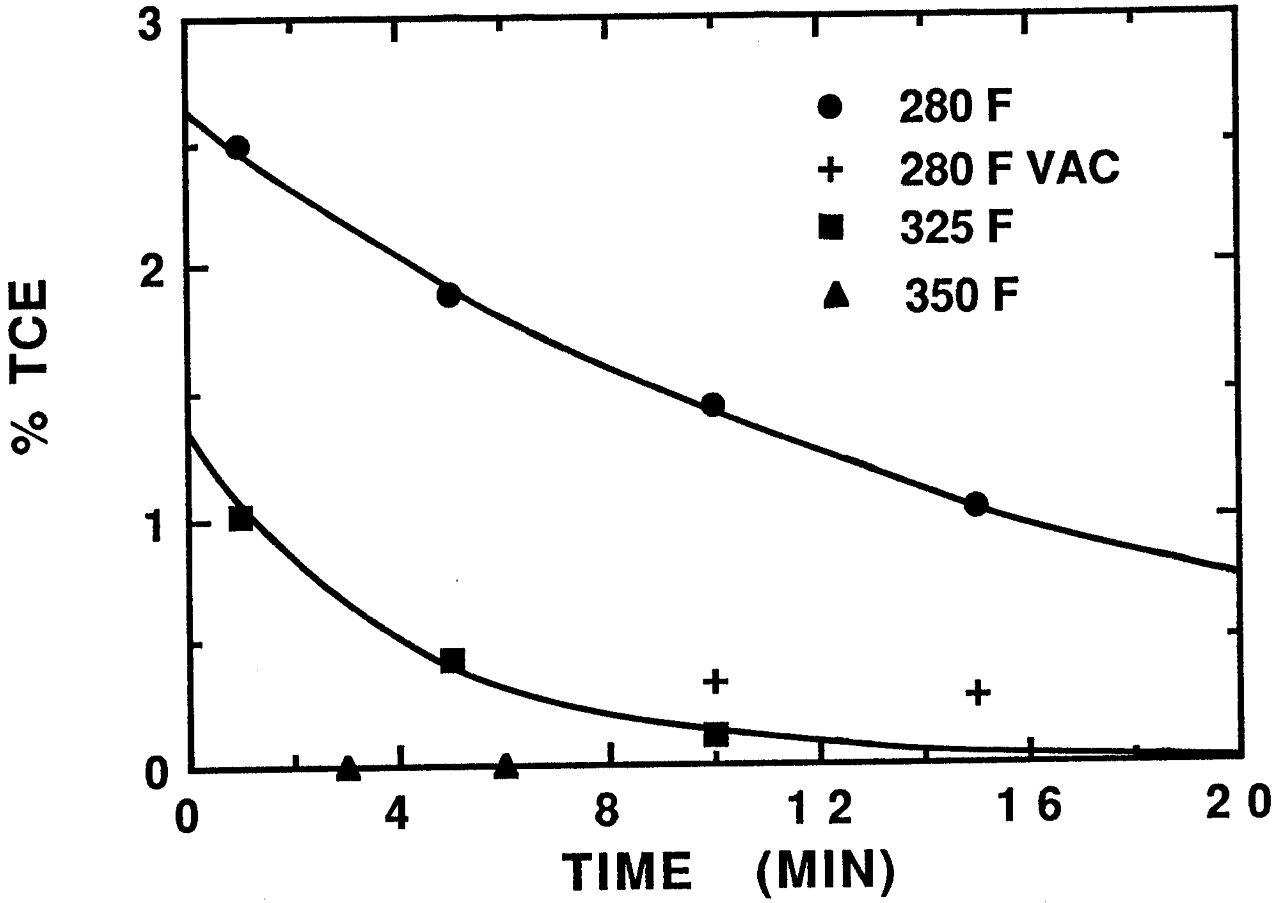


Figure III-1-11
Residual Solvent Concentrations Versus Roto-vap Recovery Time
at Three Temperatures for a 20,000 Poise (Aged) Asphalt

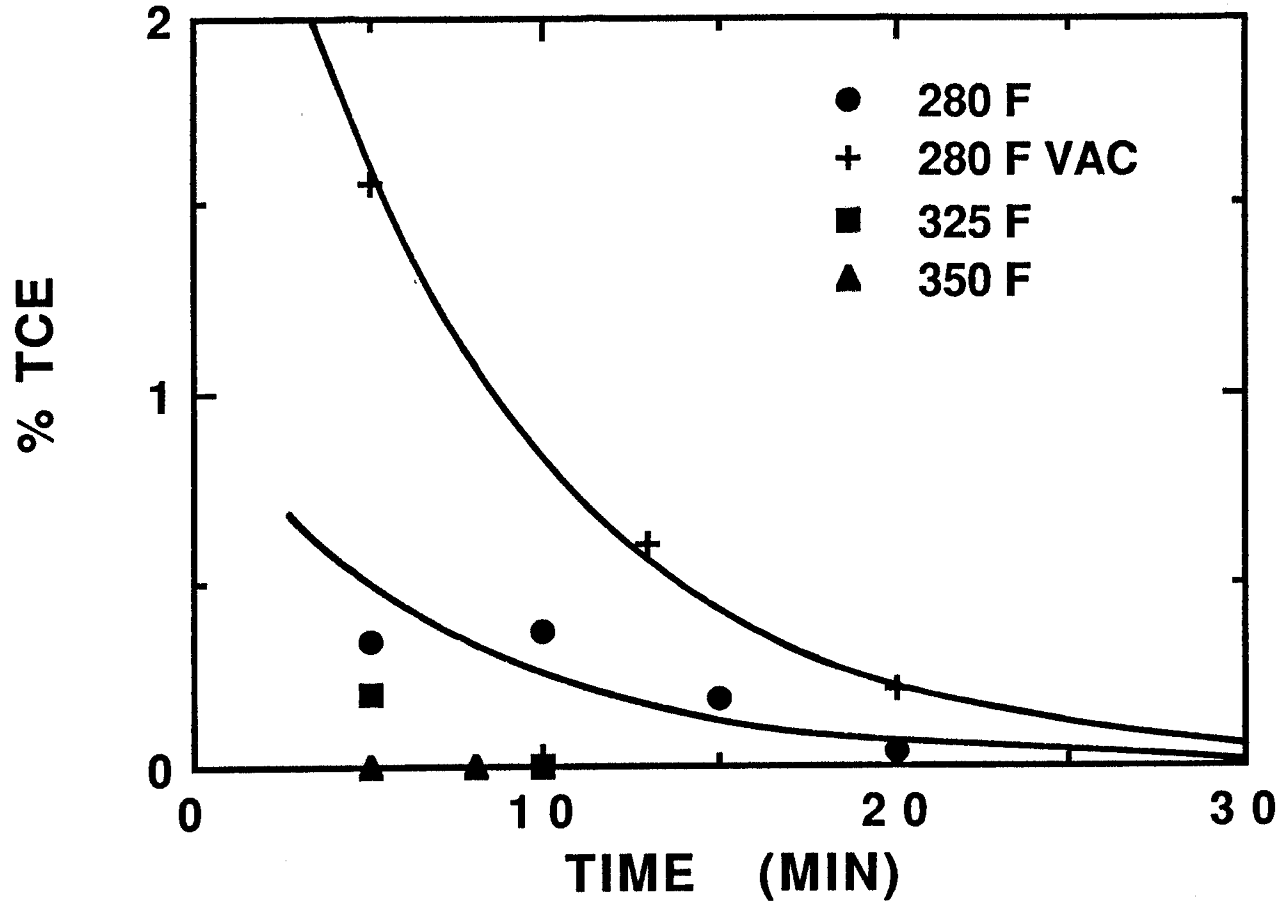


Figure III-1-12
Residual Solvent Concentrations Versus Roto-vap Recovery Time at Three Temperatures for a 200,000 Poise (Aged) Asphalt

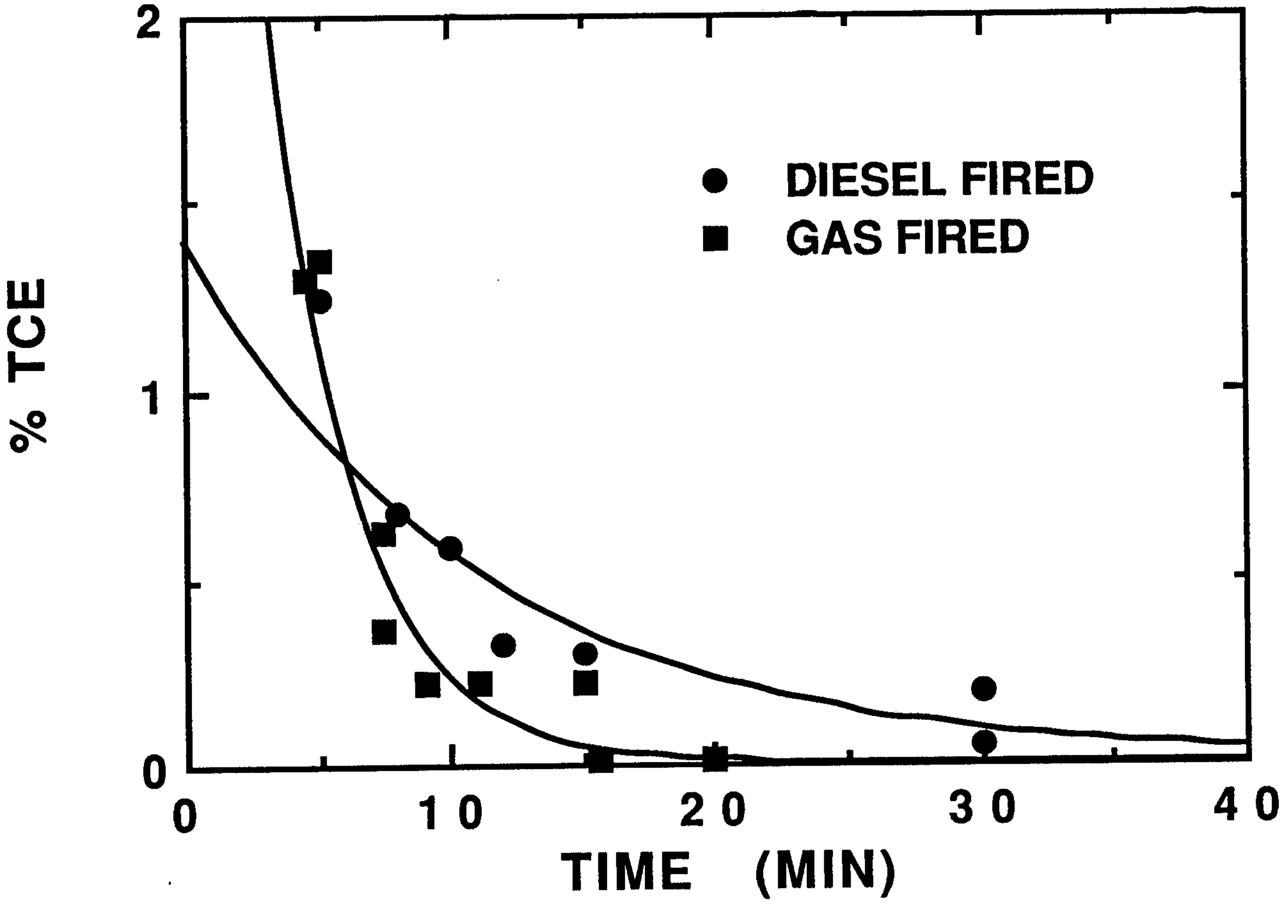


Figure III-1-13
Residual Solvent Concentration Versus Abson Recovery Time
for Two Hot-mix Extractions

The diesel fuel mixes were also different in that they evolved a long-lasting fog and deposited an oily residue on the recovery flask's surfaces. These asphalts were all mixed at drum plants fired by diesel or fuel oil. Infrared analyses of the oily film showed it to be composed of highly oxidized, low molecular weight hydrocarbons (Figure III-1-14). This is possibly from partially oxidized fuel oil. Other asphalts mixed at batch or natural gas-fired plants did not exhibit this phenomenon.

The presence of these volatiles may have given a false indication of residual solvent concentration and may account for the excessive solvent removal times of these hot mixes. To test this, a hot mix containing these volatiles was extracted with THF in a sequence of cold, batch extractions using a total amount of solvent which gave an overall concentration suitable for direct GPC analysis. Because no solvent removal was performed, all the volatile impurities remained in solution and were detected on the GPC. Several new peaks and valleys appeared near the TCE elution time, leaving open the possibility that the apparent TCE peak in the hot mix recoveries was due to residual oxidized fuel oil. Although the relative amount of this material in the asphalt was not determined, its significance to highway performance is potentially great and bears further study.

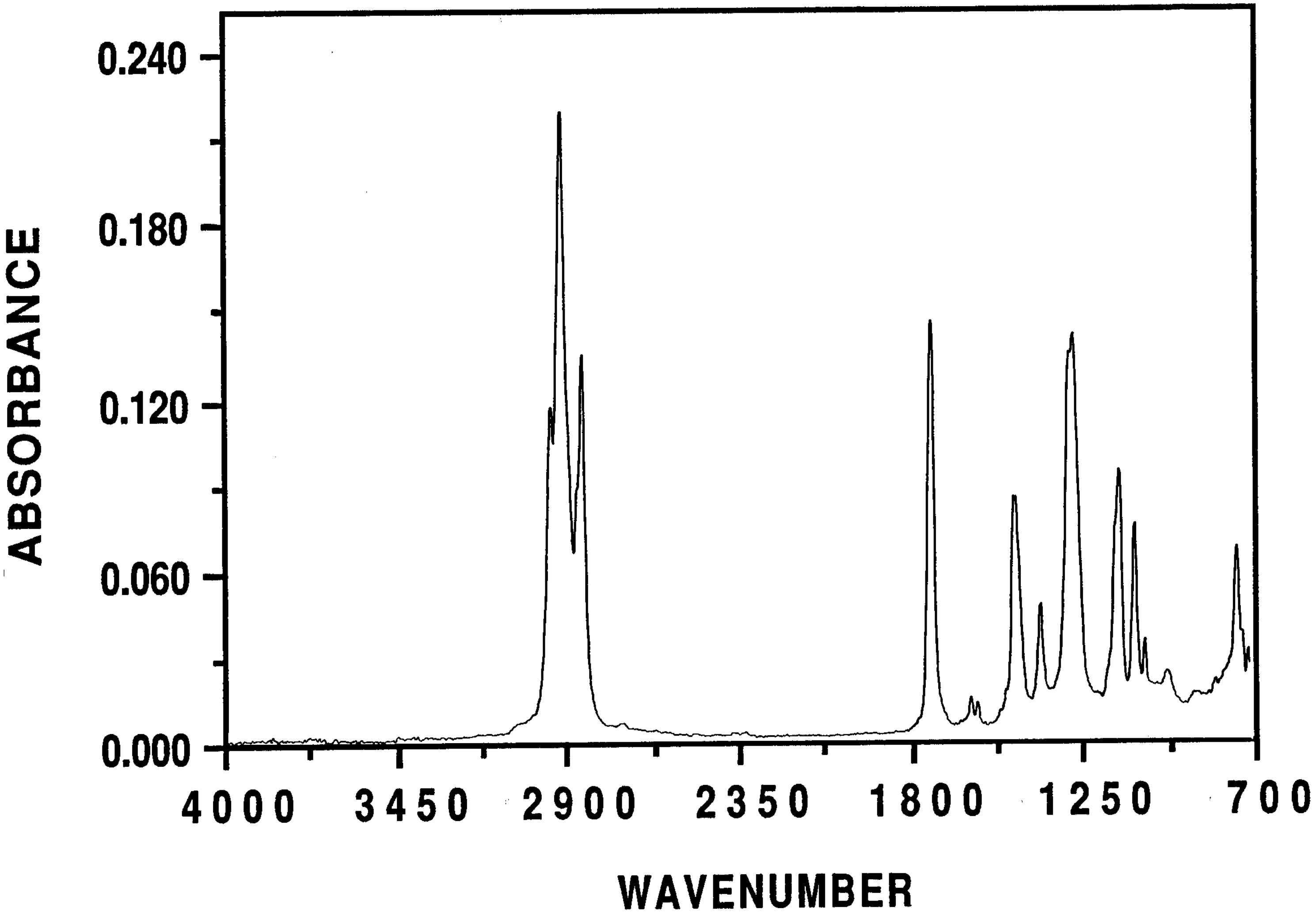


Figure III-1-14
FT-IR Spectrum for the Volatile Material Recovered from the Diesel-fired Hot-mix

CHAPTER III-2

SOLVENT HARDENING OF ASPHALT

Summary

Solvent hardening can be a serious problem in asphalt extraction and recovery. It is due to unknown reactions, and since it occurs in all solvents, it is not likely that the reactions involve the solvent (except perhaps CCl_4) but are merely made favorable by the solution state. Solvent hardening is accelerated by heat, light, and dissolved oxygen, but in the case of the latter two effects, the reaction products are different from solvent hardening in the absence of light and dissolved oxygen. At the present state of knowledge, the best course would appear to be to carry out all steps without heat, light or oxygen when possible and to finish as quickly as possible. Even so with the best techniques now in use, hardening (measured by viscosity at 140^{o}F) of about 15% is consistently experienced.

Introduction

One of the most important and alarming discoveries of this study has been the seriousness and universality of solvent hardening during the recovery of asphalt from mixes. It is our opinion that no study conducted thus far on the properties of recovered asphalt is unmarred by this phenomenon.

The history and seriousness of the problem is recounted in some detail in Chapter I-2. In particular, a study by Abson (1960) of the chlorinated solvents carbon tetrachloride and trichloroethane showed high solvent hardening when exposed for two to four hours in 15% solutions. Similarly, Abu-Eigheit et al. (1969) showed that asphalts harden when exposed to a variety of solvents with results similar to those in this study. This problem is alluded to in ASTM D1856, where extraction Method A is specified when recovery of asphalt is desired. The unsuitability of Method B was confirmed in this study during the work reported in Chapter III-1 on solvent removal.

Measuring Asphalt Solvent Hardening by GPC

Earlier in this work, we had found that samples mixed with THF for GPC analysis appeared to change if for any reason they were not run promptly. For this reason it has been a policy in this work to remix samples after a delay of more than a few hours.

A study was made of this effect by dissolving asphalts in various solvents at 7% by weight, letting them stand for various times at different temperatures and then injecting directly into the GPC. The very significant effects at 100°C in TCE are shown in Figure III-2-1 and in toluene in Figure III-2-2. The effects at 50°C in TCE and toluene are shown in Figures III-2-3 and III-2-4. The results at room temperature are not so dramatic, but the effects, as we shall see, are still quite real and serious.

Solvent Hardening During Extraction and Recovery

After this problem became apparent, much of the early work was centered on attempts to minimize the problem and do not constitute controlled experiments. Basically, we now use ASTM D1856 Method A with ethanol additions to improve extraction of strongly adsorbed material, and effort is made to complete the process as rapidly as possible. Also we now run the Roto-vap under vacuum until most of the solvent is removed. Two very important facts were established in this work. Higher temperatures accelerate the effects as do dilute solutions. As the asphalt to solvent ratio approaches unity, little hardening seems to occur.

Establishing Solvent Hardening Parameters

A variety of solvent hardening experiments were run to establish the percent increase in viscosities with different solvents, solvent concentrations, recovery procedures, and the effect of oxygen and light. Concentrations were either 20 gms of asphalt in 400 ml(5%) or 800 ml(2.5%). Most recoveries, designated "hot," were in a Roto-vap at atmospheric pressure. Those designated "cold" were under

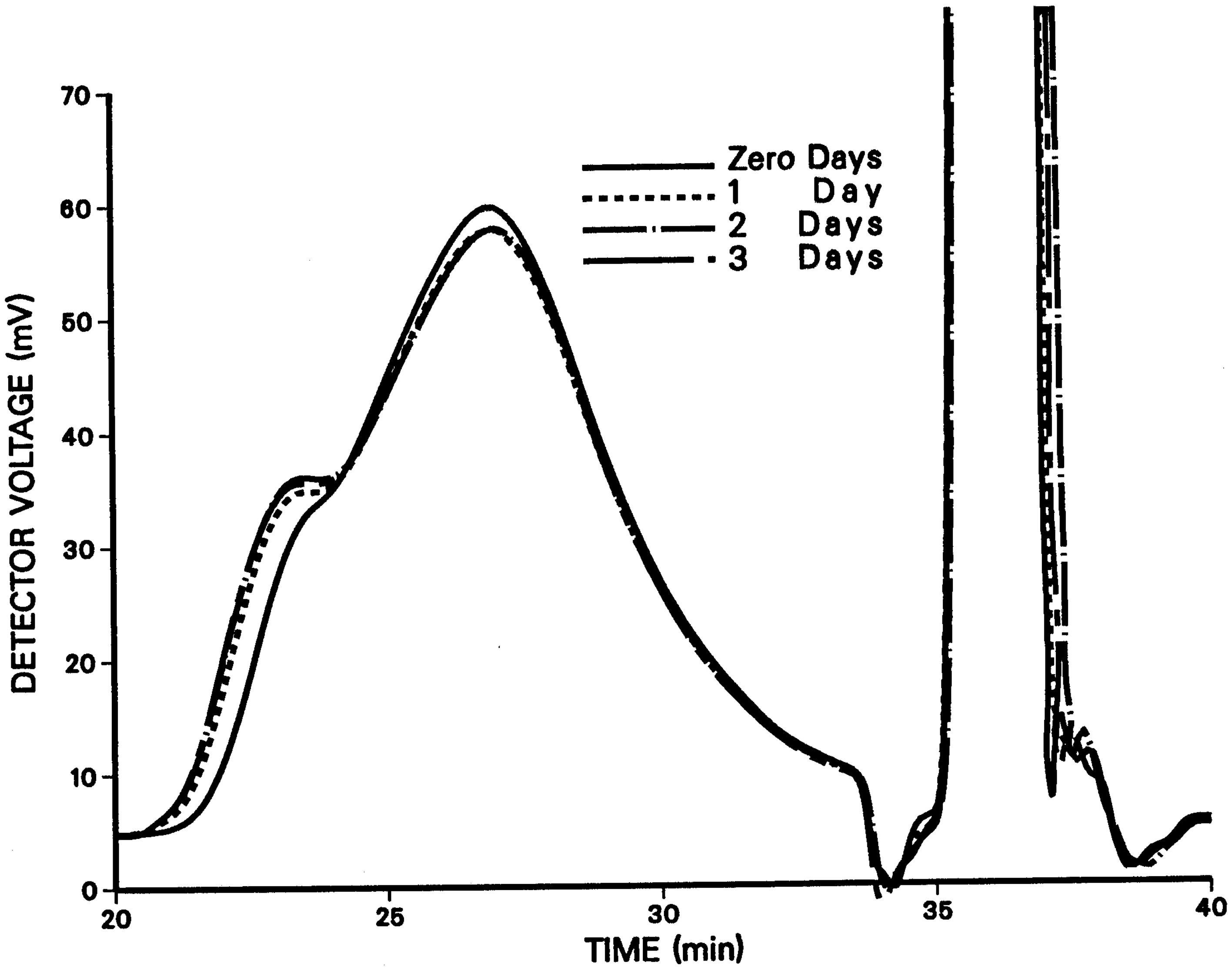


Figure III-2-1
Asphalt Solvent Hardening in a 7% Solution in Trichloroethane
at 100°C - Ampet AC-10

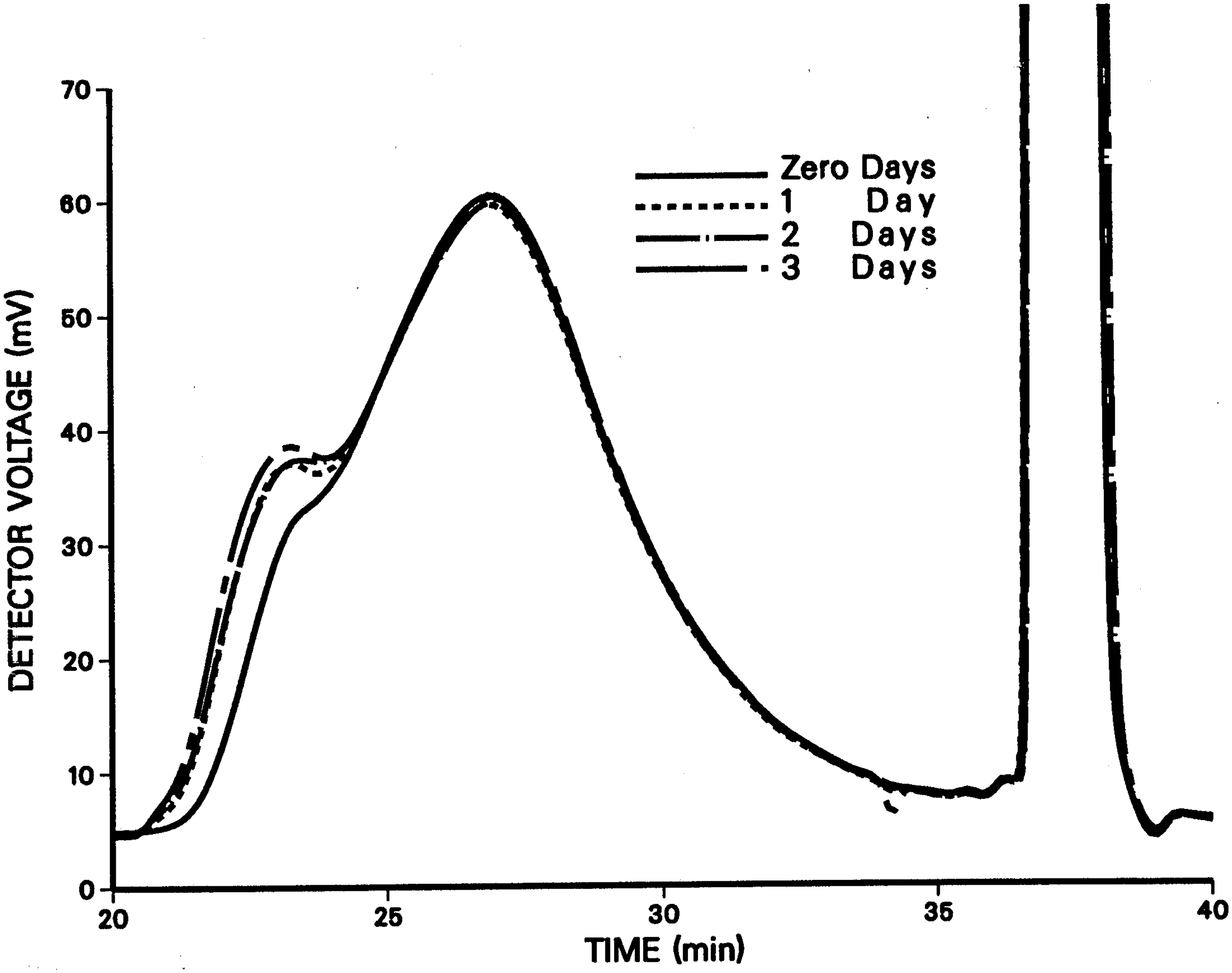


Figure III-2-2
Asphalt Solvent Hardening in a 7% Toluene Solution
at 100°C - Ampet AC-10

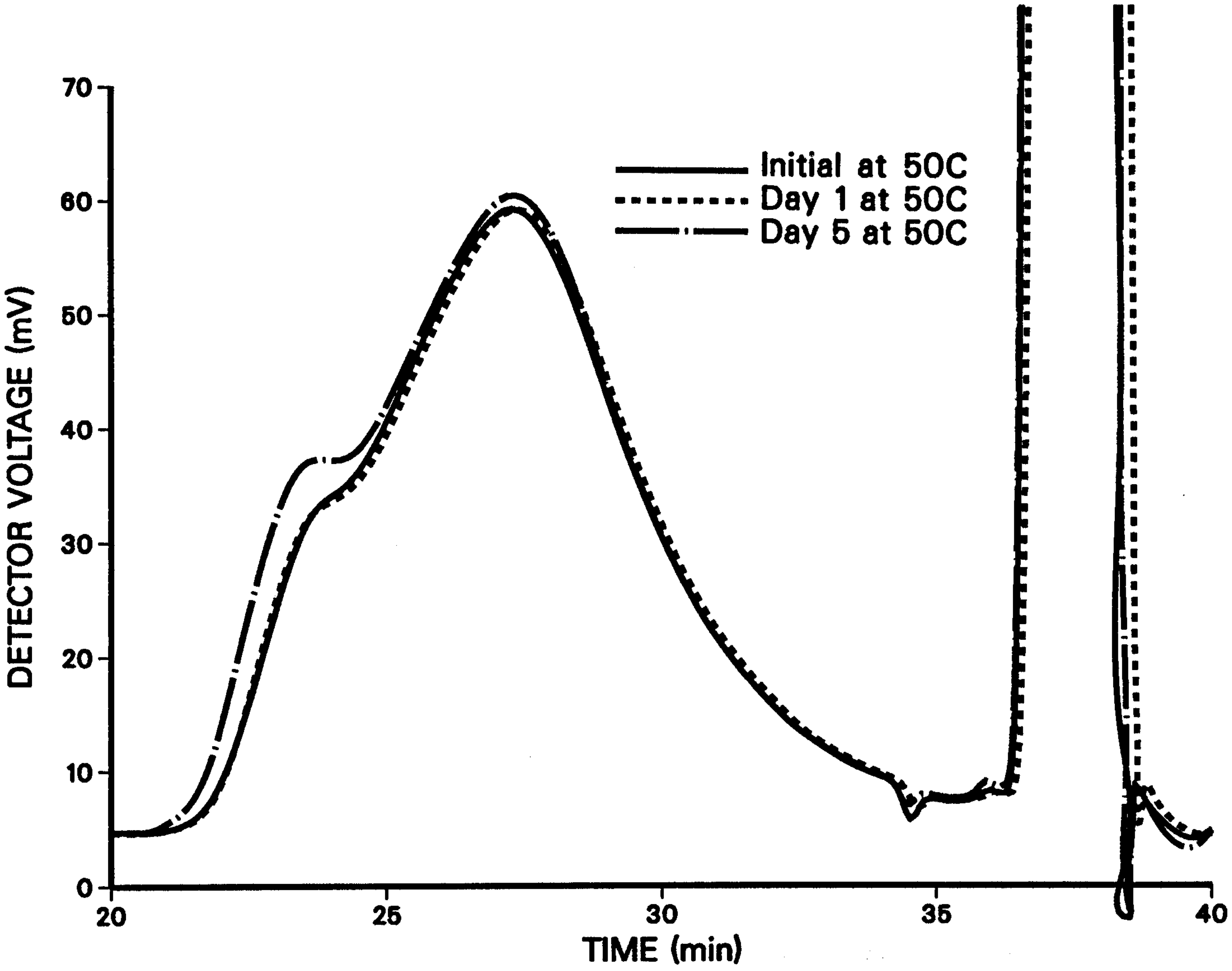


Figure III-2-3
Asphalt Solvent Hardening in a 7% Trichloroethylene Solution at 50°C - Ampet AC-10

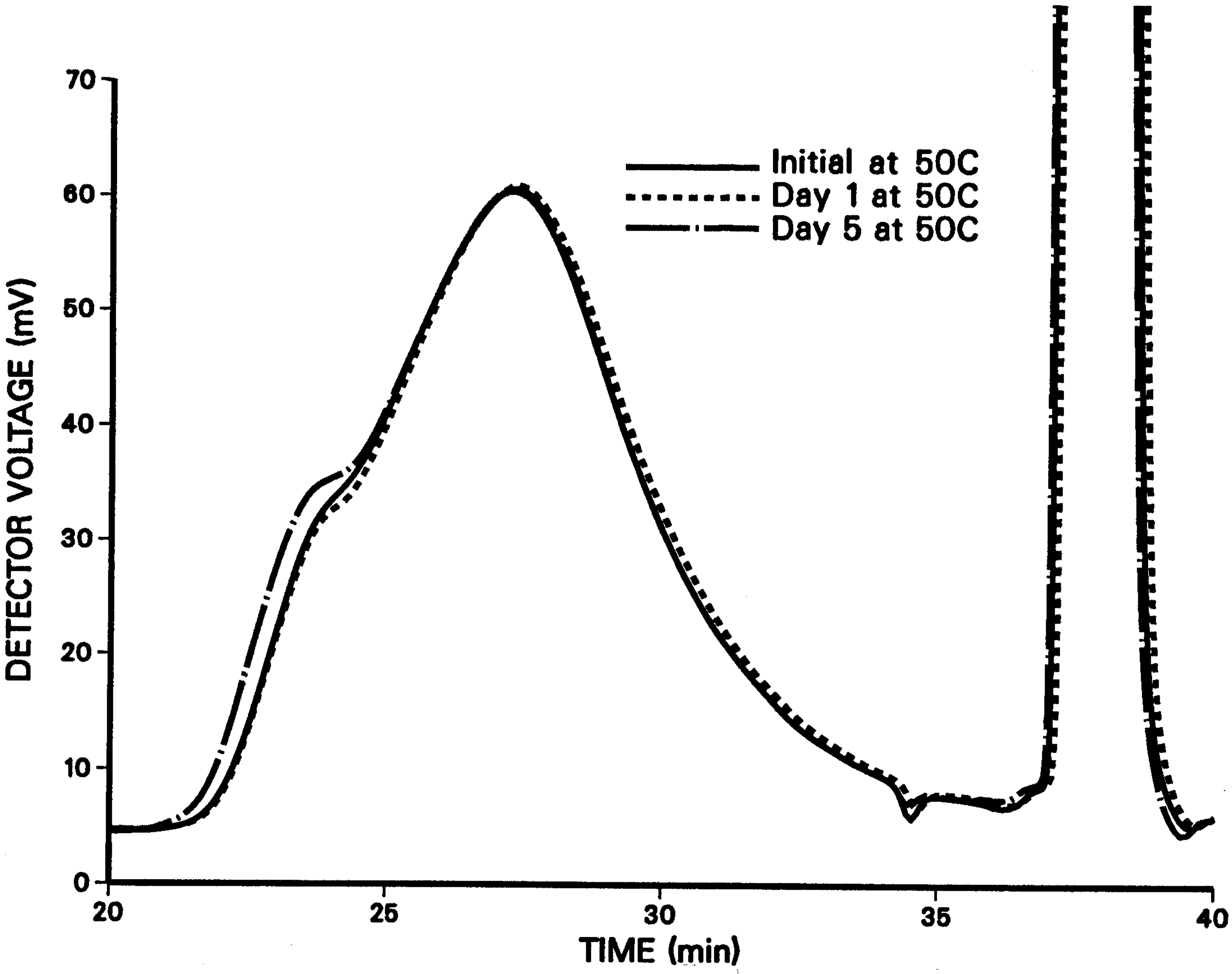


Figure III-2-4
Asphalt Solvent Hardening in a 7% Toluene Solution
at 50°C - Ampet AC-10

sufficient vacuum that the solvent temperature was near room temperature. Most samples were allowed to stand in contact with air; a few were saturated with O_2, others with N_2, or degassed by vacuum before standing. Some were aged in the dark, some at room light and others under strong light. Four runs were with asphalt hardened to 20,000 poise. All runs were at room temperature. The results are shown in Table III-2-1 and Figures III-2-5 and III-2-6. In Figure III-2-5 all the data for 5% asphalt in TCE are plotted except those with strong light and oxygen. Some hardening seems to occur very quickly and continues as long as contact continues. There is no conclusive evidence that any of the variables included in this figure are significant except time and perhaps the weak light.

