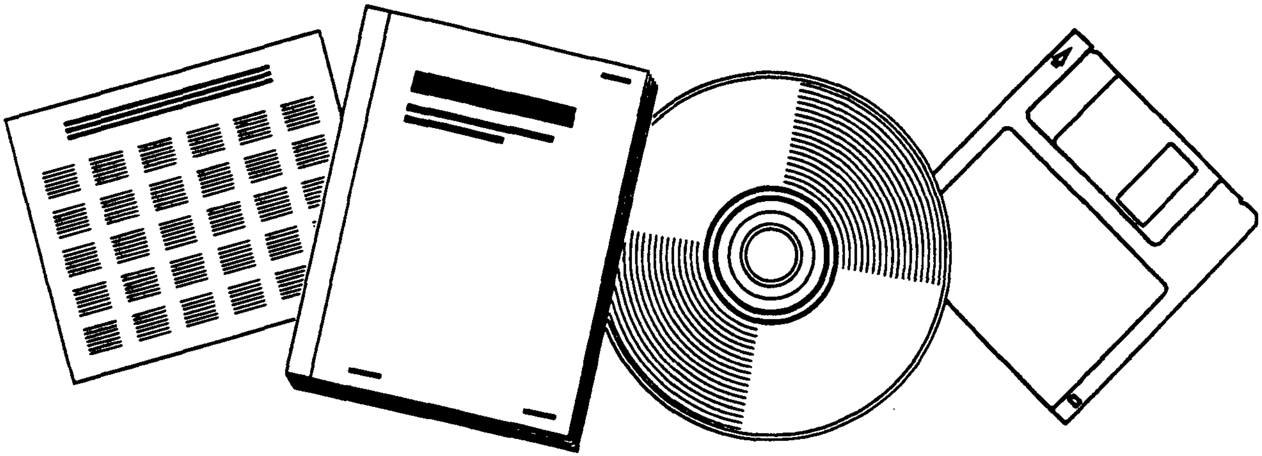
PB97-199384

LABORATORY DEVELOPMENT OF THIRD/FOURTH GENERATION SULPHLEX BINDERS

TEXAS TRANSPORTATION INST., COLLEGE STATION

JUL 97



Laboratory Development of Third/Fourth Generation Sulphlex Binders

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U.S. Department of Transportation
Federal Highway Administration

Research and Development
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FOREWORD

This final report presents the findings of Tasks A through F of a multitask program, which allows for the preparation and characterization of four generations of Sulphlex binders in accordance with the procedures generated under two previous FHWA Sulphlex projects designated Second Generation Sulphlex.

Current prices and sources for the raw materials used in the preparation of the Sulphlex binders studied in this program are reported under Task A. In Task B, Sulphlex 233 (First Generation) and Sulphlex 198 (Second Generation) were prepared individually and then blended to 50/50 proportions on a weight basis. In Task C, the equivalent of the Task B Sulphlex blend was produced in a one-pot synthesis and designated as the Third Generation Sulphlex. In Task D, a "new and improved" binder designed to enhance low-temperature fracture resistance was synthesized and designated as the Fourth Generation Sulphlex. For Task E, Sulphlex binders and their respective mixtures were subjected to a series of screening and characterization tests using Superpave, AAMAS, AASHTO and VESYS procedures to assess their roadway performance potential.

In Task F, manufacturing plans and procedures were generated for the manufacture of Sulphlex for the construction of an hypothetical road section. Current prices and sources for the raw materials and chemicals used in the preparation of the binders generated in this program are also provided.

Sincerely,

Charles J. Nemmers
Director, Office of Engineering
Research and Development

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16. Abstract

This report presents the findings of a 2-year, multitask study to provide a new generation of Sulphlex binders with enhanced low-temperature fracture resistance. The initial phases of the program dealt with the preparation and base-line characterization of Sulphlex 233 and 198, First and Second Generation Sulphlex, respectively, considered the more promising of a broad series of formulations developed under earlier FHWA programs. These binders were prepared individually and blended at ratios of 50/50 and 75/25: (198/233) and designated as Third Generation Sulphlex. The former was prepared by directly blending the two binders as well as by a one-pot synthesis. These binders were subjected to a series of screening tests including (a) Penetration @ 25°C, (b) Viscosity @ 135°C, (c) Specific Gravity, (d) Solubility in $CHCl_3$, (e) Storage Stability, and (f) Glass Transition temperature. A "new and improved" Sulphlex binder designated as Fourth Generation was formulated utilizing the rationale derived from the earlier systems.

Sulphlex mixtures along with a control using an AC-20 asphalt were prepared using a crushed limestone aggregate and tested in accordance with AAMAS, AASHTO, Superpave and VESYS procedures including, (a) Indirect Tension, (b) Diametral Resilient Modulus, (c) IDT Creep, (d) Compressive Creep, (e) Unconfined Compression, (f) Repeated Load Permanent Deformation and Aging using M_R.

A set of generic manufacturing plans and procedures were generated for the production of Sulphlex in sufficient quantity to satisfy the requirements of an hypothetical test road section.

17. Key Words
Sulphlex, plasticized sulfur, olefin, sulfur, AAMAS, Superpave, VESYS, synthesis, paving mixtures

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yards	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
NOTE: Volumes greater than 1000 l shall be shown in m^3.				
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact)		
°F	Fahrenheit temperature	5(F-32)/9 or (F-32)/1.8	Celcius temperature	°C
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.71	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact)		
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.

(Revised September 1993)

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CHAPTER 1. SUMMARY

NATURE OF SULPHLEX

The need for cost-effective alternatives to replace the asphalt binders conventionally used on the Nation's highways was felt in the early 1970's due to the Arab Oil Embargo and the subsequent energy crisis. The research and development activity that followed produced a plethora of sulfur-extended-asphalt (SEA) binders in which up to 30 percent of the weight of asphalt was replaced with sulfur (1,2,3,4,5). Consequently, attempts were made to totally replace the asphalt with sulfur, leading to the development of the "Sulphlex" concept. The harbinger of this effort was performed at the Southwest Research Institute in San Antonio, Texas by Ludwig et. al. who succeeded in producing 23 Sulphlex formulations which showed promise as a paving material.(6,7) These binders were subsequently designated as the First Generation Sulphlex binders of which the most intensively studied was Sulphlex 233.

It was initially recognized that if sulfur were to be used as a pavement binder, it would have to exhibit more plastic characteristics. The term plasticized sulfur is often used to describe the modification of sulfur to achieve the characteristics of flexibility, workability, and extensibility.

It has long been known that when elemental sulfur is heated above its transition temperature and rapidly quenched it exhibits a temporary plastic character. However, the material quickly hardens with the formation of orthorhombic, S_8 sulfur crystals. Evidence exists that above 160 °C (320 °F) molten sulfur consists of a mixture of S_8 rings and S_x chains where the value of x can be very large. Exactly how the plasticization occurs at this point is uncertain and speculative. In any case, the mechanism for plasticizing sulfur is brought about by a physical change that does not lend itself to practical application in the preparation of binders for paving.

In order to retain the desirable plasticized behavior, sulfur must be converted by a chemical reaction, a physical change, or a combination of these. Prior to research performed for the Federal Highway Administration (FHWA), efforts at sulfur plasticization had dealt with a single additive. Sulphlex binders are based on the reaction of multiple additives with elemental sulfur. Depending on the degree of plasticization, Sulphlex formulations can resemble asphalt or portland cement in terms of their behavioral characteristics and can thus be utilized in either flexible or rigid pavement applications.

Sulphlex 233, which in this report will be referred to as the First Generation Sulphlex, is a manufactured product. Specifically, molten, elemental sulfur is reacted in a vessel at 149 °C (300 °F) with a blend of plasticizers or chemical modifiers: dicyclopentadiene (DCPD), vinyl toluene, and dipentene. The formulation for the 233 binder is 70 percent by weight of elemental sulfur, 12 percent DCPD, 10 percent dipentene, and 8 percent vinyl toluene. As a binder for roadway pavements, Sulphlex 233 binders tend to exhibit good strength properties, but appear to have certain shortcomings that had to be overcome. Some of these concerns include:(8)

1. The aggregate mixes made with Sulphlex 233 have poor fatigue resistance, especially at low temperature.

2. The aggregate mixes of Sulphlex 233 without additives have poor water resistance; that is, in water the binder seems to separate from the aggregate, and the mix loses strength.

3. The properties of Sulphlex 233 change with time at ambient temperature largely due to crystallization of the free sulfur present. The Sulphlex hardens, particularly when in thin films. As a binder, its penetration drops, and in concrete its modulus increases.

4. On storage at elevated temperature, e. g., 135 °C (275 °F), Sulphlex 233 loses weight and increases in viscosity. This is of importance because it would be desirable, as with asphalt, to maintain Sulphlex in a molten condition so that it could be easily pumped from the storage tanks.

5. The temperature at which the Sulphlex is prepared has a significant effect upon binder characteristics. Sulphlex 233 prepared at a lower temperature of 150 °C (302 °F) crystallizes at a slower rate, has a lower free sulfur content and a somewhat higher molecular weight, and is more viscous. The slower rate of hardening tends to make Sulphlex more asphalt-like, while all Sulphlex 233 systems tend to harden at ambient temperature. Also, Sulphlex prepared at 150 °C (302 °F) ages better in the molten state than when prepared at 170 °C (338 °F). The higher viscosity of the Sulphlex prepared at 150 °C (302 °F) could adversely affect mixing and paving operations.

These shortcomings were addressed in an FHWA sponsored Texas A&M/Matrecon program which led to the development of Sulphlex 198, hereafter referred to as Second Generation Sulphlex.(9,10) Interestingly, this binder possessed substantially lower glass transition temperatures, T_g's, than did First Generation Sulphlex binders. From a fracture resistance perspective, J_{IC} values (i. e., the amount of work, or energy, required to promote crack growth) were higher, at or near the glass transition than First Generation Sulphlex binders. However, Sulphlex 198 binders were susceptible to permanent deformation at the higher temperatures, and it was generally necessary to blend 198 with a stiffer Sulphlex series, such as 233, in order to achieve a composite binder that would perform satisfactorily over the temperature range to which mixtures are typically subjected. Extensive mixture testing and performance predictions in an FHWA research study demonstrated that a 50/50 blend of 198 and 233 was particularly successful.[(9)] However, the final report states, "the weak link in the research done thus far from a mixture standpoint is the lack of extensive water susceptibility and aging testing of the Second Generation Sulphlex binders."

The engineering development of the Second Generation Sulphlex binders concentrated heavily on the glass transition temperature and the fracture properties, especially J_{1C} at and near their T_g. The T_g was determined through differential scanning calorimetry (DSC) and by dilatometeric methods at different heating rates. Much of the mixture testing consisted of the work with the Texas Transportation Institute (TTI) overlay tester where a slab of mixture is subjected to the exact type of stress and movement induced in the pavement during periods of temperature fluctuation and during movements in underlying cracks or joints (reflection cracking). This type of testing allowed the researchers to determine the rate of crack growth for the various mixtures tested under various stress states induced at the crack tip. An equally important phase of testing was the low temperature determination of J_{1C} using notched asphalt beams. The researchers state in the final report on the development of the Second Generation of Sulphlex binders, "The determination of transition temperatures by means of the DSC and dilatometer, J_{1C} values and the crack propagation behavior of Sulphlex mixtures under controlled displacement fatigue proved to be indispensable tools in the development of Second Generation Sulphlex binders and mixtures."

In terms of the development of the Sulphlex binders, research on the development of Second Generation binders concluded that:

1. Plasticized sulfurs based on low-purity reactants and uncontrolled mixtures of different chemical species of reactants tend to have erratic and poor properties. Future work should be continued on reactants that are as pure as possible or that are prepared under highly controlled conditions until such time as technically satisfactory products can be made and reproduced.

2. Batch-to-batch reproducibility can be achieved in the preparation of small batches of plasticized sulfurs by using reactants from the same batches and under highly controlled reaction conditions.

3. Plasticized sulfurs containing less than 18 percent free sulfur do not appear to show sulfur crystallinity, but they do appear to show some crystallinity possibly from low molecular weight reaction products of sulfur and hydrocarbons.

4. The following reactants showed promise and should be investigated further:

    a. p-Vinyl toluene (improved high temperature stability).
    b. 1, 4-Hexadiene (improved low temperature properties).
    c. Neodene C_{11} - C_{12}, internal olefins[1] (improved low temperature properties).

d. Dicylopentadiene-oligomer (low viscosity and improved properties for blending with higher viscosity plasticized sulfurs).

The important and significant findings and recommendations such as Sulphlex binder processing methodology, mix design rationale and safety considerations developed in earlier research programs provided much of the decision criteria used in this research effort.

These decision criteria were brought to bear in the design of the "new and improved," Fourth Generation Sulphlex binder (Task D). The primary objective of this task was to further enhance low temperature fracture resistance. A secondary consideration was to also extend, if possible, resistance to high temperature distress, as well. Although cost was not of prime importance in this research effort, the opportunity to exploit cheaper, more readily available raw materials was incorporated into the design criteria for this new binder.

The result was a formulation that was similar to Sulphlex 198 in that it eliminated Vinyl Toluene and Dipentene, yet novel that it added a DCPD Oligomer to provide long-term allotropic stability to the chemical composition.(11)

The result was a binder with higher penetration and lower T_g values than any of previously developed Sulphlex systems. As will be discussed later in chapter 5, these improved binder properties which would normally be indicative of good low temperature fracture resistance did not exhibit this behavior when incorporated into mixtures.

This program employed testing methodologies recommended by the Asphalt Aggregate Mixture Analysis System (AAMAS), the American-Association of State Highway and Transportation Officials (AASHTO), the Strategic Highway Research Program (SHRP or Superpave), and Viscoelastic Systems (VESYS) analysis, for the evaluation of the binders and mixtures.(12, 13, 14, 15)

[1] A group of aliphatic olefins in which double bonds are randomly distributed along the aliphatic carbon chain.

CHAPTER 2. RESEARCH OVERVIEW

PURPOSE AND OBJECTIVES

This program was designed to provide a new Sulphlex binder formulation to augment those developed on earlier Sulphlex research contracts.(6, 7, 8, 9, 10, 11, 16, 19, 20) The major drawbacks inherent with those early formulations were cost and low temperature fracture resistance. The former was dictated by the cost and availability of sulfur and chemical additives. The latter problem was the residual consequence of the performance characteristics inherent with the First and Second Generation of Sulphlex binders. The current program not only attempts to optimize these early formulations into a one-pot synthesized Third Generation Sulphlex, but also provides the opportunity to develop a new and improved Fourth Generation Sulphlex binder unrestricted by the need to use the same raw materials used in the earlier Sulphlexes. The behavioral characteristics of the Sulphlex binders and mixtures were compared with those prepared using a conventional AC-20 asphalt.

