SHRP - A/IR - 89 - 002 Revised 10/31/89

STRATEGIC HIGHWAY



RESEARCH PROGRAM

MATERIALS REFERENCE LIBRARY ASPHALT SELECTION PROCESS

Prepared by

SHRP CONTRACT A001 CENTER FOR TRANSPORTATION RESEARCH THE UNIVERSITY OF TEXAS AT AUSTIN

August 1989

SHRP MATERIALS REFERENCE LIBRARY ASPHALT SELECTION PROCESS

by

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Research Report Number SHRP-IR-A-89-002 (UT-SHRP-A-001-2)

Improved Asphaltic Materials Experiment Design, Coordination, and Control of Experimental Materials

Research Project SHRP-A-001

conducted for

Strategic Highway Research Program

by the

CENTER FOR TRANSPORTATION RESEARCH THE UNIVERSITY OF TEXAS AT AUSTIN

August 1989

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ACKNOWLEDGEMENT

The research described herein was supported by the Strategic Highway Research Program (SHRP). SHRP is a unit of the National Research Council that was authorized by Section 128 of the Surface Transportation and Uniform Relocation Assistance Act of 1987.

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Preface

The asphalt selection process reported herein was performed under the Strategic Highway Research Program Contract No. SHRP-87-A-001, by The University of Texas at Austin, which is the prime contractor for this project, with Thomas W. Kennedy as Principal Investigator. The other authors are James S. Moulthrop, Project Coordinator; Ronald J. Cominsky, SHRP Technical Support Engineer, and William E. Elmore, Development Manager.

The authors express their sincere appreciation to the Strategic Highway Research Program (SHRP), the SHRP Asphalt Selection Expert Task Group, and many State Highway Agency engineers for their valuable technical role and guidance related to the Materials Reference Library asphalt selection process. The Expert Task Group which devoted a significant amount of time and effort to the selection process consisted of the following:

> Ernest G. Bastian, Federal Highway Administration; Joseph L. Goodrich, Chevron Research Company; Ken F. Grzybowski, Gardner Asphalt Corporation; William Gunderman, Transportation Research Board; Woodrow J. Halstead, Consultant; Douglas I. Hanson, New Mexico State Highway Department; Louis E. Ott, Amoco Oil Company; Mark Plummer, Marathon Oil Company; and Laverne Miller, Petro Canada.

The selection process would have been extremely difficult without

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their knowledge and guidance. Joseph L. Goodrich, Chevron Research Company, and Edward T. Harrigan, currently with SHRP and formerly with The Asphalt Institute, are especially recognized for their professional assistance related to the selection process and the review and preparation of this report.

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CHAPTER 1. INTRODUCTION

In 1984, the Transportation Research Board published a special report (Ref 1) which identified several asphalt pavement distress conditions that were perceived to be caused by deficiencies in the asphalt cement. This report resulted in a National Cooperative Highway Research Program (NCHRP) contract for the development of research plans to identify and classify specific relationships between the physicochemical properties of asphalt cement and pavement performance. A report (Ref 2) provided the framework and research plans for the SHRP Asphalt Research Program.

These research plans recognized that the magnitude of the program would require a major effort by several different research organizations and that, in order for the total research effort to be both meaningful and effective, all researchers should have access to and use the same materials in their studies. This would reduce many of the variables and problems that would occur when analyzing the resulting data produced by many researchers using a wide variety of materials.

As a result, The University of Texas at Austin, the SHRP Asphalt Technical Assistance Contractor (SHRP Contract A-001, "Improved Asphaltic Materials, Experimental Design, Coordination, and Control of Experimental Materials") (Ref 3), was required to develop and operate a Materials Reference Library (MRL) containing sufficient quantities of selected asphalts and aggregates which will be used throughout the SHRP Research Program and possibly by future asphalt research efforts.

Facilities for storing these materials are located in Austin, Texas. A total of thirty-two asphalts, representing the output of approximately 40

percent of the asphalt refineries in the U.S. and Canada, will be sampled and stored in the library. The initial planning by the A-001 contractor provided that eight of the asphalts would be selected in the initial phase of the contract and the remaining twenty-four at a later time. The selection process utilized the outside expertise of an Expert Task Group appointed by SHRP, a review of the literature, and an Asphalt Refinery Survey prepared by The Asphalt Institute as a subcontractor.