Figure III-2-6 shows the rest of the data. Prehardened asphalt still solvent hardens at about the same rate as tank asphalt. All the solvents appear about equal in hardening except CCl_4 which causes much greater hardening. As would be expected some of the oxygen containing samples hardened considerably. Light also seems to accelerate hardening both with and without oxygen. However, run 12 and 13 appear inconsistent.

There is no proof here that cold recovery under vacuum reduces aging, but it appears logical and needs further study.

Solvent Hardening and Infrared Spectra

While there is no question that asphalts change when dissolved in solvents, there remains considerable doubt as to what actually happens. It has been proposed that in situ, the larger asphaltene molecules are surrounded by more soluble polar aromatics which aid in their dispersion. In solvents, these are dissolved away and the asphaltenes aggregate, causing an increase in viscosity. An alternate proposal is that there are reactive sites in asphalt such as free radicals which are sterically hindered in situ but which become available for reactions in solution. If reaction is occurring in solution, changes might be expected in the infrared spectra of the asphalts. Infrared spectra were made of some of the asphalts in Table III-2-1. The asphalts were exposed to solvent in the dark, in bright light and with and without oxygen.

Table III-2-1

Solvent Hardening Experiments

Asphalt	Solvent % Asphalt	Recovery	Gas	Light	Time(hrs)	%Diff Visc
1 EXXON AC-20	TCE 5%	HOT	AIR	LOW	96.000	66.900
2 EXXON AC-20	TCE 5%	HOT	AIR	NO	7.000	21.500
3 EXXON AC-20	TCE 5%	HOT	AIR	NO	20.000	26.800
4 EXXON AC-20	TCE 5%	HOT	AIR	NO	49.000	34.300
5 EXXON AC-20	TCE 5%	HOT	AIR	NO	116.000	43.400
6 EXXON AC-20	TCE 5%	HOT	AIR	NO	1032.000	105.000
7 EXXON AC-20	TCE 5%	HOT	AIR	LOW	1.000	18.600
8 EXXON AC-20	TCE 5%	HOT	AIR	LOW	0.250	13.700
9 EXXON AC-20	TCE 5%	COLD	AIR	LOW	0.250	9.800
10 EXXON AC-20	TCE 5%	HOT	O_2	BRIGHT	48.000	71.600
11 EXXON AC-20	TCE 5%	HOT	N_2	NO	48.000	37.800
12 EXXON AC-20	TCE 5%	COLD	N_2	BRIGHT	48.000	35.000
13 EXXON AC-20	TCE 5%	COLD	O_2	NO	48.000	26.000
14 EXXON AC-20	TCE 5%	HOT	DEGASED	BRIGHT	48.000	74.700
15 EXXON AC-20	TCE 5%	HOT	DEGASED	NO	48.000	39.100
16 EXXON AC-20	TCE 5%	HOT	O_2	BRIGHT	48.000	86.800

Table III-2-1 (Cont'd)

Solvent Hardening Experiments

	Asphalt	Solvent % Asphalt	Recovery	Gas	Light	Time(hrs)	%Diff Visc
17	EXXON AC-20	TCE 5%	HOT	O_2	NO	48.000	60.900
18	EXXON AC-20	$CHCL_3$ 5%	HOT	AIR	LOW	48.000	38.700
19	EXXON AC-20	CH_2CL_2 5%	HOT	AIR	LOW	48.000	33.000
20	EXXON AC-20	111 TCE ane	HOT	AIR	LOW	48.000	34.300
21	EXXON AC-20	TCE/ETOH	HOT	AIR	LOW	48.000	34.700
22	EXXON AC-20	TCE 5%	HOT	AIR	NO	48.000	34.300
23	EXXON AC-20	CCL_4 5%	HOT	AIR	LOW	48.000	91.200
24	EXXON AC-20	TOLUENE	HOT	AIR	LOW	48.000	36.900
25	EXXON AC-20	12 DCE	HOT	AIR	LOW	48.000	39.600
26	EXXON AC-20	TCE/ETOH	HOT	AIR	NO	0.250	10.800
27	EXXON AC-20	TCE/ETOH	HOT	AIR	NO	1.300	15.700
28	EXXON AC-20	TCE/ETOH	HOT	AIR	NO	4.750	20.100
29	EXXON AC-20	TCE/ETOH	HOT	AIR	NO	6.670	17.800
30	EXXON 20kP	TCE 5%	HOT	AIR	NO	69.000	45.200
31	EXXON 20kP	TCE 2.5%	HOT	AIR	LOW	0.250	17.200
32	EXXON 20kP	TCE 2.5%	COLD	AIR	LOW	0.250	7.990
33	EXXON 20kP	TCE 5%	COLD	AIR	LOW	0.250	17.700

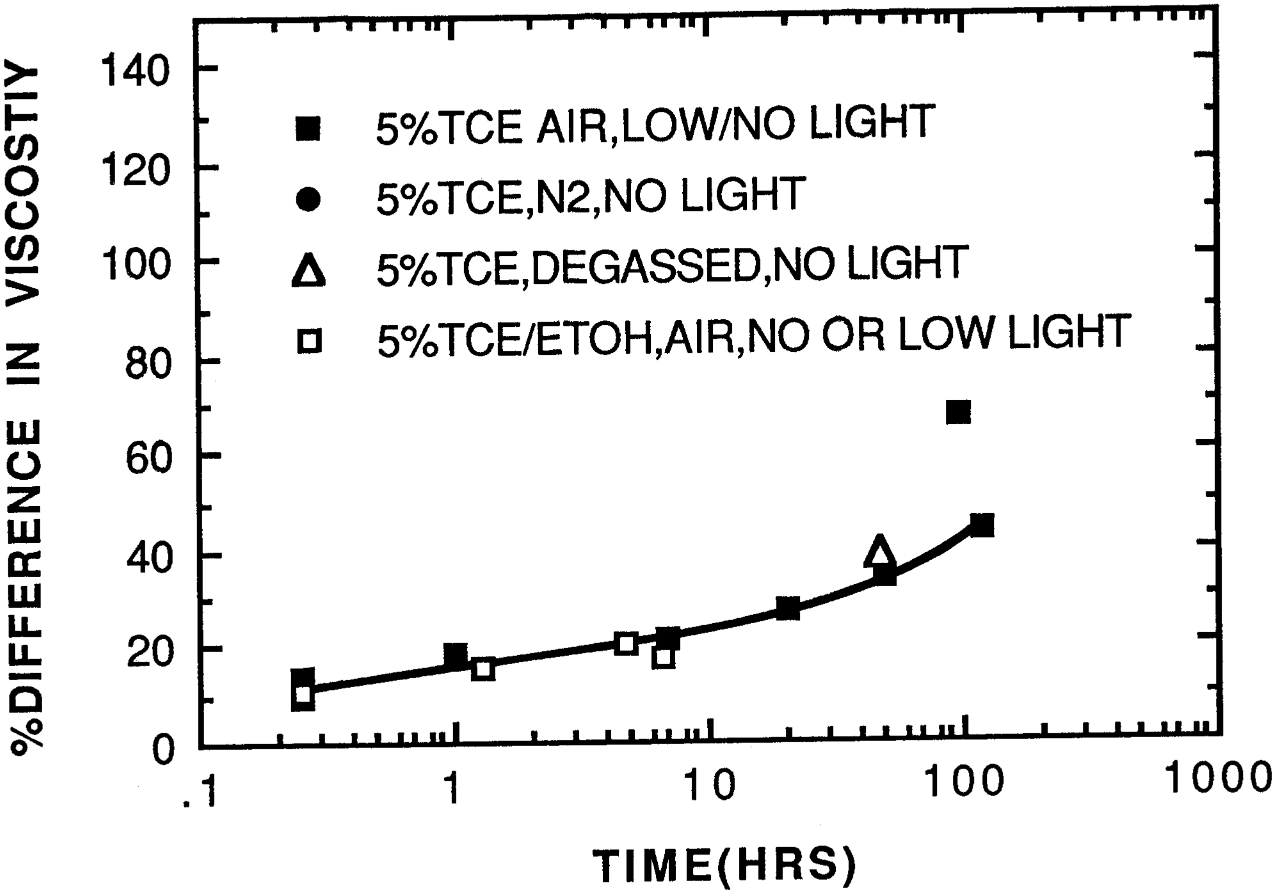


Figure III-2-5
Solvent Hardening in 5% TCE Solution Without Oxygen or Strong Light

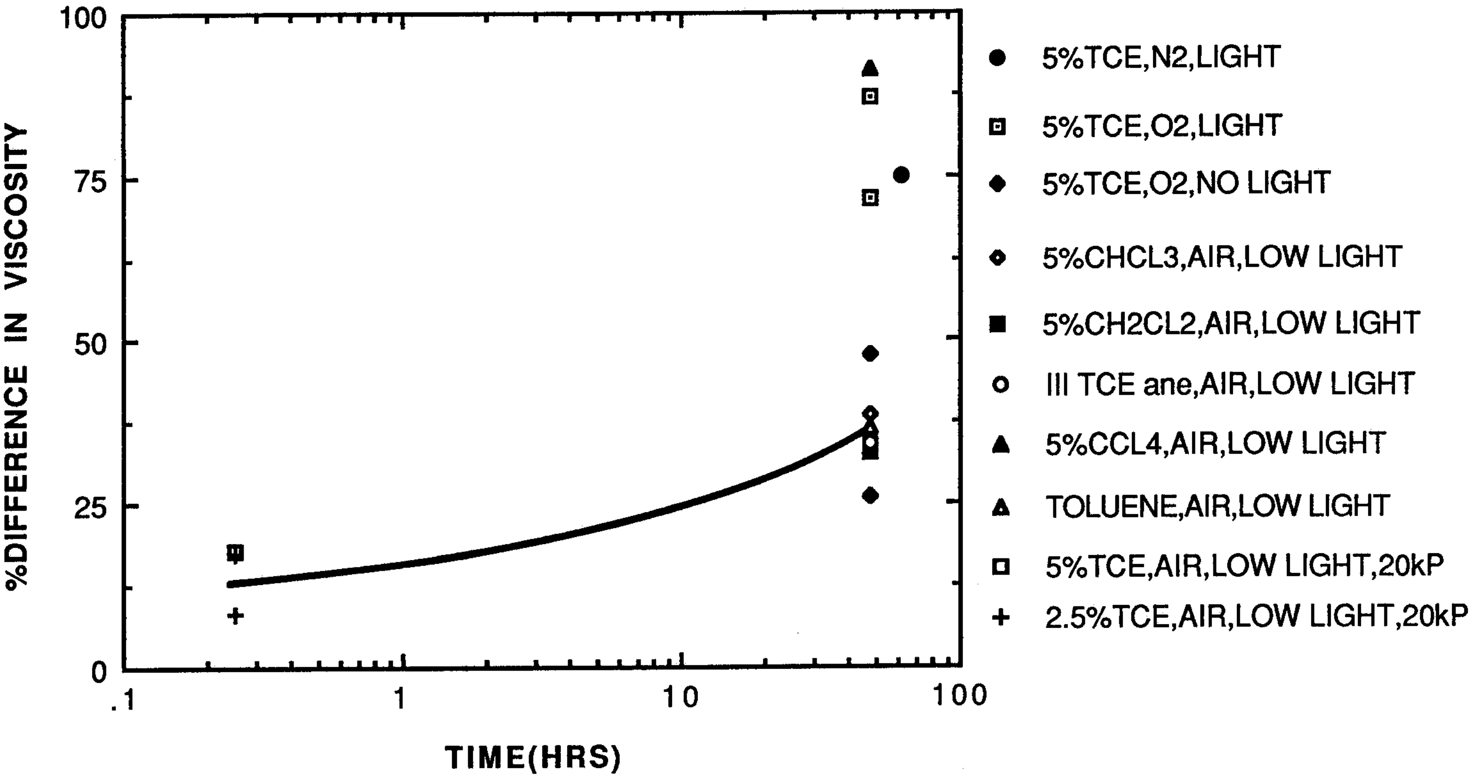


Figure III-2-6
Solvent Hardening in Various Solvents and the Effect of Oxygen and Strong Light

Figure III-2-7 shows spectra with TCE saturated with oxygen, and Figure III-2-8 is an enlargement of the carbonyl region which occurs at wave numbers around 1700. These two figures correspond to runs 16 and 17 in Table III-2-1. The results are typical of oxidized asphalt, though it is obvious that light is accelerating the reactions. There are no effects that seem peculiar to solvent hardening except for higher rates. Figure III-2-9 is the spectra for asphalts from runs 14 and 15, and Figure III-2-10 is an enlargement of the carbonyl region. In these runs, oxygen was excluded, yet we have considerable growth in the carbonyl region and in the sulfoxide region at 1030, especially with light. Perhaps the most interesting feature is the appearance of a peak at about 1730 for the asphalt hardened in the dark without oxygen. This feature is absent from the spectra with oxygen and/or light. Figures III-2-11 and III-2-12 show a spectrum of an asphalt air blown to 20,000 poise and then exposed to TCE for nearly 3 days in the dark without oxygen and then recovered. This corresponds to run 30. This asphalt has a strong carbonyl peak at 1700 that is clearly distinguished from the broad peak around 1730. In addition, peaks at 1300 and 1150 have appeared and these, too, are not found in air oxidized asphalt. The identities of these peaks are not known for sure, but sulfones have strong absorption near both 1300 and 1150. Esters show strong absorption at all three locations. Apparently, the presence of light or oxygen favors carbonyl and sulfoxide formation.

The real mystery is the source of oxygen for ester or sulfone formation, since there is no decrease in carbonyl or sulfoxide absorption nor in the broad uplift that occurs across the spectrum from about 900 to 1400, and in fact, these areas increase in absorption as the new peaks form.

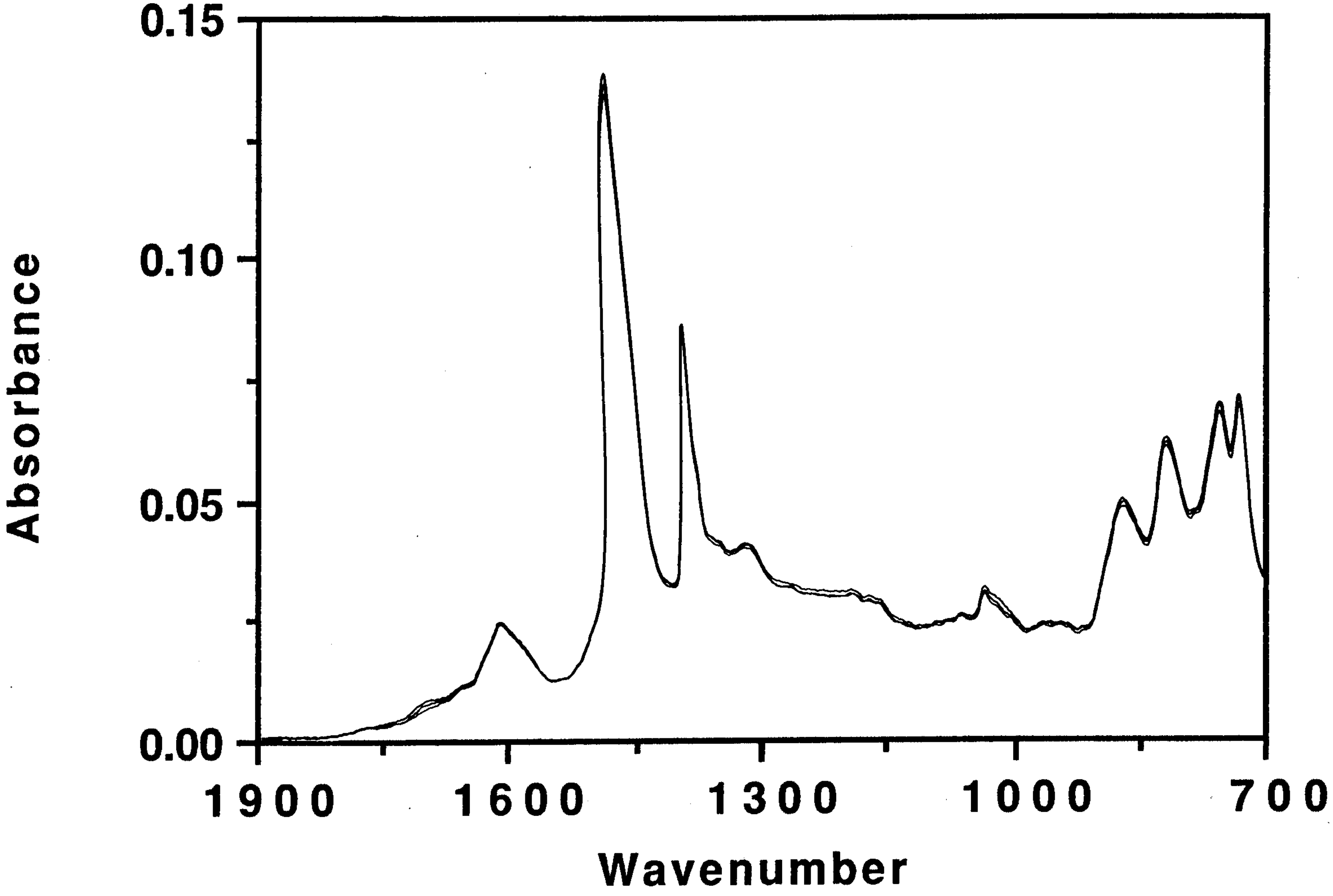


Figure III-2-7
IR Spectrum of Solvent Hardened Asphalt in
Oxygen Saturated TCE - Exxon AC-20

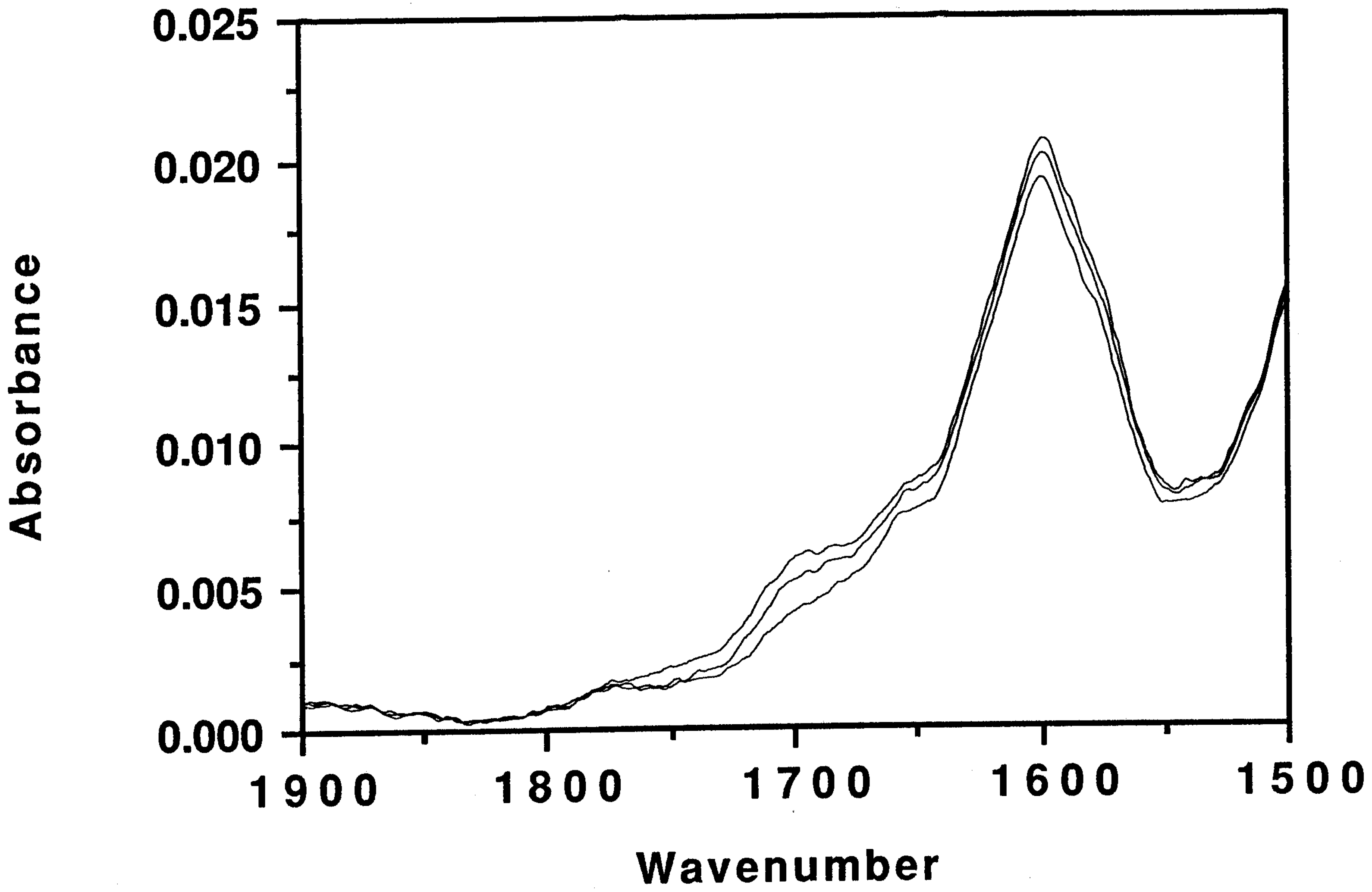


Figure III-2-8
Carbonyl Region of IR Spectrum Solvent Hardened Asphalt in
Oxygen Saturated TCE - Exxon AC-20

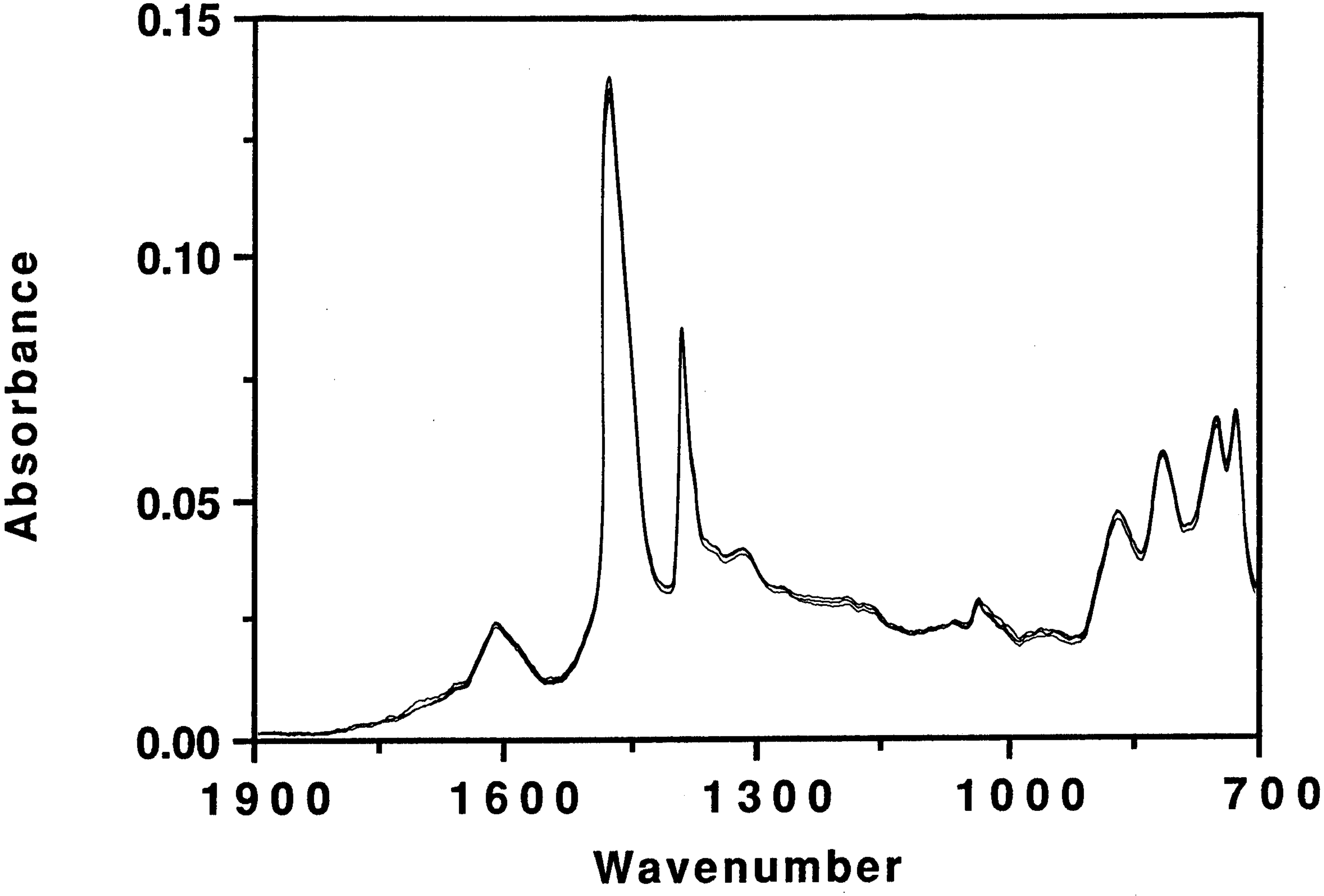


Figure III-2-9
IR Spectrum of Solvent Hardened Asphalt in
Oxygen Free TCE - Exxon AC-20

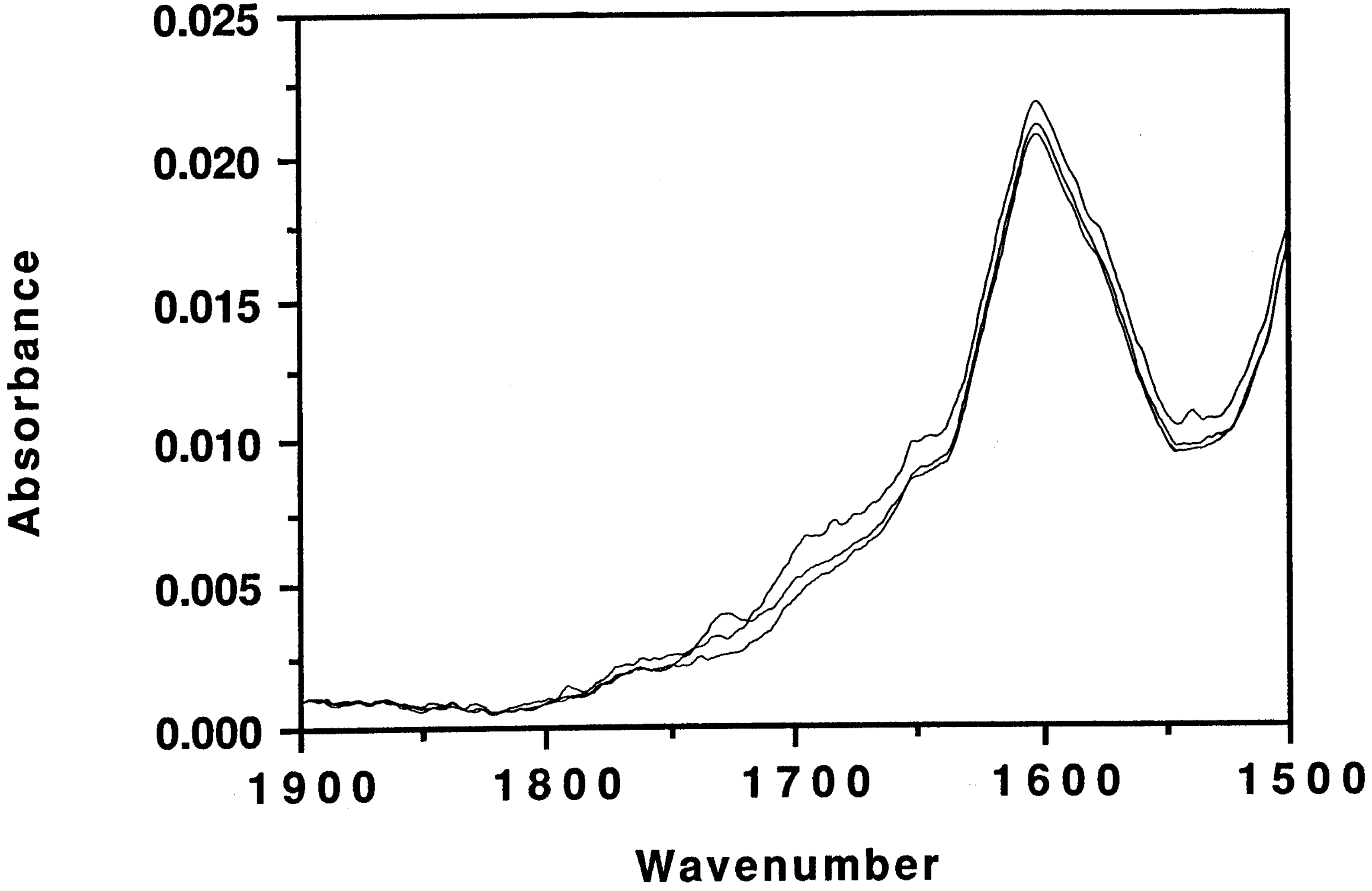


Figure III-2-10
Carbonyl Region of Solvent Hardened Asphalt in
Oxygen Free TCE - Exxon AC-20

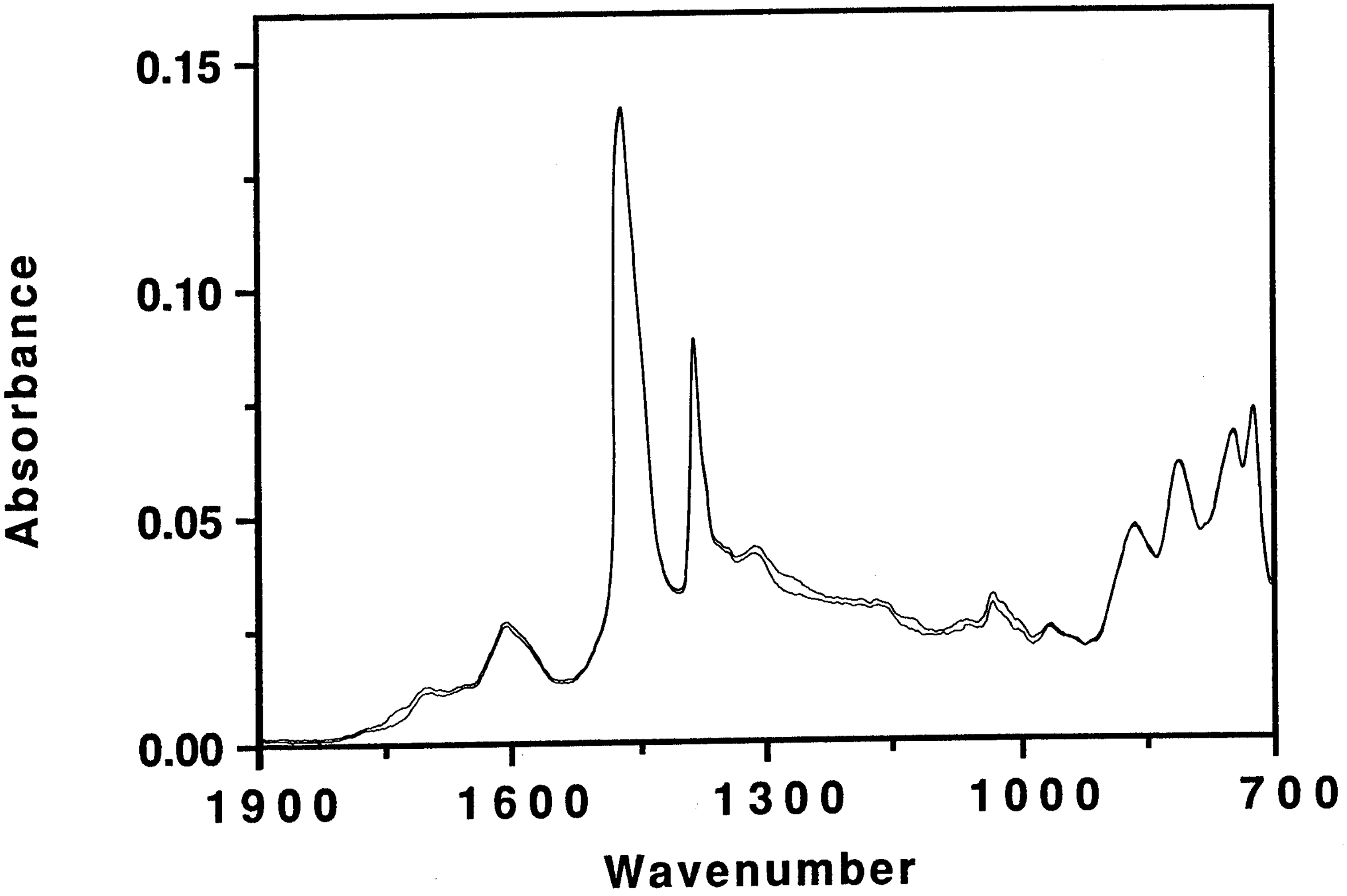


Figure III-2-11
IR Spectrum of Air Blown Exxon AC-20 Solvent
Aged for Three Days in TCE

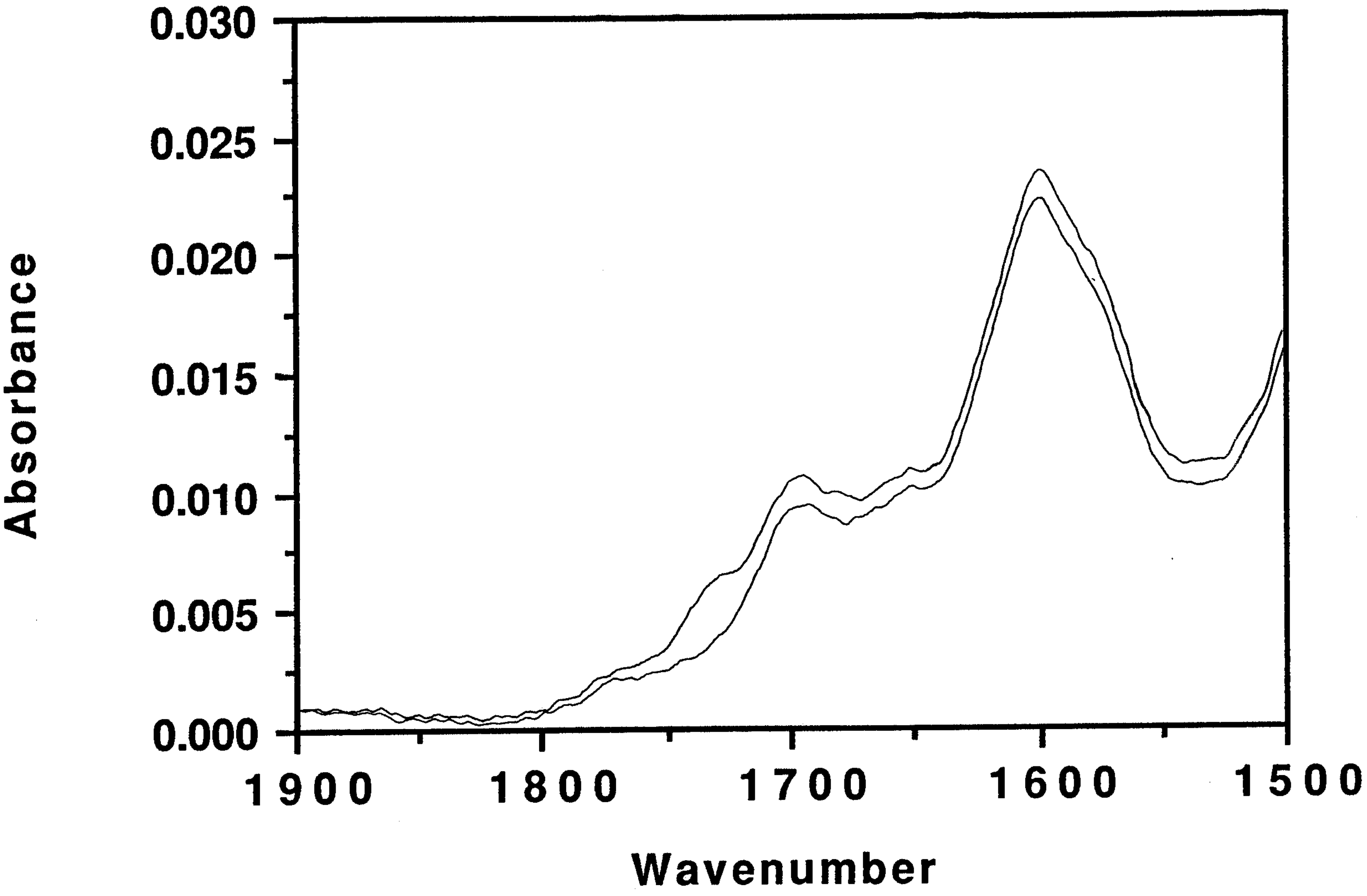


Figure III-2-12
Carbonyl Region of Air Blown Exxon AC-20 Solvent
Hardened in TCE for Three Days

SECTION IV

CORRELATION OF ROAD AND HOT-MIX AGING WITH CHEMICAL PARAMETERS

In this section the results of two major efforts of Study 458 are presented. One relates to road aging and the other to hot-mix aging. There is no characteristic of asphalt more important than its tendency to oxidize and harden, yet this process is not well-understood chemically. A very important area of research is to relate asphalt aging to its chemical composition and chemical changes and to devise aging tests which accurately reproduce the changes that occur in service.