A second requirement of this program was to develop a process and specifications whereby Sulphlex binders can be prepared in a single reaction vessel. The resulting process was subsequently scaled-up to provide a generic set of manufacturing plans and procedures. The ultimate use of these plans was for the efficient and economically frugal production of Sulphlex for an hypothetical test road section.

REPORT ORGANIZATION

The report is divided into six chapters. The first chapter is a summary of the study while chapter 2 presents the objectives and organization of the overall study. Chapter 2 also describes the test procedures and materials used throughout the program. Chapters 3 through 6 are presented consistent with the sequence of tasks (Tasks A through F) as set forth in the proposed scope of work as discussed below.

Identification of Raw Materials Sources (Task A)

In addition to providing a list of sources for sulfur and other chemical additives required for the production of Sulphlex binders, the prices of these raw materials were periodically updated throughout the course of the program.

Synthesis of Second, Third, and Fourth Generation Sulphlex Binders (Tasks B, C, and D).

In Task B, a 50/50 (198:233) blend of First and Second Generation Sulphlex binders was synthesized. The two binders, Sulphlex 233 and Sulphlex 198 were prepared using the methodology described in FHWA publication number FHWA-RD-86-016.(16)

In Task C, a Third Generation Sulphlex was prepared. This binder was similar to that produced under Task B except that, the reaction was carried out as a "one-pot synthesis" using a single reactor.

Task D provides for the synthesis of a "new and improved" Sulphlex binder. Because changes in raw materials were permitted in the formulation of this binder it was felt appropriate that it should be referred to as a Fourth Generation Sulphlex. This new formulation built on the mix design rationale developed in both the past and current Sulphlex programs to extend the temperature range over which these binders could be expected to perform. Although the primary thrust was to enhance low temperature fracture resistance, the new mix design attempted to affect high temperature performance, as well.

In all these tasks, the syntheses were carried using the facilities of McBee and Associates of Lebanon, Oregon. Their production unit consists of a 56.8-l (15-gal), sealed, agitated, steam (or water) jacketed, stainless steel reactor. Chemical additives were preblended in a 7.6-l (2-gal) pressurized stainless steel tank. Aside from the preparation of the various Sulphlex binders, this plant was also used to establish QC/QA procedures for future road construction projects.

Characterization Testing of Sulphlex Binders and Mixtures (Task E)

The Second and Third Generation Sulphlex (Tasks B and C) binders were screened through a series of tests similar to those conducted under publication number FHWA-RD-86-016 (May 1986).(16) These tests were to establish that the properties of binders produced under this study were consistent with those generated in the earlier Sulphlex programs. Except for variations which could be attributed to differences in process equipment and the improvement in the control of process variables afforded by the McBee pilot plant, the new binders appeared to exhibit properties similar to their earlier counterparts.

Upon completion of the binder screening tests, the Fourth Generation Sulphlex binder and concrete mixtures were prepared and characterized in accordance with Superpave/AAMAS performance-related procedures. These tests also provided input to QC/QA methodology for scaled-up production of Sulphlex binders and mixtures for use in road construction to be discussed in chapter 6.

Manufacturing Procedures for Sulphlex Roadway Construction (Task F)

Generic plans and procedures were prepared for the manufacture of sufficient quantities of Fourth Generation Sulphlex binder to construct an hypothetical test section 152.4 m (500 ft) long with 2 to 3.66-m (12-ft) wide lanes and a thickness of 12.7 mm (0.5 in). The plan was designed to emphasize cost-effective production and include acquisition, handling and storage requirements for all raw materials.

MATERIALS

Three classes of materials were utilized in this program: (a) Sulphlex (First through Fourth Generations), (b) AC-20 viscosity grade asphalt, and (c) a crushed limestone aggregate. The chemical additives utilized in the preparation of the four generations of Sulphlex binders studied under this program include: (a) Sulfur, (b) Dicyclopentadiene (DCPD), (c) Neodene C_{11} - C_{12}, internal olefin, (d) Vinyl toluene, (e) Dipentene, and (f) Dicyclopentadiene oligomer. These chemical designations were employed throughout this report to maintain consistency with earlier published work. For convenience of the reader, additional designations are given in the manufacturers' Material Safety Data Sheets (MSDS) found in appendix A. A listing of each reactant, its chemical structure, source and current cost is also presented in chapter 3 of this report. The processing of Sulphlex binders in laboratory and large-size batches is discussed in chapters 4 and 6, respectively.

Sulphlex

This binder was originally produced under FHWA contract.(16) Sulphlex is a trade name for a family of pavement binders composed of chemically-modified sulfur. The results of this investigation produced a listing of 21 Sulphlex formulations considered by the authors to be the most promising. Throughout this report these binders will be referred to as First Generation Sulphlex. Of the original group, Sulphlex 233 was selected for use in this study. The major shortcoming of the First Generation Sulphlex binders proved to be their low-temperature crack resistance. This lead to a new FHWA study to develop a Second Generation of Sulphlex binders.(10)

After evaluating some 99 different materials, Sulphlex 198 was created, wherein a Neodene C_{11} - C_{12} internal olefin was substituted for the vinyl toluene and dipentene fraction in Sulphlex 233. This group is referred to, herein as Second Generation Sulphlex. The composition by weight of these two formulations are given in table 1.

Table 1. Raw materials for Sulphlex 233 and 198 binders.

Raw Material[1]	Sulphlex 233 (w/o)[2]	Sulphlex 198 (w/o)[2]
Sulfur	70	70
Dicyclopentadiene (DCPD)	12	12
Dipentene (Limonene)	10	---
Vinyl Toluene	8	---
Neodene C_{11} - C_{12} Internal Olefins	---	18

[1]See appendix A for additional designations.
[2]w/o = weight percent

When blended at a 50/50 mixture of Sulphlex 198 and 233, superior low-temperature performance was achieved in laboratory testing.(10) This blend was incorporated into this study and was produced by two different methods. In the first method, each binder was produced individually and subsequently blended (Task B) in a two-pot process. In a separate synthesis, the equivalent of the 50/50 (198:233) blend was achieved in a one-pot reaction (Task C). These blended binders were designated as the Third Generation Sulphlex.

An attempt was made to optimize the properties of Sulphlex binders thereby synthesizing a "new and improved" formulation not necessarily restricted by the need to use the chemical constituents in the First, Second, and Third Generation Sulphlex formulations. The resulting binder was designated as the Fourth Generation Sulphlex with the composition given in table 2.

Table 2. Formulation of Fourth Generation Sulphlex.

Fourth Generation Sulphlex, (w/o)	
Sulfur	70
Dicyclopentadiene DCPD	7.5
Neodene C_{11} - C_{12} Internal Olefin	7.5
Oligomer of Dicyclopentadiene	15

Asphalt

The control binder in this study was an American Petrofina AC-20 asphalt obtained from Young Brothers, College Station, Texas. This control binder along with its mixtures served as the reference for all the characterization testing discussed in chapter 5 of this report. All properties of the binders met ASTM and AASHTO specifications laid down for this grade. The composition of the control asphalt using the Rostler analysis was is given in table 3.

Table 3. Composition (w/o) of control AC-20 asphalt.

Asphaltenes	15.3
Nitrogen Bases	32.1
First Acidaffins	19.8
Second Acidaffins	23.4
Paraffins	9.4

The penetration of the asphalt at 25 °C (77 °F) (100 g 5 s) was 58 and the viscosity was 196 Pa·s at 60 °C (140 °F).

Aggregate

All mixtures used in the characterization testing program utilized an aggregate comprised of a combination of limestone and field sand. The coarse fraction was a hard, durable, quality dolomitic limestone quarried in Brownwood, Texas. The field sand was a silicious, subangular material. The combination of dolomitic limestone, silicious field sand and the optimum binder produced a high quality hot mix asphalt concrete mixture. The aggregate gradation used is shown in figure 1 and was the same as that used in the testing of the Second Generation Sulphlex binders, as documented in FHWA-RD-86-016.(16)

The bulk specific gravity of the aggregate was 2.587 using the assumption that 41 percent of the total weight was coarse aggregate and the remaining was fine aggregate with specific gravities of 2.663 and 2.537, respectively.

BINDER PREPARATION

A primary objective of this research was to conduct characterization tests on Sulphlex binders prepared in a pilot plant rather than in small, laboratory-scale batches. To this end, the facilities of McBee and Associate of Lebanon, Oregon were solicited for binder production.

This facility is more fully discussed in chapter 4. The 56.8-l (15-gal) capacity of the McBee plant provided all the Sulphlex used in this study. The process controls, reaction times and temperatures and product quality assurance encountered in the production of these binders formed the basis of the manufacturing specifications generated and discussed in chapter 6.

LABORATORY TESTING

Binder Screening Tests

One of the initial objectives of this study was to assess the potential of the third generation binder for engineering applications and thereafter synthesize a new and improved Fourth Generation Sulphlex binder with enhanced low-temperature properties. A preliminary binder testing program was developed in order to characterize all the Sulphlex binders named the 50/50, 75/25 (198/233), the one-pot synthesized blends of Sulphlex 198 and 233, and the new and improved Fourth Generation Sulphlex. The binder tests on the original binders were conducted in accordance with those reported in FHWA-RD-86-016, and included in the following:(16)

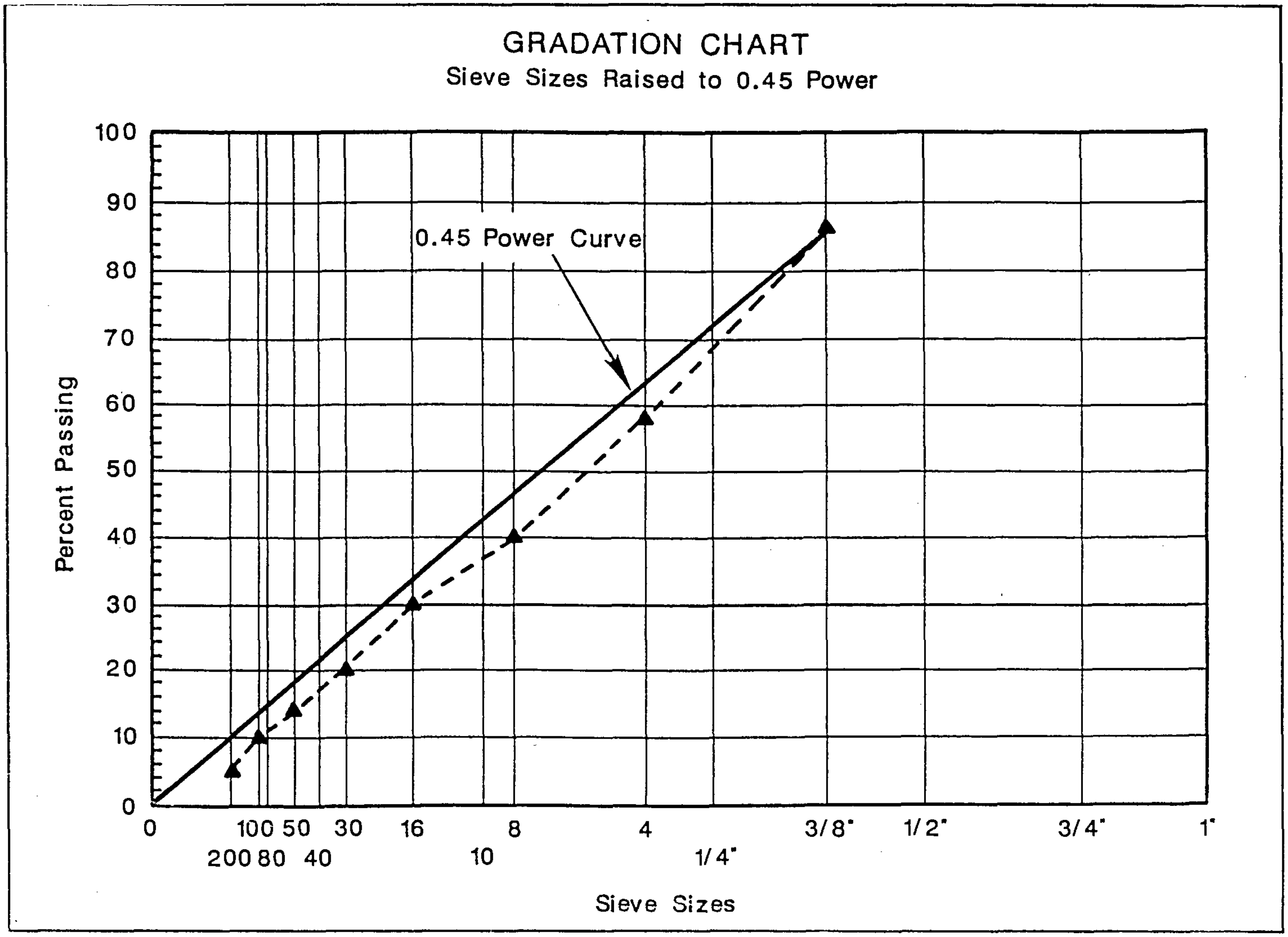

Figure 1. Aggregate gradation used in both Second Generation Sulphlex binder and control mixtures.

1. Penetration at 25 °C (77 °F) .... ASTM D 5.
2. Viscosity at 135 °C (275 °F) .... ASTM D 2170.
3. Specific Gravity .... ASTM D 70.
4. Solubility in $CHCL_3$ .... AASHTO T 44.
5. Storage Stability @ 100 °C (212 °F)
   and Ambient temperature .... ASTM E 1131.
6. Glass Transition Temperature, T_g .... ASTM D 696.
7. Brookfield Viscometer .... ASTM D 4402.
8. Dynamic Shear Rheometer .... Superpave.(14)
9. Bending Beam Rheometer .... Superpave.(14)

In addition, the Superpave tests - namely the dynamic shear rheometer, the bending beam rheometer and the direct tension test - were conducted where necessary to establish conformity with the Superpave binder specifications.(14)

Preliminary binder tests, items one through six, were conducted in accordance with their respective ASTM and AASHTO procedures at the laboratories of Matrecon, Inc. The Brookfield viscometer, the dynamic shear rheometer and the bending beam rheometer testing procedures will, however, be discussed at length, below. The results of all these tests are presented in chapter 5.

Brookfield Viscometer

The Brookfield DVII viscometer, documented under procedure ASTM D 4402 and shown in figure 2 was used to determine the viscosity of the Sulphlexes over a range of elevated temperatures. The operating principle of the viscometer was that the spindle was driven through a beryllium/copper spring and the degree to which the spring was wound, detected by a rational transducer, was proportional to the viscosity of the fluid.(17)

The most important aspect of this test is its capability of measuring the apparent viscosity of binders at elevated temperatures. It was designed specifically with the intention of developing viscosity and temperature relationships.