The following chapters describe the rationale and procedures used in the asphalt selection process. The properties of the asphalts contained in the Materials Reference Library will be summarized in a later report.

CHAPTER 2. ASPHALT SELECTION PROCESS

SELECTION HYPOTHESIS

The basic premise of the selection process was that the performance of asphalt pavements is directly influenced by the physicochemical properties of asphalt cement. Thus, asphalt cements were deliberately chosen to create a MRL containing currently available asphalt cements representing a wide range of field performance histories, crude oil sources, refinery practices, and physical and chemical properties.

Thirty-two asphalt cements were to be selected, sampled, and stored by The University of Texas at Austin for detailed analysis and evaluation during the SHRP Asphalt Research Program. The selection of the asphalt cements took place in three phases:

. eight initial or core asphalts - Phase I;

. fourteen additional asphalts - Phase II; and

. ten final asphalts - Phase III.

All phases have been completed and the thirty-two asphalts have been identified. At this time (September 1989) twenty-two of the asphalts have been sampled and stored in the MRL.

PHASE I involved the selection of eight initial asphalts that represent a common set of core asphalts to be tested by all contractors. An attempt was made to obtain asphalts produced by a straight run distillation process from a single source crude oil in order to minimize the number of variables. More importantly, however, was the need to have asphalts that exhibited a wide range of field performance and physicochemical characteristics.

PHASE II involved the identification of fourteen additional asphalts with a range of physicochemical properties, crude oil sources, refinery

processes, and performance histories. The Refinery Survey information was used extensively in the section of these fourteen asphalts.

PHASE III involved the selection of the final ten asphalts. Initial data developed under the A-002 and A-003 contract, as well as the Refinery Survey, were used in the selection process.

SELECTION CRITERIA

The specific selection criteria which have been used in the three phases of the selection process are discussed in the following sections.

The primary selection criteria were:

. pavement performance;

- . crude oils, including the physicochemical and performance-related properties of asphalts produced from them; and
- . Refinery processes used in the manufacture of asphalt.

Pavement Performance

Major emphasis and consideration were given to asphalts that had been used in pavement performance studies for which performance information was generally available and for which the physical and chemical properties had been reported. Table 1 provides a listing of various roadway studies relating asphalt composition and characteristics to pavement performance.

An attempt was made to characterize the various asphalts as good or poor performers based on the <u>perceived</u> performance in these studies or in normal field use. The distress related performance factors considered, which are the focus of the entire SHRP Asphalt Research Program, were the following:

TABLE 1 STUDIES RELATING ASPHALT COMPOSITION TO ROAD PERFORMANCE (After Reference 3)

	Performance Found Related to		
	Construction Variables?	Physical Tests?	Asphalt Composition?
Michigan Test Road (1954)		Yes	Poor
Texas Test Roads (1954-1959)		No	No
Zaca-Wigmore (1954-1955)	Yes	Yes	Yes
Pennsylvania Test Roads (1961-62,1976)	Yes	Yes	No
Texas Test Roads (1963-1966)		Yes	Poor
California Test Roads (1964-1973)	Yes	Yes	Poor
Australian Test Roads (1966-1976)	Yes	Yes	Yes
California Durability Study (1974-1980)	Yes	Yes	Some
Recycling Agent Study (1979-1980)		Yes	Some
Montana Asphalt Study (-1977)		Yes	Some
South African Study (-1984)	·	Yes	Some

- . thermal cracking;
- . fatigue cracking;
- . permanent deformation (rutting);
- . adhesion and water sensitivity; and
- . aging.

California Valley (San Joaquin), Middle East, Smackover, Venezuela, Wyoming high sulfur, and Lloydminster crude sources were identified as asphalts which have generally good performance histories. California Coastal, Boscan, Maya, Utah, and Redwater crude sources were identified as asphalts that generally were perceived to perform poorly with respect to one or more types of pavement distress. It should be noted that while these asphalts may perform poorly with respect to one distress, they may perform quite well with respect to others. Thus, it is difficult to select asphalts that are truly good or poor. In fact, the effect of the asphalt may often be very subtle and performance is also highly dependent on other factors such as aggregate characteristics and construction quality.