In the first chapter, the continual aging of the 1982-1983 Study 287 test sections is examined and compared to some old roads cored in southern Texas. Shortly after laying the Study 287 test sections, two of the three locations were found to have consistently high voids. As would be expected, these sections have aged much more rapidly than those at the other location. The work in Study 458 endeavored to relate this aging to void content and the chemical changes that accompany aging. Significant relations were found between carbonyl formation and viscosity and penetration, and between property changes and voids.

The second chapter examines the interchangeability of the Thin Film Oven Test (TFOT) and the Rolling Thin Film Oven Test (RTFOT) and whether these tests duplicate the changes that occur in hot-mix plants. At standard test times the two oven tests were found to be identical in all respects including both chemical and physical properties. In general, hot-mix asphalts were harder than oven-aged asphalts and showed greater chemical changes. The divergence varied with the test, but carbonyl formation was higher and sulfoxide formation much higher in the hot-mix asphalts.

Evidence of fuel contamination in oil-fired drum plants is examined.

CHAPTER IV-1

ASPHALT AGING IN TEXAS TEST SECTIONS

Summary

This study has demonstrated again the extremely detrimental effect of high voids. Though this effect has been known for decades, it seems to resist implementation. It will be impossible to predict the progressive hardening of road asphalt with age apart from knowledge of the percent voids and perhaps knowledge of the aggregate used. It may be that sulfoxide formation is desirable. In this event, high sulfur asphalts and aggregates that promote the oxidation of sulfur would be preferred. Lower viscosity grades should be used where possible.

Carbonyl formation is an excellent measure of oxidative aging and correlates with changes in physical properties. If other asphalt properties such as compatibility were included, the correlations would likely improve (see Section VI). The use of GPC to measure asphalt aging is also very useful, but is more difficult to correlate because each asphalt yields a chromatogram with a distinctive shape which is also very dependent on the procedures used.

Introduction

Test Sections. In 1982-83, test sections were constructed at three locations in Texas using asphalts from five refineries. Both AC-10 and AC-20 grades were used for a total of 20 sections. Seven sections were placed East of Dickens, Texas in 1982 on the Westbound travel lane of U.S. 82. Seven sections were located North of Dumas, Texas on the Northbound travel lane of U.S. 287. These sections were also put down in 1982. In 1983, six sections were installed on the Northbound lane of two-lane U.S. 96 about 25 miles South of San Augustine, Texas. These are referred to as the Lufkin sections in this report.

The aggregate used at Dickens was mined near the site. The course and intermediate fractions were crushed siliceous gravel and the fines were similar material. The Dumas aggregate was an absorptive crushed limestone. The Lufkin aggregate consisted of a mixture of limestone and iron ore gravel plus field sand.

The principal objective of Study 287 was to relate both physical and chemical laboratory properties to field pavement performance. In connection with this study, a variety of properties were measured on the original asphalts, and some of these are used in the present study (Table IV-1-1 from Adams and Holmgreen, 1986). Following construction, it was found that the Dumas and Dickens sites had very high void contents. Cores were taken at Dickens and Dumas after one week and after one and two years and at Lufkin after one week and one year. The voids after each period are shown in Table IV-1-1. At Dumas, the Dorchester section failed after a year and had to be replaced. The Exxon section was also in bad condition and had to be partially replaced. At Dickens, all the test sections began to show raveling and were fog sealed in 1985.

The present study has as an objective the correlation of chemical properties to physical properties and road performance. In connection with this objective, the test sections were recored in 1987. By this time the Exxon and Diamond Shamrock AC-10 at Dumas had been completely replaced and the remaining sections at Dumas had been seal coated. Only the Lufkin sections remained with original surfaces and these were all in good condition. One Lufkin section listed as Dorchester AC-20 was omitted from the study, as the asphalt source was actually believed to be Texaco. This left 16 sections to be cored; the 1987 data for the cores and extracted asphalts are shown in Table IV-1-2. Additional characteristics of asphalt extracted from these 1987 cores are given in Table IV-1-3.

South Texas Sites. It was decided to expand the study by including some old roads that were still in good condition. District 21 in the southern tip of Texas was chosen as this area has a generally hot, dry climate significantly different from the other locations. This district in cooperation with the Texas State Department of Highways and Public Transportation (SDHPT) in Austin and with Texas A & M has established a database on their roads containing pertinent information about construction, use and condition of their roads. Using this database, only six roads could be found that were uncracked and at least five years old. One more with

Table IV-1-1

Viscosities of Virgin Asphalts and Core Voids

	Viscosity (Poise)		% Voids		
	140°F	275°F	1 week	1 year	2 years
Dickens					
D.S. AC-10	1220	4.51	16.0	14.3	9.1
D.S. AC-20	2175	7.15	13.4	10.0	12.7
MacM AC-20	2523	4.64	15.6	9.9	14.0
EXX AC-20	2576	3.55	14.8	9.9	13.6
Dorch AC-20	2151	4.53	11.7	14.1	13.0
Cos AC-10	1264	2.55	14.4	14.5	10.6
Cos AC-20	1515	2.87	15.0	10.5	12.3
Dumas					
D.S. AC-10	958	4.65	20.4	7.2	2.1
D.S. AC-20	2155	6.39	13.9	11.6	9.2
MacM AC-10	961	3.63	12.2	13.7	10.5
EXX AC-10	1388	3.06	16.5	15.4	
Dorch AC-10	1030	3.21	12.6	12.2	8.6
Cos AC-10	1038	2.48	20.4	13.8	7.3
Cos AC-20	2354	3.17	17.1	10.5	10.2
Lufkin					
D.S. AC-20	1728	5.05	8.6	2.6	
MacM AC-10	932	3.63	4.8	6.2	
EXX AC-20	1811	3.19	6.6	3.0	
Dorch AC-10	1040	2.88	3.2	4.2	
Dorch AC-20	1913	3.96	7.4	2.2	
Cos AC-20	1858	2.83	6.5	3.2	

Diamond Shamrock (D.S.)
Dorchester (Dorch)
MacMillan (MacM)
Cosden (Cos)
Exxon (EXX)

Table IV-1-2

Physical Properties of Test Section 1987 Cores and Extracted Asphalt

	Percent Voids	Viscosity		Penetration at 77°F (0.1 cm)	Percent Asphalt
		140°F (Kilopoise)	275°F (Poise)		
Dickens					
MacM AC-20	8.0	159	23.1	16	6.2
Dorch AC-20	13.0	222	22.4	10	4.6
EXX AC-20	9.0	900	70.7	12	5.1
D.S. AC-20	12.0	260	34.2	18.5	---
D.S. AC-10	9.0	48.9	17.9	25	5.3
Cos AC-20	11.0	376	26.4	10.5	4.0
Cos AC-10	12.0	342	18.2	11.5	5.6
Dumas					
MacM AC-10	5.5	13.3	9.2	38	5.5
D.S. AC-20	8.1	32.5	18.9	27.5	5.9
Cos AC-10	9.5	23.4	26.7	18	5.9
Cos Ac-20	8.5	55.6	11.7	15.5	5.9
Lufkin					
MacM AC-10	2.4	4.8	6.5	39	6.6
Cos AC-20	1.8	5.4	5.7	22	6.9
D.S. AC-20	2.1	9.1	11.2	30	6.5
EXX AC-20	2.5	3.9	5.8	40.5	7.7
Dorch AC-10	2.1	2.4	4.6	38.5	5.6

MacMillan (MacM)
Diamond Shamrock (D.S.)
Dorchester (Dorch)
Cosden (Cos)
Exxon (EXX)

Table IV-1-3

Parameters Used in Aging Correlations

	Carbonyl Peak Height	Sulfoxide Peak Height	Percent LMS	Aging Index 140°F	Aging Index 275°F
Dickens					
MacM AC-20	34	23	33.6	63	5.0
Dorch AC-20	29	18	25.4	103	4.9
EXX AC-20	37	20.5	38.8	350	19.9
D.S. AC-20	35.5	13.5	53.9	119	4.8
D.S. AC-10	29.5	16.25	46.0	40	4.0
Cos AC-20	32	18	26.8	247	9.2
Cos AC-10	31	22	30.1	271	7.1
Dumas					
MacM AC-10	15.5	30	24.4	13.8	2.5
D.S. AC-20	25	22.25	45.9	15.0	3.0
Cos AC-10	17	29	19.6	22.5	10.7
Cos AC-20	20.5	25	23.2	20.5	3.7
Lufkin					
MacM AC-10	10	13	33.7	10	1.8
Cos AC-20	8.5	32.25	18.5	8.5	2.0
D.S. AC-20	22	10.25	45.0	22	2.2
EXX AC-20	8	25.75	23.5	8	1.8
Dorch AC-10	5	19	23.5	5	1.6

MacMillan (MacM)
Diamond Shamrock (D.S.)
Dorchester (Dorch)
Cosden (Cos)
Exxon (EXX)

slight transverse cracking was included. These roads were cored in June 1988 and are listed in Table IV-1-4.

State Highway 186 in Willacy county was sampled at two locations. At milepost 25.8, the pavement was laid in the fall of 1982. The road showed a small amount of raveling but was otherwise in very good condition. At milepost 34, the pavement was laid in August 1980.

United States Highway 77 was also sampled in two locations. At milepost 16 in Willacy county, the road was in good condition. It was laid in August 1982 and was a high traffic area. In Cameron county, US 77 was sampled at milepost 27. This was the highest traffic spot sampled, located near Harlingen, Texas. It was paved in August 1982 and was seal coated in 1987, possibly to solve a raveling problem.

The only other high traffic road sampled was US 281 in Hidalgo county. This site at milepost 37.5, near McAllen, was laid in January of 1979 and seal coated in May 1985. Raveling was obviously a problem with this stretch of road because the verge of the road was covered with aggregate from the original asphalt, not from the seal coat.

Two Texas farm-to-market roads were included. In Cameron county FM 2925 was sampled at milepost 12. The asphalt here was laid in April 1983. This pavement was cracked transversely about every 8 feet. The road was made up of a thin pavement over the base and the high level of boat traffic to the Gulf of Mexico may have contributed to the cracking. The other farm-to-market road was officially listed as a seal coat only. FM 1017 in Hidalgo county was cored at milepost 7.5. This road was easily the oldest in the study, having been laid in May 1969 over what appeared to be an old gravel road. The pavement was rutted by the oil field trucks travelling it but was in very good condition, considering its age and construction. In fact, only about 0.6 miles of the 1969 road still exist, the rest having been replaced. All of the pavements in the south Texas test sites were constructed with aggregate resembling river gravel, which may have contributed to the raveling in many roads. These locations and those of the original test sections are shown in Figure IV-1-1.

Table IV-1-4

Data for South Texas Roads

Highway	Carbonyl Peak Height	Sulfoxide Peak Height	% LMS	Viscosity 140°F (kpoise)	Viscosity 275°F (poise)	Penetration (0.1 cm)	Age (yrs)
FM 2925	23.5	26.75	26.4	67.8	15.4	14	5
US 77/27[a]	10.75	33	25	27.5	12.3	23.5	5+1[b]
US 77/16[a]	18	28.5	24	43.3	12.5	14.5	6
SH 186/25[a]	30.75	36	30.5	130	21.0	14	6
US 281	22	28.75	26.4	22.0	8.5	22	6+3[b]
SH 186/36[a]	30.75	23	29.7	282	23.5	10	8
FM 1017	36.75	13.5	33.8	248	21.1	13	19

[a] Milepost
[b] Years Under Sealcoat

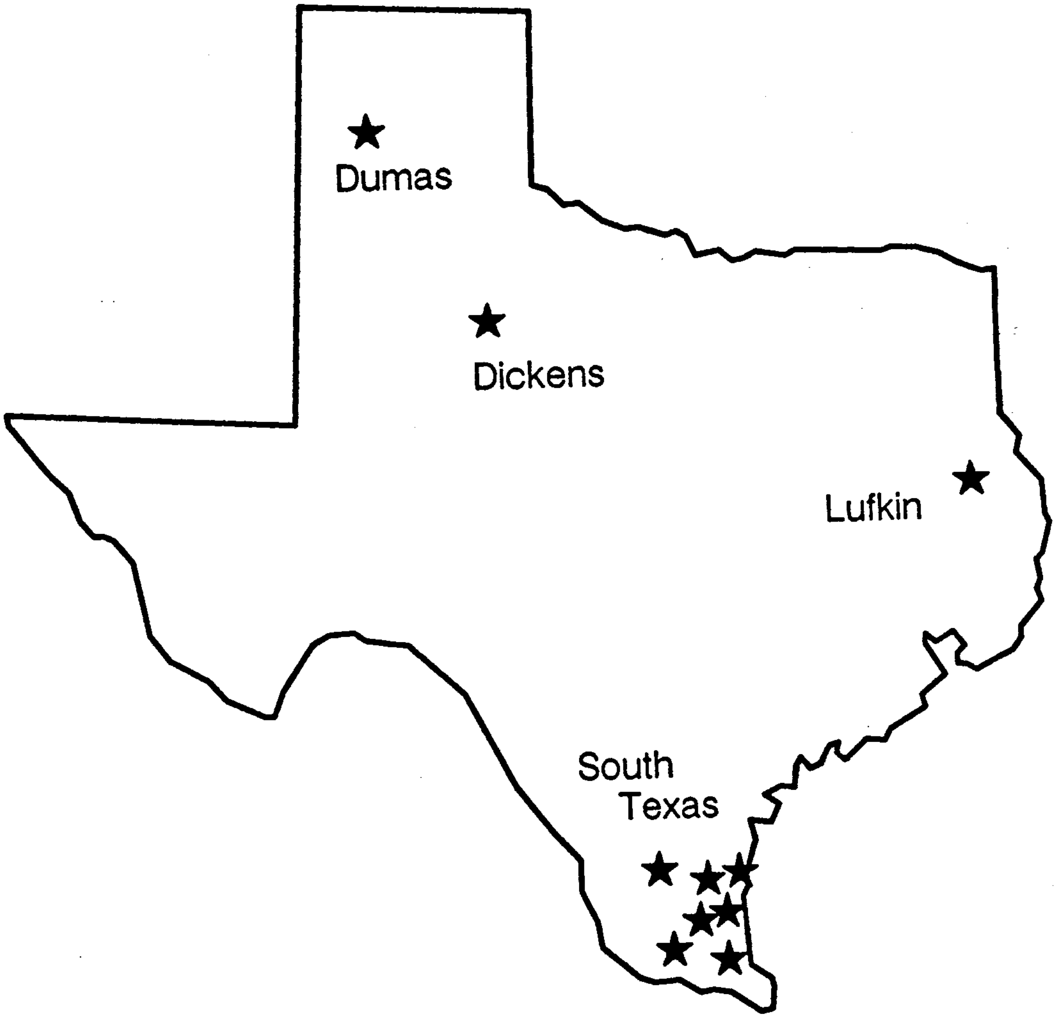


Figure IV-1-1
Location of the Test Sections Near Dickens, Dumas, and Lufkin and of Highways Cored in South Texas District 21

Procedures

All of the cores were extracted by a modified ASTM D 2172-81 Method A, except at Lufkin where all but the Cosden AC-20 were extracted by Method B. The procedure was changed after it was realized that Method B can change the asphalt. In both instances, ethanol was added to improve removal from the aggregate. In the Method B procedure, a 95%-5% trichloroethylene-ethanol mixture was used. In Method A, several extractions with trichloroethylene were followed by a 90%-10% trichloroethylene-ethanol mixture. The small amount of ethanol considerably enhances removal of the last few percent of asphalt.

Solvent was removed by either the Abson or Roto-vap procedure. When running Gel Permeation Chromatography (GPC) on the recovered material, it was found that many samples still contained solvent and additional solvent removal was required so as to avoid erroneously soft asphalt. It has since been found that the times specified in the standard procedures are frequently inadequate for complete solvent removal, especially from viscous, core material.

Voids and percent asphalt were calculated and are recorded in Table IV-1-2. Penetrations at 77°F, ASTM D 5, were run on the recovered material as were viscosities at 140°F and 275°F using ASTM D 2173. These are found in Tables IV-1-2 and IV-1-4.

GPC chromatograms were obtained using an IBM 9533 Liquid Chromatograph controlled by an IBM 9000 computer, as described in Section II, Chapter 1. Briefly, two Polymer Laboratories PL gel chromatographic columns were used in series, a 500 Å followed by a 50 Å pore size. The detector was a Waters R401 differential refractometer. Purified tetrahydrofuran (THF) was used as the solvent. Asphalt samples were made to exactly 7% by weight in THF and sonicated for about 3 hours. The sonicated material was then filtered through a 0.45 micron filter to remove fines. The filtered material was placed in a 1.8 ml septum-capped vial and placed in an automatic sampler. A 100 microliter sampling loop was used.

Infrared spectra of the recovered material were obtained on a Nicolet 60 SX B Fourier-Transform Infrared Spectrometer. All the data were obtained by a KBr pellet procedure, which is described in Section II, Chapter 2 and by Glover et al. (1989).

To use either GPC or IR spectra to correlate properties, some simplified characteristic was desired because the spectra are complex. For GPC, the percent large molecular size (LMS) as suggested by Jennings et al. (1980) was used. Arbitrarily, the entire spectrum was taken as 20 to 35 minutes and the LMS from 20 to 25 minutes. The percent LMS was calculated from the areas under the curve during these intervals.

There are two areas of the IR spectrum that relate specifically to oxidation. One is the carbonyl peak occurring at about a wavenumber of 1700 and the other a sulfoxide peak at a wavenumber of 1030. Since these peaks both occur in areas where absorption of other entities is present, the choice of peak height is somewhat arbitrary. For the sulfoxide peak, the method recommended by Peterson (1986) is used as shown in Figure IV-1-2. A tangent line is drawn below the peak of interest touching the low points on either side. A similar procedure was used with the carbonyl peak. The parameter used in this work was the height of each peak above this tangent line. Spectra for these asphalts are presented in Appendix C.

Results and Discussion

Properties of the 1987 test section cores and the extracted asphalts are listed in Table IV-1-2. Sulfoxide and carbonyl peak heights from the IR analyses and percent LMS from the GPC experiments are listed in Table IV-1-3, along with viscosity aging indexes at both 140°F and 275°F. This is the ratio of the viscosity of the 1987 core extracts divided by the viscosity of the virgin asphalt from Table IV-1-1. Properties of the asphalt extracted from the South Texas cores is given in Table IV-1-4.

Correlation of Voids and Aging. One of the surprising elements of the data in Tables IV-1-1 and IV-1-2 is the inexplicably high voids level in the test sections at Dumas and Dickens that has led to rapid aging and the early demise of three sections. It has been recognized for decades that high voids leads to shortened road

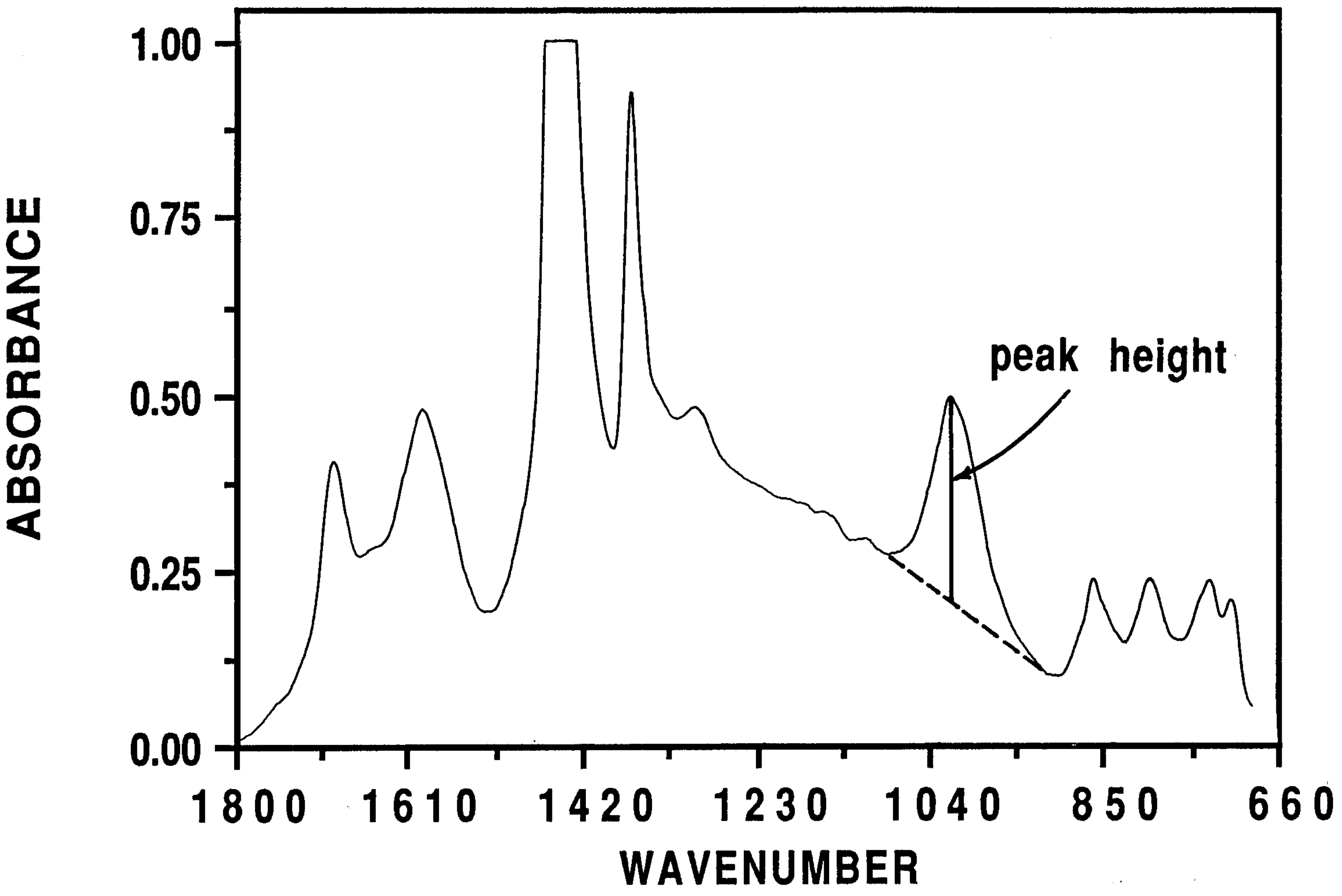


Figure IV-1-2
Example FT-IR Spectrum Showing the Method of Determining the Sulfoxide Band Peak Height Near 1000 cm^{-1}. The Carbonyl Peak Height Near 1700 cm^{-1} is Determined Similarly.

life, yet it continues to be a problem even in carefully monitored test sections. This is discussed in detail in Section I, Chapter 3.

In Figure IV-1-3, carbonyl peak height is plotted versus percent voids. These are 1987 core voids which give better results than averaging the void data. This is likely because of variation in voids within the roadbed, so that earlier cores may not represent the cores being studied. It is obvious that oxidation as reflected in the growth of the carbonyl peak increases rapidly with voids. Also it appears that the Dickens sections, which are represented by the seven highest carbonyl peaks, are showing a greater response than the Dumas sections. It also may be noted that in general those sections constructed with the lower viscosity grade are oxidizing less rapidly. In the three direct comparisons with the same supplier and site, Cosden at Dickens, Diamond Shamrock at Dickens and Cosden at Dumas, this is the case. Though the Exxon at Lufkin appears to be oxidizing no more than the other asphalts, the Exxon at Dickens is the most oxidized of all. The data are simply not sufficient, however, to conclude that any asphalt is more susceptible to oxidation.

In Figure IV-1-4, the aging index at 275°F is plotted versus the percent voids. The results are similar to those in the previous graph. The Exxon has a high aging index along with its high carbonyl content. Both of the Cosdens appear to be abnormally aged at Dickens. However the Dumas Cosden datum at 8.5 percent voids is inconsistent with the 140°F data and with earlier cores and is probably in error. Figure IV-1-5 is a similar plot with 140°F aging indexes. Again the Exxon value is quite high, with high values for the Cosdens and perhaps for the McMillan. At Dumas we see that both Cosdens are near the curve. As mentioned earlier, there is an inherent problem in the study of voids versus aging in that roadbed variability makes it impossible to obtain an accurate voids history of the particular core being studied. So 1987 voids rather than average voids have been used which no doubt accounts for much of the scatter.

Correlation of Carbonyl Content and Physical Properties. Since both viscosity aging index and carbonyl peak height correlate with voids, they should cross-correlate. Figure IV-1-6 and IV-1-7 indicate that they do. Somewhat surprisingly, however, viscosity seems to correlate as well as the aging index, and this

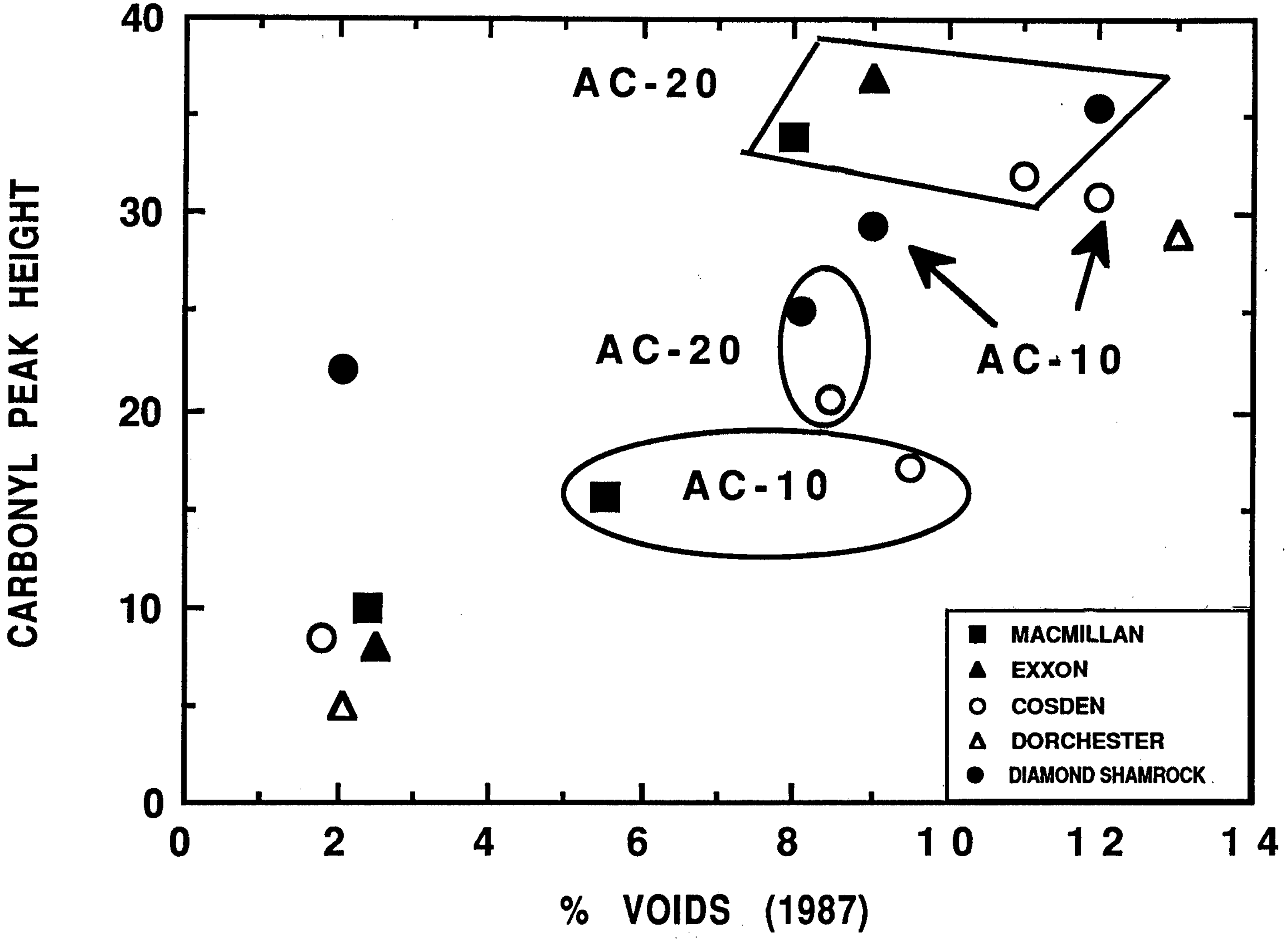


Figure IV-1-3
Carbonyl Aging Versus Voids for Asphalt from
1987 Cores of the Test Sections

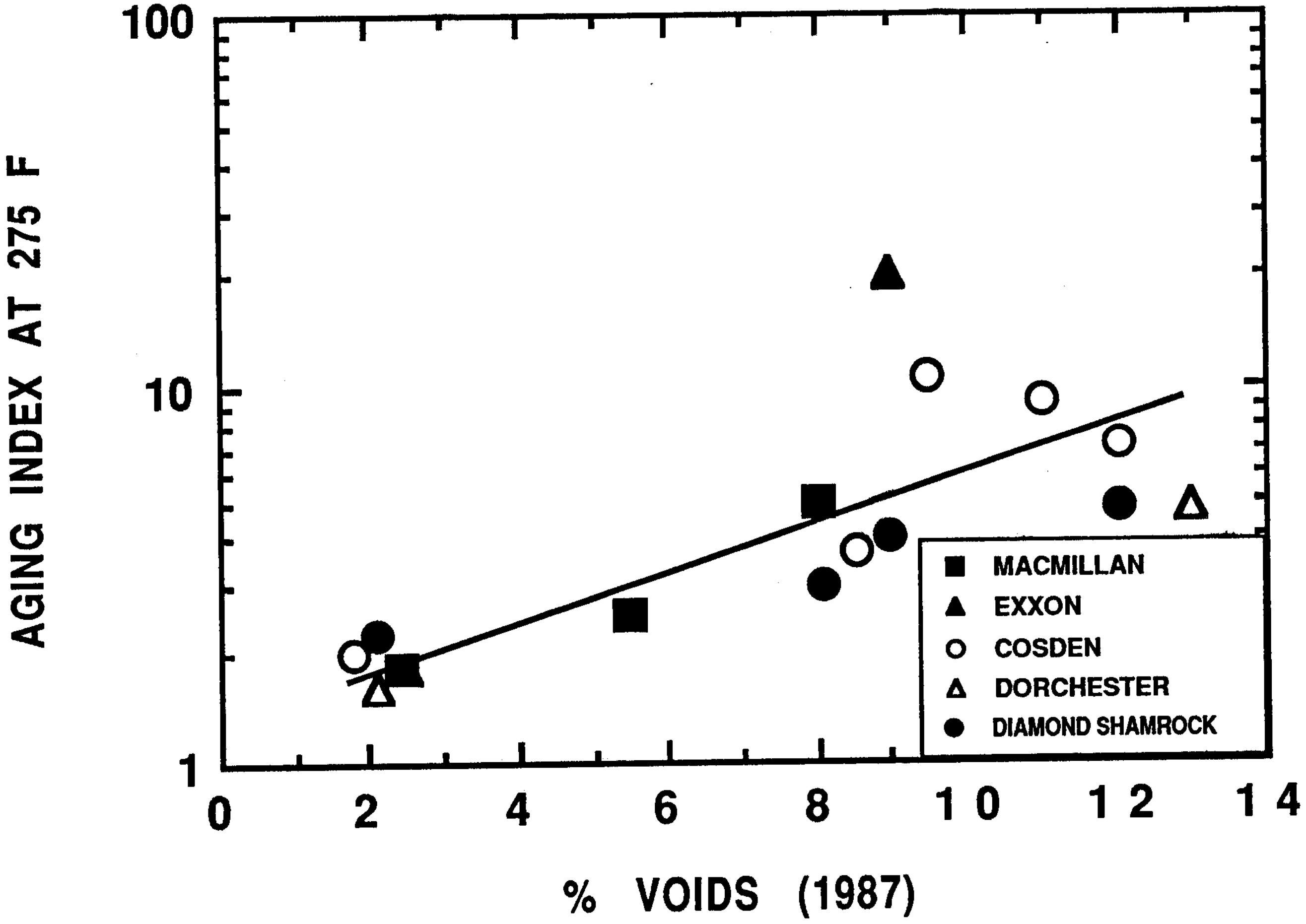


Figure IV-1-4
The 275°F Aging Index Versus Voids for Asphalt from
1989 Cores of the Test Sections