Temperature measurements were achieved using the Brookfield Thermosel system which included a digital proportional temperature controller with a Resistance Temperature Detector (RTD) sensor. The viscometer was capable of controlling the spindle speed within a range of 0.5 to 100 r/m.(17)

The Brookfield DVII viscometer was used with the Brookfield DV-Gather *software. The software was designed to facilitate testing procedures by preprogramming certain commonly used data gathering techniques. It was also automatically controlling the

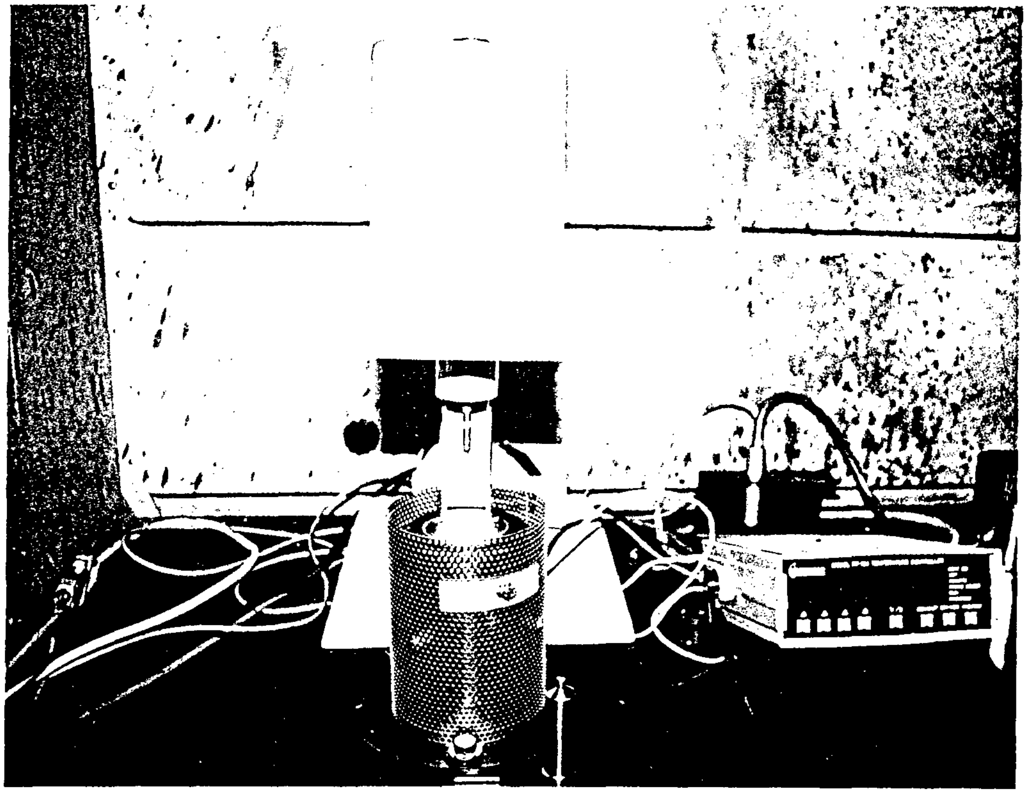

Figure 2. The Brookfield viscometer.

viscometer rotational rate and collecting the corresponding rheological data.

Dynamic Shear Rheometer

The dynamic shear rheometer was used to determine the rheological properties of the Sulphlex binders.(14) This instrument was developed about 30 years ago and finds use in many corporations for research and also for quality control for a wide range of materials.

Its theory of operation is based on introducing a small sample of the binder between two parallel, circular plates 25 mm in diameter and 1 mm apart. The upper plate is oscillated by a precision electronic motor, controlled by a personal computer. The rotation of the upper plate is precisely measured by an optical encoder which consists of a transparent disc with a pattern of opaque segments on its surface. With movement, these segments interrupt a light beam, the frequency of which, can be translated electronically into either linear or angular speed. From the torque and rotation, the rheological properties were calculated by the computer. The modulus of the asphalt, which is a measure of its overall stiffness, was computed from the applied torque and the resulting deflection.

The dynamic shear rheometer data is used to measure and control the properties of the binders at high temperatures. This data is used in conjunction with the bending beam rheometer data to predict the rheological behavior of the binder over a range of temperatures and loading times.(4) Adequate binder performance is ensured by allocating allowable values for specific rheological parameters related to low temperature cracking, permanent deformation, and fatigue cracking.

The specification test for this program involves the measurement of rheological properties of the binder at a fixed frequency of 10 rad/s over a range of temperatures prescribed by the Superpave binder specifications.(14)

Figure 3 shows the Carri-Med CSL dynamic shear rheometer located in the Chemical Engineering Department at Texas A&M and used in this program. This rheometer is one of two used in rheological testing of Sulphlex binders at TTI. The second is a Rheometrics Model RDS II rheometer.

Bending Beam Rheometer

This test was conducted in accordance with Superpave procedures in order to establish conformity with Superpave specifications.(14) The bending beam rheometer,

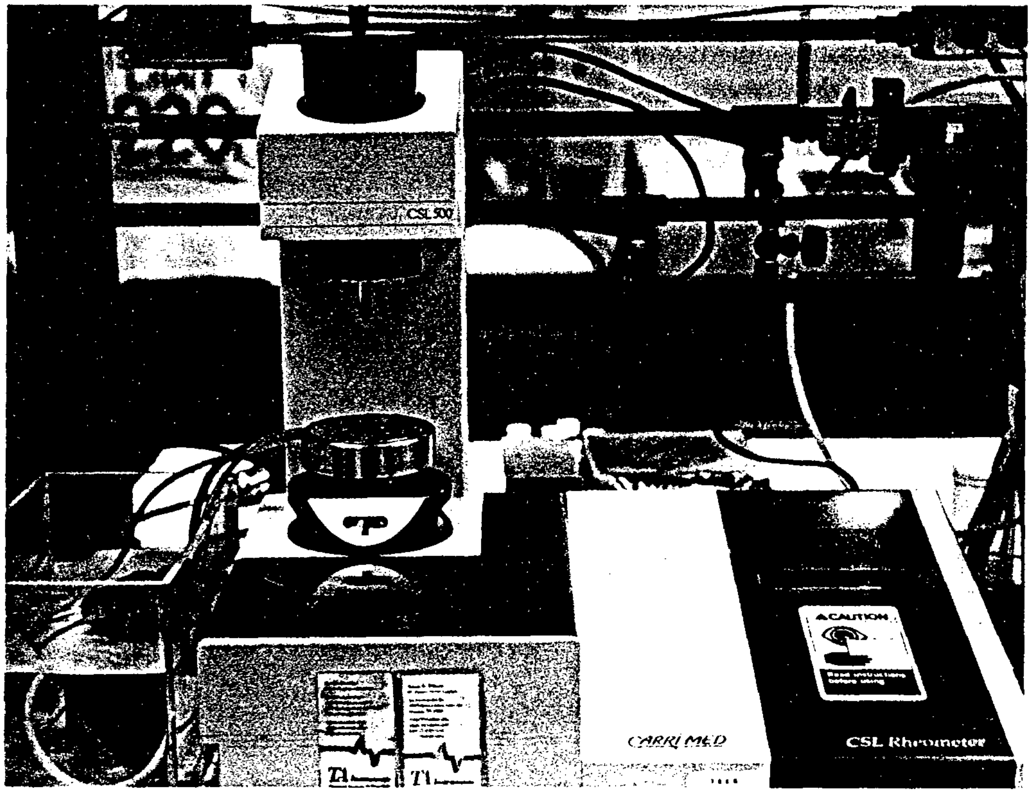

Figure 3. The Carri-Med CSL dynamic shear rheometer.

shown in figure 4, was used for measuring the low-temperature rheological properties of the Sulphlex binders. This instrument was recently developed at Penn State University and was used to measure the resistance of asphalt binders to deformation at very low temperatures. Due to the similarity observed between Sulphlex and asphalt binders from previous characterization programs, this test was deemed applicable for use on Sulphlex binders.

Its theory of operation was based on loading a Sulphlex specimen in the form of a beam, 125 mm (4.9 in) long, 12.5 mm (0.49 in) wide, and 6 mm (0.24 in) thick, with a constant load. The beam, supported by half-round supports placed 100 mm (3.9 in) apart, was loaded at the midspan with a constant load of 50 to 100 g. The loading platform was placed in a refrigeration bath which maintains the test temperature at -15 °C (5 °F). The deflection of the beam at the midspan was measured continuously over a period of 4 min, and the flexural stiffness was calculated automatically by a computer software program. The stiffness of the asphalt, which reflects its resistance to deformation, was calculated from the applied load and the resulting deflection as a function of time. Adequate binder performance was ensured by specifying maximum requirements for stiffness at low temperatures, by minimum requirements for permanent deformation at high temperatures, and by minimum creep rate "m" at intermediate temperatures designated in the Superpave binder specifications.(14)

The specification test under this program involved the measurement of the stiffness of the Sulphlex binder as a function of loading time over a 4-min time period under a constant load of 100 g at temperatures ranging from -15 °C (5 °F) to 30 °C (86 °F). The binder was subjected to rolling thin film oven and the pressure aging vessel conditioning before being tested in the bending beam rheometer.(14) From this test, both the creep stiffness and slope of the creep stiffness versus time of loading at 60 s of loading were determined at the test temperatures.

Direct Tension

The apparatus normally used to determine the failure properties of binders in direct tension was not used in this testing program.

CHARACTERIZATION TESTS OF SULPHLEX AND CONTROL MIXTURES

The Third Generation Sulphlexes designated as 50/50, 75/25 (198:233) two-pot, and one-pot synthesized along with the Fourth Generation asphalt and an AC-20 asphalt were subjected to a series of mixture screening tests which included the following:

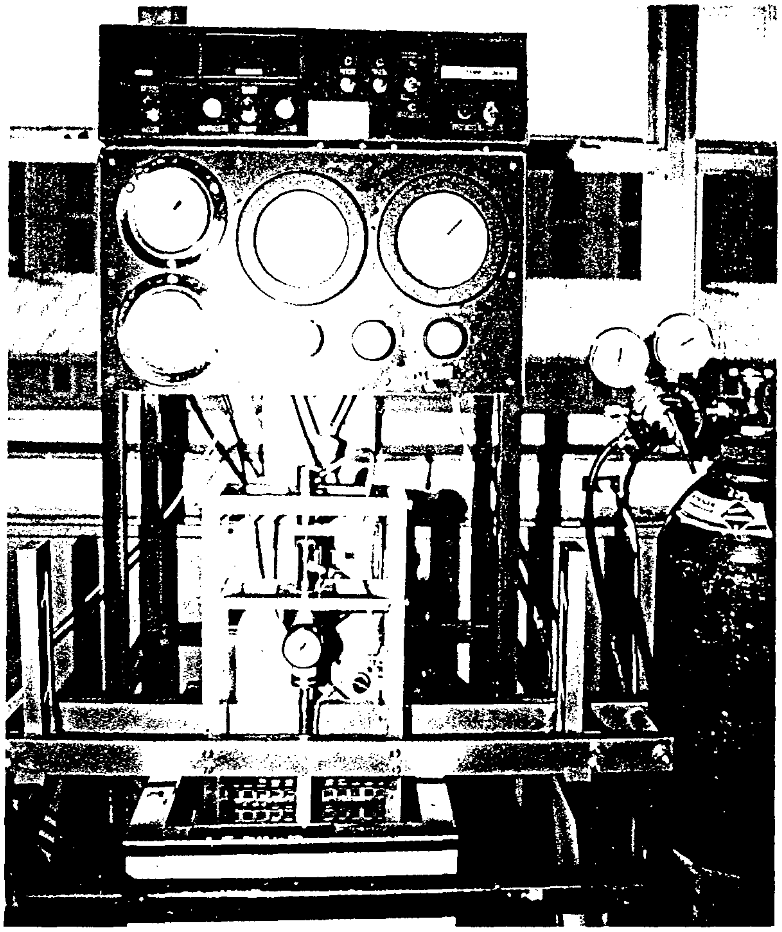

Figure 4. The bending beam rheometer.

1. Diametral Resilient Modulus (AAMAS) at -24, 5, 25, and 40 °C (-10, 41, 77 and 104 °F).(12)

2. Indirect Tensile Creep (AAMAS) at 5 °C (41 °F).(12)

3. Uniaxial Compressive Creep (AAMAS) at 40 °C (104 °F) for 3600 s at stress levels of 103 and 414 kPa (15 and 60 psi).(12)

4. Repeated Load Permanent Deformation for 10,000 cycles.

5. Unconfined Compressive Strength (AAMAS).(12)

6. Indirect Tension to Failure (AAMAS) at -24, 5, 25, and 40 °C (-10, 41, 77, and 104 °F).(12)

7. Aging at 25 °C (77 °F).

Table 4 is a summary of the testing procedures followed in this study for the engineering characterization of Sulphlex and control mixtures. Table 5 lists the distress mechanisms addressed and the testing procedures associated with them.

Diametral Resilient Modulus and Indirect Tension

The indirect tensile testing was done in accordance with AAMAS procedures on 6.35 mm high by 10.2 mm diameter cylindrical samples.(12) The resilient modulus test was conducted according to ASTM D 4123, which is also the standard followed by AAMAS. Indirect tensile testing was conducted at the four temperatures given above. Three specimens were tested at each temperature.

The repeated load indirect tension test for determining resilient modulus, as shown in figure 5, was conducted by applying compressive loads with an offset sine wave (commonly, but incorrectly called a "haversine") followed by a rest period having a long duration in relation to the duration of the sinusoidal pulse. The load was applied along the vertical diametral axis of the specimen. The resulting diametral horizontal and vertical deformations of the specimen were measured. The total resilient modulus and Poisson's ratio were calculated using the total recoverable deformation which includes both the instantaneous and the time-dependent, continuing recoverable deformation during the unloading and rest-period portion of one cycle. The Poisson's ratios associated with the four test temperatures are summarized in table 6.

Table 4. Summary of the test procedures used in the engineering characterization of Sulphlex mixtures.(16)

Test Category	Test Name	Test or Material Properties of Significance	Test Procedure Used
Mixture Design	Marshall Stability	Marshall Stability and Flow	ASTM D 1559
	Bulk Specific Gravity	Bulk Density	AASHTO T-166
	Rice Specific Gravity	Maximum Specific Gravity	AASHTO T-166
	Void Content	Air Voids	Asphalt Institute(18)
		Voids in Mineral Aggregate	Asphalt Institute(18)
Modulus	Diametral Resilient Modulus	Resilient Modulus	ASTM D 4123
Deformation	Indirect Tensile (IDT) Creep	IDT Creep Modulus	AAMAS, Ref. 12, pp. 35-38
	Uniaxial Compressive Creep	Creep Modulus	AAMAS, Ref. 12, pp. 35-38
	Repeated Load Permanent Deformation Test	Dynamic Resilient Modulus and	VESYS Users Manual(15)
		Total Permanent Deformation	VESYS Users Manual(15)
Strength	Unconfined Compression	Compressive Strength	AASHTO T-165, T-167
	Indirect Tension to Failure Test	Stress and Strain at Failure	AAMAS(12)
Aging	Diametrial Resilient Modulus	Resistent Modulus	AAMAS(12)
	Indirect Tension to Failure Test	Stress and Strain at Failure	ASTM D 4123(19,20,21)

Table 5. Summary of the distress mechanisms and associated testing procedures of mixtures.