An evaluation of the performance-related physical and chemical properties was undertaken as a secondary means of selecting asphalts with the widest possible range of performance levels.

There are limited published data available that can be used to specifically quantify the relationship between asphalt cement properties and field performance. Field performance is highly dependent on loading, environment, mix design, and construction variables. Thus, the performance rating for various asphalts was to some extent qualitatively established based on the experience and perceptions of the A-001 research personnel, the SHRP Expert Task Group, State Materials Engineers, and

other researchers throughout the United States and Canada. When quantitative data were available, however, such data took precedence in the selection process.

"Good" and "poor" performance criteria, of course, are unique to the distress that is considered. For instance, California Valley asphalts traditionally have been considered good with respect to age hardening, but poor with respect to temperature susceptibility. Similarly, Boscan asphalt has a relatively high aging index, but it is characterized as a low temperature susceptible material.

Petroleum Crude Origin

Because of the difficulty of classifying all asphalts with respect to performance and the lack of information related to distress factors and performance, asphalts were selected based on crude oil source and the physicochemical properties of these crude oils and asphalt cements produced from them.

The properties of asphalts manufactured from numerous domestic and imported crude oil sources were measured or estimated and then evaluated. Particular attention was given to those crude oils that are major contributors to the North American asphalt supply. It was recognized that since a crude oil may contain petroleum recovered from numerous wells within a field, the asphalt properties from a single-source crude are not necessarily uniform. Still, there are several well known single-source asphalts which have been extensively evaluated in test roads and laboratory studies. Some of them are still available and are expected to be available for future use. These single crude sources include Boscan, California Coastal, California Valley

(San Joaquin Valley), and Lloydminster.

<u>Chemical Properties</u> While it is recognized that asphalt chemistry, or composition, determines the physical properties and the ultimate field performance of asphalt, there are few well-established and accepted relationships between asphalt chemistry and pavement performance. This is evidenced by the fact that a major goal of the SHRP asphalt research effort is to establish the relationship between fundamental chemical properties and pavement performance. Thus, the focus in the selection process was to include asphalts that represented a wide range of chemical, or compositional, properties which were considered to be related to pavement performance. The range of chemical properties, representing a wide range of performance factors, was assured by evaluating the geochemistry, the heteroatom composition, and the geographic origin of asphalt crude sources, all of which are closely interrelated.

The formation of petroleum crude oil is the result of the accumulation and decomposition of organic matter from plants and animals in both marine and non-marine environments. The type and amount of heteroatom elements in the crude, both of which can provide an estimate of the performance of the resulting asphalts, are generally indicative of the organic matter, i.e., plant or animal, and the environment in which the petroleum was formed.

Heteroatoms in asphaltic crude oils include elements other than carbon and hydrogen. Elemental analysis indicates that asphalts typically contain 1 to 7 percent sulfur, 0.5 to 3 percent nitrogen, 0.25 to 2 percent oxygen, 100 to 1500 ppm vanadium and 20 to 200 ppm nickel. The amount of each heteroatom element present in the crude oil is strongly cross-correlated to those of the other heteroatoms and with the geochemical origin of the crude

As an example of an important geochemical process that influences asphalt performance, sulfur was a minor constituent in the plants and animals that decomposed to form petroleum. In non-marine environments such as swamps and bogs, the sulfur in organic sediments, derived principally from plant sources, typically was acted upon by anaerobic, sulfur-reducing bacteria, resulting in the production of hydrogen sulfide.

If the sediments which covered and surrounded the organic sediments were high in iron, as is typically the case for non-marine deposited material, the hydrogen sulfide would be eliminated through the precipitation of iron sulfide and, thus, the sulfur effectively removed from the organic sediments. Thus, petroleum derived from such deposits tends to be low in sulfur and high in the waxy organic compounds generally found in algae and other plant materials, e.g., branched saturates. Asphalts refined from these low sulfur, high wax content crude oils generally exhibit poor performance.