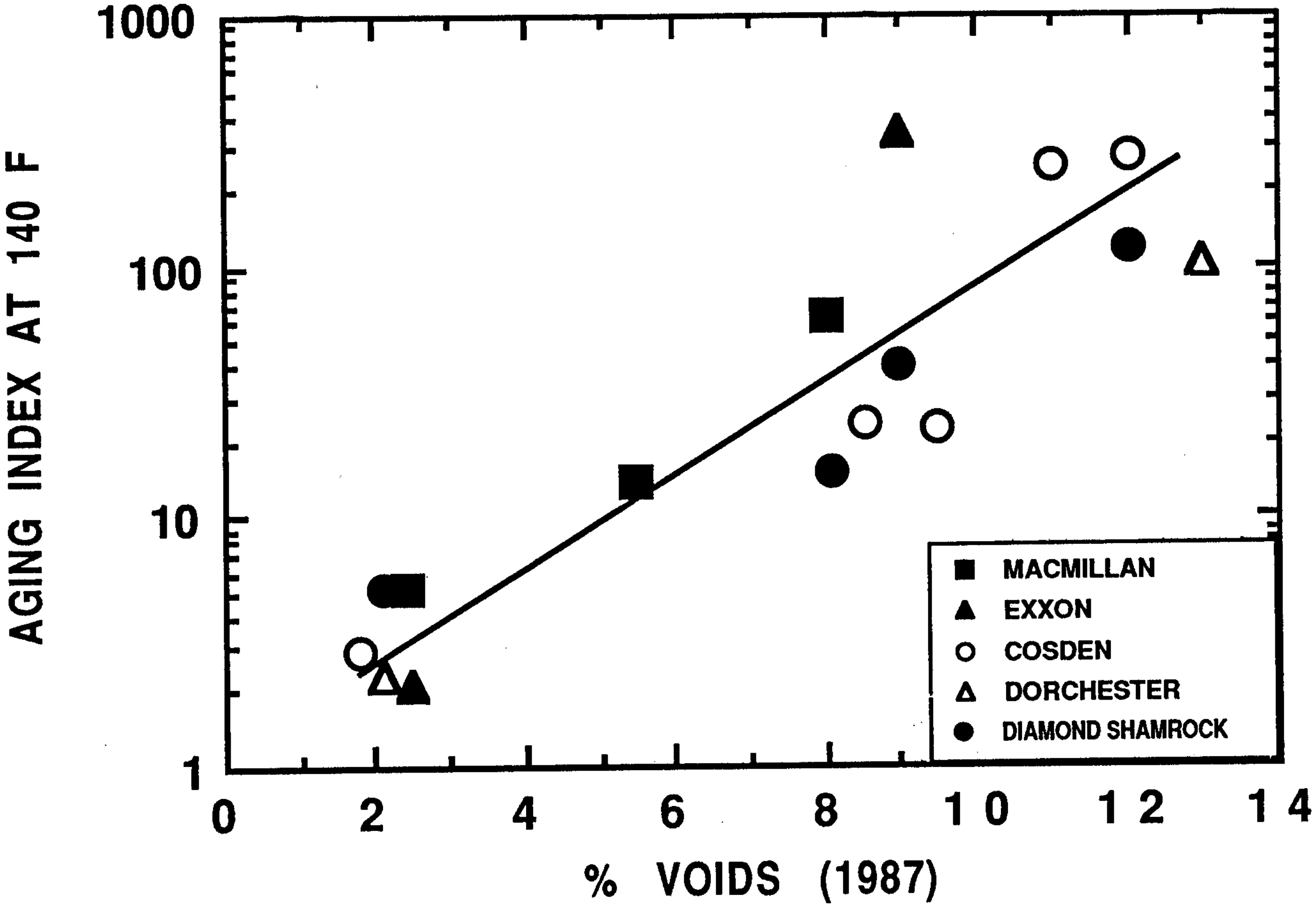


Figure IV-1-5
The 140°F Aging Index Versus Voids for Asphalt from
1987 Cores of the Test Sections

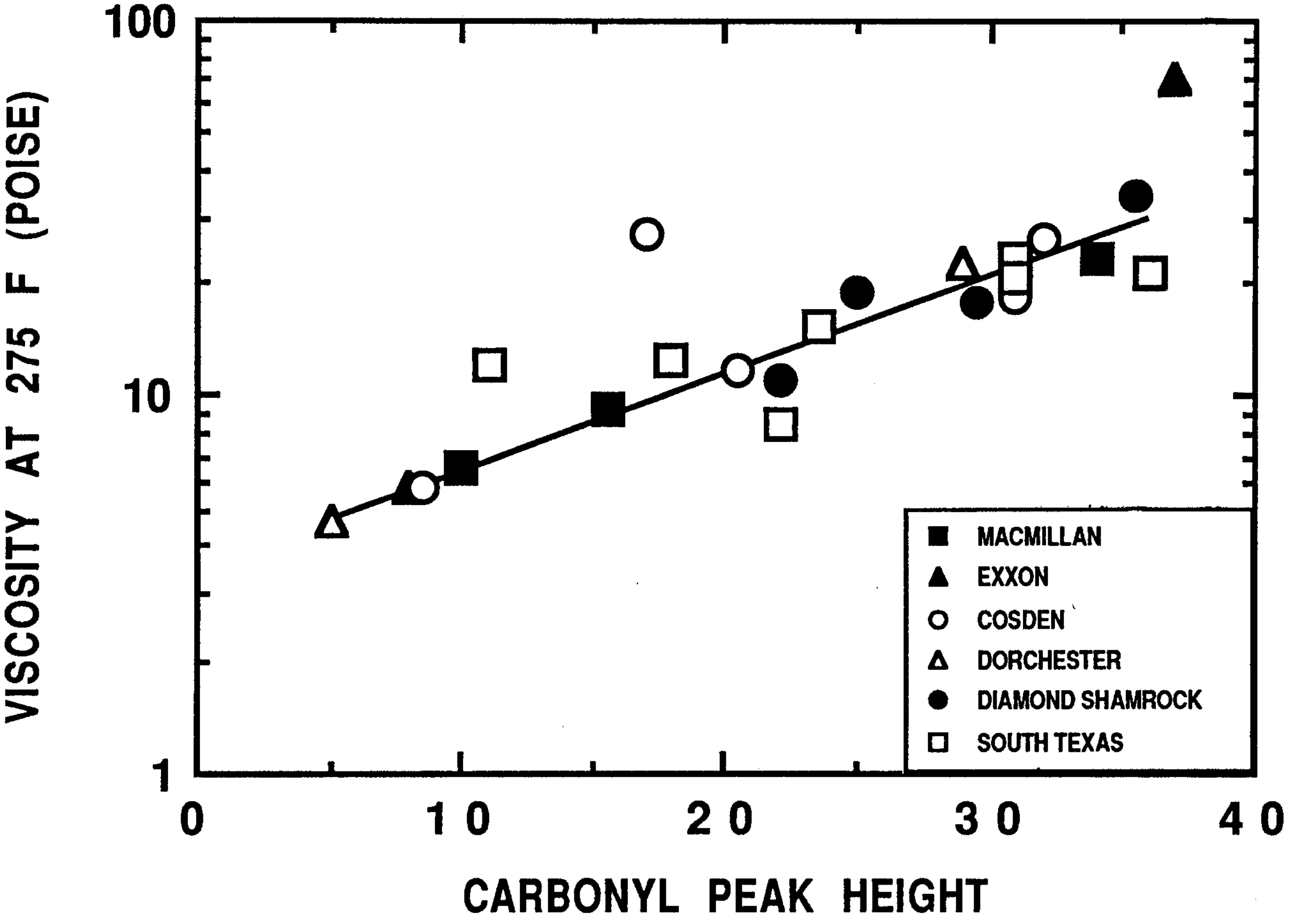


Figure IV-1-6
Viscosity at 275°F Versus Carbonyl Peak Height from 1987 Cores of the Test Sections and from the South Texas Highway Cores

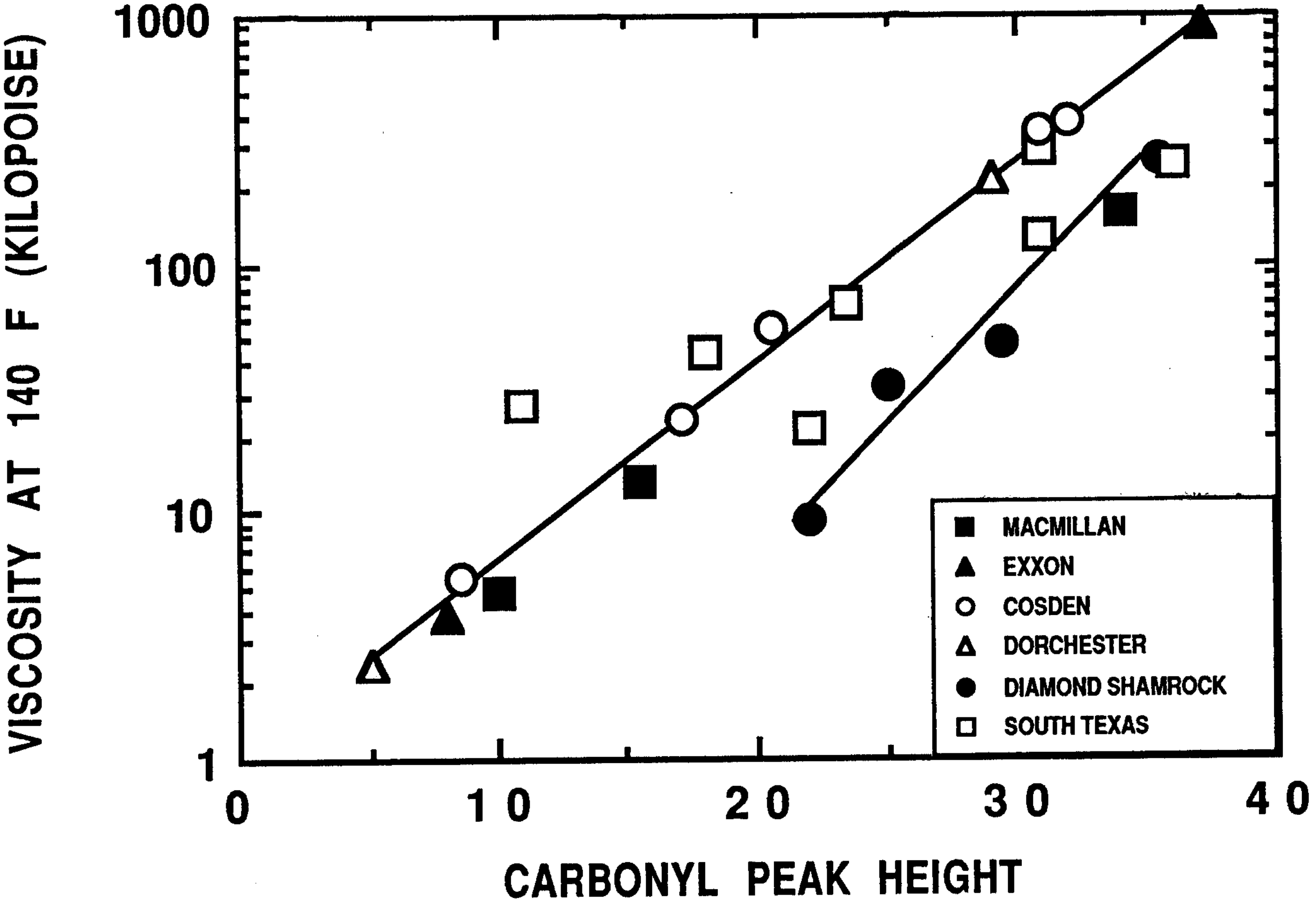


Figure IV-1-7
Viscosity at 140°F Versus Carbonyl Peak Height from 1987 Cores of the Test Sections and from the South Texas Highway Cores

allows the inclusion of the South Texas data for which original viscosities are not available. At 275°F, Figure IV-1-6, the Exxon Dickens value is very high. The high Cosden value is the suspect point previously discussed. Otherwise all but some South Texas data fit very well.

At 140°F, Figure IV-1-7, the Diamond Shamrock data have completely separated from the others. The Dickens Exxon is now on the curve while South Texas data plot with a different slope than the other data. Looking again at Figure 6, it is seen that the South Texas data would plot better here too with a lower slope.

In Figure IV-1-8, penetrations at 77°F are plotted versus carbonyl peak height. Further separation of individual asphalts has occurred, but surprisingly, Exxon and McMillan have almost merged with Diamond Shamrock while Cosden has approximately joined South Texas with an entirely different slope. Interestingly, the 19-year-old South Texas FM 1017 has only a slightly higher penetration than the 5-year-old Dickens Exxon. Several of the Dickens roads are approaching dangerously low penetrations, as is Highway 186/MP 36. This low penetration on 186/MP 36 is consistent with its very high viscosity at both 140°F and 275°F.

Except for this road and Highway 281/MP 37.5, which has an abnormally high Pen and low viscosities, the other South Texas roads show remarkable conformity. In Figure IV-1-9 and IV-1-10, viscosities of the South Texas roads are plotted versus carbonyl peak height at 275°F and 140°F. The 140°F correlation is particularly good except for the two data points referred to above. All of these data tend to indicate that carbonyl peak height is a very good measure of road aging for any particular asphalt with respect to both viscosity and penetration. It can likely be used as an effective parameter in laboratory aging tests. It also may be concluded that it cannot be related to road age in years as percent voids and probably other factors exert too much influence on aging. One of these other factors is almost certainly asphalt compatibility (Altgelt and Harle, 1975). This could account for much of the divergence of individual asphalts noted here.

The Effect of Sulfoxides. Surprisingly, the correlations so far have been made without reference to sulfoxide peak height which for some of the aged asphalts is higher than the carbonyl peak. One would expect sulfoxide formation to be

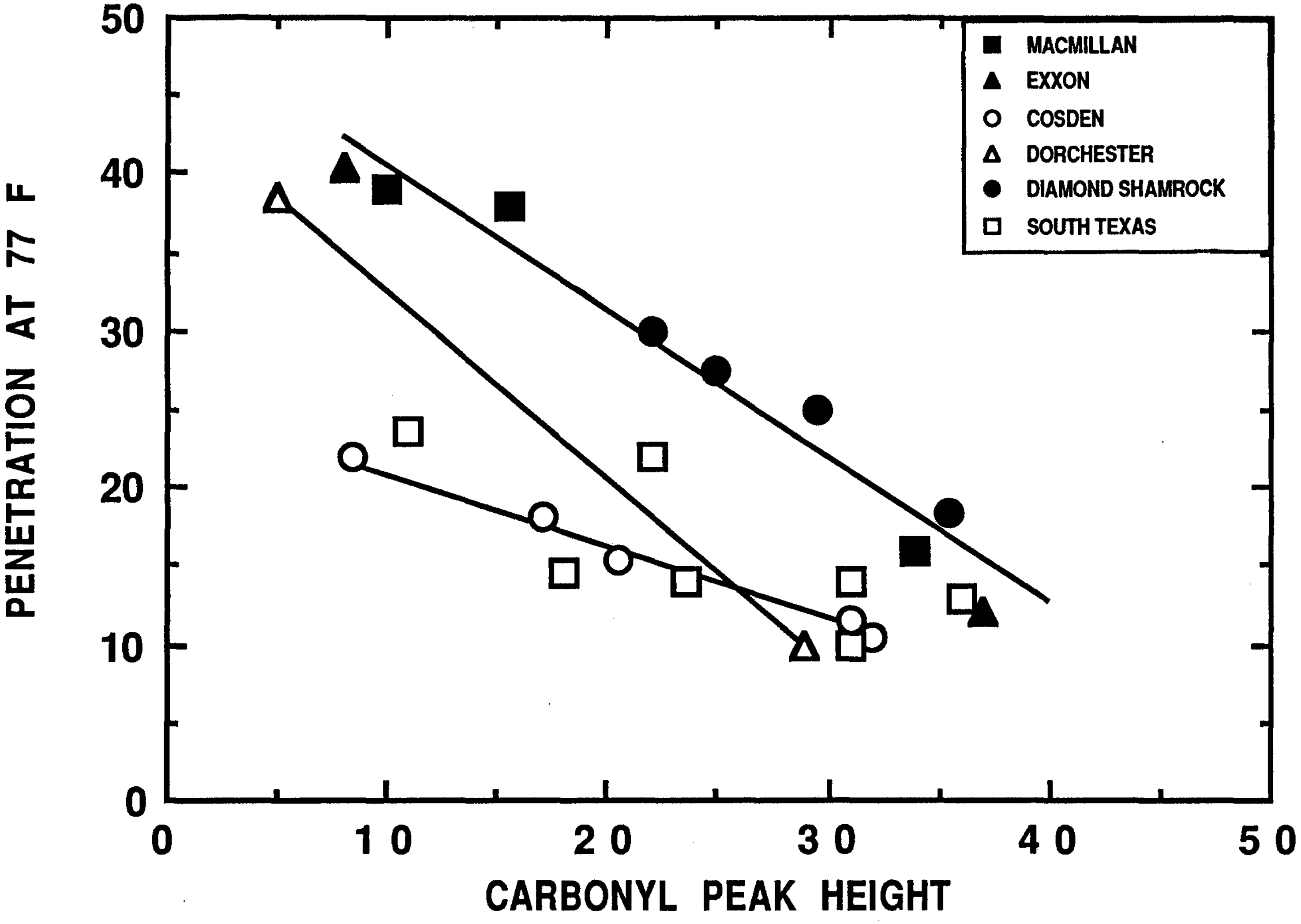


Figure IV-1-8
Penetration at 77°F Versus Carbonyl Peak Height from 1987 Cores of the Test Sections and from the South Texas Highway Cores

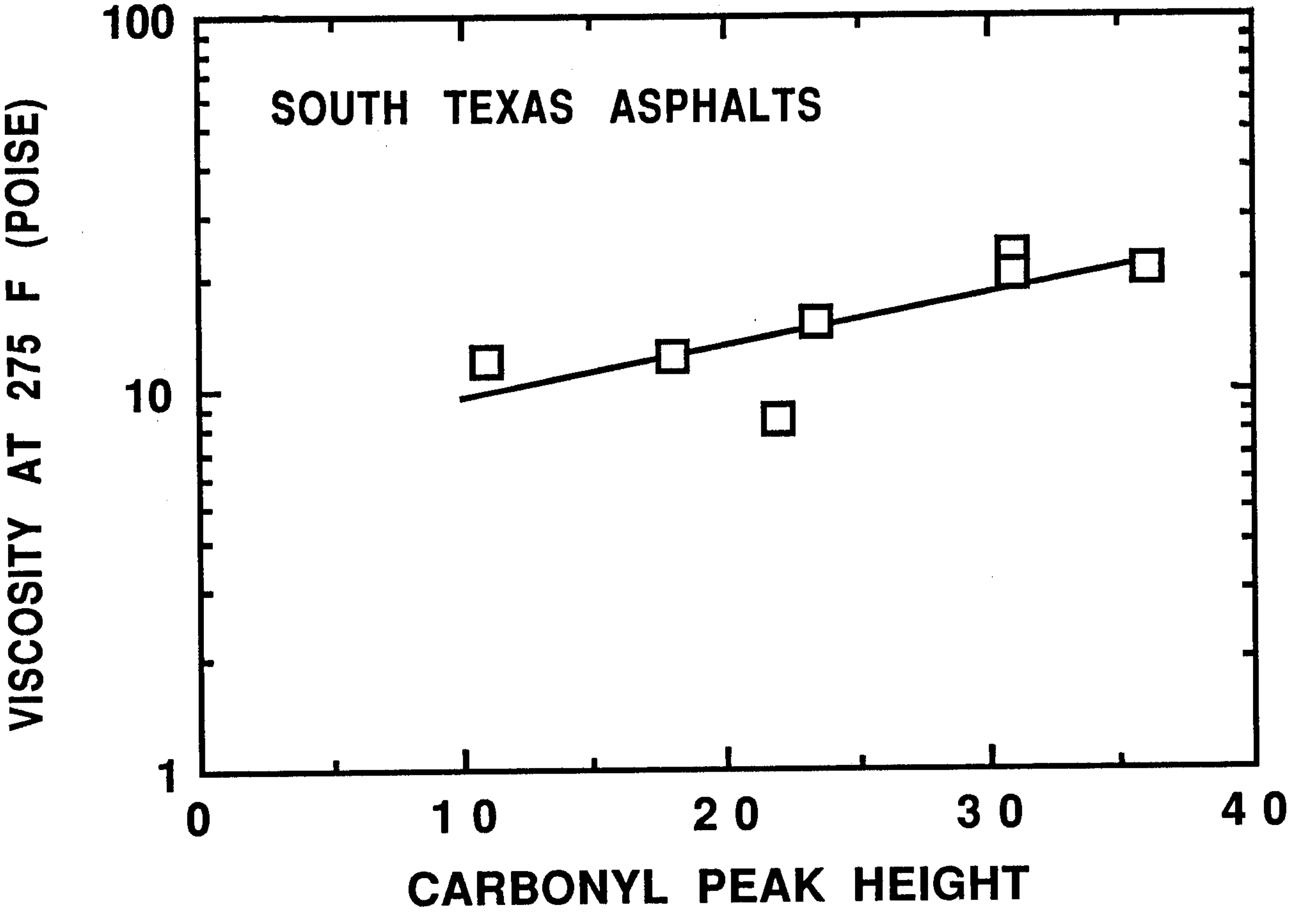


Figure IV-1-9
Viscosity at 275°F Versus Carbonyl Peak Height for Asphalts from the South Texas Highway Cores

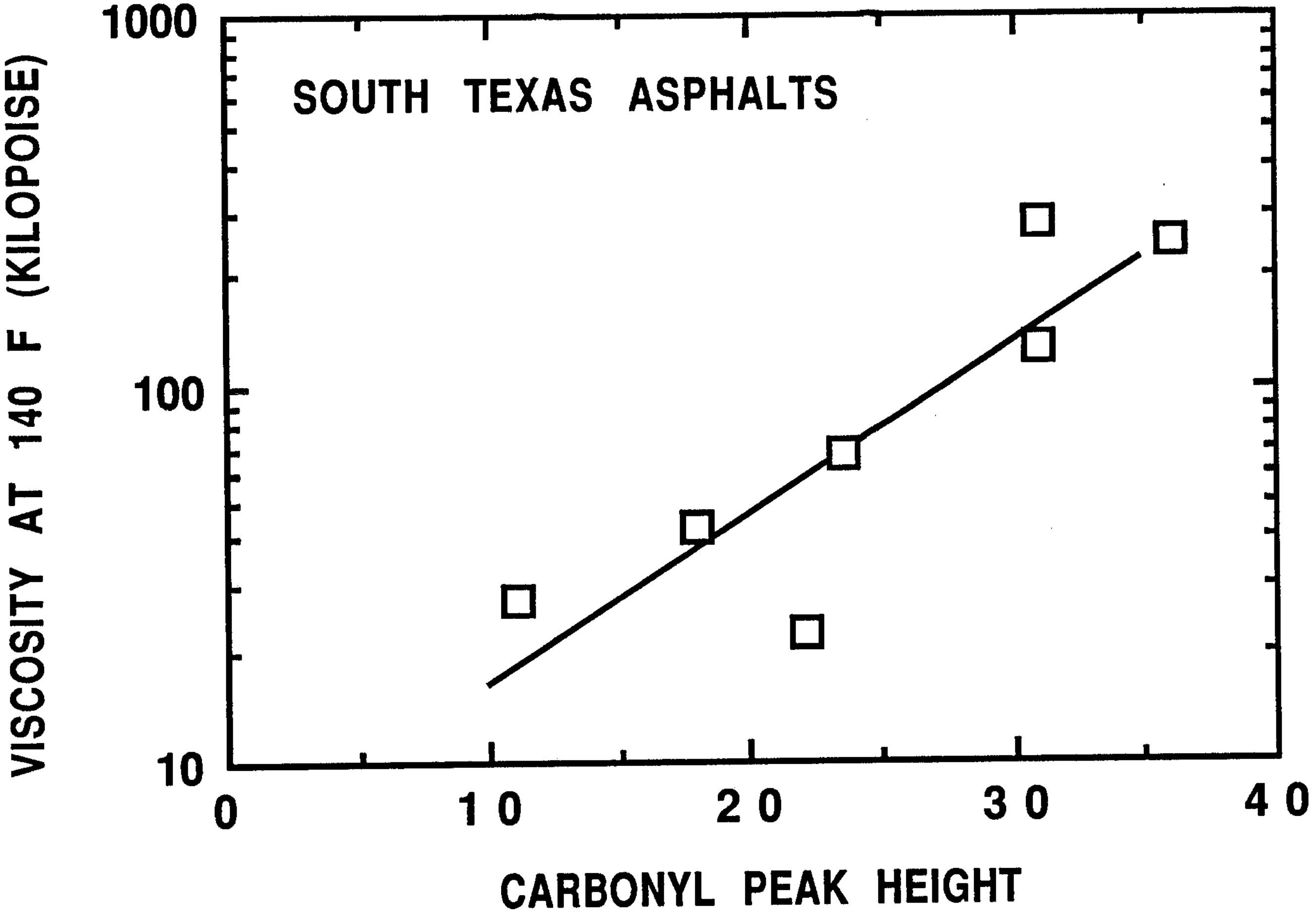


Figure IV-1-10
Viscosity at 140°F Versus Carbonyl Peak Height for
Asphalts from the South Texas Highway Cores

complicated by the wide variations encountered in sulfur content. Figure IV-1-11 shows sulfoxide peak height versus sulfur content for those asphalts for which sulfur content is available. While there is overall a distinctly upward bias with increasing sulfur content, it is obvious that location is having a much stronger effect. It may be recalled that the Dickens sites had consistently higher carbonyl peaks and viscosities and generally lower penetrations; yet we find that Dumas has consistently higher sulfoxide peaks. This is emphatically so when one compares the asphalts from the same supplier.

This indicates a reverse correlation between sulfoxide and carbonyl peak heights, which is seen in Figure IV-1-12. The scattered data at the bottom represented by the lower curve are from Lufkin where both carbonyl and sulfoxide tend to be lower because of the small extent of aging. All of the other data fall reasonably well on the upper curve except for highway 186/MP 25 that shows a high value for both peaks. The asphalt extracted from this road fits the other correlations very well, giving further evidence that sulfoxide formation has little effect on physical properties, except as it affects carbonyl formation.

Apparently there is competition between sulfoxide and carbonyl formation, and because sulfoxide appears to contribute little to hardening, its preferential formation is desirable. The question remains why sulfoxide formed preferentially at Dumas. A possible answer is the aggregate which at Dumas is an absorptive limestone while the Dickens aggregate is sandstone. It has been reported by March (1977) that sulfoxide formation is base catalyzed.

Correlation with GPC. Figure IV-1-13 shows GPC results for Cosden AC-20 at all three locations. Similar chromatographs for the other sections are in Appendix C. The progressive aging with time and the higher aging at Dickens and Dumas is clearly shown. Figure IV-1-14 shows a plot of percent large molecular size (LMS) versus carbonyl content. It is not surprising that the correlation is not good as the chromatograph of each asphalt source tends to have its distinctive shape, and this is only crudely represented in LMS. The unique shape of Diamond Shamrock chromatographs is reflected in this graph, but the scatter is disappointing, as it is for several other asphalts.

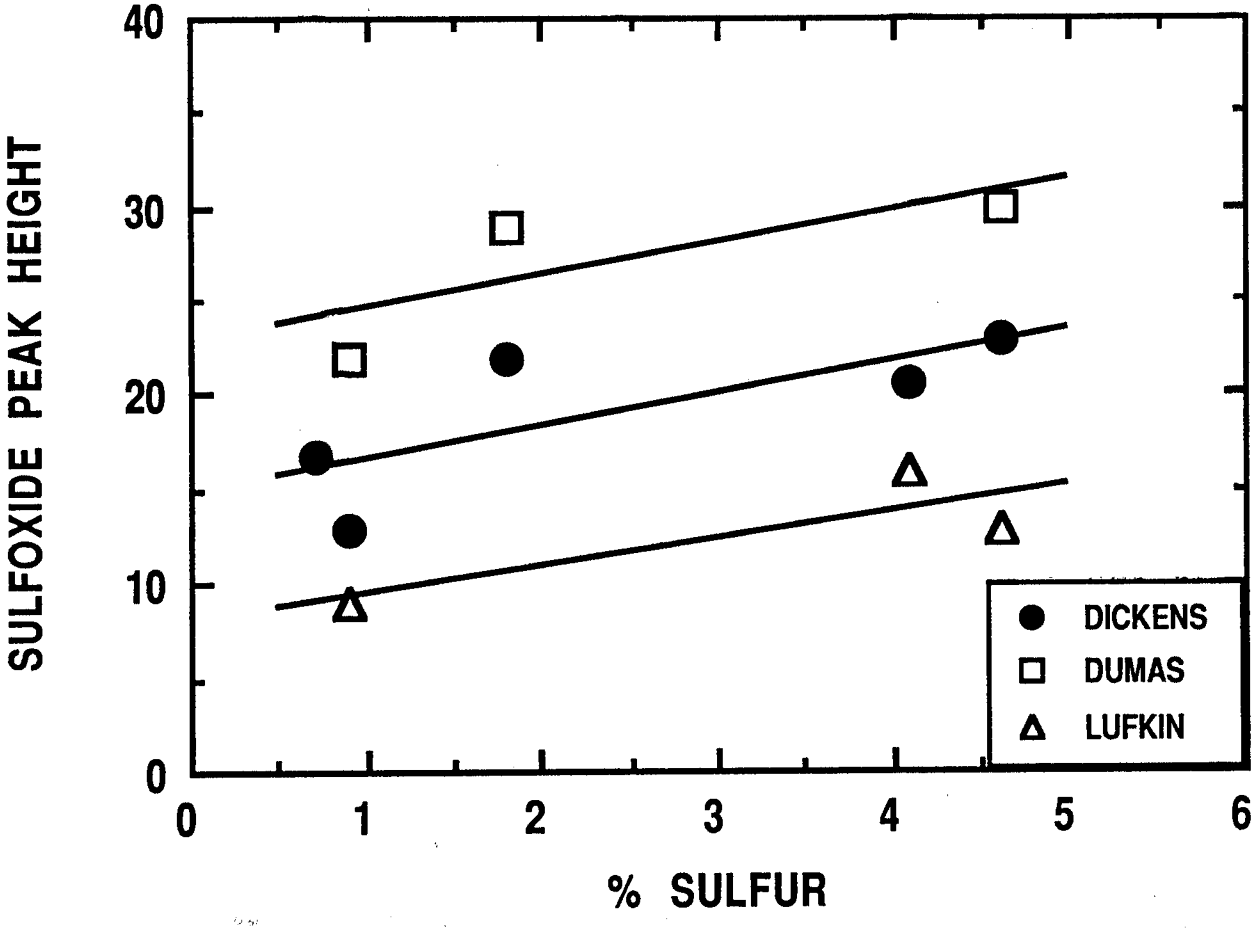


Figure IV-1-11
Sulfoxide Peak Height Versus Sulfur Content for Asphalt from 1987 Cores of the Test Sections

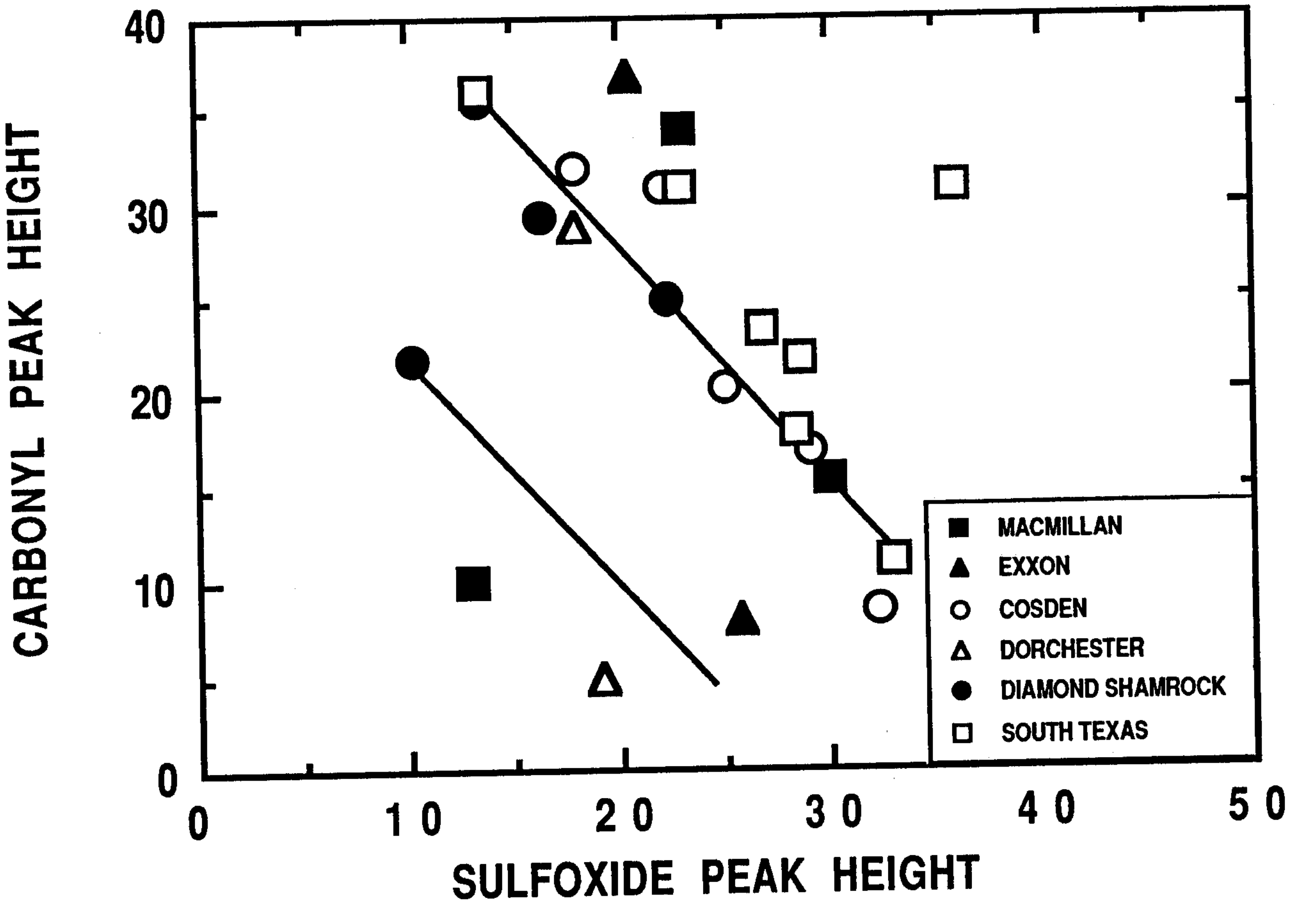


Figure IV-1-12
Carbonyl FT-IR Peak Height Versus Sulfoxide Peak Height from 1987 Cores of the Test Sections and from the South Texas Highway Cores