Distress Mechanism Addressed	Testing Procedure	
Load-Induced Fatigue Cracking	Indirect Tensile Tension (IDT) to Failure Test	AAMAS(12)
	IDT Resilient Modulus	
Resilient Response and Elasticity	IDT Resilient Modulus	
	Dynamic Resilient Modulus	AAMAS(12)
Resistance of Mixture to Consolidation and Long-Term Deformation	Uniaxial Compressive Creep	AAMAS(12)
	Unconfined Compressive Strength	AASHTO T-165, T-167
	Repeated Load Deformation	VESYS (15)
Low Temperature Fracture	IDT Creep	Ref 14
	IDT Stress and Strain at Failure	
Moisture Resistance	Superpave Stripping Test	Ref 12
Aging Resistance	AAMAS Aging	

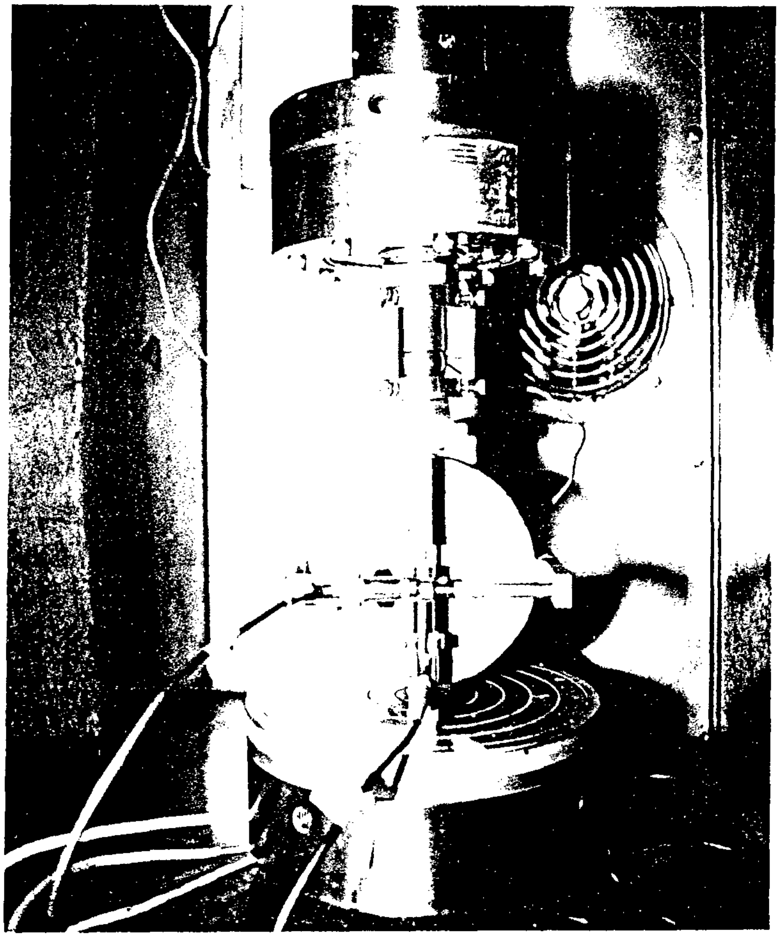

Figure 5. The repeated load indirect tension test set-up for determining resilient modulus.

Table 6. Poisson's ratio at the four test temperatures.

Temperature °C	Poisson's Ratio
-24	0.20
5	0.25
25	0.35
40	0.40

After the resilient modulus was determined, the specimens were tested in indirect tension to obtain the indirect stress and strain at failure. In this test, the specimens were vertically loaded at a constant rate with a compressive load, along the diametral axis of a 102-mm (4-in) diameter by 51-mm (2-in) long specimen until failure occurs. The diametral horizontal deformation during the entire loading time, or until the load sustained by the specimen began to decrease, was recorded. The peak load and the load at failure were recorded from which the tensile stress and strain at failure (i. e., where actual break occurs) were calculated. The deformation rate was varied at different temperatures to obtain representative results. At temperatures of 5 and -24 °C (41 and -11 °F) the deformation rate was 0.5 mm/min (0.02 in/min) while at temperatures of 40 °C (104 °F) and 25 °C (77 °F) the rate was 51 mm/min (2 in/min).

Specimens for this test were prepared using the Texas gyratory compactor (Texas Test Method: Tex 206F). The average specimen height was 51 mm (2 in) with a minimum diameter of 102 mm (4 in). The specimens were compacted at a stress level of 345 kPa (50 psi) with a final seating load of 11 kN (2500 lb). The AAMAS test procedure used was as follows:

1. The bulk specific gravity and the Rice (maximum) specific gravity of the specimens were measured in accordance with AASHTO T-166 to compute air voids and VMA (voids in mineral aggregate).
2. The test specimens were then kept in temperature-controlled cabinets for 12 h prior to testing, to bring them to their respective test temperatures.
3. Four loading strips were then glued on to the specimen spaced equally on the circumference.

4. The electronic load-deformation measuring system was then balanced. The instrumented specimen was placed in the testing machine as a unit. The specimen was manually aligned along the central axis of the actuator. The testing machine actuator was moved to put a static load of 44.5 - 89 N (10 to 20 lb) (but not more than 20 percent of the average failure load applied to similar mixes) to the specimen.

5. The transducers were checked and adjusted.

6. The specimen was then brought to the test temperature.

7. A sinusoidal waveform load with an amplitude of 40 percent of the average failure load of the mix was applied over a period of 0.1-s followed by a rest period of 0.9-s. A total of 50 cycles of loading was applied to the specimen. As a minimum, load and deflection data were recorded for the last five cycles of loading. Figure 6 is a schematic of the typical load and deformation versus time relationship for repeated-load indirect tension test.

8. The specimen was then rotated through 90 degrees, and steps 4 through 7 were repeated.

9. After the resilient modulus test was completed, a compressive load at a controlled deformation rate was applied along the axis with the larger resilient deformations. The horizontal deformation during the entire loading time, or when the load sustained by the specimen decreased, was recorded. The stresses and strains at failure were then computed based on the load and deformation at failure. A deformation rate of 51 mm/min (2 in/min) was used at temperatures of 25 °C (77 °F) and 40 °C (104 °F). A lower rate of 0.5 mm/min (0.02 in/min) was used at 5 and -24 °C (41 and -1 °F). The apparatus used to conduct the splitting tensile test according to prescribed procedures is shown in figure 7.

The outlined procedure and following relationships were used in calculating the resilient modulus and the indirect tensile strength and strain at failure as shown in equations 1 through 4.(12)

Resilient Modulus

$$E_{RT} = \frac{P(\nu_{RT} + 0.27)}{t \Delta H_T} \qquad (1)$$

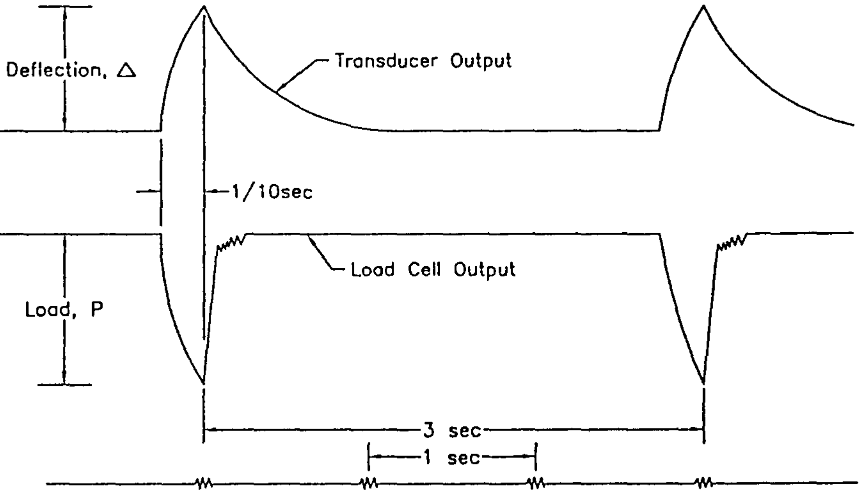

Figure 6. Typical load and deformation versus time relationships for repeated-load indirect tension tests.

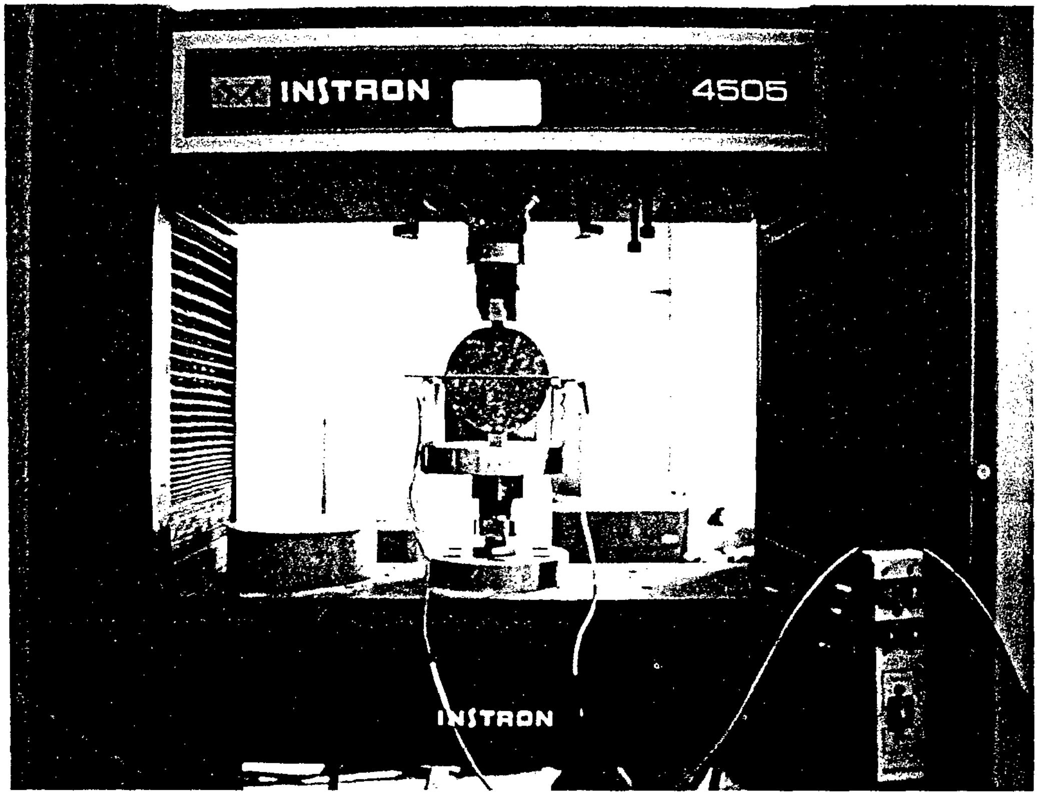

Figure 7. Indirect tension test apparatus.

$$\nu_{RT}=\frac{3.59\Delta H_T}{\Delta V_T-0.27} \tag{2}$$

where:

E_{RT} = total resilient modulus of elasticity, psi.
ν_{RT} = Poisson's ratio.
P = repeated load, lb.
t = thickness of specimen, in.
ΔH_T = total recoverable diametral horizontal deformation, in.
ΔV_T = total recoverable vertical deformation, in.

Indirect Tensile Strength

$$S_t=\frac{P_f A_0}{h} \tag{3}$$

where:

S_t = indirect tensile strength, psi.
P_f = total load sustained by the specimen, lb.
A_0 = 0.156 for 102 mm (4 in) diameter specimens.
h = specimen height, in.

Indirect Tensile Strain

$$\epsilon_f=\Delta_h\left[\frac{A_5+\nu_R A_6}{A_1+\nu_{RT} A_2}\right] \tag{4}$$

where:

ϵ_f = tensile strain at yield or failure, in/in.
Δ_h = total horizontal deformation at failure or where yielding occurs, in.
ν_{RT} = Poisson's ratio.
A_5 = 0.03896 for 102 mm (4 in) diameter specimens.
A_6 = 0.1185 for 102 mm (4 in) diameter specimens.
A_1 = 0.0673 for 102 mm (4 in) diameter specimens.
A_2 = 0.2494 for 102 mm (4 in) diameter specimens.

Indirect Tensile Creep

The indirect tensile creep test was conducted in accordance AAMAS procedures on 6.35 mm high by 10.2 mm diameter cylindrical samples.(12) The tests were conducted at 5 °C (41 °F) and at a stress equal to 5 percent of the indirect tensile strength. Three specimens of each type were tested.

In this test, a static load of fixed magnitude was applied along the diametral axis of a preconditioned specimen for a fixed duration of time. The total horizontal (tensile) deformation of the specimen was measured for a period of 1 h of loading. After the load was released, the resilient (recoverable) deformation was measured for a period of 1 h. From the recorded data, the indirect tensile creep modulus at a specified duration of time and the indirect tensile recovery efficiency from a static load were calculated.

Specimens for this test were prepared using the Texas gyratory method (Tex Method 206 F). The average specimen height was 51 mm (2 in) with a minimum diameter of 102 mm (4 in). The specimens were compacted at a stress level of 345 kPa (50 psi) with a final seating load of 11 kN (2500 lb). The procedure for carrying out indirect tensile creep testing was as follows:

1. The bulk specific gravity and the Rice (maximum) specific gravity of the specimens were measured in accordance with AASHTO T-166 to compute air voids and VMA (voids in mineral aggregate).

2. The test specimens were then kept in a temperature controlled cabinet for 12 h prior to testing, to bring them to the test temperature of 5 °C (41 °F).

3. The test specimen was placed on its diametral axis in the loading apparatus, positioned and adjusted. The LVDT's were strapped on to the specimen and adjusted. The electronic measuring system was then balanced.

4. The ambient temperature was then lowered to the test temperature of 5 °C (41 °F), by the use of carbon dioxide gas.

5. The fixed load to be used in the test was that which would induce a tensile stress in the specimen of 5 to 20 percent of the indirect tensile strength, and result in a horizontal diametral deformation greater than 25.4 x 10^{-3}mm (0.001 in).

6. The specimen was preconditioned by applying a repeated haversine load without impact using a loading frequency of 1 Hz (0.1-s load application and 0.9-s rest period) for a minimum period sufficient to obtain uniform deformation readout (less than 2 percent deviation).

7. The horizontal recoverable deformations were recorded to compute the total or instantaneous resilient modulus.

8. After preconditioning, the electronic measuring systems were rezeroed and a static load of fixed magnitude was applied to the specimen.

9. The horizontal deformation during the entire loading time of 60 min, ± 15 s was monitored and recorded.

10. After the fixed load had been applied for 60 min, the load was released and the rebound or resilient deformation (horizontal) monitored and recorded for an additional 60 min, ± 15 s. The permanent horizontal deformation was measured and recorded from the strip chart recorder for the entire duration of the test.