In marine environments, the covering sediments were low in iron and the organic sediments contained compounds derived from a larger proportion of sulfur-rich, planktonic (animal) sources than are found in non-marine environments. Consequently, the sulfur remained available for incorporation in the petroleum. Thus, crude oils derived from marine deposits have more organic compounds derived from planktonic sources and contain higher sulfur contents and lower wax contents. Asphalts produced from these crude oils generally perform well. Furthermore, these asphalts will be generally low in iron and have a high vanadium to nickel ratio due to the relative absence of metal precipitation by hydrogen sulfide during

oil.

crude oil formation.

Many observations and hypotheses have been advanced which relate the heteroatom chemistry of the crude oil to pavement performance properties. Asphalts with higher sulfur content tend to be less temperature susceptible than asphalts with lower sulfur contents. In addition, vanadium compounds commonly found in asphalt may serve as a catalyst which promotes oxidation of the asphalt and causes premature hardening or aging. It has also been reported that water sensitivity problems may be related to the presence of nitrogen compounds in the asphalt which may affect the asphalt-aggregate bond. Thus, asphalts with higher nitrogen contents may be more resistant to moisture damage or stripping.

A review of the nitrogen content of numerous asphalts indicates that California asphalts have high nitrogen contents relative to other world wide sources. Thus, it could be hypothesized that California crudes should exhibit good adhesion and stripping characteristics.

Therefore, the sulfur, nitrogen, and metal content, were used to evaluate crude oil sources and were considered in the asphalt selection process. Figures 1 through 5 represent sulfur versus vanadium-to-nickel ratios for various crude sources and Figure 6 illustrates the range of nitrogen contents for asphalts produced from a range of crude oils.

<u>Physical Properties</u> The selection process specifically considered the following two physical properties which are related to performance:

. temperature susceptibility; and

. aging.

It has been hypothesized that temperature susceptibility is indicative of thermal cracking and permanent deformation. Temperature susceptibility



Figure 1. Heteroatoms in asphalts made from single crudes (After Reference 4)



Figure 2. Heteroatoms in asphalts made from single crudes (After Reference 4)



Sulfur In Asphalt, %





Figure 4. Heteroatoms in asphalts made from single crudes (After Reference 4)



Sulfur In Asphalt, %

Figure 5. Heteroatoms in asphalts made from single crudes (After Reference 4)



Figure 6. Nitrogen content of AC-20 asphalts refined from single crudes (After personal communication with J.L. Goodrich)



Figure 7. Range of PVN and Aging Index for single source crudes (After Reference 5)

was evaluated using the penetration-viscosity number (PVN) which is an estimate of the slope of the temperature-viscosity relationship using the penetration at 77F (25C) and viscosity at 140F (60C). Asphalts typically have PVN values ranging from +0.5 to -3.0. A low PVN, e.g. -2.0, indicates a very temperature susceptible asphalt.

Aging characteristics were evaluated in terms of the aging index, which is the viscosity (140F) after laboratory aging using the thin film oven test (TFOT) divided by the original viscosity of the asphalt cement. A high aging index number indicates the asphalt is more susceptible to oxidative aging or hardening. Values typically range from 1.0 to 3.5.

Figure 7 illustrates the range of temperature susceptibility and viscosity ratios of asphalts from numerous single-source crudes (Ref 5). It is apparent that these two performance-related physical properties exhibit a wide range of values. The more <u>desirable</u> asphalts would be located in the upper, left corner of Figure 7. These asphalts would have the best combination of properties, i.e., high resistance to age hardening and low temperature susceptibility, and should produce durable, high performance pavements. The most undesirable asphalts would be located in the lower right corner. These asphalts would tend to age rapidly and be very temperature susceptible. Figure 8 is a summary of the perceived relationships between asphalt physical and chemical properties and pavement performance that were employed in the overall asphalt selection process.

Refinery Processes in the Manufacture of Asphalts

The principal refining processes used to manufacture asphalt cements are as follows:

- . atmospheric and vacuum distillation;
- . solvent deasphalting; and
- . distillation followed by air-blowing.

Figure 9 represents a schematic of the various processes. Atmospheric and vacuum distillation is the predominant refinery process used in the manufacture of asphalts in the United States.