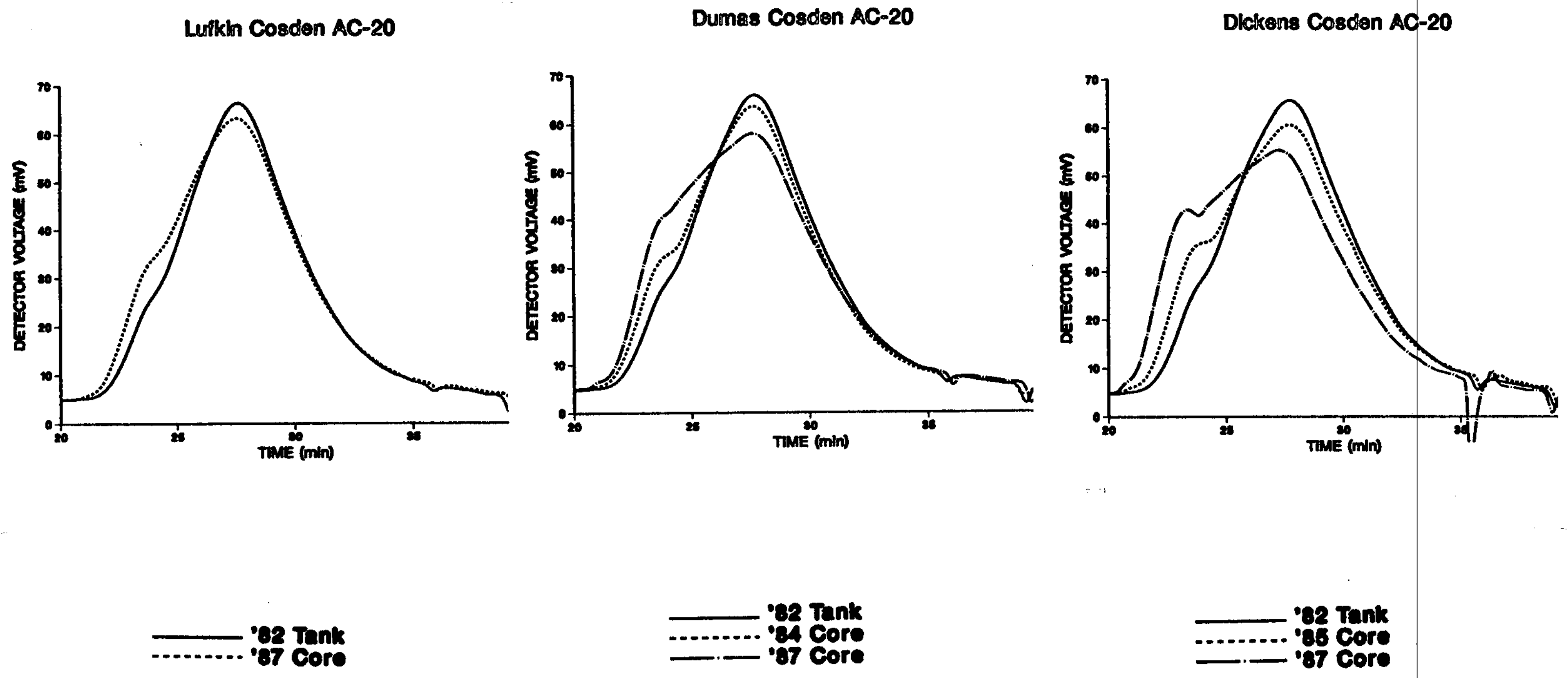


Figure IV-1-13
GPC Chromatograms of the Cosden AC-20 Asphalt as Sampled Prior to Hot-mixing (Tank) and as Extracted and Recovered from the Three Test Section Locations

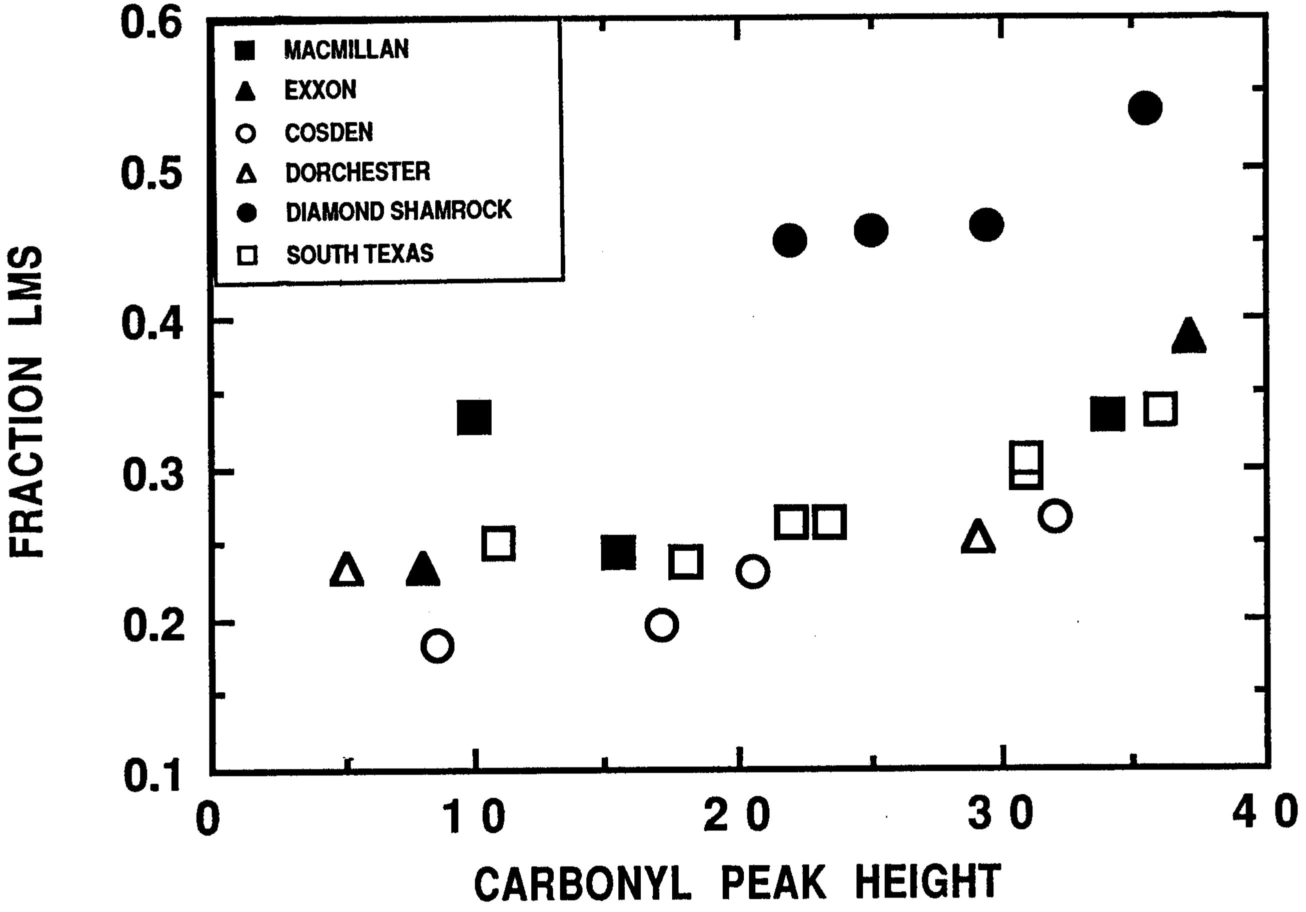


Figure IV-1-14
GPC Chromatogram Large Molecular Size (LMS) Fraction Versus
Carbonyl Peak Height from 1987 Cores of the Test Sections
and from the South Texas Highway Cores

The most consistent set of data are for Cosden and South Texas for which also the most data are available. Figure IV-1-15 is a plot of percent LMS versus carbonyl peak height for South Texas, and except for highway 77/MP 16, the correlation is excellent. Figure IV-1-16 shows the GPC chromatograms for South Texas, and it can be seen that the chromatogram for this asphalt is anomalous, having the lowest shoulder but not the lowest LMS. In Figures IV-1-17 and IV-1-18, viscosity is plotted versus LMS for the South Texas asphalts. The points off the line are for the most part the same ones that did not correlate with carbonyl versus viscosity. In Figure IV-1-18, the highest and lowest point are for the same asphalts that are off the line in Figure IV-1-10. The third point represents the asphalt that deviated from the line in Figure IV-1-15. The remaining four points form a near perfect straight line.

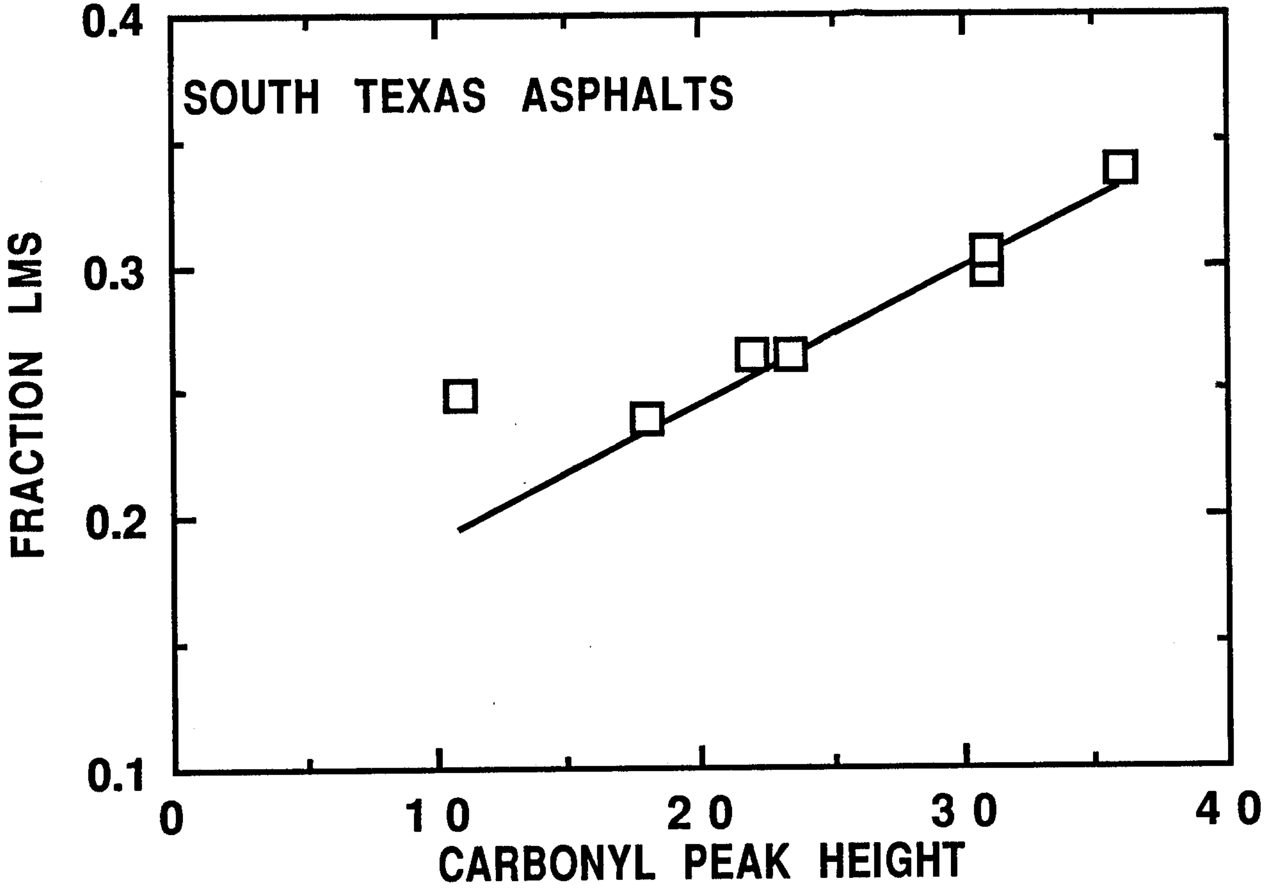


Figure IV-1-15
GPC Chromatogram Fraction LMS Versus Carbonyl Peak Height for Asphalts from the South Texas Highway Cores

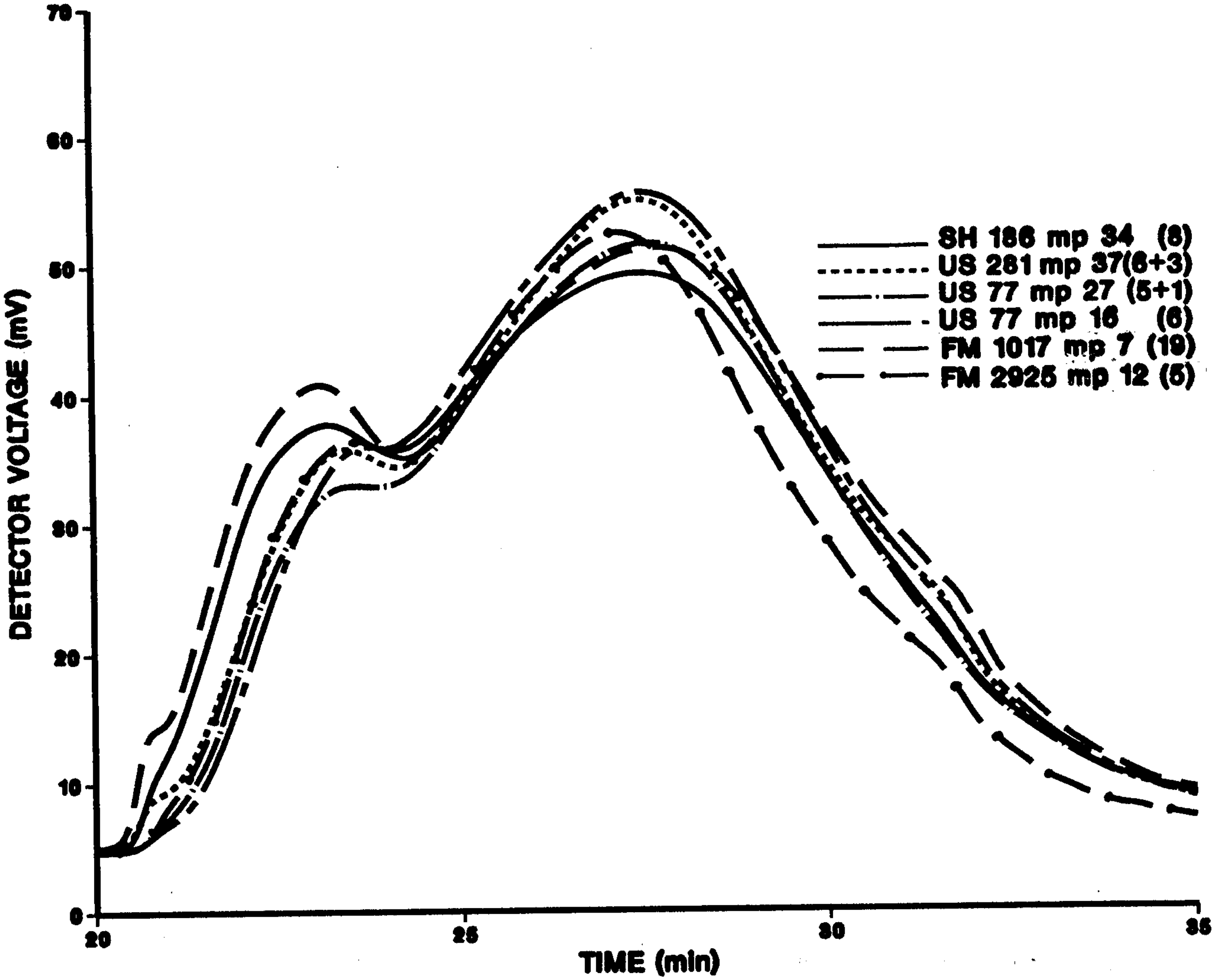


Figure IV-1-16
GPC Chromatograms for Asphalts from the South Texas Highway Cores

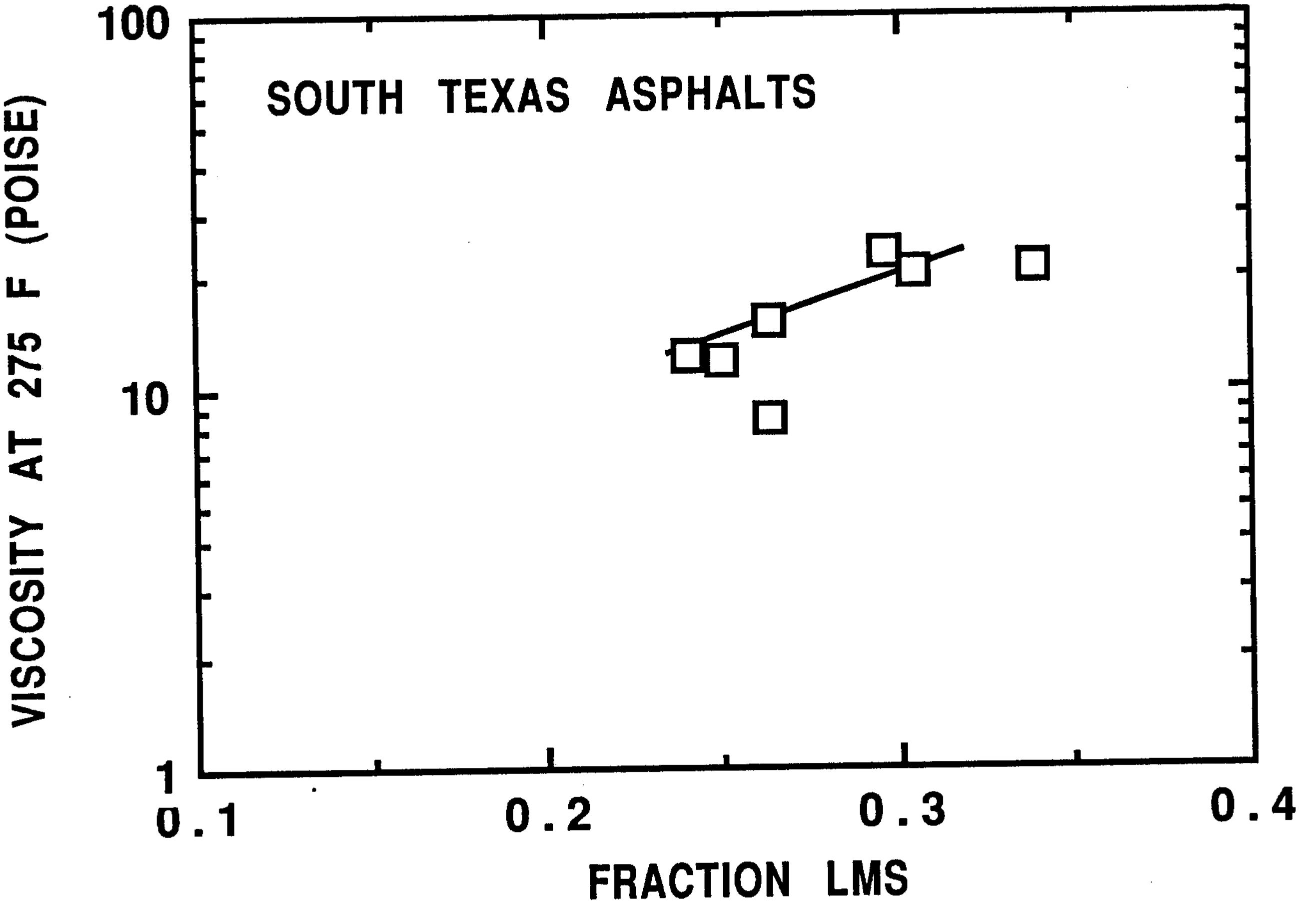


Figure IV-1-17
Viscosity at 275°F Versus GPC LMS Fractions for Asphalts from the South Texas Highway Cores

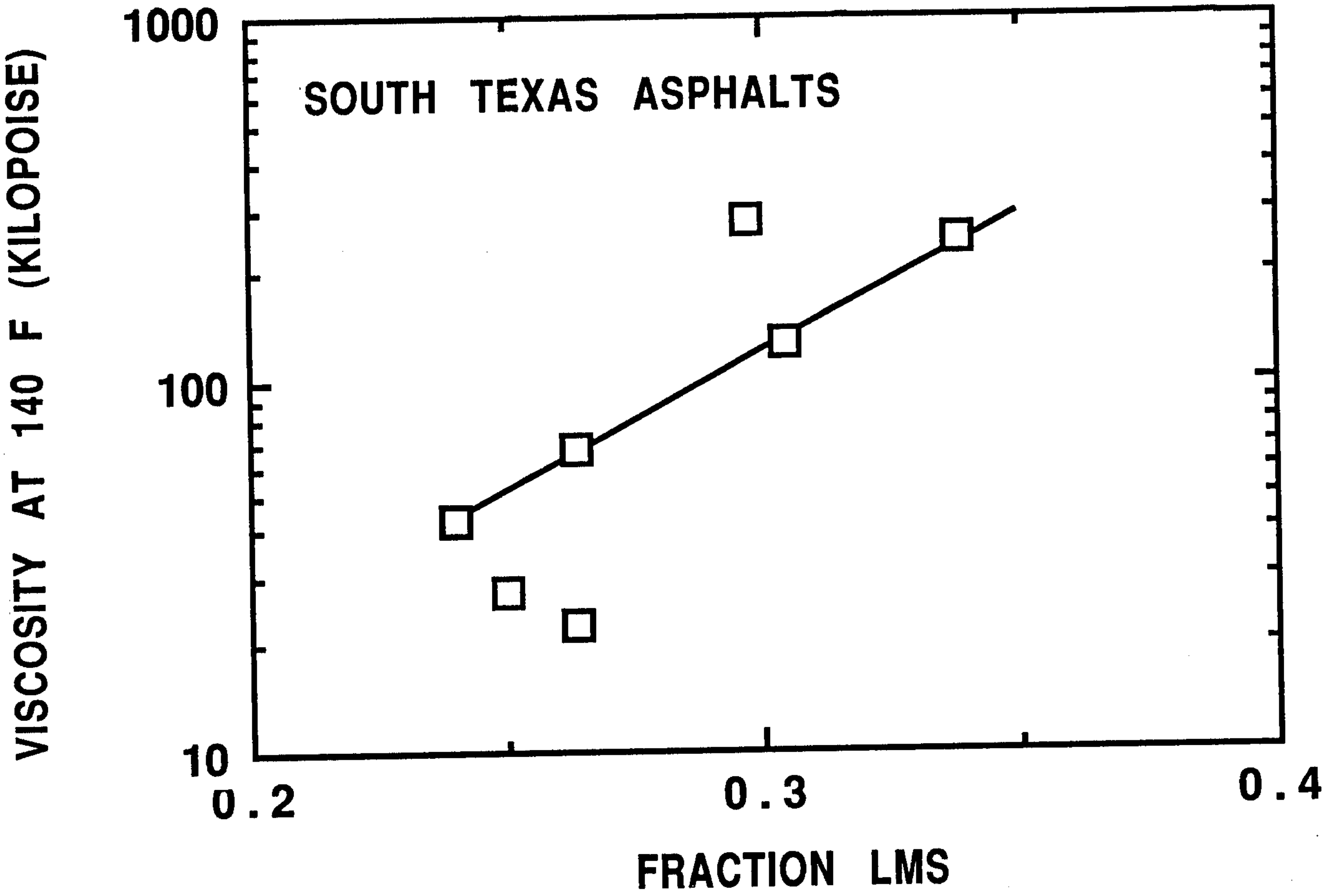


Figure IV-1-18
Viscosity at 140°F Versus GPC LMS Fractions for Asphalts from the South Texas Highway Cores

CHAPTER IV-2

HOT MIX AND OVEN COMPARISONS

Summary

Using a variety of tests, the interchangeability of the thin film oven test and the rolling thin film oven test is demonstrated. It is also shown that by most criteria for most asphalts, the hot-mix aging is more severe than the oven tests. The significance of the infrared spectra is discussed, as is a problem of fuel contamination of some hot-mix samples.

Introduction

Several hot-mix asphalt and corresponding tank asphalt samples were obtained from various locations in Texas. These mixes were extracted and their properties compared to those obtained from laboratory aging experiments. The samples were analyzed to determine the physical and chemical property differences between the hot-mix and oven tested versions.

The hot-mix asphalt samples were extracted from the aggregate using a modified ASTM D 2172 Method A, and the asphalt was recovered from the solvent by ASTM D 1856, using the modifications mentioned in Chapter 1 of this section and in Section III, Chapter 1. These procedures may introduce the largest amount of variability and error in the analysis due to the effects of solvent aging, volatiles' loss, and incomplete removal of the asphalt from the aggregate. These phenomena are discussed in Chapter III-1.

ASTM methods D 1754 and D 2872, the Thin Film Oven Test (TFOT) and the Rolling Thin Film Oven Test (RTFOT), respectively, were performed on the tank samples. The standard times as well as the extended times of 14.5 hours for the TFOT (ETFOT) and 3.5 hours for the RTFOT (ERTFOT) resulted in four oven-aged samples for each asphalt. The tank and oven-aged asphalts provided a range in which the extracted hot mix would fall and give an indication of the accuracy of the standard oven tests in predicting the chemical and physical properties of the hot mix.

Penetrations (ASTM D 5) and viscosities (ASTM D 2171) at 140°F and 275°F comprised the physical tests performed on the asphalt samples. The chemical characterization techniques consisted of Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FT-IR). The GPC gives a molecular size distribution, while the FT-IR provides an indication of the chemical functional groups that are present. These methods show significant changes in the chemical properties during the oven tests and hot-mix process that coincide with the physical property results. The GPC and FT-IR methods are described in detail in Section II.

Chromatograms obtained from the GPC show the shifts in molecular size associated with the oxidative aging of the asphalt. The average molecular size increases with aging and can be measured by calculating the percent large molecular size (%LMS) by determining the percent area of the chromatogram eluting before 25 minutes. Some hot-mix samples gave chromatograms which not only differ in molecular size, but also show significantly different shapes. This cannot be easily explained, and apparently no amount of oven aging can reproduce the shapes of some hot mixes.

The spectra obtained from the FT-IR indicate a definite increase in carbonyl absorption with oxidative aging. The amount of carbonyl absorption was measured by calculating the area under the curve given by the spectra in the carbonyl region. Changes also occur in regions representing increases in carbon-oxygen bonds. The sulfoxide absorbance area is of interest, but it could be masked by the presence of micron size dust and aggregate particles whose silicon oxide bands absorb at approximately the same location. This could be the cause of the radically different absorbance of some hot mixes in the sulfoxide region compared to the oven tests. Throughout the rest of the spectrum, however, the changes in chemical compositions attributed to the hot-mix procedure seemed to be proportional to the changes resulting in the oven tests.

Results

Nine different hot-mix asphalts were analyzed with the corresponding oven tests and tank samples. The standard TFOT and RTFOT methods were compared for each asphalt to determine the interchangeability of the tests. These standard oven tests were also compared with the hot-mix results to determine their validity. The six variables of penetration at 77°F, viscosity at 140°F, viscosity at 275°F, carbonyl area of infrared spectrum, percent LMS from the GPC, and the calculated VTS compare the chemical and physical properties of the samples. The differences or similarities of the values obtained by these methods indicate whether our hypotheses of the equality of the oven tests and the hot mix are correct. Complete GPC data and IR spectra are in Appendix C. A number of measured and derived parameters are given in Tables IV-2-1 and IV-2-2.

Oven Test Comparisons

The two oven tests are similar in design and the temperatures are identical. The RTFOT yields a more homogeneous product than the TFOT due to its constantly renewed surface. The exposure times of the tests differ significantly, with the RTFOT's shorter time being generally more desirable. Since these methods were designed to accomplish the identical task of simulating the changes of asphalt properties occurring during the hot-mix process, they would be expected to produce at least similar outputs with identical inputs.

The data in Table IV-2-1 and Figures IV-2-1 through IV-2-6 show that the TFOT and RTFOT chemical and physical properties are indeed comparable. The diagonal lines represent lines of equality on each plot. The plots of the viscosities at 275°F (135°C), the percent LMS, and the penetration values (Figures IV-2-1, 2 and 3 respectively) seem to characterize the RTFOT as being a slightly more severe aging test. Meanwhile, Figure IV-2-4 representing the viscosities at 140°F appear to indicate the TFOT as being more severe. These differences are small, however, and the carbonyl area and the VTS values shown in Figures IV-2-5 and -6 indicate that one test could not be considered different from the other.

Table IV-2-1

Properties of Hot-Mix Study Asphalts

Names	Asphalts	Penetration	Viscosity @ 60^0C	Viscosity @ 135^0C	%LMS	Carbonyl	VTS
AMPET AC-20 1989	Tank	69.7	1835	3.91	15.7	0.392	3.49
	RTFOT	47.3	3287	4.58	18.2	0.445	3.59
	TFOT	47.9	3100	4.61	18.0	0.493	3.56
	Hot Mix	28.7	4792	5.75	20.0	0.703	3.56
	ERTFOT	35.0	5437	5.60	20.8	0.553	3.62
	ETFOT	29.7	7533	6.73	22.0	0.695	3.60
COASTAL AC-20 1987	Tank	57.7	1998	4.19	19.4	0.522	3.47
	RTFOT	39.2	5722	6.58	23.2	0.607	3.52
	TFOT	41.1	5374	6.33	22.0	0.614	3.52
	Hot Mix	32.1	9227	6.83	26.2	0.763	3.66
	ERTFOT	29.5	15644	12.05	25.8	0.739	3.44
	ETFOT	27.1	27095	9.64	26.5	0.828	3.78
COSDEN AC-10 1989	Tank	89.0	970	2.61	11.4	0.364	3.57
	RTFOT	47.0	2571	3.33	15.2	0.488	3.76
	TFOT	50.7	2193	3.18	14.3	0.462	3.73
	Hot Mix	27.5	9854	4.40	19.7	0.894	4.03
	ERTFOT	27.0	7442	6.39	19.1	0.679	3.64
	ETFOT	29.0	7078	4.94	18.6	0.773	3.82
COSDEN AC-20 1989	Tank	76.7	2061	3.85	26.3	0.497	3.55
	RTFOT	46.0	5763	5.96	29.6	0.624	3.60
	TFOT	50.5	4695	5.25	28.6	0.605	3.62

Table IV-2-1 (Cont'd)

Properties of Hot-Mix Study Asphalts

Names	Asphalts	Penetration	Viscosity @ 60^{0}C	Viscosity @ 135^{0}C	%LMS	Carbonyl	VTS
COSDEN	Hot Mix	47.0	5945	4.98	29.7	0.751	3.75
AC-20	ERTFOT	33.2	12533	7.94	32.5	0.788	3.66
(Cont'd)	ETFOT	32.7	16620	8.80	32.8	0.793	3.68
EXXON	Tank	61.2	1974	3.64	13.4	0.450	3.58
AC-20 1987	RTFOT	38.8	4372	4.91	15.9	0.544	3.64
BATCH #2	TFOT	38.0	4195	5.02	15.2	0.552	3.61
	Hot Mix	45.9	3304	4.13	18.3	0.571	3.68
	ERTFOT	26.4	8539	6.58	18.5	0.641	3.66
	ETFOT	23.5	11347	7.82	19.6	0.760	3.64
EXXON	Tank	62.8	1809	3.12	10.9	0.377	3.67
AC-20 1987	RTFOT	46.6	2846	3.76	13.1	0.500	3.70
BATCH	TFOT	49.6	3004	3.68	13.0	0.517	3.74
	Hot Mix	41.8	2902	4.02	15.6	0.521	3.65
	ERTFOT	31.8	5056	4.69	15.6	0.607	3.74
	ETFOT	31.1	6564	5.24	16.6	0.715	3.74
EXXON	Tank	64.6	1864	3.43	10.9	0.421	3.60
AC-20 1988	RTFOT	47.6	3203	4.22	13.4	0.469	3.65
	TFOT	47.5	3204	4.28	13.3	0.517	3.64
	Hot Mix	46.6	3615	4.29	16.9	0.683	3.68
	ERTFOT	34.6	5733	5.51	15.9	0.601	3.66
	ETFOT	31.8	7529	6.17	17.1	0.721	3.67

Table IV-2-1 (Cont'd)

Properties of Hot-Mix Study Asphalt

Names	Asphalts	Penetration	Viscosity @ 60^{0}C	Viscosity @ 135^{0}C	%LMS	Carbonyl	VTS
TEXACO AC-20 1989	Tank	86.6	2070	4.24	19.3	0.411	3.47
	RTFOT	58.4	4372	5.66	21.7	0.460	3.53
	TFOT	52.0	4646	5.70	21.8	0.490	3.55
	Hot Mix	44.7	5547	6.23	23.8	0.543	3.55
	ERTFOT	39.1	9651	7.60	24.3	0.569	3.60
	ETFOT	40.4	13678	8.77	25.0	0.641	3.62
TEXAS GULF AC-20 1989	Tank	78.4	2209	3.58	16.5	0.472	3.64
	RTFOT	40.1	6496	5.39	19.7	0.578	3.72
	TFOT	47.1	5610	5.00	19.2	0.583	3.72
	Hot Mix	34.8	8607	5.99	21.4	0.653	3.74
	ERTFOT	29.3	18902	7.68	22.2	0.710	3.83
	ETFOT	28.9	29344	9.07	23.6	0.830	3.85

Table IV-2-2

Derived Correlating Parameters from Hot-Mix Study Asphalts

Names	Asphalts	Pen Index	Viscosity Index @ 60^{0}C	Viscosity Index @ 135^{0}C	Carbonyl Index	Carbonyl Difference	LMS Area
AMPET	Tank	1.000	1.00	1.00	1.00	0.000	85.56
AC-20 1989	RTFOT	0.679	1.79	1.17	1.14	0.053	--
	TFOT	0.687	1.69	1.18	1.26	0.101	94.07
	Hot Mix	0.412	2.61	1.47	1.79	0.311	109.92
	ERTFOT	0.502	2.96	1.43	1.41	0.161	--
	ETFOT	0.426	4.10	1.72	1.71	0.303	114.10
COASTAL	Tank	1.000	1.00	1.00	1.00	0.000	97.92
AC-20 1987	RTFOT	0.679	2.86	1.57	1.16	0.085	--
	TFOT	0.712	2.69	1.51	1.18	0.092	123.17
	Hot Mix	0.556	4.62	1.63	1.46	0.241	144.75
	ERTFOT	0.511	7.83	2.88	1.42	0.217	--
	ETFOT	0.470	13.56	2.3	1.59	0.306	141.61
COSDEN	Tank	1.000	1.00	1.00	1.00	0.000	60.36
AC-10 1989	RTFOT	0.528	2.65	1.28	1.34	0.124	--
	TFOT	0.570	2.26	1.22	1.27	0.098	76.22
	Hot Mix	0.309	10.16	1.68	2.46	0.530	110.75
	ERTFOT	0.303	7.67	2.45	1.86	0.315	--
	ETFOT	0.326	7.30	1.89	2.12	0.409	96.66

Table IV-2-2 (Cont'd)

Derived Correlating Parameters from Hot-Mix Study Asphalts

Names	Asphalts	Pen Index	Viscosity Index @ 60°C	Viscosity Index @ 135°C	Carbonyl Index	Carbonyl Difference	LMS Area
COSDEN	Tank	1.000	1.00	1.00	1.00	0.000	141.90
AC-20 1989	RTFOT	0.600	2.80	1.55	1.26	0.127	--
	TFOT	0.658	2.28	1.36	1.22	0.108	154.33
	Hot Mix	0.613	2.88	1.29	1.51	0.254	165.59
	ERTFOT	0.433	6.08	2.06	1.59	0.291	--
	ETFOT	0.426	8.06	2.28	1.60	0.296	190.51
EXXON	Tank	1.000	1.00	1.00	1.00	0.000	77.46
AC-20 1987 #2	RTFOT	0.634	2.22	1.35	1.21	0.094	--
	TFOT	0.621	2.12	1.38	1.23	0.102	81.74
	Hot Mix	0.750	4.67	1.14	1.27	0.121	104.16
	ERTFOT	0.431	4.33	1.81	1.42	0.191	--
	ETFOT	0.384	5.75	2.15	1.69	0.310	98.76
EXXON	Tank	1.000	1.00	1.00	1.00	0.000	58.92
AC-20 1987	RTFOT	0.742	1.57	1.20	1.33	0.123	--
BATCH	TFOT	0.790	1.66	1.18	1.37	0.140	66.06
	Hot Mix	0.666	1.60	1.29	1.38	0.144	88.60
	ERTFOT	0.506	2.80	1.50	1.61	0.230	--
	ETFOT	0.495	3.63	1.68	1.90	0.338	83.85