For each specimen tested, the creep moduli at times of 1, 10, 100, 1,000, and 3600 s, were calculated as shown in equations 5 and 6.

$$E_{ct4}(t)=\frac{\sigma_{t4}}{\epsilon_{t4}(t)} \tag{5}$$

where:

$E_{ct4}(t)$ = indirect tensile modulus at time t, psi. (where subscript 4 refers to diameter of samples in inches)
σ_{t4} = tensile stress along the diametral axis of a 102 mm (4-in) diameter specimen, psi. = 0.156 P/h
$\epsilon_{t4}(t)$ = tensile creep strain at time t for specimens with a 102 mm (4-in) diameter, cm/cm.
P = load applied to the specimen, lb.
h = sample height, in.

$$\epsilon_{t4}(t)=\Delta_H(t)\left[\frac{0.03896+(\nu)0.1185}{0.0673+(\nu)0.2494}\right] \tag{6}$$

where:

$\Delta_H(t)$ = the horizontal deformation at time t, in.
ν = Poisson's ratio.

Uniaxial Compressive Creep

The uniaxial compressive creep test was conducted in accordance with AAMAS procedures.(12) The tests were conducted on all the binders at 40 °C and at two stress levels of 0.1 and 0.4 MPa (15 and 60 psi). Three specimens of each type were tested at the two stress levels.

In this test, a static load of constant magnitude was applied along the cylindrical axis of a preconditioned cylindrical specimen for a fixed duration of time. The total uniaxial (compressive) deformation of the specimen was measured over a period of 1 h of loading. After the load was released, the resilient (recoverable) deformation was measured for a period of 1 h. From the recorded data, the compressive creep modulus at a specified duration of time and the compression recovery efficiency from a static load were calculated.

Specimens for this test were prepared using the California kneading compactor. The average specimen height was 102 mm (4 in) with a minimum diameter of 102 mm (4 in). The specimens were compacted in two layers with 30 and 60 blows 2 at 1725 kPa (250 psi) being imparted to the first and second layers, respectively, to obtain the required air voids. A final seating load of 55.6 kN (12,500 lb) was then applied to the specimens. The AAMAS testing sequence used for these specimens was as follows:

1. The bulk specific gravity and the Rice (maximum) specific gravity of the specimens were measured in accordance with AASHTO T-166 to compute the air voids and VMA (voids in mineral aggregate).

2. The test specimens are then kept in a temperature controlled oven for 12 h prior to testing, to bring them to the test temperature of 40 °C (104 °F).

3. The test specimen was placed in the loading apparatus, positioned and adjusted. The LVDT's (linear variable differential transducer) were strapped on to the specimen and adjusted. The electronic measuring system was then balanced.

4. The fixed load to be applied on the specimen was computed based on the stress levels of 103 and 412 kPa (15 and 60 psi). These load levels were

values which would induce a compressive stress of 5 to 25 percent of the unconfined compressive strength as measured by AASHTO procedure T-167, and result in a vertical deformation greater than 25.4×10^{-4}mm (0.0001) in.

5. The specimen was preconditioned by applying a repeated haversine load (large enough to cause a deformation of approximately from 100 to 250 microstrain) without impact using a loading frequency of 1 H_z (0.1-s load application and 0.9-s rest period) for a minimum period sufficient to obtain a uniform deformation readout (less than 2 percent deviation).

6. The vertical, uniaxial, recoverable deformations were recorded to calculate the total or instantaneous resilient modulus.

7. After preconditioning, the electronic measuring systems were rezeroed and a static load of fixed magnitude was applied to the specimen.

8. The vertical deformation during the entire loading time of 60 min, ± 15 s was monitored.

9. After the fixed load was applied over a period of 60 min, the load was released and the rebound or resilient deformation monitored and recorded for an additional 60 min, ± 15 s. The permanent vertical deformation was measured and recorded from the strip chart recorder for the entire duration of the test.

For each specimen tested, the creep moduli at times of 1, 10, 100, 1,000, and 3,600 s, was calculated as shown in equations 7 and 7.1.

$$E_{cq}(t) = \sigma_c / \epsilon_c(t) \tag{7}$$

where:

$E_{cq}(t)$ = creep modulus at time t, psi.
σ_c = compressive stress applied to the specimen, psi.
$\epsilon_c(t)$ = uniaxial strain at time t, in/in.
$\epsilon_c(t) = \Delta_v(t)/l$ (7.1)
l = gauge length which is the distance between the LVDT's, or the average height of the specimen being tested, if clamps are not used on the specimen, in.
$\Delta_v(t)$ = uniaxial vertical deformation at time t, in.

The Recovery Efficiency, X, is calculated as shown in equation 8 below.

$$X = \frac{\Delta_r(3600)}{\Delta_{v(H)}(3600)} \tag{8}$$

where:

$\Delta_r(3600)$ = The recoverable vertical deformation for uniaxial compression tests or horizontal deformation for indirect tensile tests at the end of the test (i. e., after 3,600 s of no load).

$\Delta_{v(H)}$ = The vertical deformation for uniaxial compression tests or the horizontal deformation for indirect tensile tests just prior to removing the load from the specimen (load time equals 3,600 s).

Unconfined Compressive Strength

The unconfined compressive strength test was conducted in accordance with AAMAS procedures following AASHTO T-167 guidelines. The tests were conducted at 40 °C (104 °F) on three specimens of all Sulphlex blends and a control asphalt mix.

The unconfined triaxial compressive strength of the specimen was measured at a temperature of 40 °C (104 °F). A compressive vertical strain rate of 0.38 mm/min (0.15 in/min) per inch height of specimen was used. The load sustained by the specimen at failure was recorded and used to calculate the stress at failure.

The test specimens were prepared using the California kneading compactor. The average specimen height was 102 mm (4 in) with a minimum diameter of 102 mm (4 in). The specimens were compacted in two layers with 30 and 60 blows at 1725 kPa (250 psi) being imparted to the first and second layers, respectively, to obtain the required air voids. A final seating load of 55.6 kN (12,500 lb) was then applied to the specimen. The testing and data reduction procedures for this test were as follows:

1. The bulk specific gravity of each specimen was determined in accordance with AASHTO procedures (AASHTO T-166).

2. The specimens were then tested in axial compression without lateral support at a uniform rate of vertical deformation of 0.38 mm/min (0.15 in/min).

3. The compressive strength of the specimen was calculated by dividing the maximum vertical load obtained during deformation at the specified rate by the original cross-sectional area of the test specimen. The value of this compressive strength was reported in pascals or pounds per square inch.

Repeated Load Permanent Deformation

The repeated load permanent deformation test was conducted in accordance with VESYS procedures.(15) The acronym VESYS was used by FHWA to identify a sophisticated linear viscoelastic systems (VESYS) pavement performance model. The tests were conducted at 40 °C (104 °F) and at a stress level of 0.1 MPa (15 psi). The stress level was increased to 276 kPa (40 psi) depending upon the stiffness and the ultimate strength of the specimens. Three specimens were tested under each category at the specified test temperature.

The specimens used for this test were prepared using the California kneading compactor. The average specimen height was 102 mm (4 in) with an average diameter of 102 mm (4 in). The specimens were compacted in two layers with 30 and 60 blows at 1725 kPa (250 psi) being imparted to the first and second layers respectively to obtain the required air voids. A final seating load of 55.6 kN (12,500 lb) was then applied to the specimens.

The test procedure and data reduction were carried out as follows:

1. The bulk specific gravity of the specimens was measured in accordance with AASHTO T-166.

2. The specimens were then kept in a temperature controlled cabinet for 12 h prior to testing, to bring them up to the test temperature of 40 °C (104 °F).

3. Metal clamps were glued on to the samples to hold the LVDT's in place. The whole assembly was then placed in the testing machine as one unit. The gauge length was fixed at 51 mm (2 in).

4. The ram was brought down on the sample to apply a seating load of about 44 - 88 N (10-20 lb). The LVDT's were rezeroed along with the electronic measuring system.

5. The chamber was brought to the test temperature of 40 °C (104 °F).

6. A repeated haversine load was applied to the specimen such that each load application had a magnitude equal to the stress level of 103 kPa (15 psi). The load pulse had a duration of 0.1-s followed by a rest period of 0.9-s. In all, 10,000 load cycles were applied and the accumulated deformation was measured through the entire period of loading.

7. The load was released after 10,000 cycles and the rebound or recovery was measured for an additional 15 min.

8. The accumulated deformation at the end of 1, 10, 100, 200, 1,000, and 10,000 cycles was computed.

9. The dynamic resilient modulus at the end of the 200th cycle was computed by dividing the constant stress by the strain at the 200th cycle.

10. The total permanent deformation at the end of 10,000 cycles and a 15-min recovery was determined.

Aging at 25 °C (77 °F)

The aging test was conducted on the 50/50 blend of Sulphlex 198 and 233, and the one-pot synthesized binder to evaluate the effects of aging on the Sulphlex binders. The specimens used for the test were 51 mm (2 in) thick by 102 mm (4 in) diameter and were molded using the Texas gyratory compactor. After initial curing at 10 °C (50 °F) for a period of 1 week, the samples were stored at room temperature 25 °C (77 °F) and the resilient modulus was determined over a period of 8 weeks at 1-week intervals. At the end of 8 weeks, the samples were subjected to the IDT stress and strain at failure test and the appropriate parameters were measured.

The procedures and relationships used were in accordance with AAMAS procedures.(12) The period and temperatures of curing and aging were based on previous studies conducted on the Sulphlex binders.

CHAPTER 3. IDENTIFICATION OF RAW MATERIALS (TASK A)

The chemical additives utilized in the preparation of the four generations of Sulphlex binders treated in this study include: (a) Sulfur, (b) Dicyclopentadiene (DCPD), (c) Neodene C_{11} - C_{12} internal olefin, (d) Vinyl toluene, (e) Dipentene (Limonene), and a (f) Cyclopentadiene (DCPD) oligomer. A listing of these raw materials, their trade names, purity and source is given in table 7 and their chemical structures are given in figure 8. More detailed information on each is also given in their respective Material Safety Data Sheets in appendix A.

The sulfur, also referred to as anchor velvet flowers, consists of fine particles of crystalline sulfur predominantly in the rhombic form. The sulfur used in this study was a commercial grade with a purity of +99.9 percent with a chemical structure of S_8. The sulfur was supplied by Martin Chemical Corporation of Odessa, Texas.

Dicyclopentadiene (DCPD) is a Diels-Alder reaction product of primarily cyclopentadiene with small amounts (i .e., less than 5 percent each) of methylcyclopentadiene and small amounts of cyclic and acyclic saturated compounds, like styrene, vinyl toluene, isoprenes and piperylenes incorporated into the polymeric structure. It is composed of an 80 percent polyester grade DCPD and 20 percent reactive codimers. It has a specific gravity of 0.97 at 16 °C (61 °F) and a flash point of 2.2 °C (36 °F).(14) The chemical was supplied by Dow Chemical Corporation of Freeport, Texas.

Neodene C_{11}-C_{12} internal olefin is a randomly double-bonded olefin uniquely manufactured using the Shell Higher Olefin process. Its composition consisted of 1 percent C_{10} and lower carbon olefins, 53 ± 6 percent C_{11} olefins, 46 ± 6 percent of C_{12} olefins and 1.5 percent of C_{13} or higher carbon olefins. It had a flash point of 70 °C (158 °F).(14) The Neodene was purchased from Shell Chemical Company of Houston, Texas.

The vinyl toluene has a purity of 99.2 percent and consisted of a mixture of meta- and para- Vinyl toluenes. It is a colorless liquid with a specific gravity of 0.920 at 25 °C (77 °F) with a flash point of 54 °C (129 °F).(14) The vinyl toluene was supplied by Del Tech Corporation in Baton Rouge, Louisiana.

Dipentene, is the trade name for Limonene, a terpene solvent with monocyclic terpene hydrocarbons and minor amounts of terpene alcohols and ketones. It has a specific gravity of 0.84 at 21 °C (69.8 °F), with a flash point of 43 °C (109 °F) and a viscosity of 1.0 cP (centipoise) at 70 °C (158 °F).(14) The Dipentene used in this study was a 60 percent technical grade and 40 percent phellandrene and was furnished by Spectrum Chemical Corporation of Gardena, California.

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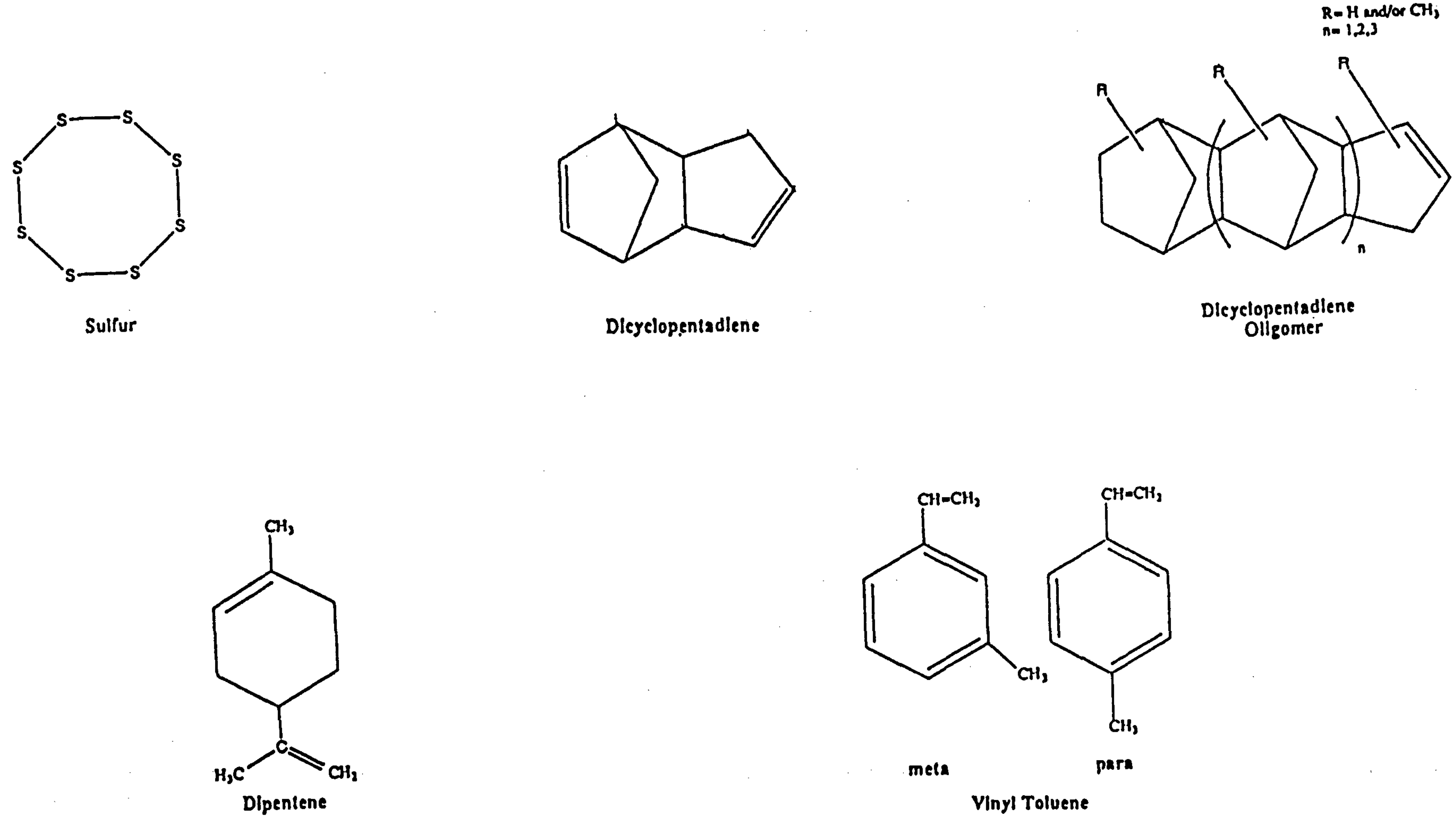
Table 7. Sources and purity of raw materials used in the preparation of Sulphlex binders.