	Pavement Distress Factors				
Asphalt Cement Characteristics	Thernaling	Failons	.0 Pernaner	ation Advestor	Solution Point
Vanadium / Nickel Ratio	м	v	м	м	v
Sulfur Content	v	м	0	0	S
Temperature Susceptibility	v	M	v	0	м
Nitrogen Content	0	V	0	v	0

Significance of Effects on Performance

Very SignificantVSignificantSMinor SignificanceMNo SignificanceO

Figure 8. Perceived relationship of asphalt cement properties to pavement performance

Vacuum Asphalt **Tube Heater** Heater Distillation Atmospheric Storage Crude 315-370 °C 370-426 °C 386 °C Distillation 150 °Č Petroleum (600-700 °F) (700-800 °F) (725 °F) (300 °F) Steam Steam **B. AIR-BLOWING** Water Air Blowing Red. Crude Asphalt Cooler Heater or Flux Vessel Storage 205-230 °C 215-280 °C 165 °C 230-270 °C 205 °C (400-450 °F) (420-500 °F) (450-520 °F) (400 °F) (326 °F) Air C. SOLVENT PRECIPITAITION Reduced Extractor Heater Flash Asphalt Crude or 38-93 °C 230 °C Stripper Storage Drum Flux (100-200 °F) (450 °F) Liquid Propane

A. STRAIGHT-RUN ASPHALT

Figure 9. Manufacture of petroleum asphalts (After Reference 6)

CHAPTER 3. SELECTION OF ASPHALTS

As previously discussed, the 32 asphalts were selected in three phases.

EIGHT CORE ASPHALTS - PHASE I

The selection of the eight "core" asphalts focused on asphalts with established or perceived performance histories. Emphasis was placed on selecting asphalts produced by atmospheric and vacuum distillation in order to minimize compositional and refining variables. However, when important crude oil sources with a wide range of physical and chemical properties were not available, asphalts manufactured by other refining processes were considered. Equally, if not more important, was the need to choose asphalts with a range of performance histories.

From an original list of thirteen sources, identified by the Expert Task Group, eight asphalts were selected as having sufficiently diverse performance histories as well as chemical and physical properties, to warrant their being selected as the core or common asphalts in the Asphalt Research Program. Core asphalts are to be tested by every asphalt researcher so that a fractional factorial cell can be developed permitting a systematic analysis of the data. Two grades of these eight asphalts were sampled, a normal paving grade for the locale where the refinery was located, as well as a softer grade which could be modified, if necessary.

Three performance pairs were included in the eight core asphalts, and are shown in relation to the various distress factors in the following tabular summary.

DISTRESSES	CALIFORNIA VALLEY VS CALIFORNIA COASTAL	LLOYDMINSTER VS REDWATER	WEST TEXAS INTERMEDIATE VS WEST TEXAS SOUR
low temperature cracking	х	X	
fatigue cracking	x		
permanent deformation (rutting)		x	
aging	X		
adhesion, water sensitivity			x

ASPHALT PAIRS

Six of the eight core asphalts were from the distillation process and two were from solvent deasphalting processes.

FOURTEEN ADDITIONAL ASPHALTS, PHASE II

During PHASE II, fourteen additional asphalts were identified which extended the matrix of performance and physicochemical properties found in the core asphalts and included additional asphalts produced by solvent refinery processes in order to evaluate the effect of different refinery techniques. Special consideration was given to the following variables in the selection of the PHASE II asphalts:

- a. current Major Sources of North American Asphalts;
- b. current Refinery Processes;
- c. asphalts with Extreme or Unusual Properties; and
- d. future Refinery Processes, e.g. using Cracked Residua.

As with the selection of the eight core asphalts, plots of temperature susceptibility versus aging index were used to ensure that a broad range of asphalts were represented. Figure 10 is a plot of temperature susceptibility versus aging index for many of the crude oil sources available to refineries in the United States and Canada.