Table IV-2-2 (Cont'd)

Derived Correlating Parameters from Hot-Mix Study Asphalts

Names	Asphalts	Pen Index	Viscosity Index @ 60^{0}C	Viscosity Index @ 135^{0}C	Carbonyl Index	Carbonyl Difference	LMS Area
EXXON	Tank	1.000	1.00	1.00	1.00	0.000	60.30
AC-20 1988	RTFOT	0.737	1.72	1.23	1.11	0.048	--
	TFOT	0.735	1.72	1.25	1.23	0.096	72.24
	Hot Mix	0.718	1.94	1.25	1.62	0.262	89.44
	ERTFOT	0.536	3.08	1.61	1.43	0.180	--
	ETFOT	0.492	4.04	1.80	1.71	0.300	87.25
TEXACO	Tank	1.000	1.00	1.00	1.00	0.000	99.12
AC-20 1989	RTFOT	0.674	2.11	1.33	1.12	0.049	--
	TFOT	0.600	2.24	1.34	1.19	0.079	110.77
	Hot Mix	0.516	2.68	1.47	1.32	0.132	110.77
	ERTFOT	0.452	4.66	1.79	1.38	0.158	--
	ETFOT	0.467	6.61	2.07	1.56	0.230	124.12
TEXAS GULF	Tank	1.000	1.00	1.00	1.00	0.000	89.40
AC-20 1989	RTFOT	0.511	2.94	1.51	1.22	0.106	--
	TFOT	0.601	2.54	1.40	1.24	0.111	100.78
	Hot Mix	0.444	3.90	1.67	1.38	0.181	100.09
	ERTFOT	0.374	8.56	2.14	1.50	0.238	--
	ETFOT	0.369	13.28	2.53	1.76	0.358	118.72

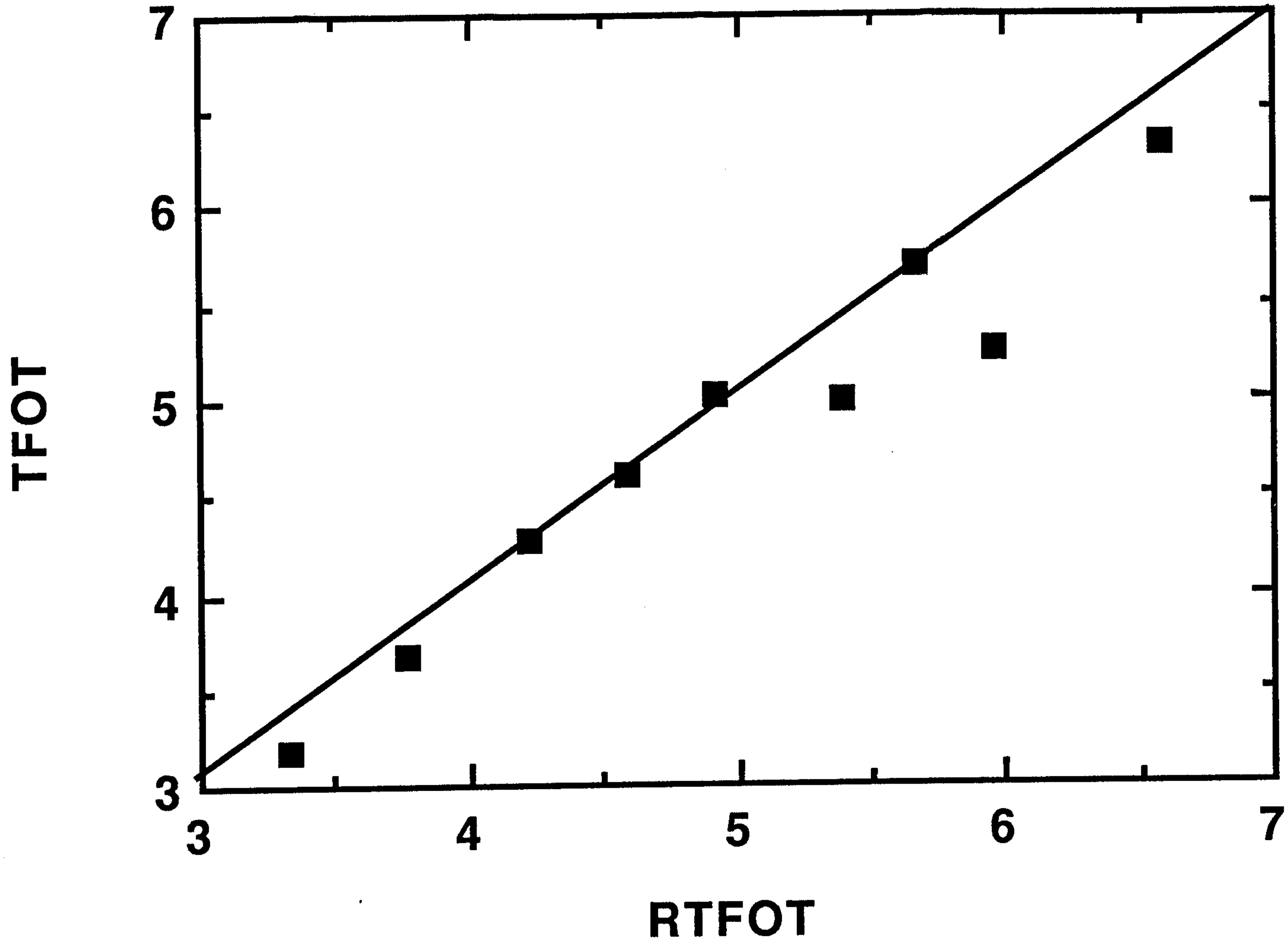


Figure IV-2-1
Comparisons of TFOT and RTFOT Viscosity at 135°C

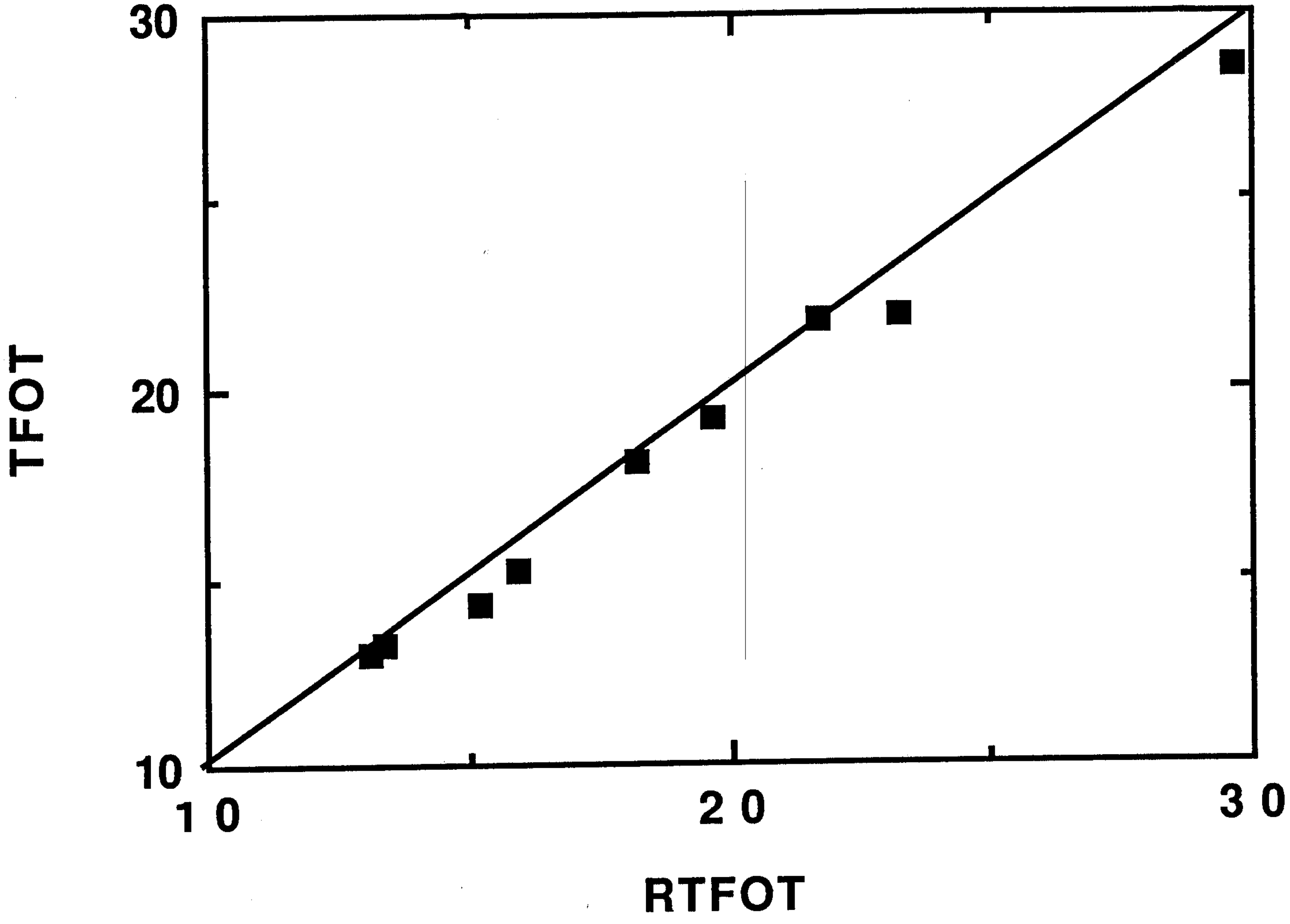


Figure IV-2-2
Comparison of %LMS for TFOT and RTFOT Aged Asphalts

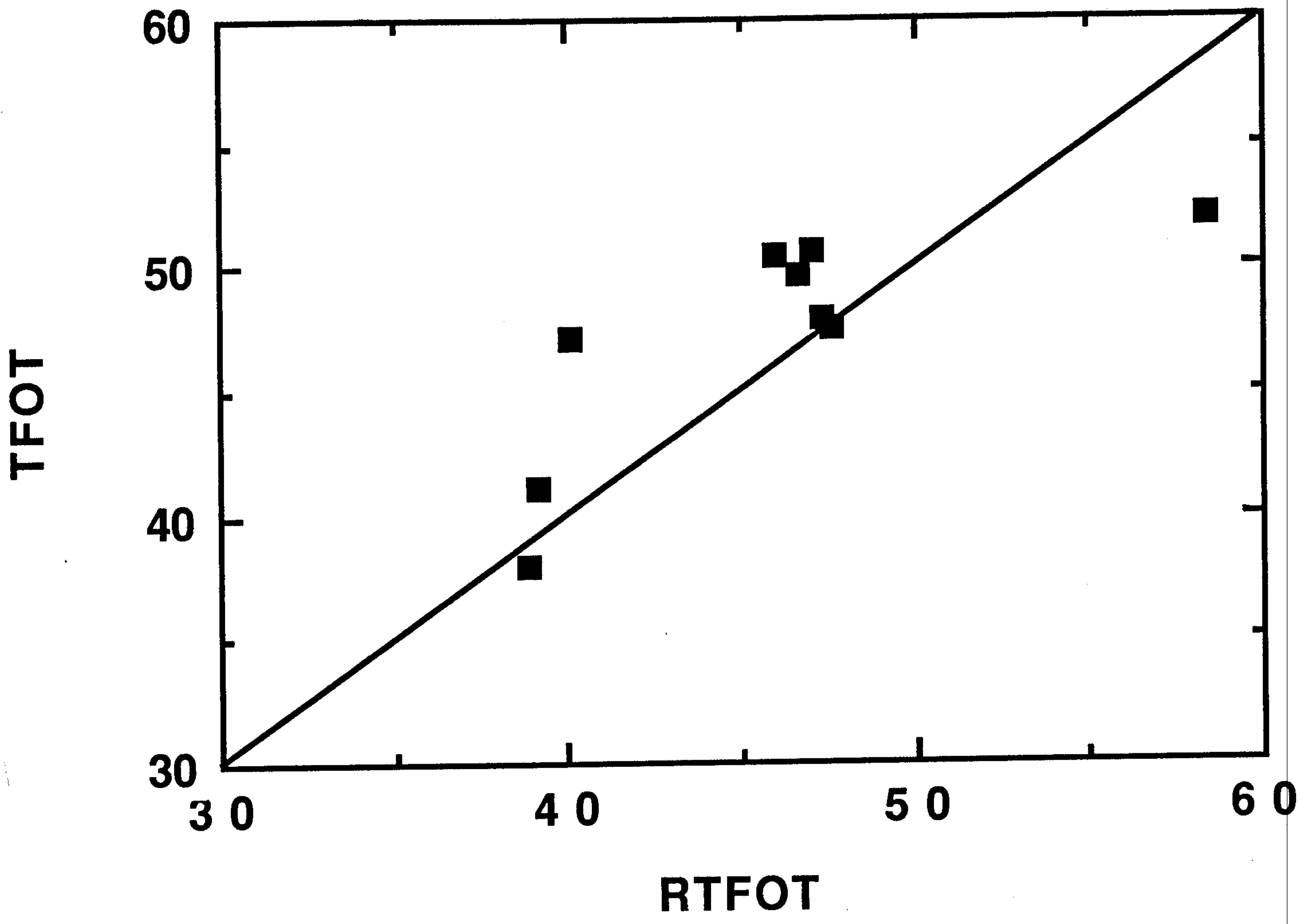


Figure IV-2-3
Comparison of the Penetrations of TFOT and RTFOT Aged Asphalts

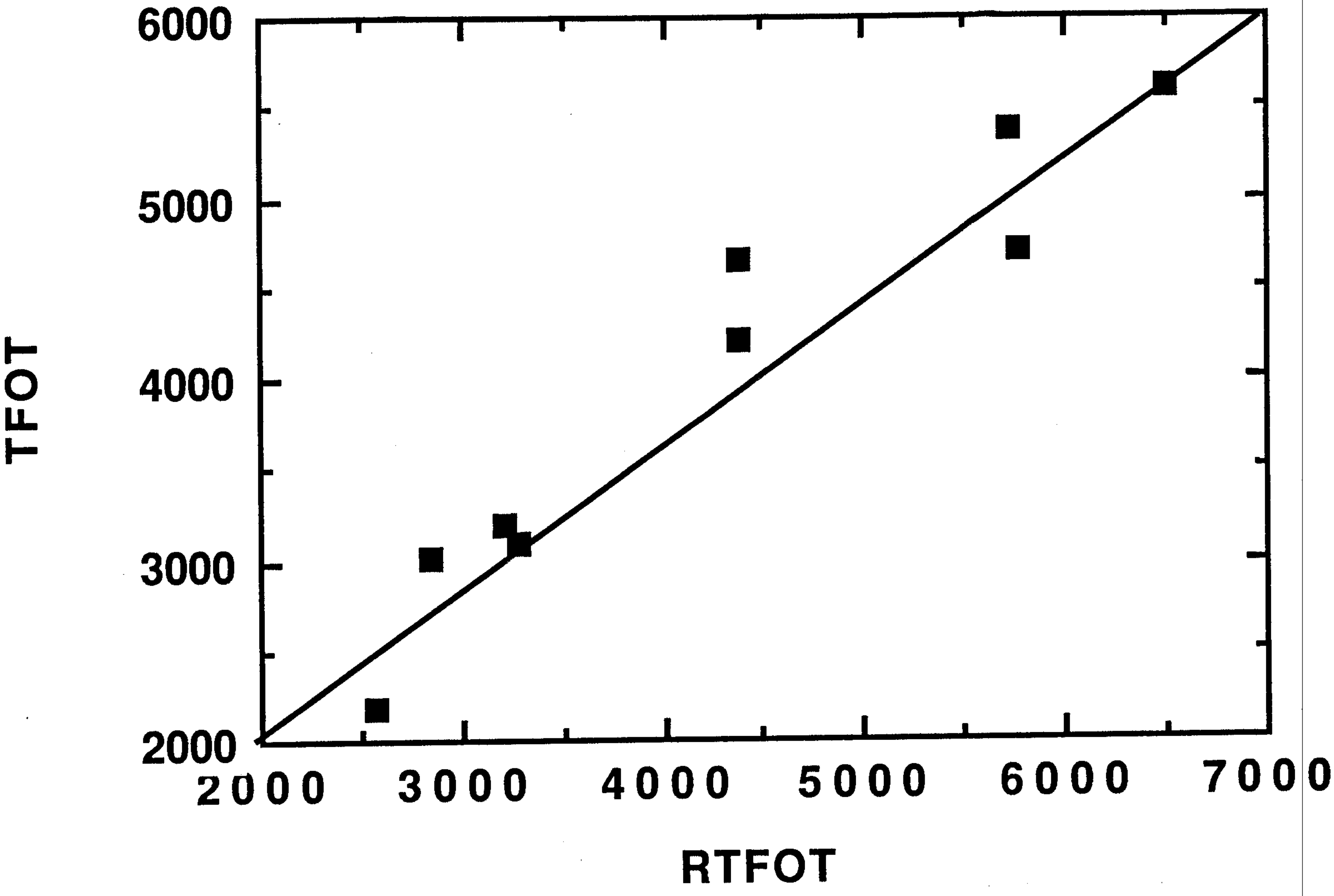


Figure IV-2-4
Comparison of the 60°C Viscosities of TFOT and RTFOT Aged Asphalts

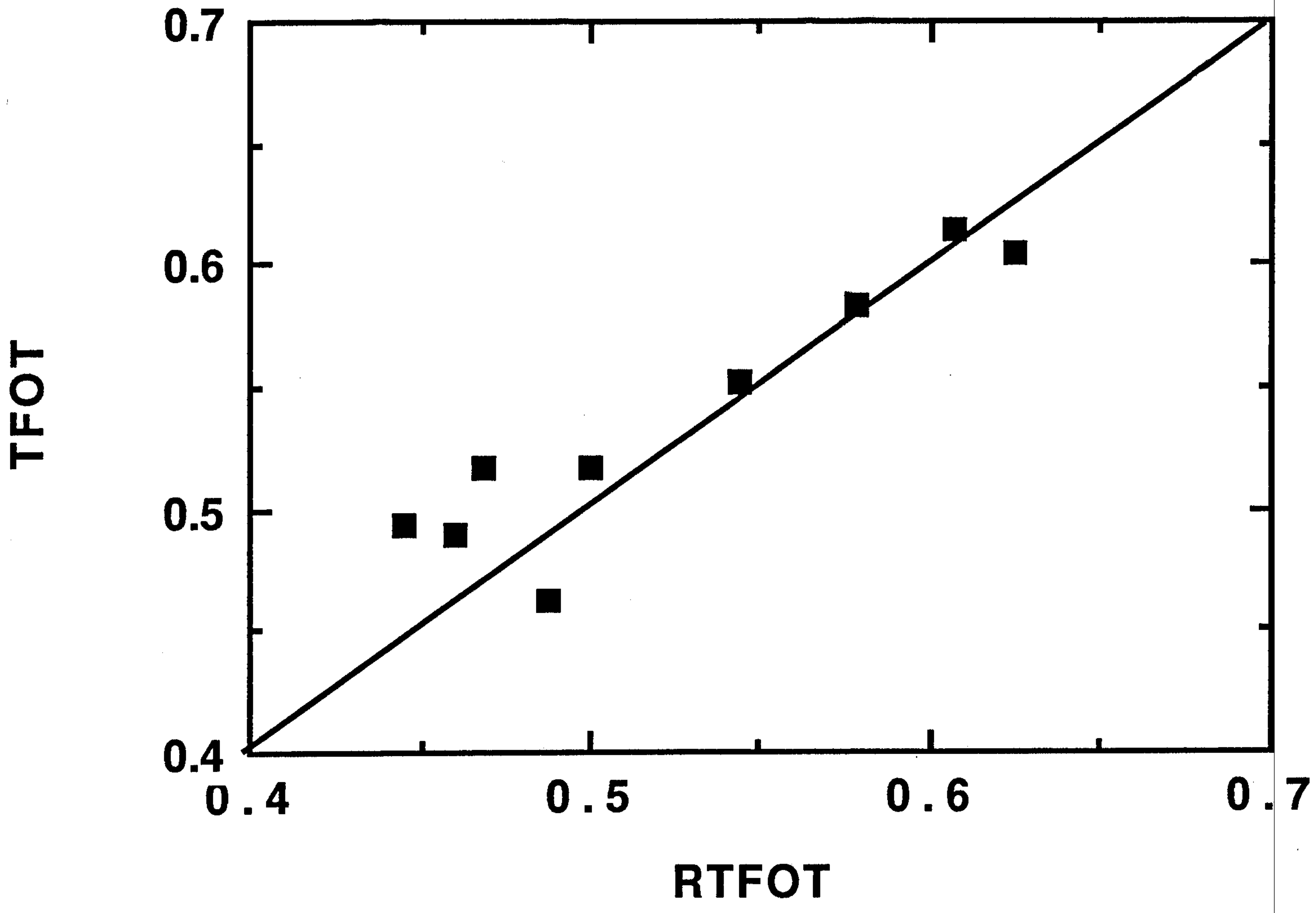


Figure IV-2-5
A Comparison of the Carbonyl Areas of the IR Spectra of
TFOT and RTFOT Aged Asphalts

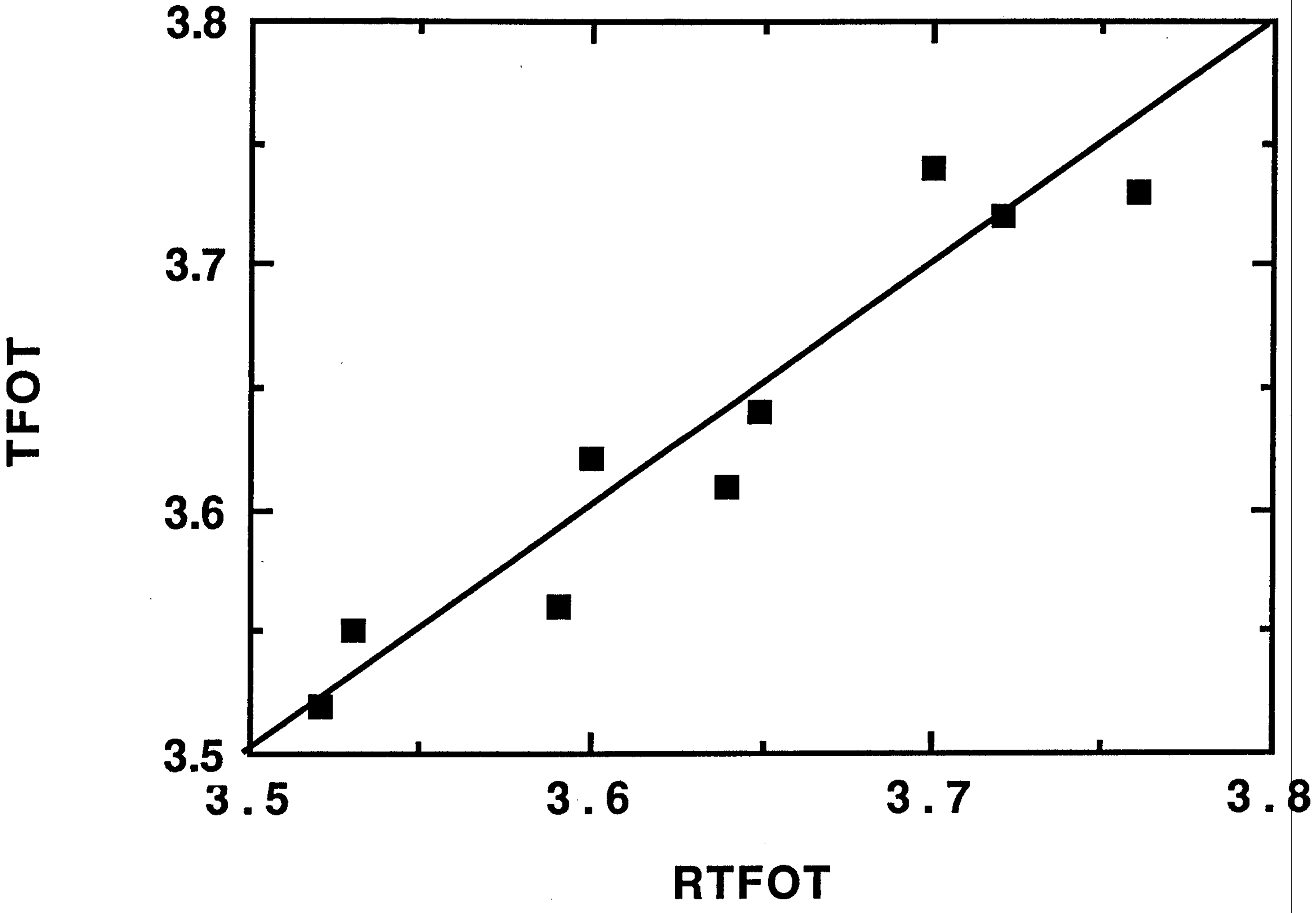


Figure IV-2-6
Comparison of the Viscosity Temperature Susceptibility
of TFOT and RTFOT Aged Asphalts

Figure IV-2-7 shows the identical GPCs for the two oven tests with Ampet AC-20, and as shown later, Figure IV-2-15 exhibits almost identical IR spectra for both tests with the Cosden AC-20. Other comparisons may be made from the data in Table IV-2-1 and the chromatograms and spectra in Appendix C.

Considering the inherent error in the oven tests and analysis techniques and the variability of asphalt samples, the apparent differences between the two oven tests are small if not insignificant. Indeed, their possible subtle differences do not warrant the use of both tests. Therefore, it is concluded that the TFOT and RTFOT methods are interchangeable and cannot be considered independent.

Hot Mix and Oven Test Comparisons

For many years the TFOT and RTFOT have been used to simulate and predict the chemical and physical changes of asphalt during the hot-mix process. This report clarifies that some of the methods used in the process to determine the validity of the hot mix simulations introduce error that may give misleading results. Examples of these errors include solvent aging and insufficient removal of the asphalt from the aggregate during the extraction, as well as incomplete solvent removal and volatiles loss during the recovery. More research is needed to handle these problems. Results may need to be simply corrected if some problems are not practically soluble. It is important, however, that we recognize the error inherent in the extraction and recovery, along with the anticipated error introduced by the different hot-mix plant types, fuels, and operating conditions. The same variables used to compare the oven tests are used to investigate the hot-mix performance.

The hot-mix data are considerably more scattered due at least in part to the previously mentioned error contributions. Figures IV-2-8 through IV-2-13 show that the hot-mix and oven test data fail to support the strong linear relationship that the oven test comparisons exhibit. Only the percent LMS, Figure III-2-13, shows linear variation, but it is displaced to higher hot-mix values. Some of this may be solvent aging as shown in Section III, Chapter 2. Also percent LMS alone does not reflect all of the aging changes that occur in the GPC chromatograms, as may be seen by comparing the asphalt chromatograms in Appendix C. Consider the case of the