Reactant	IUPAC[*] or Trade Name	Purity Percent (cost in $/lb)[**]	Sources
Sulfur	Elemental Flaked Sulfur	+99.9 ($0.02)	Martin Chemical Corp. Odessa, Texas 915-381-2321
Dicylcopentadiene (DCPD)	Dicyclopentadiene Polyester Grade with Reactive Codimers	80 (0.30)	Dow Chemical Corp. Freeport, Texas 409-238-2011
Neodene C_{11}-C_{12} Internal Olefins	Neodene (R) 1112 Internal Olefin	Not Specified (0.55 to 0.60)	Shell Chemical Co. Houston, Texas 713-544-4199
Vinyl Toluene	Vinyl Toluene	99.2 (0.49 to 0.77)	Del Tech Corp. Baton Rouge, La. 504-775-0150
Dipentene or Limonene	1-Methyl-4-(1-Methylethenyl) cyclohexene	60 (0.43)	Spectrum Chemical Corp. Gardena, California 310-516-8000
DCPD Oligomer Hydrocarbon Resin Oil	OREPREP RI-300	Not Specified (0.53)	Techmark Industries and OREPREP Chemical Co. Galena Park, Texas 713-455-1206

[*] Union of Pure and Applied Chemists.

[**] Prices shown are based on laboratory quantities.



Sulfur

Dicyclopentadiene

Dicyclopentadiene Oligomer

Dipentene

meta

para

Vinyl Toluene

Figure 8. Chemical structure of raw materials used in Sulphlex binder production. (Neodene structure not available).

The oligomer of dicyclopentadiene (DCPD) is a proprietary resin intermediate (RI) produced by Techmark Industries, and OREPREP Chemical Company of Galena Park, Texas, under the trade name of OREPREP RI-300. Its composition was 2 percent C_5 monomer, 35 percent C_{10} dimer, 20 percent C_{15} trimer, 8 percent C_{20} tetramer, and the remainder as a hydrocarbon olefin. Its purity and chemical structure were not specified by the vendor.

Table 8 shows the range of sulfur prices at various locations in the United States, and in Alberta, Canada as of May 1994.(23) A comparison is also shown with sulphur prices in May 1992. Relative costs associated with recovered (secondary) sulfur and that obtained using the Frasch source are also given.

Table 8. Prices of recovered and Frasch sulfur at various geographic locations in the United States and Canada.(23)

Recovered	Prices ($/Ton)*		Percent Change
	May 1994	May 1992	
Tampa	36-40	85	-60
New Orleans	20-25	75	-73
Houston	10	70	-85
West Coast	2-5	20	-75
Alberta, Canada	1-3	23	-87
Frasch			
Tampa	42	98	-57
New Orleans	36	83-86	-58

*Metric Ton = 10^3 kg = 1.102 Ton

The data in table 8 indicate a significant reduction in the price of sulfur in both the United States and Canada over the past 24 months. Although not as dramatic, the price of Frasch sulfur also dropped nearly 60 percent in this same time period. There appears to be a gradual decrease in sulfur cost from the East Coast to Texas. The price then drops precipitously to below $5/ton on the West Coast. In addition to the favorable economic impact they have on Sulphlex production, these price trends should also have a major impact on the use of sulfur as an alternative to asphalt in other roadway mixtures incorporating sulfur-modified binders.

Table 9 presents the results of a survey of some additional commercial sources for Sulphlex raw materials including selected vendors and their respective quotes as of the May 1994 preparation date of this report. Because of a wide range of the prices for sulfur, the reader is advised to seek out current prices in his locality.

Table 9. Costs and sources* for Sulphlex raw materials.

Vendor	Product	Address/Phone	Person Contacted	Response
Unocal Chemicals Div/Nitrogen Group	Sulfur	Lodi, CA (714) 572-7464	John Padilla	$28/ton Galveston, Texas
Chevron Chemical Company	Sulfur	San Francisco, CA (415) 894-4770	Tim Arias	$0 - $1.00/ton West Coast $35 - $40/ton Houston, Texas
Phillips Petroleum Company	Sulfur	Bartlesville, OK (918) 661-6600 Ext. 8962	Paul Beach	$31 - $55/ton Borger, Texas Base Price; $68/ton Tampa, Florida
Shell Oil Company	Sulfur	Houston, Texas (713) 544-4199	Matt Morre	$53/ton + Freight; Deer Park, Texas
Exxon Chemical Company	Dicyclopentadiene	Houston, Texas (800) 231-6633	June Dillingham	$0.32/lb Baton Rouge, Louisiana
Chem Central	Vinyl Toluene	San Antonio, Texas (210) 533-0123	Darla Hurley	1 drum (410 lb) @ $1.02/lb 4 drums @ $0.96/lb 10 drums @ $0.93/lb
Union Camp Corporation	Citrus Limonene or Unitene (Dipentene)	Wayne, New Jersey (201) 628-2000 (800) 874-9220	Verna Darly	Limonene 5100 (55 gallon (392 lb) @ $0.81/lb F.O.B. Jacksonville, Florida Unitene @ $0.36/lb F.O.B. Jacksonville, Florida

Vendor	Product	Address/Phone	Person Contacted	Response
SCM GLIDCO Organics	Dipentene	Jacksonville, Florida (904) 768-5800	Patty Coppedge or Alice Stokes	Dipentene Extra (1-9 drums) 400 lb $0.63/lb Dipentene GICA (1-9 drums) 400 lb $0.53/lb Dipentene LPX (1-9 drums) 400 lb $0.60/lb Dipentene PG (1-9 drums) 400 lb $0.93/lb F.O.B. Jacksonville, Florida
Exxon Chemical Company	Internal Olefins	Houston, Texas (713) 870-6084	Dale Reynolds	Tetramer M C11-C12 -40.28/lb
Goodrich	Internal Olefins	Cleveland, Ohio (216) 239-1000 (800) 331-1144	Goodrich	No Response
Shell Chemical Company	Internal Olefins	Houston, Texas (713) 246-8128 or (713) 246-8129	Pam Duncan (Customer Service)	Neodene 6-10: $0.60/lb 10-12: $0.58/lb 12-14: $0.55/lb 16-18: $0.55/lb 14-16: $0.55/lb
Techmark Industries	OREPREP RI-300	Galene Park, Texas (713) 455-1206	Don Penshaw	1 drum (420 lb) @ $0.53/lb

*This table is intended to be only a limited, and not complete, source list for these materials.

CHAPTER 4. SYNTHESIS OF FIRST, SECOND, THIRD, AND FOURTH GENERATION SULPHLEX BINDERS (TASKS B, C AND D)

BINDER PREPARATION

The production of the Sulphlex binders used in this study was carried out using the facilities at McBee and Associates of Lebanon, Oregon. The production unit, as shown in figure 9, consists of a 57.8 L (15-gal), sealed, agitated, steam (or water) jacketed stainless steel reactor. The agitator was a 51 mm (2 in) propeller-type impeller whose speed could be varied from 0 to 800 r/m using a 0.75 horsepower DC motor. A 7.6 L (2-gal) capacity stainless steel tank was used to pre-blend the reactants. Reaction temperatures were monitored and controlled using a vertical Type K thermocouple well which extends into the lower central region of the vessel close to the agitator. Heat was provided by a 1.5 Brake Horsepower (BHP) steam generator that operated at a pressure of 0 to 1.03 MPA (0 to 150 psi). A scaled-up production plant used for larger batch sizes to be discussed in chapter 6 is shown in figure 10.

The Sulphlex cement was manufactured by initially melting the elemental sulfur in the reactor and stabilizing it at a temperature of 150 °C (302 °F). The reactants were weighed and poured into the pre-mix tank in their proper proportions. The premixed chemicals were then injected into the sealed reactor at ambient temperatures from the pressurized stainless steel auxiliary tank. During injection, which lasted for approximately 30 min, the pre-mix tank pressure was maintained at 70 kPa (10 psi) by venting excess air back to the tank to minimize polluting the workplace. No change in temperature was observed in the pre-mix tank while charging the reactor. The temperature in the reactor was maintained at 150 °C (302 °F) to 180 °C (356 °F) by varying steam pressure. The exothermic heat generation which followed was controlled by circulating cooling (ambient) water through the reactor's steam jacket. The top of the reactor was not heated to permit the volatiles to reflux back into the mixture ensuring a more complete reaction and total consumption of the reactants. Viscosity and temperature of the mixture were continually monitored using a Brookfield viscometer mounted on the top of the reactor. The reaction was considered complete when the viscosity stabilized, which was usually after 6 to 7 h.

All Sulphlex binders for this study were reacted for 6.5 h. A range of short-duration variations in production temperatures was created by the exothermic reactions encountered during the addition of the reactants. Passing cold air through the annular jacket around the reactor kept these thermal excursions to a minimum. This process produced a binder with a viscosity of 350 to 450 cP at 135 °C (275 °F).

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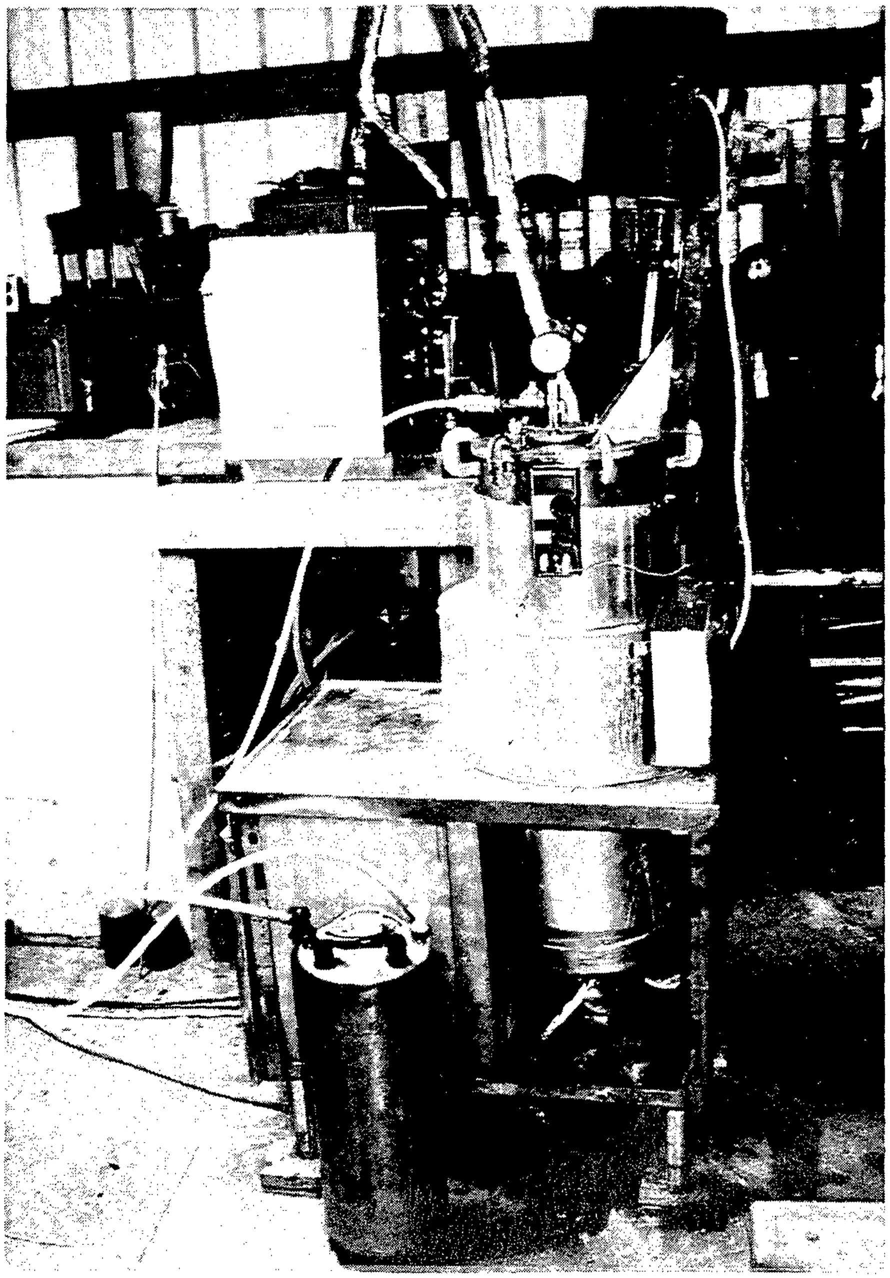
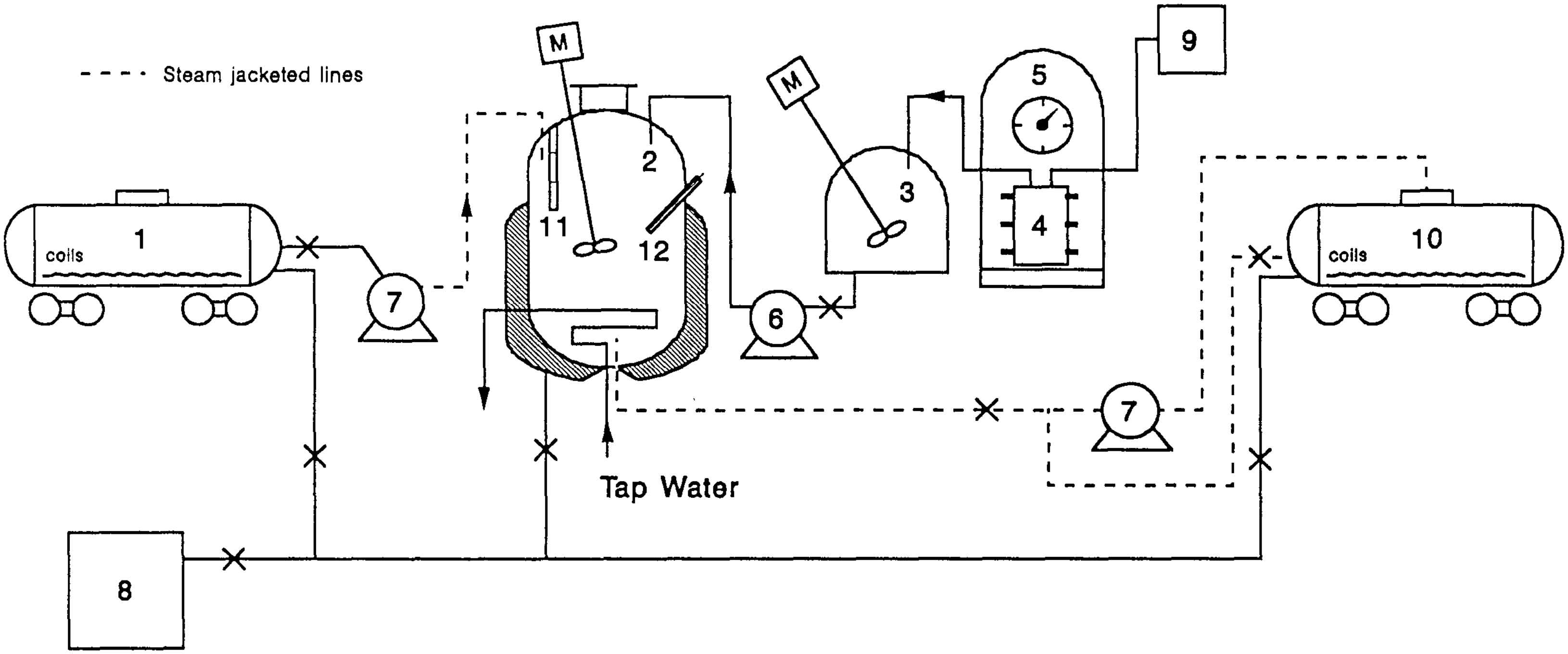


Figure 9. McBee and Associates reactor assembly used for the production of Sulphlex binders.