SELECTION OF THE FINAL TEN ASPHALTS, PHASE III

During PHASE III, the final ten research asphalts were selected. Gaps in asphalt properties or performance histories identified by the early research data previously obtained from the SHRP Asphalt Program had a strong influence on the selection of the final ten asphalts. In addition, data developed for the previously sampled MRL asphalts were utilized. Thus, the PHASE III asphalt selection criteria were focussed on the completeness of the Phase I and II selection process.

ASPHALTS CURRENTLY AVAILABLE

Sampling of asphalts began in August 1988 and is expected to continue through 1989. The asphalt sources sampled, and which are available in the MRL, are noted in Figure 11. Prior to sampling, codes which are noted in Table 2, were assigned to each source in order to maintain confidentiality. All asphalts will be identified by these codes. At times it may be necessary to use these codes plus the name of the crude source.



CODE

- 1. California Coastal
- 2. California Coastal
- 3. Boscan
- 4. Lloydminster
- 5. Redwater
- 6. Wyoming High Sulfur
- 7. West Texas Intermediate
- 8. Arabian Heavy
- 9. Alaska North Slope
- 10. Maya
- 11. Maya/Wyoming Sour (40-60)
- 12. Maya/Arabian Heavy (80-20)
- 13. CA Valley/CA Coastal
- 14. ANS/CA Coastal
- 15. Cold Lake
- 16. Bow River
- 17. West Texas Sour/Maya (65-35)

- 20. Arabian Light/Maya (50-50) 21. Raspo More
 - 22. Baxterville
 - 23. Oklahoma Mix

18. Boscan/Maya

- 24. Rangley

19. Boscan/Bachaquero

- *25. Wyoming/Canadian Mix *26. Wyoming/Canadian Mix
- *27. Cracked 1
- *28. Cracked 2
- *29. Cracked 0
- *30. Wilmington
- 31. Lloydminster-Oxidized
- *32. El Paso-Oxidized
- *33. Kansas/Oklahoma
- * Data not Available
- Figure 10. Properties of crudes most often used in U.S. and Canada in asphalt production (After Reference 5)





ASPHALT ID CODES FOR MATERIALS REFERENCE LIBRARY

- AAA Loydminster
- AAB Wyoming High Sulfur
- AAC Redwater
- AAD California Coastal
- AAE Lloydminster (Air Blown)
- AAF West Texas Sour
- AAG California Valley
- AAH Rangely
- AAJ Oklahoma Mix (SDA)
- AAK Boscan
- AAL Cold Lake
- AAM West Texas Intermediate (SDA)
- AAN Bow River
- AAO Arabian Heavy
- AAP Oklahoma Mix
- AAQ Wyoming Mix (SDA)
- AAR Maya/Wyoming High Sulfur
- AAT Maya/Lloydminister
- AAU Alaska North Slope/CA Coastal
- AAW West Texas Sour/Maya
- AAY Maya/Arabian Heavy
- ABA West Texas Intermediate/West Texas Sour (Air Blown)
- Note: All sources used distillation process unless specifically noted. i.e., Solvent de-asphalted (SDA) or Air Blown

 Table 2. MRL Asphalt Codes for Materials Sampled to Date

FUTURE REPORT

Samples of asphalt cements contained in the MRL have been sent to two contract laboratories for analysis. Data obtained from these two labs, The Asphalt Institute and Matrecon, Inc., will be presented in a future report and are for the purpose of providing information which will allow the various asphalt researchers to effectively select asphalts for analysis. Table 3 contains a list of physical and chemical tests that will be performed on the MRL asphalts.

Test	Method		
1631	ASTM	AASHTO	
Viscosity			
140°F (60°C) 275°F (135°C)	D2171 D2170	T202 T201	
Penetration (100g, 5 sec) 39.2°F (4°C) 77°F (25°C)	D5	T49	
Ductility 60°F (15.6°C)	D113	T51	
Ring and Bell Softening, °F	D36	T53	
Thin Film Oven (TFO) Test	D1754	T179	
Viscosity 140°F (60°C)	D2171	T202	
Component Analysis	D4124		
Elemental Analysis for Sulfur, Nickel, Vanadium, Nitrogen	Microanalysis and Atomic Absorption		

TABLE 3 PHYSICAL AND CHEMICAL TESTS FOR MRL ASPHALTS

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