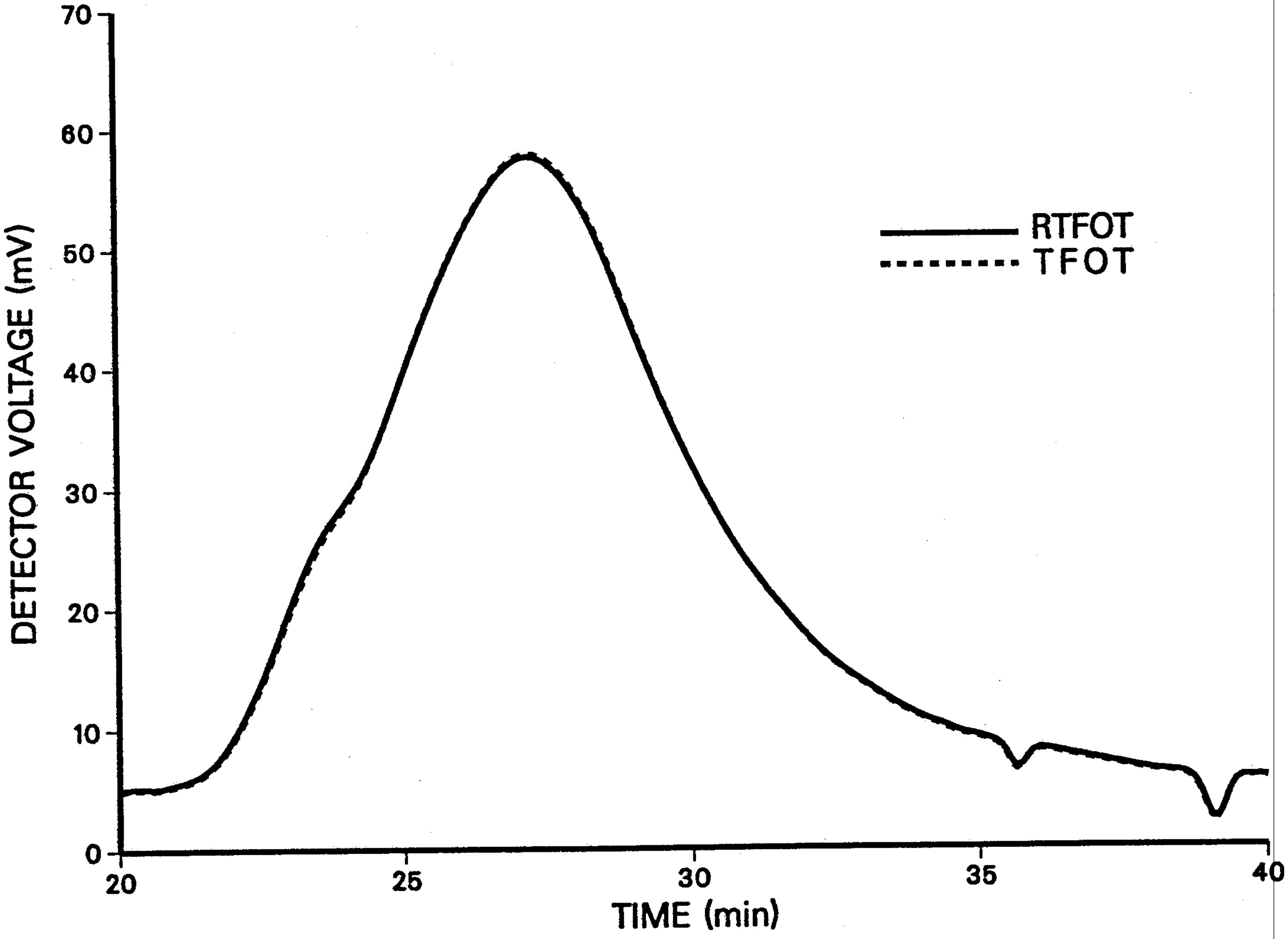


Figure IV-2-7
GPC Chromatograms for TFOT and RTFOT of 1989 AMPET AC-20

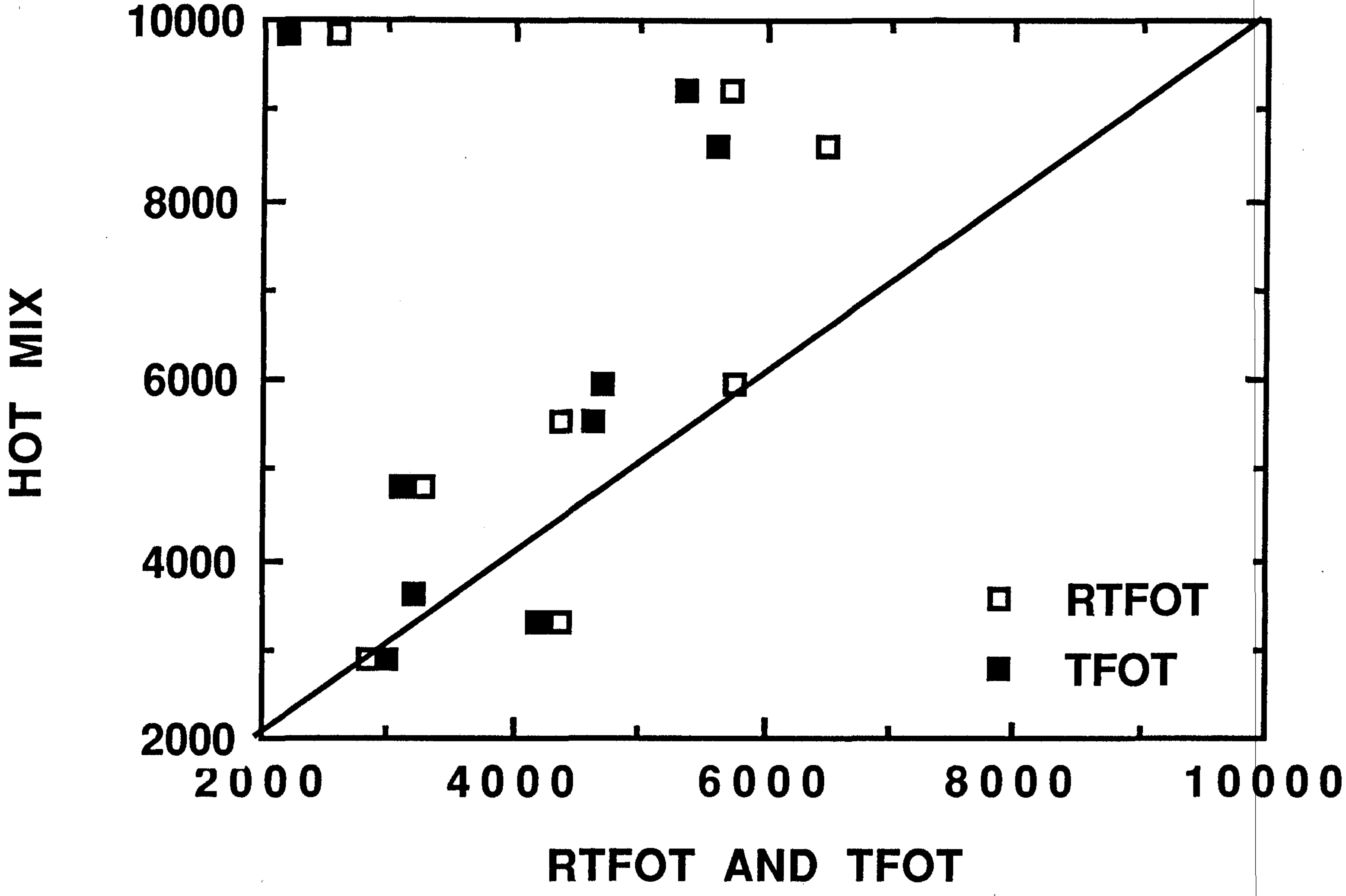


Figure IV-2-8
A Comparison of 60°C Viscosities of Hot-mix and Oven-aged Asphalts

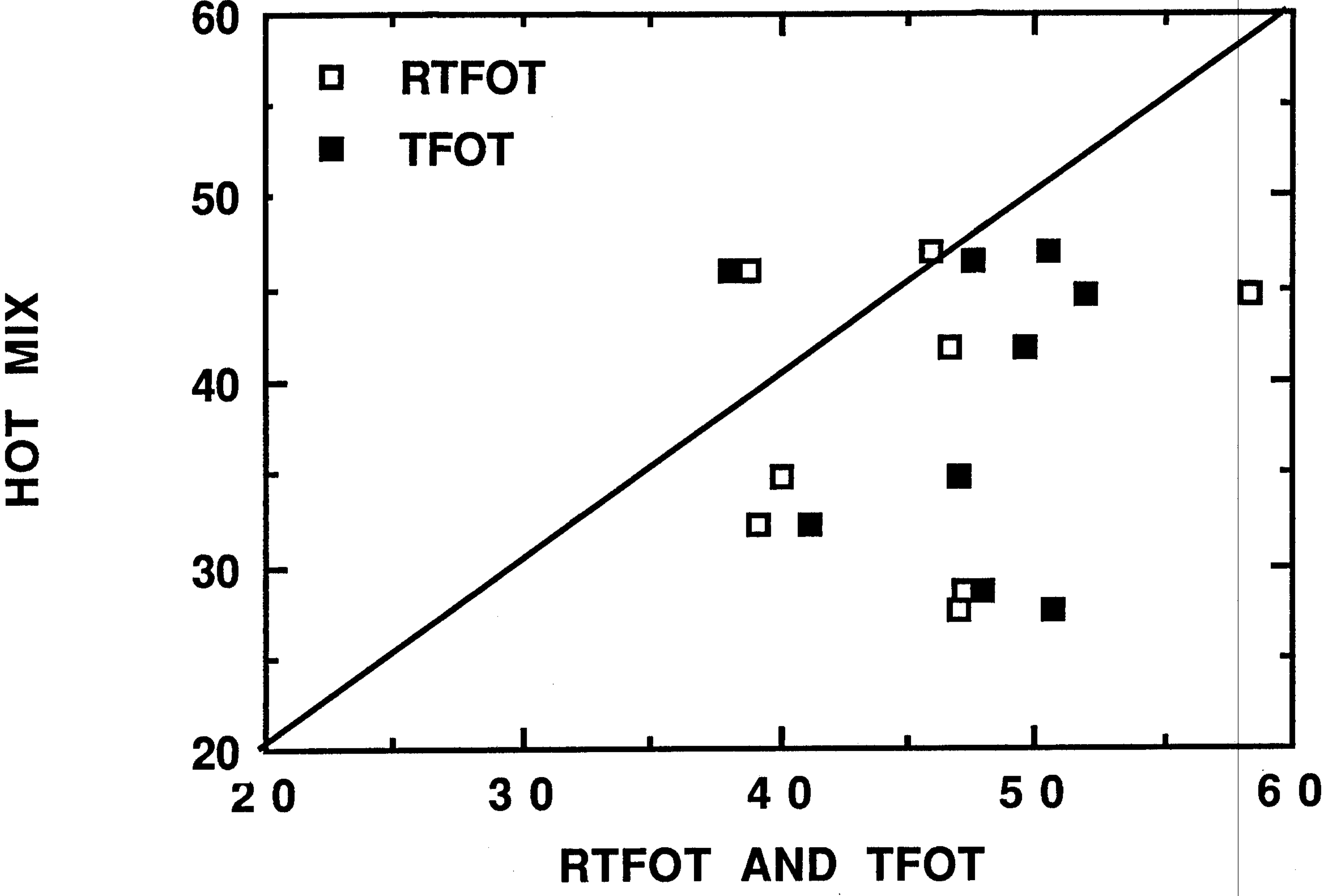


Figure IV-2-9
A Comparison of the Penetration of Hot-mix and Oven-aged Asphalt

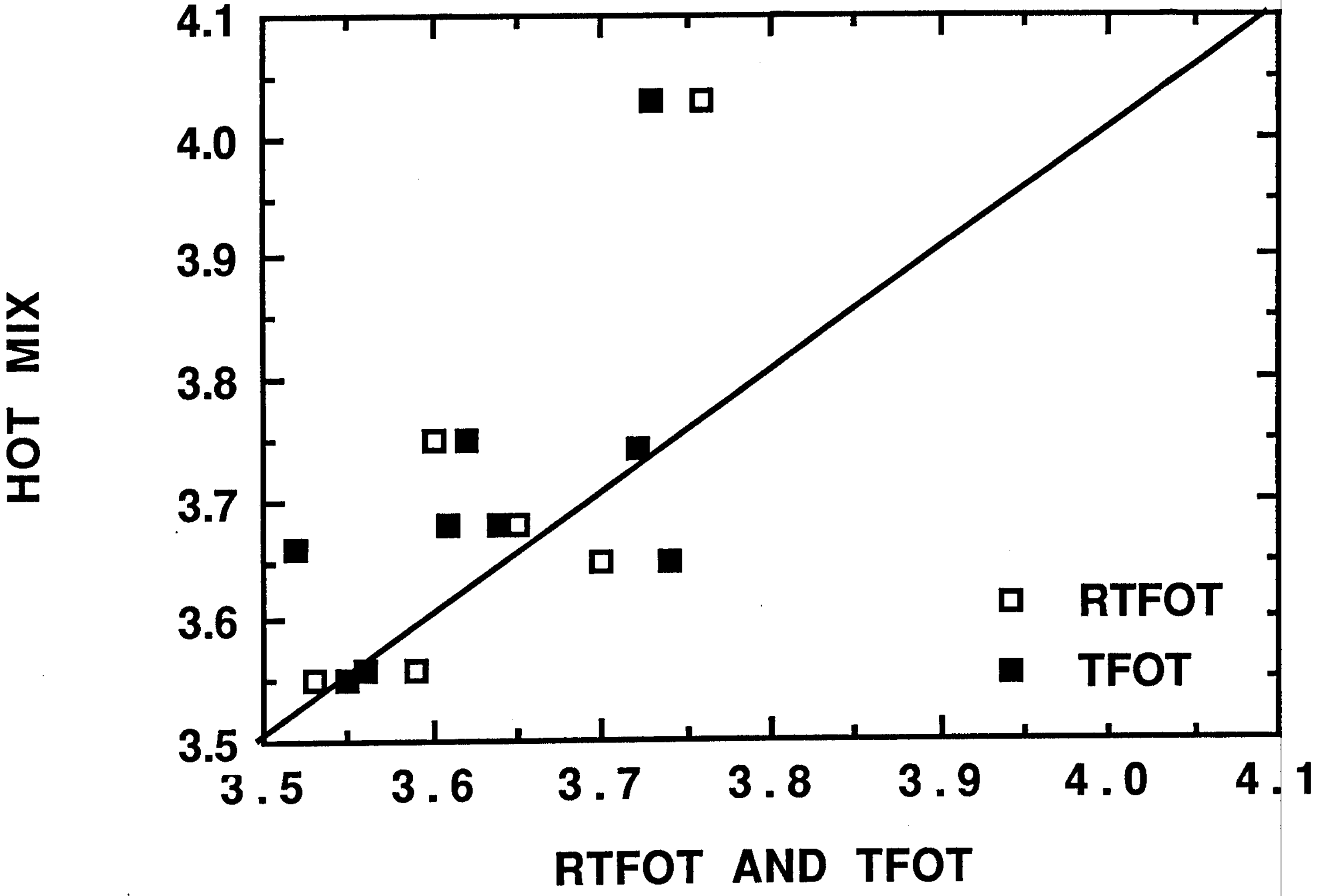


Figure IV-2-10
A Comparison of Viscosity Temperature Susceptibility of Hot-mix and Oven-aged Asphalt

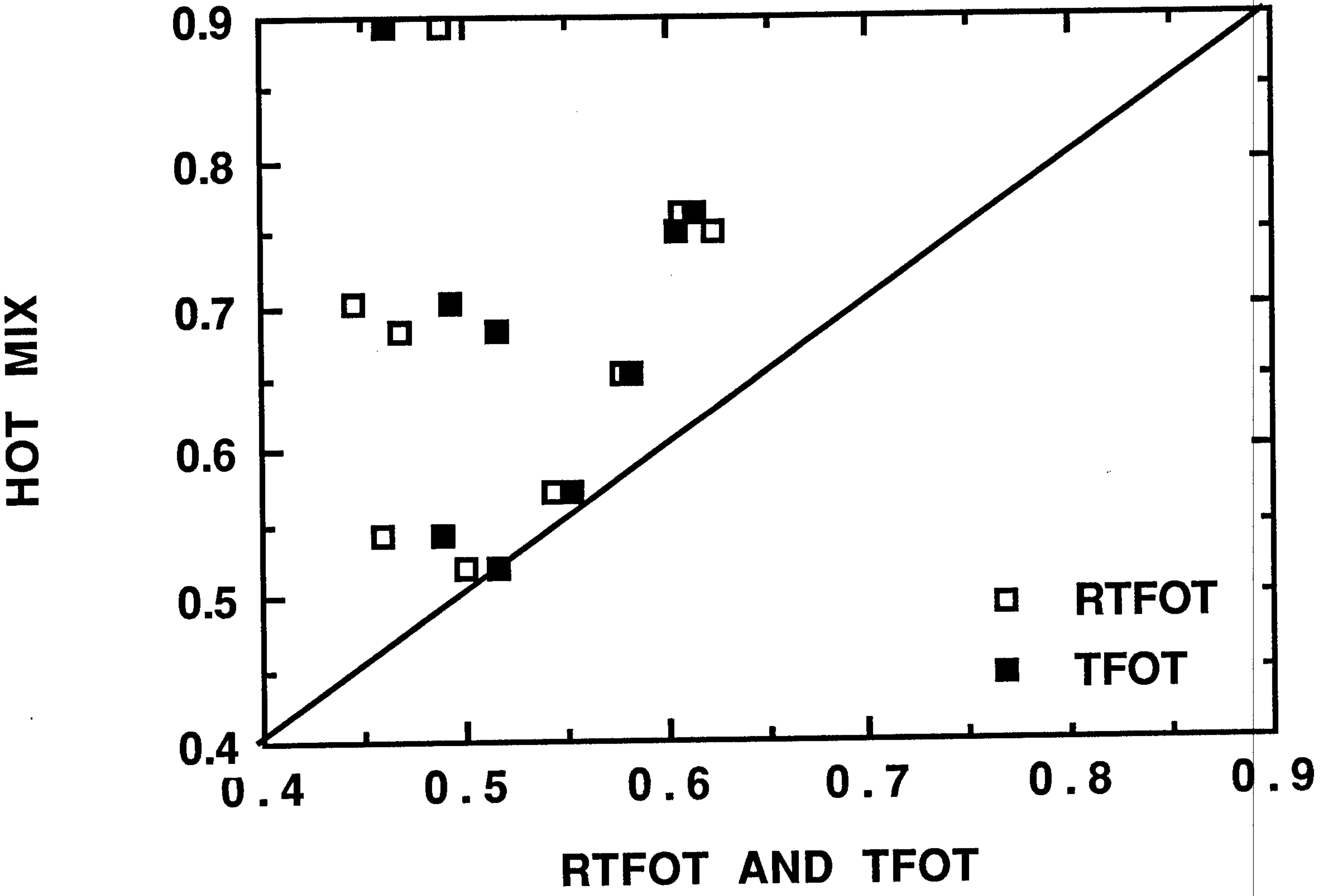


Figure IV-2-11
A Comparison of the IR Carbonyl Areas of Hot-mix
and Oven-aged Asphalt

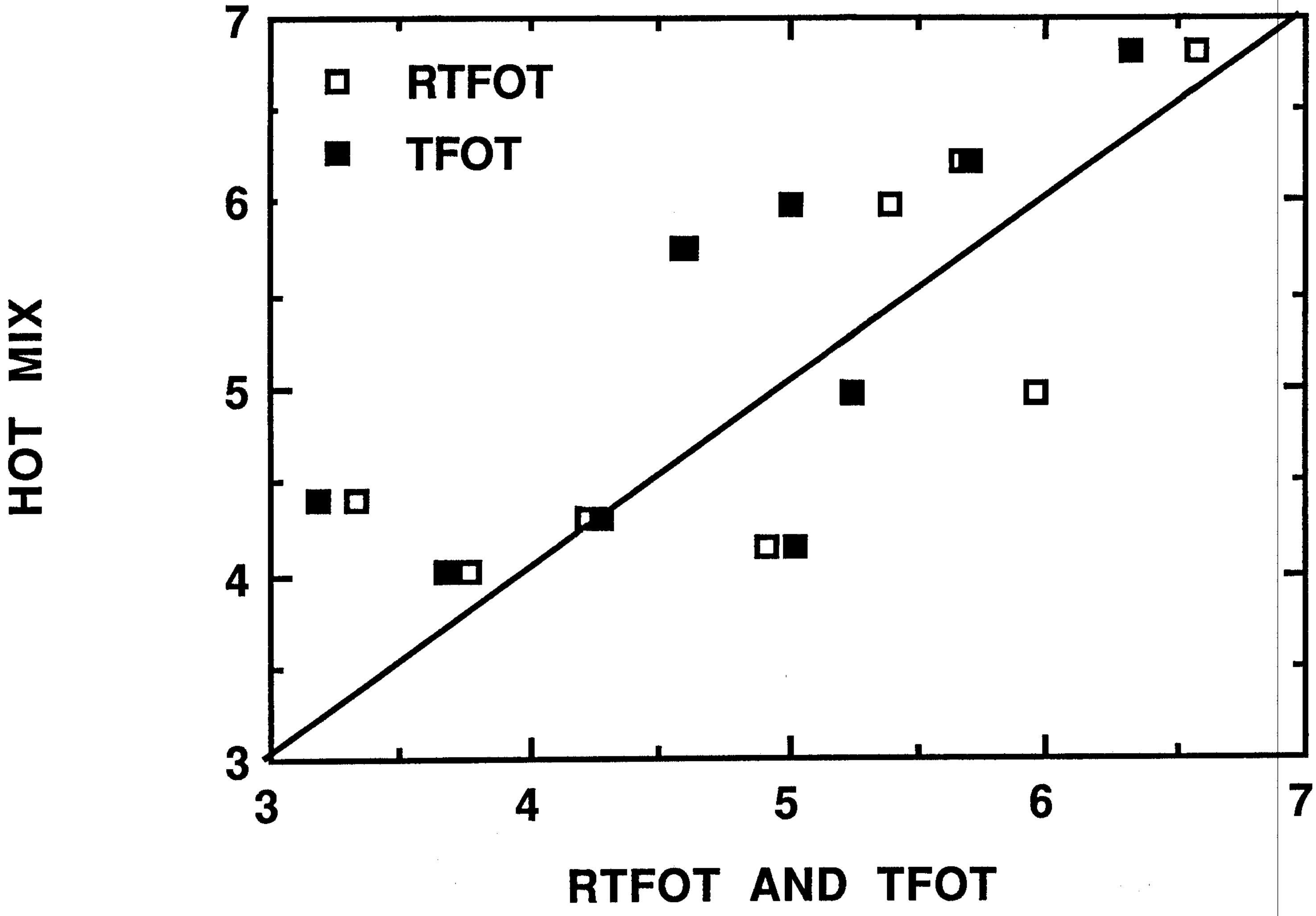


Figure IV-2-12
A Comparison of 135°C Viscosities of Hot-mix and Oven-aged Asphalt

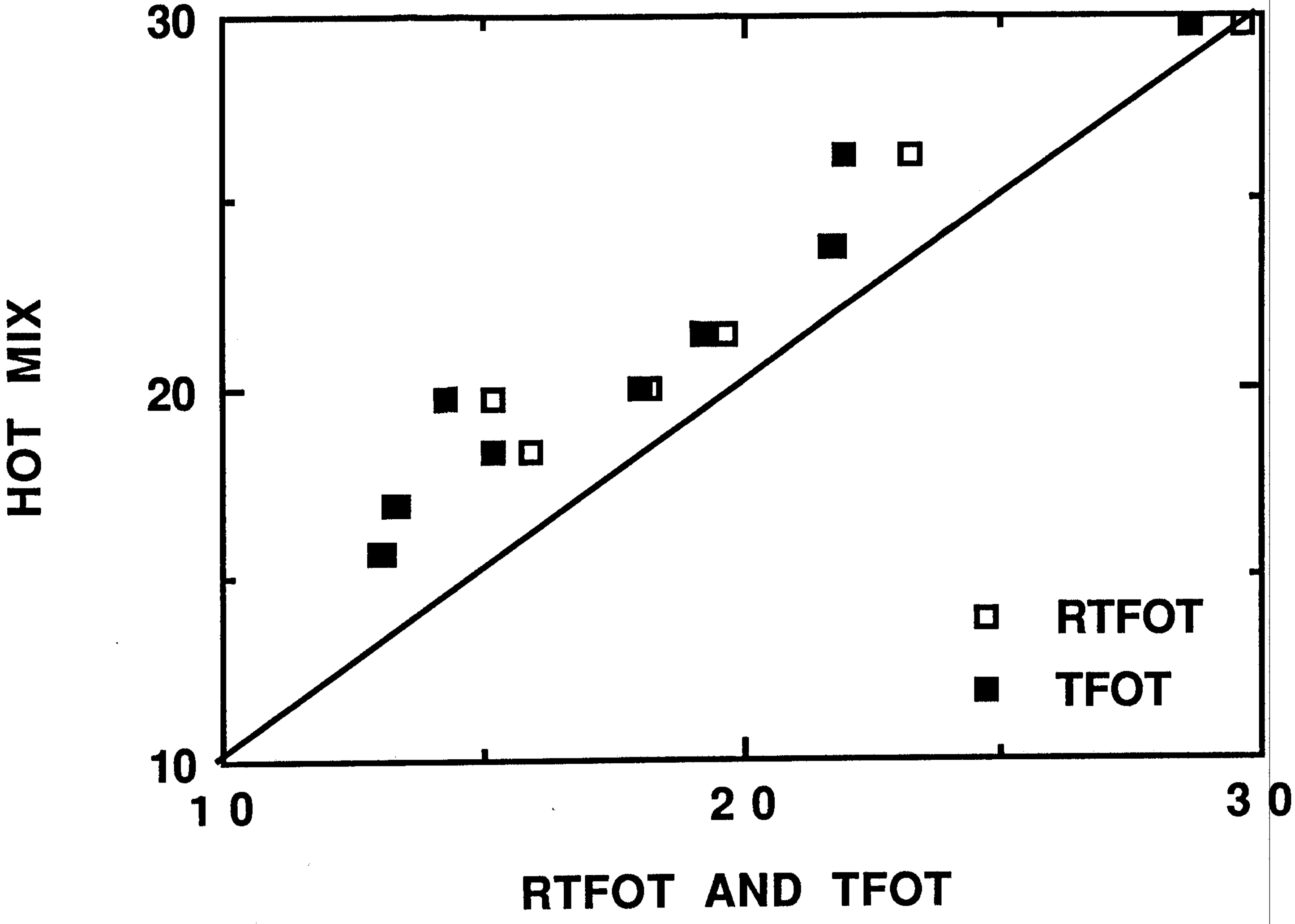


Figure IV-2-13
A Comparison of the %LMS for Hot-mix and Oven-aged Asphalts

Texaco AC-20. The data in Table IV-2-1 show that the percent LMS for the hot mix and the extended rolling film oven test are close, but in Figure IV-2-14 the chromatograms are seen to be quite different. The viscosity at 275°F (135°C), Figure IV-2-12, show less deviation than most but with considerable scatter. The plots of the parameters suggest that the hot-mix process is significantly more severe than either of the oven tests.

The IR spectra in Figures IV-2-15 to IV-2-17 and Appendix C are particularly instructive. In Figure IV-2-15 the good agreement of the oven tests and their gross disagreement with the hot mix is clearly evident with greater hot-mix aging across the spectrum. Figure IV-2-16 however, shows agreement in the carbonyl region between the standard oven test and the hot mix but gross divergence in the sulfoxide region. As mentioned earlier, some of this, at least, could be silica contamination, and this is supported by the sharp and unusual peak at about 900 which is probably carbonate. In Figure IV-2-17 we again see good agreement in the carbonyl region between the hot-mix and oven test, but in the sulfoxide region agreement is close between the ETFOT and the hot mix. The upper curve shows the great hardening for material that is not normally extracted and which is absent from the hot-mix spectra. If this material could be extracted with the rest, the divergence between oven tests and hot mix would be greater.

The data strongly indicate that the oven tests do not accurately predict the chemical and physical changes occurring in the asphalts during the hot-mix process. Some of the differences between the hot mix and oven tested asphalt can be attributed to the fact that the properties of the extracted asphalt are changed during the extraction and recovery processes. Leaving small amounts of asphalt on the aggregate during the extraction can affect the resulting bulk properties, because the asphalt closest to the aggregate surface tends to be more oxidized. Also, incomplete solvent removal from the asphalt during the recovery step will produce inaccurate results. These oversights can indicate a softer extracted asphalt than actually exists. The hot-mix properties may also be influenced by the source of the asphalt. In Figure IV-2-8 of the 140°F viscosities, the lowest three hot-mix values result from Exxon AC-20 asphalts, and the oven-test values coincide. For this asphalt, using the

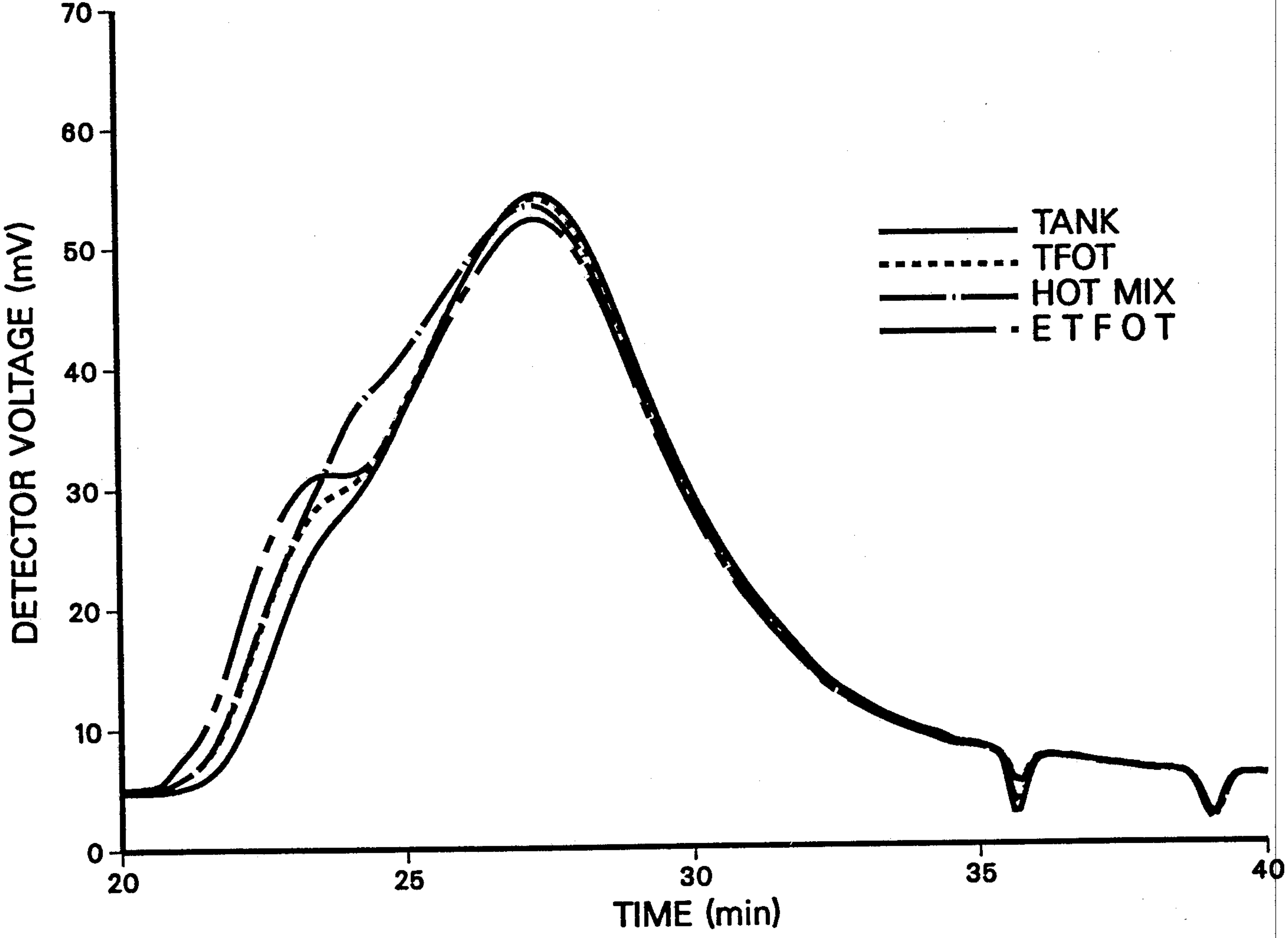


Figure IV-2-14
GPC Chromatograms of Tank, TFOT, ETFOT and Hot-mix - 1989 Texaco AC-20

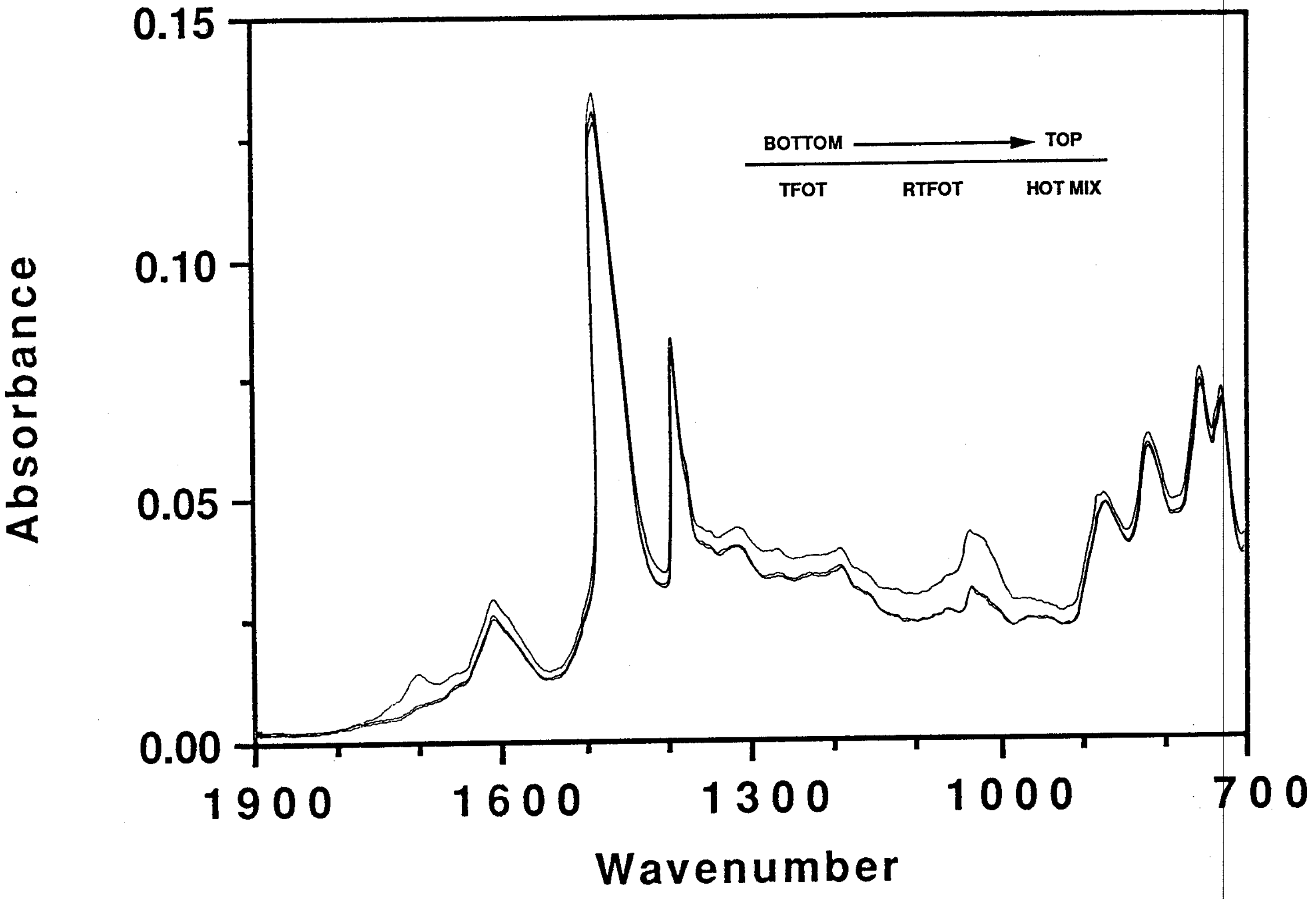
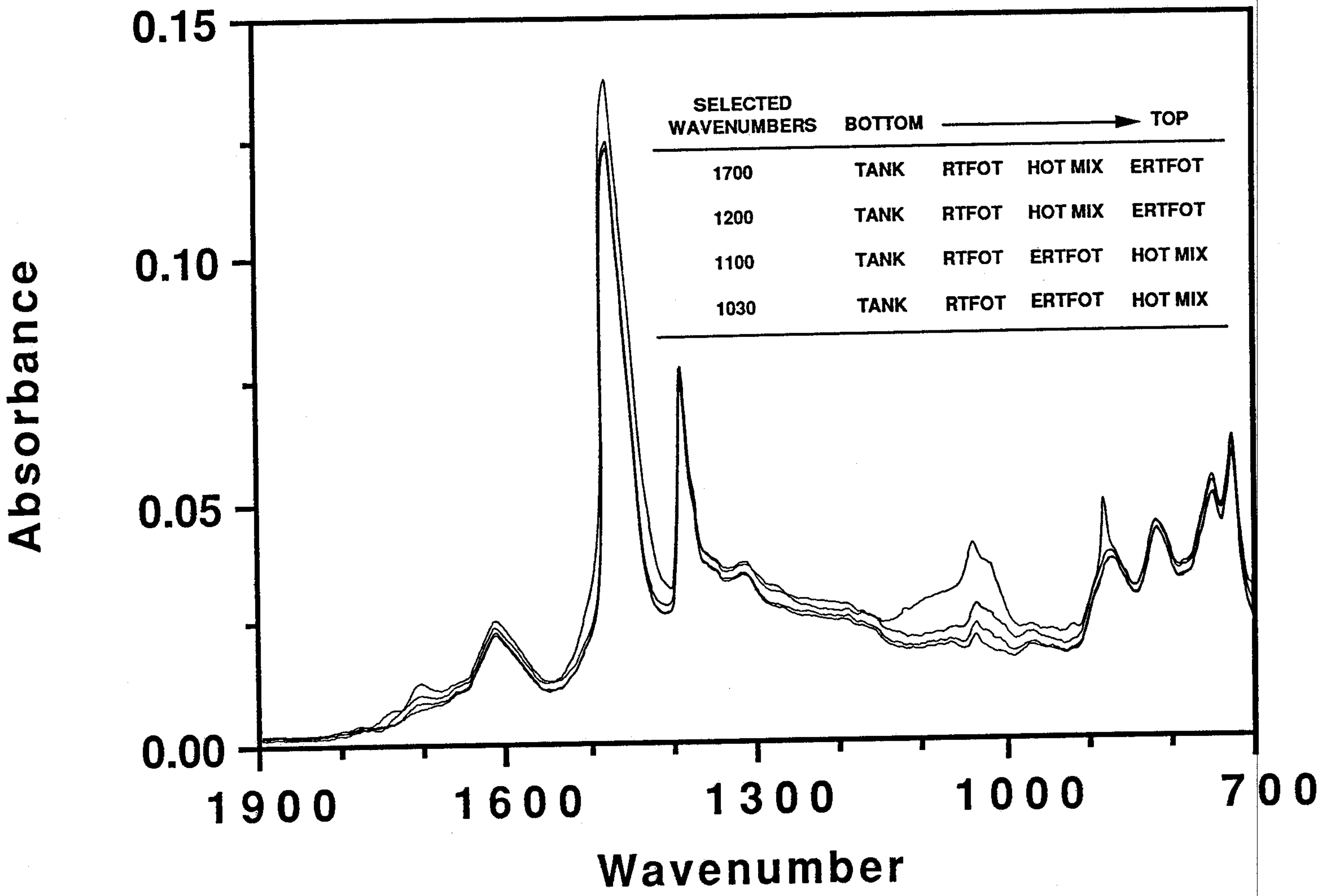


Figure IV-2-15
Comparison of IR Spectra for TFOT, RTFOT and Hot-mix - 1989 Cosden AC-10



SELECTED WAVENUMBERS	BOTTOM	⟶		TOP
1700	TANK	RTFOT	HOT MIX	ERTFOT
1200	TANK	RTFOT	HOT MIX	ERTFOT
1100	TANK	RTFOT	ERTFOT	HOT MIX
1030	TANK	RTFOT	ERTFOT	HOT MIX

Figure IV-2-16
Comparison of IR Spectra RTFOT, ERTFOT, and Hot-mix -
1989 Cosden AC-20

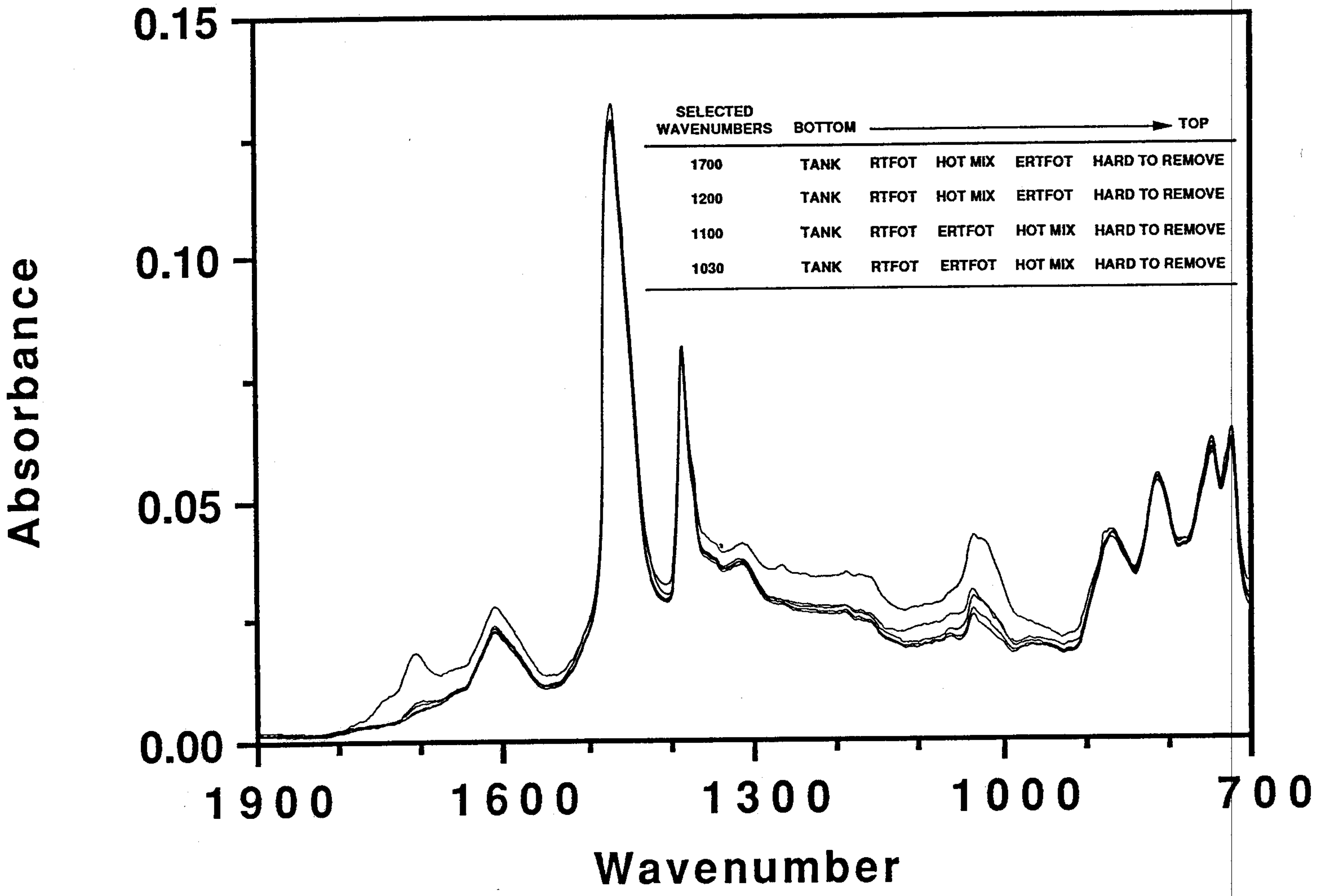


Figure IV-2-17
Comparison of IR Spectra for Oven Test and Extended Oven Test with Hot-mix and Hard to Remove Material - 1987 Exxon #2 AC-20

140°F viscosity, the oven tests seem to predict the hot-mix properties, but this is not so for the other asphalts. Consequently, the hot-mix properties will be extremely difficult to simulate with any test without accounting for the inherent inaccuracies in the extraction and recovery procedures and the differences in the virgin asphalts and perhaps the effect of the aggregate.