1) 3800 gallon sulphur transport trailer (same as item 10)
2) 1500 gallon sealed jacketed chemical reactor (stainless steel) with agitator
3) 800 gallon stainless steel chemical pre-mix tank with agitator
4) 55 gallon chemical additive supply drum(s)
5) 1000 pound platform scale
6) 25 gpm chemical pump
7) 100 gpm steam jacketed positive displacement pump
8) 7 horsepower steam generator
9) 3 horsepower air compressor
10) 3800 gallon Sulphlex storage tank
11) Viscometer
12) Thermocouple

Figure 10. Batch-type Sulphlex production plant.

The one-pot synthesized binder (Task C) and the Fourth Generation Sulphlex (Task D) were produced by preblending the reactants, as discussed above, at the desired mix proportions in a pressurized stainless steel auxiliary vessel prior to their introduction into the reactor. The process temperature was controlled by adjusting the flow of steam and/or cold air. The reaction was carried out at an average temperature of 150 °C, +5 to -2 °C (302, +9 to -3.6 °F) for 6.5 h of which 1 h was used to charge the reactor. The temperature variations in this production sequence were significantly lower than those for the 50/50 (198:233) binder. The target viscosity for the processed Sulphlex binders was between 350 and 450 cP at 135 °C (275 °F). One part of a previously produced Sulphlex 198/233 blend was premixed with 9 parts of the reactants to act as a catalyst for the reaction.(16)

Table 10 is a summary of the individual composition of the First, Second, Third, and Fourth Generation Sulphlex binders along with the type of process (blended, one-pot, etc.) under which they were produced and their respective physical properties. Essentially, the same process conditions mentioned above are recommended for all Sulphlex binders.

TOXICITY OF SULFUR-INITIATED POLLUTANTS

The production of Sulphlex binder is normally carried at 150 °C (302 °F) which is well above the melting point of Sulfur (i. e., 120 °C (246 °F). In this state, sulfur can produce both gaseous and particulate effluents which could, if not regulated, be hazardous to personnel. Therefore, a discussion of the safety aspects of sulfur initiated pollutants, namely hydrogen sulfide (H_2S), sulfur dioxide (SO_2) and particulate sulfur follows. Additional safety and handling information, is provided for Sulphlex and its raw materials in chapter 6 and appendix A, respectively.

Relative Toxicity of Hydrogen Sulfide (H_2S)

Hydrogen sulfide is known for its characteristic "rotten egg" odor. Although this odor is noticeable at concentrations as low as 0.02 ppm, odor is not a good indicator of concentration level.(24) Hydrogen sulfide can have a paralyzing effect on the sense of smell. Therefore, high concentrations of H_2S can escape recognition. The effect of exposure to various concentrations of H_2S is given in table 11.

On the basis of these effects a Maximum Allowable Concentration (MAC) value of 5 ppm is normally specified as the upper threshold limit for continuous exposure to H_2S emissions in areas normally expected to be occupied by construction or plant personnel.

Table 10. As-mixed chemical composition and physical properties for 233, 198, 50/50, one-pot synthesized blend and Fourth Generation Sulphlex binders.

Chemical Composition	233 (Percent)	198 (Percent)	50/50 Blend of 198/233 Task B (Percent)	One-Pot Synthesized 50/50 (198/233) Task C (Percent)	Fourth Generation Sulphlex Task D (Percent)
Sulfur	70	70	70	70	70
Dicyclopentadiene	12	12	12	12	7.5
Vinyl Toluene	8	-	9	9	-
Dipentene (Limonene)	10	-	5	5	-
Neodene C_{11}-C_{12} Internal Olefins	-	18	4	4	7.5
DCPD Oligomer	-	-	-	-	15
PHYSICAL PROPERTIES					
Penetration @ 25 °C (77 °F), 100 g, 5 s	165	168	165	131	241
Viscosity @ 135 °C (275 °F), cSt	350	402	356	388	321
Specific Gravity @ 25 °C (77 °F)	1.550	1.490	1.509	1.500	1.532
Solubility in $CHCl_3$	95	88	91	88.1	99.99
Glass Transition Temp, °C (°F)	-6 to-12 (21.2 to 10.4)	-12 to-14 (10.4 to 6.8)	-14 to -18 (6.8 to -0.4)	-11 to -15 (12.2 to 5)	-28 to -33 (-18.4 to -27.4)

Table 11. Toxicity levels for H_2S exposure.

H_2S Concentration, ppm	Effect
5-10	Suggested maximum allowable concentration (MAC) for prolonged exposure
70-150	Slight symptoms after exposure of several hours
170-300	Maximum concentration which can be inhaled for 1 hr without serious consequences
400-700	Dangerous after exposure of ½ to 1 h
600	Fatal with ½ h exposure

Relative Toxicity of Sulfur Dioxide (SO_2)

Sulfur dioxide (SO_2) is a colorless gas with a pungent odor which unlike H_2S gives ample warning of its presence. The principle health hazard from SO_2 comes from inhalation of excessive quantities above its MAC. The basis for establishing the relative toxicity of emissions generated during construction would be the relationships between SO_2 concentrations and human effects as specified by the National Institute for Occupational Safety by Health and the Manufacturing Chemists Association shown in table 12.(25,26)

Table 12. Toxicity levels for SO_2 exposure.

SO_2 Concentration, ppm	Effect
0.3-1	Detected by taste
1	Injurious to plant foliage
3	Noticeable odor
5	MAC (ACGIH)
6-12	Immediate irritation of nose and throat
20	Irritation of eyes
50-100	MAC for 30-60 min exposures
400-500	Immediately dangerous to life

The present Federal standard for SO_2 in an 8-h time weighted average is 5 ppm (see 29CFR, 1910, 93 published in the Federal Register, Volume 37, page 22139 (October 18, 1972). This is the MAC specified as the upper threshold limit concentration for SO_2 emissions in areas normally expected to be occupied by construction or plant personnel over an 8-h work day.

Relative Toxicity of Particulate Sulfur

Vapors given of during mixing and dumping operations contain a certain amount of undissolved and unreacted sulfur. As the vapors come in contact with air and cool, the sulfur crystallizes into small particles which are carried by the wind in a manner similar to dust and find sands. Since there is no practical way to eliminate this pollutant, its effects on both environment and personnel need to be considered. A detailed discussion of the relative hazards associated with sulfur dust may be found in reference.(27)

The principal problems associated with sulfur dust lie in its contact with eyes. Sulfur is virtually nontoxic and there is no evidence that systemic poisoning results from the inhalation of sulfur dust. However, sulfur is capable of irritating the inner surfaces of the eye lids. Sulfur dust may rarely irritate the skin. These problems are minimized by the requirement that goggles and long sleeve shirts be worn in areas subject to this pollutant such as at the hot mix plant and in the vicinity of the paver.

The primary hazard in handling solid sulfur results from the fact that sulfur dust suspended in air may be ignited and explode. This problem is almost always limited to enclosures and unventilated areas such as storage silos and hoppers.

To minimize possible irritation, unnecessary contact with skin and eyes should be avoided. Following the work period, sulfur dust should be removed with mild soap and water. For relief of eye irritation, eyes should be thoroughly flushed with large quantities of plain water or physiological saline. Inadequate amount of water may actually increase eye irritation.

CHAPTER 5. CHARACTERIZATION TESTING OF SULPHLEX BINDERS AND MIXTURES (TASK E)

BINDER TESTS

Screening Tests

The binders produced at the facilities of McBee and Associates, in Lebanon, Oregon, were shipped to Matrecon, Alameda, California, for quality control analysis. These binders were subjected to a series of screening tests to compare their engineering and physical properties with the binders produced under the Second Generation Sulphlex program.(16)

The results reveal that there is a reasonable agreement between respective values for specific gravity, solubility in chloroform, viscosity and storage stability at room temperature between Second Generation binders and new Sulphlex binders. However, there is less agreement in penetration and storage stability at 100 °C (212 °F). This difference might be attributed, in part, to the difference in purity of the reactants and equipment used in the production of the binders. The purity of the dicyclopentadiene used in the Second Generation study was close to 97 percent while 80 percent polyester grade with 20 percent codimer was used in the current study. The purity of the vinyl toluene used in the Second Generation study was 100 percent while that used in the current study was 99.2 percent. A second factor to which these variations might be attributed is the difference in the production plants and methodology used to produce the binder. The 94.6 L (25-gal) reactor at TTI's facilities used to produce the Second Generation binders was not as well sealed as the plant at the McBee facility. The binders developed in the earlier studies at the facilities of Matrecon were processed in 500 ml flasks. Neither of these apparatuses were able to achieve as effective a temperature control as that of the McBee plant. Furthermore, reactants were introduced more quickly in the Matrecon apparatus than in the TTI apparatus. These differences in the production process have hence been identified as at least a partial and significant cause of the marginal differences observed in the screening test data.(16)

Glass Transition Temperature

The continuous rearrangement of atoms and molecules in an organic material is due to thermal agitation. As the temperature of a material is raised, thermal agitation is heightened producing an increase in intermolecular spacing and free volume. Conversely, as the temperature is decreased the molecules tend to pack closer to one another due to less thermal agitation; hence a decrease in free volume results. This continues until a temperature is reached where the free volume is at a minimum. Any

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beyond this point is due to molecular vibrations of smaller amplitudes. At this temperature, the material takes on a sudden change in the rate of volume change. Such a phenomenon is called a second order transition. This second order change in volume occurs at a temperature commonly called the glass transition temperature, T_g, and is defined as the temperature below which the material loses its viscous behavior and, hence, its flexibility and toughness.

The viscous component of the rheological behavior of polymeric materials is responsible for the materials toughness, and hence, its ability to withstand fracture. Therefore, it appears reasonable to assume that by lowering a material's T_g, the viscous behavior of the binder is extended to lower temperature and as a result its resistance to low-temperature cracking will be enhanced.(16) It is for this reason that the glass transition temperature, T_g, was used as a preliminary index of a material's ability to perform in a cold climate.

Various methods have been used to measure the T_g of Sulphlex binders.(16) The most critical condition for this test is the rate of temperature change to which the sample is subjected. It has been shown that when cooling or heating rates are high, i. e., above 10 °C/min (18 °F/min), thermal gradients can be created within the specimen which will either mask the true transition point or shift it to lower (when cooling) or higher (when heating) values.

In this study, the second order transitions of the binders were measured using the Perkin Elmer differential scanning calorimeter (DSC) in accordance with ASTM D 3418. Table 13 is a summary of the DSC results detailing the T_g values for the first and second scans for the binders tested under this program. Both scans were achieved as test temperatures were increasing. For a better understanding of the test results a typical DSC scan is shown in figure 11.