Fuel Oil Contamination

Several of the extracted asphalts showed evidence of fuel oil contamination. As discussed in Chapter III-1, an aerosol appeared as the last drops of solvent was distilled from the recovered asphalt. This persisted for some time and some collected on the inside of the flask. The infrared spectrum of this material was given in Figure III-1-14. The absence of many features normally in asphalt, such as significant aromatic peaks and the presence of a large, sharp carbonyl peak, is what would be expected of an oxidized fuel oil.

SECTION V

CORRELATION OF PHYSICAL AND CHEMICAL PROPERTIES

Summary

Using data from Section II and Section IV, various correlations were obtained for viscosity, penetration, and aging indexes in terms of percent LMS, carbonyl peak or area from the infrared spectra, and Heithaus (Chapter II-5) parameters. The infrared carbonyl absorption is shown to be a powerful correlating property of aged asphalts. Of the other parameters, the maximum flocculation ratio from the Heithaus data gave the best results.

Introduction

Many attempts have been made to correlate chemical and physical properties with only limited success. Certainly no correlations have sufficient dependability to permit calculation of reliable physical properties from chemical parameters only. This does not mean it cannot be done, only that asphalt is quite complex and it will require more knowledge then we now possess. Nor does the inadequacy of these correlations mean the attempt is not worthwhile, since considerable qualitative understanding of asphalt performance may be gained. In a previous study (Glover et al., 1987) relations between tenderness and Heithaus flocculation ratio, tenderness and percent asphaltenes, and also tenderness and percent LMS were found. Not surprisingly percent asphaltenes correlated well with percent LMS except for the anomalous Diamond Shamrock asphalt. Some rather crude correlations between viscosity and percent asphaltenes and percent saturates were obtained. Without question some relation must exist, as saturates always lower viscosity and asphaltenes always raise it. This still does not lead to a general correlation because of the large difference in properties of asphaltenes from different asphalts.

Correlation of Test Section Core Properties

In Section IV, Chapter 1 of this report, good relations between carbonyl peak height and viscosity of asphalts extracted from test section cores were found. For instance, the 275°F viscosities, Figure IV-1-6, without the South Texas data, gives

$$\log \text{viscosity } (275^{\circ}\text{F}) = 1.156 + .0663(\text{IR}),\ r^2 = 0.9125$$

where log is the natural logarithm. At 140°F neither the South Texas asphalts nor Diamond Shamrock could be correlated by using only the IR peak because the former showed a different slope and the latter formed an entirely different line, Figure IV-1-7. However, the remaining data show an excellent correlation.

$$\log \text{viscosity } (140^{\circ}\text{F}) = 6.943 + 0.177(\text{IR}),\ r^2 = 0.962$$

When the penetration at 77°F is plotted, Figure IV-1-8, each asphalt shows a linear plot of Pen vs IR peak but each is different. These are perhaps the best correlations ever obtained relating infrared results to properties, but it is obvious that this is not sufficient information.

Inspection of the three figures referred to above, Figures IV-1-6 through IV-1-8, shows that as the temperature increases, the relation between IR peak height, which is a measure of oxidation, and properties becomes more general. This is not too surprising as specific interactions in a fluid decrease with increasing temperature. At lower temperatures, some measure of the asphalt tolerance for oxidation is needed.

To study this, correlation of viscosity and penetration with IR and either a Heithaus parameter or LMS was attempted. The Heithaus parameters are shown and discussed in Section II, Chapter 5. The two parameters used are FR_{max} and HP3 which is $(1 - FR_{max})(1 - X_{min})$. Because parameters are available only for the tank asphalts and the properties are for aged cores, too much should not be expected. Even so, some interesting correlations resulted. For instance, the 140°F viscosity correlations without Diamond Shamrock became

$$\log \text{viscosity } (140^{0}\text{F}) = 5.756 + 7.248(\text{FR}_{\text{max}})^{1.5} + 0.256(\text{IR})^{0.9},\ r^{2} = 0.983$$

$$\log \text{viscosity } (140^{0}\text{F}) = 5.054 + 0.5762(\text{LMS})^{-.6} + 0.2817(\text{IR})^{0.9},\ r^{2} = 0.968$$

$$\log \text{viscosity } (140^{0}\text{F}) = -1.636 + 8.07(\text{HP3})^{0.1} + 0.394(\text{IR})^{0.8},\ r^{2} = 0.968$$

Including Diamond Shamrock would require that a value of zero be assigned to FR_{max} and HP3. It is probably futile to attempt to include Diamond Shamrock and get meaningful viscosity results. It is the only asphalt that does not correlate reasonably well at 140°F with IR only. If LMS is used, the large values of LMS and lower viscosity of Diamond Shamrock would force the viscosity to decrease with LMS, which is exactly opposite from what occurs during aging.

The penetration at 77°F is a more interesting challenge, as the asphalts have definitely separated according to source. The best correlation without Diamond Shamrock was

$$\text{Pen}_{77} = 103.98 - 217.8(\text{FR}_{\text{max}})^{1.9} - 33.53(\text{IR})^{0.22},\ r^{2} = 0.909$$

Including Diamond Shamrock and assigning a zero value for FR_{max} yields

$$\text{Pen}^{77} = 101.14 - 1454(\text{FR}_{\text{max}})^{3.9} - 36.39(\text{IR})^{0.22},\ r^{2} = 0.905$$

Considering that these are tank Heithaus values, this is encouraging. It seems reasonable that asphalt compatibility, of which FR_{max} is a measure, should be a factor in asphalt hardening.

Correlation of Hot-Mix, Oven Test Results

In these correlations, LMS area rather than percent LMS was used. This is the area under a curve of LMS versus concentration from 0% to 6% asphalt and its derivation is discussed in Section II, Chapter 1. Also because the IR carbonyl peaks are small, either the area under the IR curve from wavenumber 1650 to 1830 was used, or the difference over this range between the area for the aged asphalt and that for the tank asphalt was used. Because these asphalts are much less aged than the previous ones, the range of variables is much smaller, resulting in poorer correlations. Correlation of viscosity at 135°C(275°F) was very poor. It was better at 140°F(60°C). Using IR as the only independent variable

$$\log \text{viscosity } (140^{o}\text{F}) = 5.632 + 4.862(\text{IR}),\ r^2 = 0.744$$

Inclusion of other parameters increased r^2 so little that they are not considered significant.

For these data, penetration correlated better than viscosity, yielding

$$\text{Pen}_{77} = 15.47 + 8.863(\text{IR})^{-2},\ r^2 = 0.721$$
$$\text{Pen}_{77} = 70.05 + 0.002635(\text{FR}_{\text{max}}) + 64.89(\text{IRDIF})^{0.4},\ r^2 = 0.823$$

where IRDIF is the difference in aged and unaged carbonyl areas. A result nearly as good was obtained using LMS areas.

$$\text{Pen}_{77} = 70.91 + 6.06 \times 10^{-7}(\text{Area})^3 + -66.0(\text{IRDIF})^{0.4},\ r^2 = 0.819$$

Somewhat better results were obtained with various aging indexes. For penetration

$$\text{PIND} = 0.3349 + 0.6476(\text{IRIND})^{-3.5},\ r^2 = 0.842$$

which is only slightly improved by

$$\text{PIND} = 0.3475 + 0.6774(\text{IRIND})^{-3} + -3.304(\text{FR}_{\text{max}}),\ r^2 = 0.865$$

in which

$$\text{PIND} = \frac{\text{Pen Sample}}{\text{Pen Tank}}$$

$$\text{IRIND} = \frac{\text{IR Area Sample}}{\text{IR Area Tank}}$$

Attempts to correlate the viscosity aging index at 140°F gave very poor results, but redefining the aging index in terms of the natural logarithms of viscosity gave much better results,

$$\text{LVIND} = 1.329 + -0.356(\text{IRIND})^{-1.8} + 17.85(\text{Fr max})^{4.8},\ r^2 = 0.775$$

in which

$$\text{LVIND} = \frac{\text{log viscosity, sample}}{\text{log viscosity, tank}}$$

Attempts to correlate viscosity temperature susceptibility (VTS) failed completely with any of the aged asphalts. Interestingly, an earlier attempt (Glover et al 1989) in this study to correlate VTS for the test section asphalts had been more successful. Using only the percent LMS and percent small molecular size, (SMS) the following results were obtained:

$$\text{Tank - All Grades(18 points)} = 3.27 + -.00889(\text{LMS}) + .0275(\text{SMS}),\ r^2 = 0.88$$
$$\text{Tank - AC-10(8 points)} = 2.48 + 0.0058(\text{LMS}) + 0.0543(\text{SMS}),\ r^2 = 0.95$$
$$\text{Tank - AC-20(10 points)} = 3.78 + -0.0174(\text{LMS}) + 0.0129(\text{SMS}),\ r^2 = 0.93$$
$$\text{Cores - All Grades(25 points)} = 2.56 + 0.00600(\text{LMS}) + 0.0930(\text{SMS}),\ r^2 = 0.49$$

Discussion of Results

Without question the infrared carbonyl area correlates strongly with asphalt hardening and is perhaps the best chemical variable to track asphalt aging. Attempts to include other IR spectra changes are worthwhile, but as discussed in Section IV, Chapter 1, there seems to be no correlation between sulfoxide formation and asphalt hardening in the test section cores. This should be further investigated.

In general the Heithaus parameter, FR_{max}, was more useful than HP3 and also better than LMS. This is probably because FR_{max} is a direct physical measure of compatibility and correlates with the ability of the asphalt to tolerate oxidation. Percent LMS, on the other hand, is strongly related, in most asphalts, to percent asphaltenes and will likely give results similar to inclusion of asphaltenes as a parameter. As LMS grows with increasing carbonyl formation, there is considerable cross-correlation between these two parameters which could diminish the usefulness of using them together. Finally LMS is very sensitive to solvent effects, and this could have affected these values for the extracted samples.

A better and easier measure of compatibility is needed, one that will include an asphalt like Diamond Shamrock which contains no asphaltenes and thus yields no precipitation on heptane addition.

SECTION VI

ONGOING PROGRAMS

Introduction

There are a number of projects that have received considerable attention in Study 458 but have not produced sufficient results to report. For instance hot-mix and tank samples have been collected at a number of locations to be used as ad hoc test sections. Some of these were used in the work reported in Section IV. Others were cored in 1988-89 and the cores are in the freezer. There are plans to establish more sections this spring.

Asphalt aging is a crucial problem and better tests are needed. A Pressure Oxygen Bomb (POB) has been constructed so that high oxygen pressure rather than high temperature can be used to accelerate aging. This should better represent road aging. Because of the considerable work done on hot-mix aging, the POB road simulation has not progressed far. The test sections will be invaluable in calibrating these tests.

In Section III, the failure of standard ASTM extraction and recovery methods was discussed and parameters for better solvent removal determined. The problem of solvent hardening was clearly demonstrated but not completely solved and no doubt colors some results in this study, as it has all previous studies of extracted asphalt. Work is continuing to better understand this phenomenon and to find better procedures for extracting and recovering asphalt.

Test Section Corings and Analysis

Over the last several years a number of ad hoc test sections have been established. The complete list is given in Table VI-1 showing date of coring for those that have been cored. The only analysis thus far is the hot-mix aging study in Section IV. In addition, there are the older Study 287 test sections discussed in Section IV, and these are listed in Table VI-2. Finally, there are a number of other

Table VI-1

List of Study 458 Test Sections

Date	Type Asphalt	Hot Mix	Core	Location of Pavement
4-27-87	Exxon AC-20	X		Hwy 21 east. St. 1075+50 No Spec
5-5-87	Exxon AC-20	X		Hwy 6 north. St. 191 Overlay on right
5-14-87	Exxon AC-20	X		Hwy 21 west. St. 1100 No Spec
6-17-87	Coastal AC-20	X		Hwy 290 east. St. 813 Overlay on right
7-15-87	Exxon AC-20	X		Hwy 21 west. St. 475+90 Overlay on right
7-23-87	Exxon AC-20	X		FM 1155 St. 32+50 Overlay on right
7-27-87	Exxon AC-20	X	X	Hwy 21 west. St. 1230 2nd lift on right
8-3-87	Exxon AC-20	X		Hwy 21 west. St. 1413+50 1st Lift on right
8-10-87	Exxon AC-20	X		Hwy 36 north. St. 69+40 2nd Lift on right
8-17-87	Coastal AC-20			None Taken
8-18-87	Exxon AC-20	X		Hwy 36 north. St. 95+50 2nd Lift in middle
8-25-87	Exxon AC-20	X		Hwy 36 north. St. 77+50 1st Lift on right
8-31-87	Exxon AC-20	X		FM 2818 west. St. 311+75 1st Lift in middle
9-1-87	Exxon AC-20	X	X	Hwy 21 west. St. 1458 2nd Lift on left
9-2-87	Exxon AC-20	X	X	Hwy 21 west. St. 1394 2nd Lift on right
9-3-87	Exxon AC-20	X	X	Hwy 21 west. St. 1295 2nd List in middle
9-4-87	Exxon AC-20	X	X	Hwy 21 west. St. 1277+50 2nd Lift on left
9-8-87A	Exxon AC-20	X		Hwy 21 west. St. 1518 1st Lift on right
9-8-87B	Exxon AC-20	X	X	Hwy 21 west. St. 1517+85 2nd Lift on right

Table VI-1 (Cont'd)

List of Study 458 Test Sections

Date	Type Asphalt	Hot Mix	Core	Location of Pavement
9-9-87A	Exxon AC-20	X	X	Hwy 21 west. St. 1483 2nd List in middle
9-9-87B	Exxon AC-20	X	X	Hwy 21 west. St. 1483 2nd Lift on right
9-10-87A	Exxon AC-20	X	X	Hwy 21 west. St. 1465+50 2nd Lift on left
9-10-87B	Exxon AC-20	X	X	Hwy 21 west. St. 1314 2nd Lift on left
6-15-88	Exxon AC-20	X		Hwy 21 west. St. 1385 Surface on right
6-16-88	Exxon AC-20	X		Hwy 21 west. St. 1478 Surface on left
6-17-88	Exxon AC-20	X	X	Hwy 21 west. St. 1483 Surface in middle
6-18-88	Exxon AC-20	X		Hwy 21 west. St. 1518 Surface on right
6-18-88	Exxon AC-20	X	X	Hwy 21 west. St. 1483 Surface on right
6-2-89	Ampet AC-20	X		U.S. 190 east. St. 280 + 50 Right lane
6-6-89	Texaco AC-20	X		U.S. 69 east. St. 105 + 25.28
6-13-89	Texas Gulf AC-20	X		FM 3083 east. St. 126 + 00
7-28-89	Cosden AC-10	X		IH-10 west. St. 605 Passing lane shoulder
8-10-89	Cosden AC-20	X		U.S. 87 south. St. 459 + 70

Table VI-2

List of Study 287 Test Sections

	Tank Samples	84 Core	85 Core	87 Core Study 458
Dickens	Ampet AC-10		X	X
	Cosden AC-10			X
	Cosden AC-20			X
	DiaSham AC-10			X
	DiaSham AC-20			X
	Exxon AC-20		X	X
	MacM AC-20		X	X
Dumas	Ampet AC-10	X	X	X
	Cosden AC-10			X
	Cosden AC-20	X		X
	DiaSham AC-10	X		X
	DiaSham AC-20	X		X
	Exxon AC-10	X	X	X
	MacM AC-10	X	X	X
Lufkin	Ampet AC-10	X	X	X
	Cosden AC-20			X
	DiaSham AC-20			X
	Exxon AC-20		X	X
	MacM AC-20	X	X	X
	Cosden AC-10		X	
	Texaco AC-20	X		X

A few other cores are on hand from other projects.

TTI test sections for which tank and core asphalts are being stored in the freezer. These are listed in Table VI-3.

These sections will be invaluable in future studies of road aging, as it is only from such data that the true changes that occur can be determined. In fact by using an array of physical and chemical tests, a better picture of asphalt performance is obtained than by road conditions which depend on so many unrelated factors. In Section IV, Chapter 1, a seeming inverse correlation between carbonyl and sulfoxide formation was investigated. These sections will allow further study of this phenomenon which could have significance in asphalt design and perhaps aggregate selection. These sections can also be used to study further the great effect of voids and also to see how this varies with lift location. This could have significance in roadway design. Finally, there has been little study of the long-term effect of additives. Large amounts of money are being spent for these materials with little real knowledge of what is being achieved.

Pressure Oxygen Bomb (POB) Aging

There is a great need for a realistic laboratory aging method that has been correlated to road samples using a variety of parameters. From the standpoint of understanding and predicting asphalt performance, the properties of aged asphalt are more important in many respects than the properties of the original material. Years after laying, when a roadway is deteriorating, the asphalt properties may be greatly different from the original properties, but if failure is due to the asphalt cement, it will be the properties of the aged material which are causing the problem.

This has been recognized for many years, and many test procedures have been devised to predict aging. Aging really occurs in two modes: first, the very rapid aging that occurs in the hot-mix plant at high temperature on the aggregate surface and second, the much slower, low temperature aging in the road. It is likely that the mechanisms in these modes of aging are quite different. This is borne out by the persistent failure of tests developed to predict hot-mix aging to prove useful in predicting road aging.

Table VI-3

List of Study 187 Asphalt Additives Test Sections

Date	Type Asphalt	Tank	Core	Additive Type	Location of Pavement
8-18-86	Texas Fuel and Asphalt AC-20 (Control)	X	X	None	San Benito US 8377
8-19-86	Texas Fuel and Asphalt AC-10	X	X	Kraton	San Benito US 8377
8-18-86	Texas Fuel and Asphalt AC-10	X	X	Ultrapave Latex	San Benito US 8377
8-19-86	Texas Fuel and Asphalt AC-10	X	X	Carbon Black	San Benito US 8377
8-18-86	Texas Fuel and Asphalt AC-10	X	X	EVA Polybilt	San Benito US 8377
10-14-86	Texas Fuel and Asphalt AC-20	X	X	None	San Benito US 8377
10-15-86	Total Asphalt Co AC-10	X	X	Ultrapave Latex	Sherman US 75
10-16-86	Total Asphalt Co AC-10	X	X	EVA	Sherman US 75

Table VI-3 (Cont'd)

List of Study 187 Asphalt Additives Test Sections

Date	Type Asphalt	Tank	Core	Additive Type	Location of Pavement
10-14-86	Total Asphalt Co AC-20 (Control)	X	X	None	Sherman US 75
10-15-86	Total Asphalt Co AC-10		X	Carbon Black	Sherman US 75
10-14-86	Total Asphalt Co AC-10	X	X	Novaphalt	Sherman US 75
10-15-86	Total Asphalt Co AC-10	X	X	Kraton	Sherman US 75

A variety of aging tests have been developed to simulate road aging, but most of these are simply lower temperature variations of the oven tests. The problem is twofold: the temperature is still much above road temperature, and in general, only a few parameters have been used in their correlation. The most realistic aging procedures would seem to be the low temperature Pressure Oxygen Bomb (POB) tests. As proposed by Lee (1968), the hot-mix step was first simulated by TFOT aging. This material, still in the TFOT dish, was placed in a pressure vessel and aged at 150°F at various pressures. A standard procedure was prepared by Lee (1973) in which TFOT residues were aged at 150°F and 20 atm. for 1000 hours. They used a variety of criteria to correlate aging, including viscosity, penetration, softening point, microductility and percent asphaltenes. Though the results are promising, the rankings of various asphalts by each criterion according to POB vs field aging were not very consistent, indicating that actual road aging was not being duplicated. They also found an overwhelming effect of voids that complicated relating properties to age. Jamieson (1970) reports POB results using 7mm films at 65°C and 300 psi, which did not agree with road performance.

Edler (1985) reports some results in which 30 micron asphalt films were contacted with oxygen at 300 psi and at 149°F for 96 hours, but the results were not compared to field data. Kim et al., (1984) aged compacted cores at 100 psi and 60°C up to 5 days. Comparison to field cores was on the basis of the resilient modulus and Corbett analysis of extracted material. There was generally fair agreement in two of three cores. There was also a problem of diffusion into the cores. It is probable that all of the POB work has either been at too high a temperature or used too thick films, or both.

The pressure oxygen bomb, which has been constructed, is shown in Figure VI-1 and VI-2. Asphalt is coated on the glass slides in thin films. The slide holder is placed in the bomb where it is exposed to oxygen at a controlled temperature and pressure. Initial work involved depositing uniform thin films on the slides.

It is desirable that the aging not be diffusion controlled or it will be nonlinear and uneven. This will require thin films. On the other hand, the test will be easier and quicker with greater film thickness. A series of runs will be made varying film

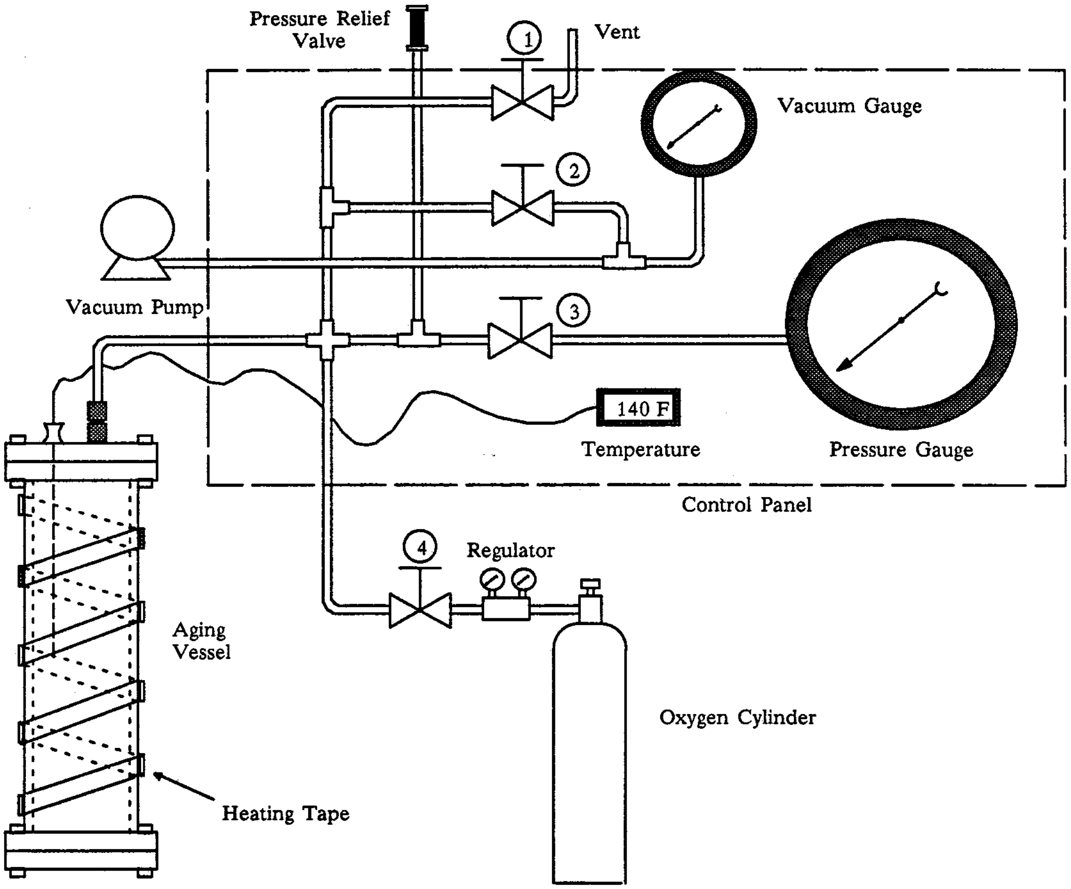


Figure VI-1
Pressure Oxygen Bomb Apparatus

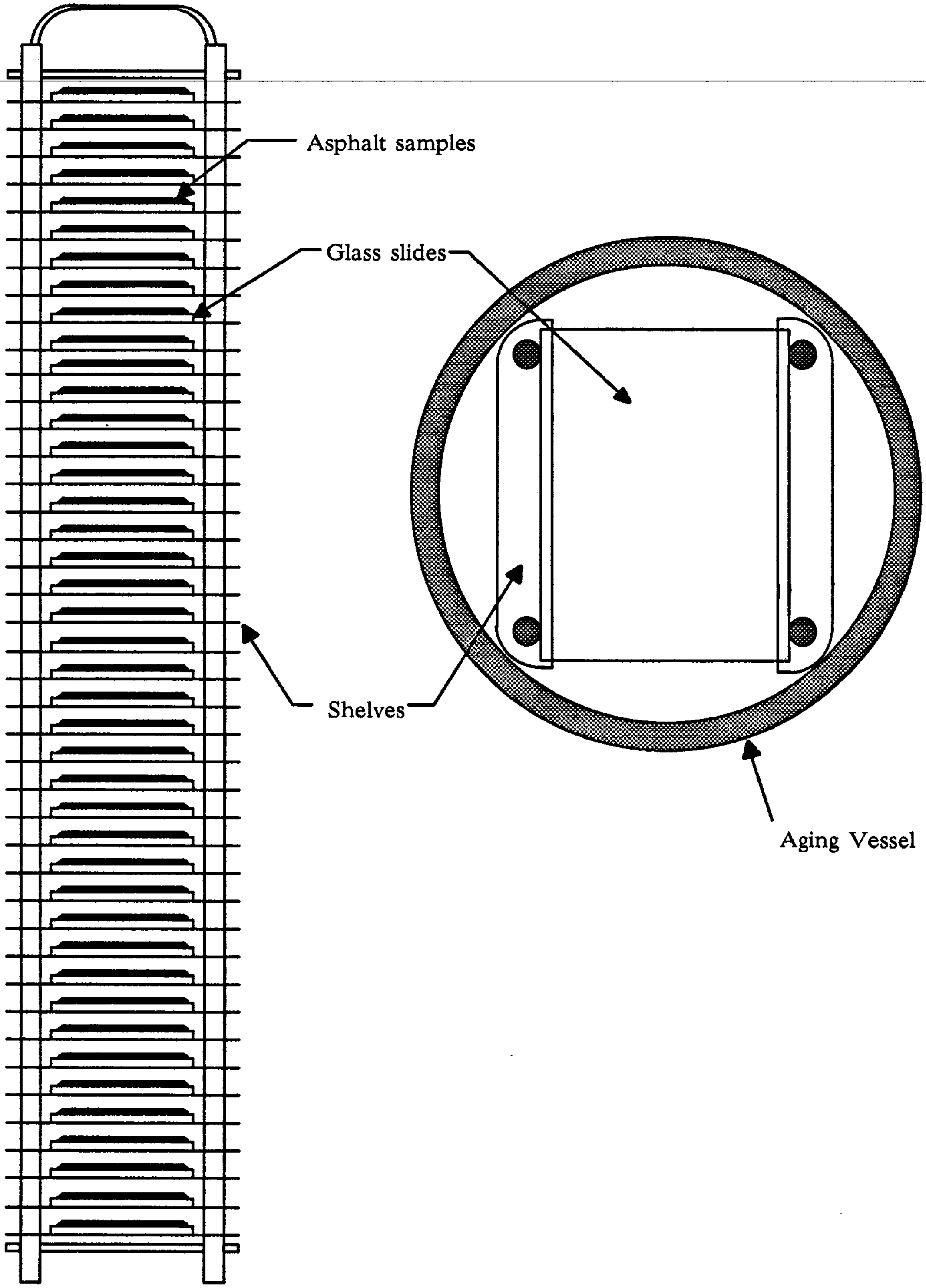


Figure VI-2
Sample Holder for Pressure Oxygen Bomb

thickness at several temperatures and pressures to determine the maximum practical thickness.

It is desirable that the test be as short as possible which will favor higher temperatures and pressure. The criterion, however, is that aging in the POB must track aging in the cores with all measured properties moving in tandem. Asphalts subjected to simulated hot-mix aging will be further aged in the POB over a range of times, temperatures and pressures. This asphalt will be analyzed by GPC and IR. Penetrations and viscosities will be run as will Corbetts when it is believed optimum conditions are being approached. These results will be compared with the analysis of recovered core material from the test sections shown in Table VI-1 to VI-3. Several additional test sections will be established as soon as possible. An aging test must be closely calibrated with cores from roadways. One asphalt only will be used until near optimum conditions are found, and then asphalts from other test sections will be included.

It should again be emphasized that the goal is not to reproduce a certain age, as asphalt aging in the field is so very dependent on voids and climate. The goal is to reproduce the aging history of actual aging road asphalts, so that if the viscosity from the POB matches that of the core material, then penetration, IR, GPC, Corbett, etc. will also match. It should then be possible to establish aging criteria which will assure long asphalt life in a properly constructed roadway. This work would not be possible without the availability of documented cores, such as those in Table VI-1 to VI-3, to serve as a calibration base for the aging test.

Improved Extraction

The literature review in Chapter 2 of Section I strongly indicates deficiencies in extraction and recovery methods as applied to asphalt mixes. Solvent removal parameters are established in Chapter 1 of Section III, and initial studies of the solvent hardening of asphalt are given in Chapter 2 of that section. For the most part, solvents seem to all harden asphalt to roughly the same degree. The only exception found in those studied thus far is carbon tetrachloride with which the phenomenon was much more severe. Light and oxygen were factors, but these are easily excluded. The principal remaining variables seem to be time, concentration and temperature of contact. The goal must be to develop a procedure in which all contact is at room temperature or below and where there is only minimum time at low concentrations, even at room temperature.

Another problem with standard procedures is that trichlorethylene may leave as much as 4% of the asphalt on the aggregate. It was found in this study that addition of 10%-15% ethanol allows rapid removal of most of this material, but even then there may remain a small quantity that will dissolve only over a long period of time. All of the hard-to-remove material is in a highly oxidized state. See Chapter 2 of Section IV.

A study is planned in which graded fines that have already been thoroughly extracted with TCE will be contacted with various solvents at fixed fines to solvent ratio to see if still better solvents or solvent combinations can be found. A more complete study is also planned on the effects of concentration and temperature on hardening. With these data in hand, a contacting and recovery procedure will be devised to minimize the extent of solvent hardening while extracting all or nearly all of the absorbed asphalt.

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER VII-1

CONCLUSIONS

Work described in this report leads to the following conclusions:

1. GPC is a fast and reliable method for detecting changes and differences in asphalt. It can distinguish between asphalt sources and detect changes in manufacturing. It is very sensitive to the changes that occur during aging and solvent hardening. It has been very effective in detecting residual solvent in recovered asphalt.
2. FT-IR has been developed into a fast and accurate procedure for detecting and investigating chemical changes in asphalt. It is able to detect the changes that occur during oxidation and those that occur during solvent hardening.
3. The TFOT and the RTFOT are essentially equivalent but do not correlate well with hot-mix aging.
4. Standard procedures for extracting asphalt usually leave unextracted material and cause solvent hardening of the extracted material. Addition of 10%-15% ethanol considerably improves extraction of hard-to-remove material but still may leave a small amount.
5. The hard-to-remove material that resists extraction has been highly oxidized relative to the bulk material.
6. Standard solvent recovery methods may leave significant solvent residues in the recovered asphalt, but this may be remedied by using longer times or higher temperatures.
7. The Corbett fractionation procedure suffers from several problems besides uncertainty in cut points. These are similar to those encountered in extraction and recovery: incomplete removal of adsorbed material from the column, incomplete solvent removal from the fractions, and solvent hardening.
8. Solvent hardening of asphalt is accelerated by oxygen, light and temperature.
9. IR spectra show changes during solvent hardening in the absence of oxygen and light that are different from those produced by oven, road or hot-mix aging.

10. Growth in the carbonyl region of the IR spectrum is an excellent indicator of road and hot-mix aging and correlates well with changes in physical properties.
11. Sulfoxide formation, though a major chemical change during asphalt oxidation, shows no correlation with hardening and in old roads correlates inversely with carbonyl formation.
12. Compatibility is an important factor in asphalt aging.
13. High air voids is one of the more serious problems in road construction. Asphalt oxidation increases rapidly with increasing voids.
14. Fuel contamination can be a problem in oil-fired drum plants.

CHAPTER VII-2

RECOMMENDATIONS

Based on the results of this study, the following recommendations are made:

1. Tighten specification or specification enforcement to assure low air voids.
2. Modify Abson and Roto-vap solvent recovery procedures to assure complete solvent removal. The standard Abson time should be increased to 25 minutes, especially at higher viscosity and sample sizes over 50 gms. An alternative is to raise the temperature to 380°F. A Roto-vap time of 20 minutes past the last drop is recommended.
3. Continue development of better extraction procedures to maximize asphalt extraction and lessen solvent hardening. In Method A ASTM D 2172, additives of 15% ethanol to trichloroethylene will increase removal of hard-to-remove material.
4. Continue efforts to understand the nature of solvent hardening.
5. Continue efforts to understand the chemical basis of asphalt aging and performance so that improved asphalts can be developed.
6. Develop better aging tests based on a variety of chemical and physical tests using hot mixes and test section cores to be sure that laboratory methods approximate the changes that actually occur in the field.
7. Continue to monitor the existing test sections and establish additional sections to obtain a history of the changes that occur in the field and how these affect performance.
8. Develop a better measure of asphalt compatibility.
9. Improve GPC analysis so that the shape of the chromatogram and not just the percent LMS can be used as correlating parameters.
10. Improve the Corbett analysis or replace it by a high pressure liquid chromatographic procedure.

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