From table 13, one may observe that the T_g values for the Sulphlex binders range from -6.2 °C (20.8 °F) to -33 °C (-27.4 °F). Average values for the 50/50 (198:233) blend were calculated as -16 °C (3.2 °F) for the first scan and -14 °C (6.8 °F) for the second scan. The specimens were heated twice from -40 °C (-40 °F) to 160 °C (320 °F) at 10 °C/min (18 °F/min). The first heating scan reveals the glass transition temperature, T_g, and the melting peaks (T_{M1}, T_{M2}, and T_{M3}) at 76 °C (168.8 °F), 103 °C (217.4 °F), and 143 °C (289.4 °F), respectively. Referring to figure 11, the shaded area under the first scan represents the heat of fusion, ΔH_f. The specimens were then quenched in the DSC at around 165 °C/min (297 °F/min) and allowed to reheat at 10 °C/min (18 °F/min). Since no crystallization occurs during the quenching phase, only the glass transition is observed in the second scan. The tests on the Fourth Generation Sulphlex were also run using both the DSC (ASTM D 3418) and the dilatometer using test procedures in accordance with ASTM D 696.(16) The T_g values using the latter technique

Table 13. Glass transition temperatures (T_g) of Sulphlex 198, Sulphlex 233, their blends, and Fourth Generation Sulphlex measured using the DSC (ASTM D3418) and Dilatometer.[16]

Sample	Container	DSC Scan[d] -40 ° to 160 °C (-40 ° to 320 °F)	T_g °C (°F)
Sulfur	----	----	None
Sulphlex 198 McBee	As Received[a]	1st 2nd	N/O N/O
	Penetration Test	1st 2nd	-15.7 (3.7) -17.8 (0)
Sulphlex 233 McBee	As Received[a]	1st 2nd	-6.2 (20.8) -11.7 (10.9)
Matrecon Two-Pot Blend of 50/50 (198:233)	6oz[b]	1st 2nd	-15.2 (4.6) -18.1 (-0.6)
	Penetration Test[c]	1st 2nd	-12.2 (10.0) -14.2 (6.4)
McBee Blend of 50/50 (198:233) One-pot synthesis	As Received[a]	1st 2nd	-14.2 (6.4) -18.7 (-1.7)
	Penetration Test[c]	1st 2nd	-11.7 (10.9) -14.7 (5.5)
Sulphlex 75/25 (198/233) one-pot synthesis	As Received[a]	1st 2nd	-12.2 (10.0) -11.7 (10.9)
	Penetration Test[c]	1st 2nd	-14.7 (5.5) -15.7 (3.7)
Fourth Generation	As Received	1st 2nd	-18 to -24 (-0.4 TO -11.2)
Fourth Generation	As Received	Dilatometer (16)	-28 to -33 (-18.4 TO -27.4)
AC-20	Control	Dilatometer(16)	-9.5 (14.9)

N/O None Observed

[a] Container as received by McBee

[b] Container in which the 50/50 (198:233) blend was made by Matrecon

[c] Three-ounce tin exposed for storage stability at room temperature

[d] Each scan was conducted under an increasing temperature mode

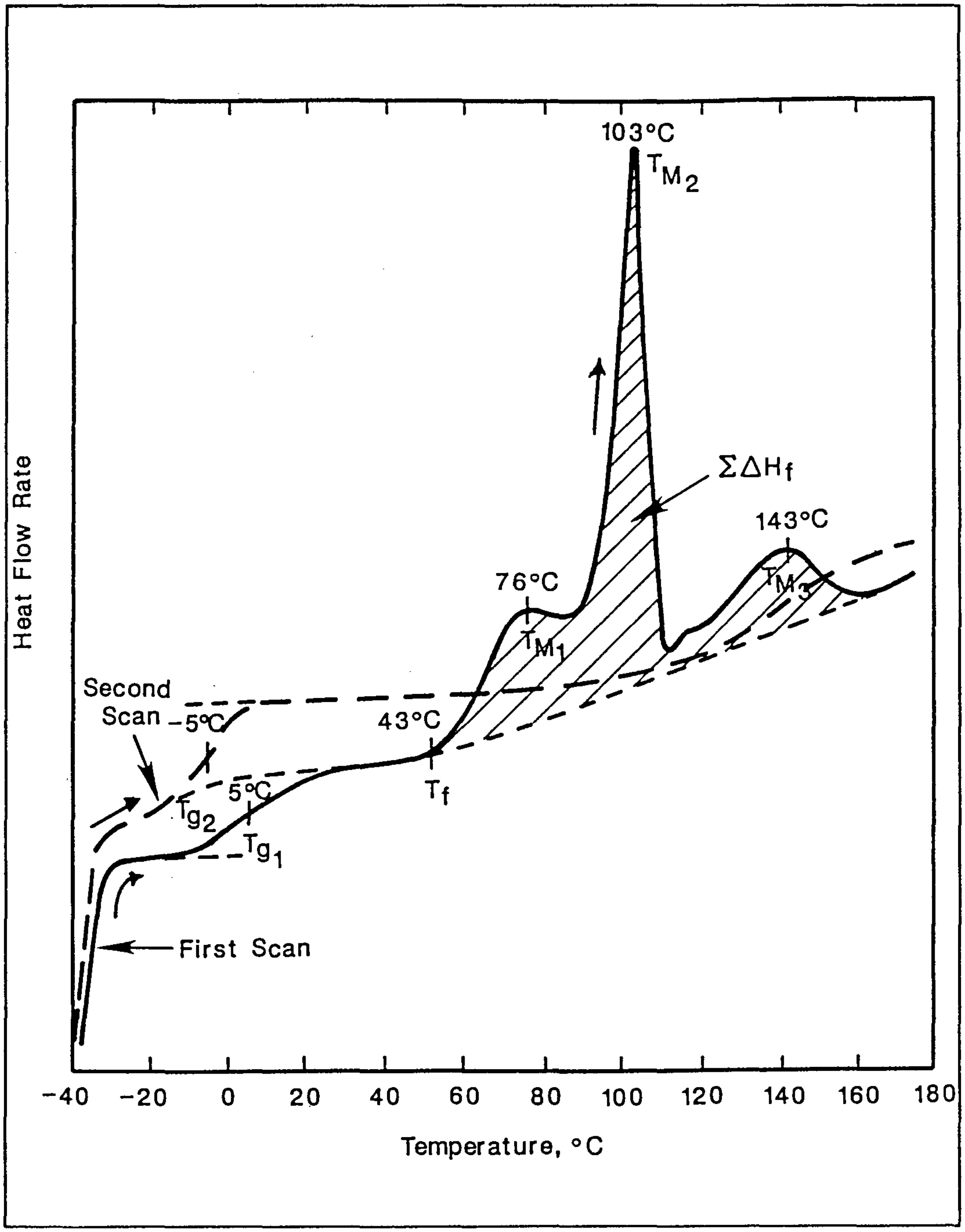


Figure 11. Typical thermograms for Sulphlex binders.

were much lower than those obtained with the DSC and ranged from -28 to -33 °C (-18.4 to -28.4 °F). However, the DSC results reflect a lower T_g -18 to -24 °C (0.4 - 11.2 °F) than early generations of Sulphlex binders. This could be an indication that the low temperature fracture resistance had been improved with the Fourth Generation Sulphlex binder.

These data should however be viewed relatively. The glass transition temperatures determined using the dilatometer can be 15 °C (59 °F) to 30 °C (86 °F) lower than those determined using the DSC. The heating rate of 10 °C/min (18 °F/min) used in the DSC is considerably higher than the 1 °C/min (1.8 °F/min) heating rate used in the dilatometer and is responsible for this difference. From a broader perspective, the T_g values for the early generation Sulphlex binders were essentially the same. The effect of the size of the test container did not seem to significantly alter the test results. The Fourth Generation Sulphlex binder had the lowest T_g values at -18 to -24 °C (-0.4 to -11.2 °F) using the DSC and -28 to -33 °C (-13.4 to -28.4 °F) using the dilatometer. It might be concluded from these results that the low-temperature fracture resistance had been enhanced with the "new and improved" Fourth Generation Sulphlex formulation. All Sulphlex, second-scan, T_g values were lower than -9.5 °C (14.9 °F) obtained with the AC-20 asphalt.

Brookfield Viscometer

The viscosity of the Sulphlex binders in this program was measured over a range of temperatures using the Brookfield viscometer. The temperatures ranged from 104 °C (220 °F) to 166 °C (330 °F). Figures 12 through 15 document the results obtained for the four original (unaged) Sulphlex blends tested under this program. The data show that over the temperature range the Fourth Generation Sulphlex binder has a higher viscosity than the other binders. The 50/50 (198:233) one-pot synthesized binder showed about a 25 percent reduction in viscosity along the range of temperatures while the 50/50 and 75/25 two-pot blends of Sulphlex 198 and Sulphlex 233 show appreciably lower viscosities, over the same temperature range. All the binders, however, fall within the Superpave binder specifications which prescribe a maximum viscosity of 3 Pa·s at a temperature of 135 °C (275 °F). The results of the Brookfield viscosity were used in conjunction with the other Superpave binder and mixture tests to more fully characterize the binders.

Superpave Binder Tests - General

Superpave binder specifications were developed to provide fundamental relationships between asphalt properties and mixture properties. Superpave binder specifications are designed to provide performance-related properties than can be related in a rational manner to pavement performance.

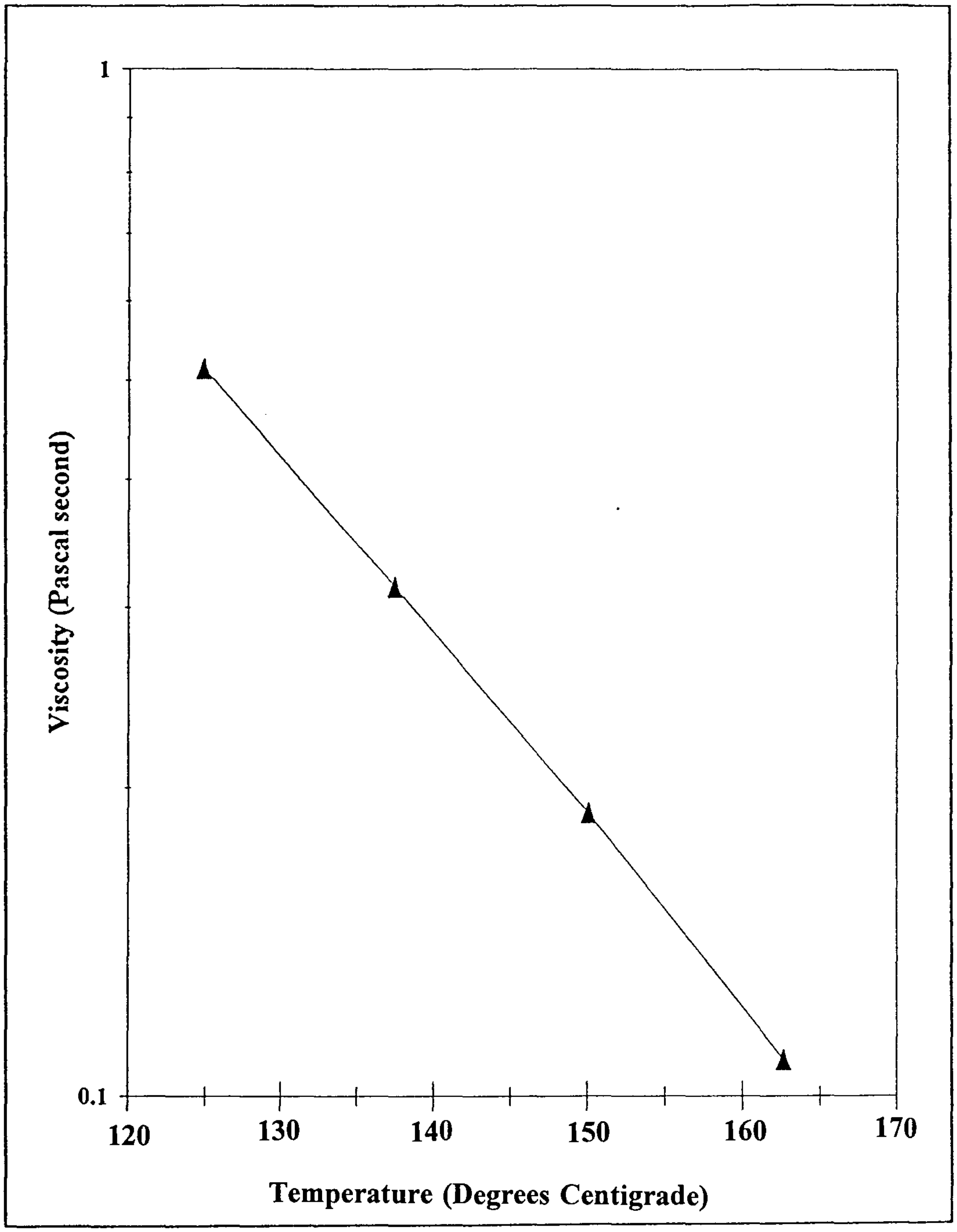


Figure 12. Viscosity versus temperature plot for the 50/50 (198:233) two-pot Sulphlex binder using the Brookfield viscometer .

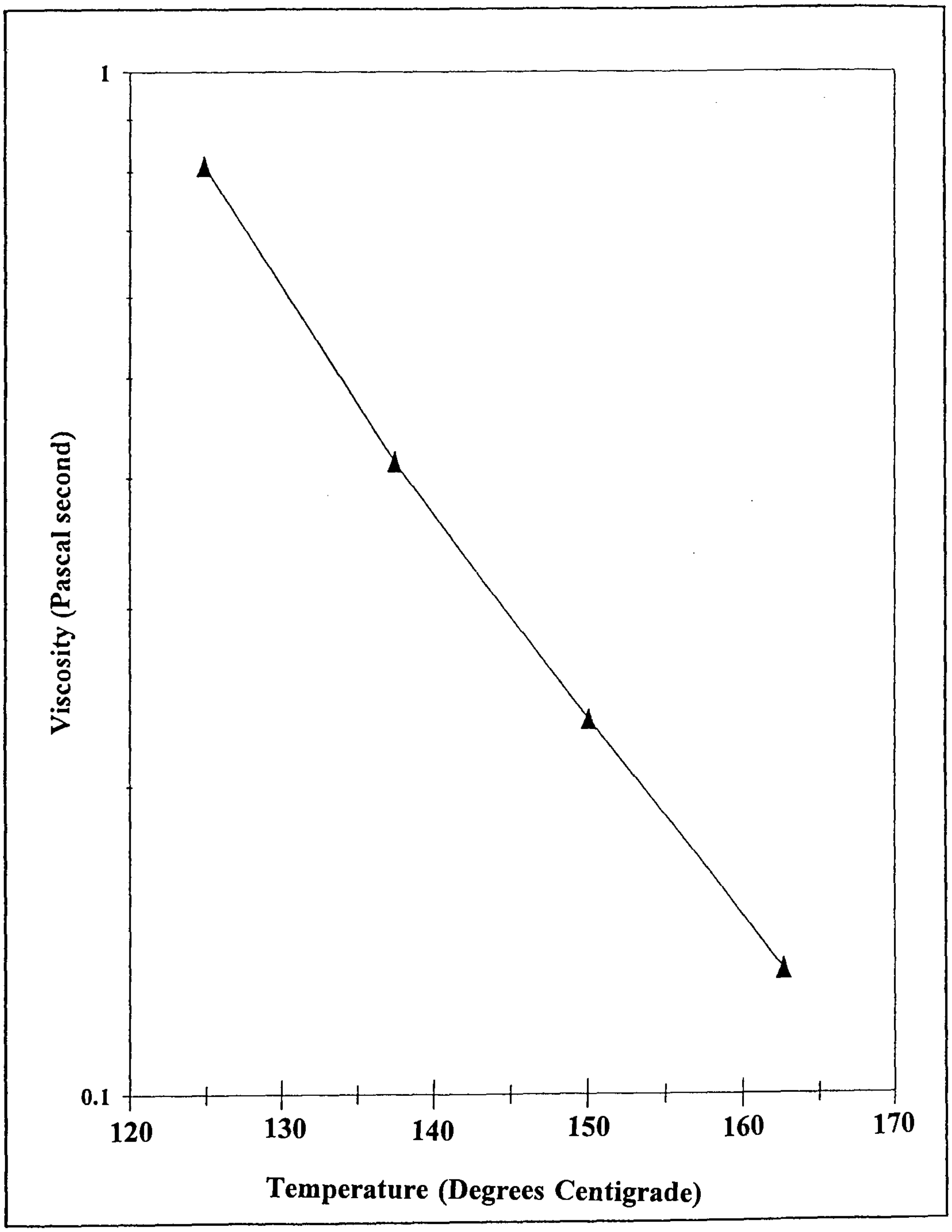


Figure 13. Viscosity versus temperature plot for the 50/50 (198:233) one-pot synthesized binder using the Brookfield viscometer.

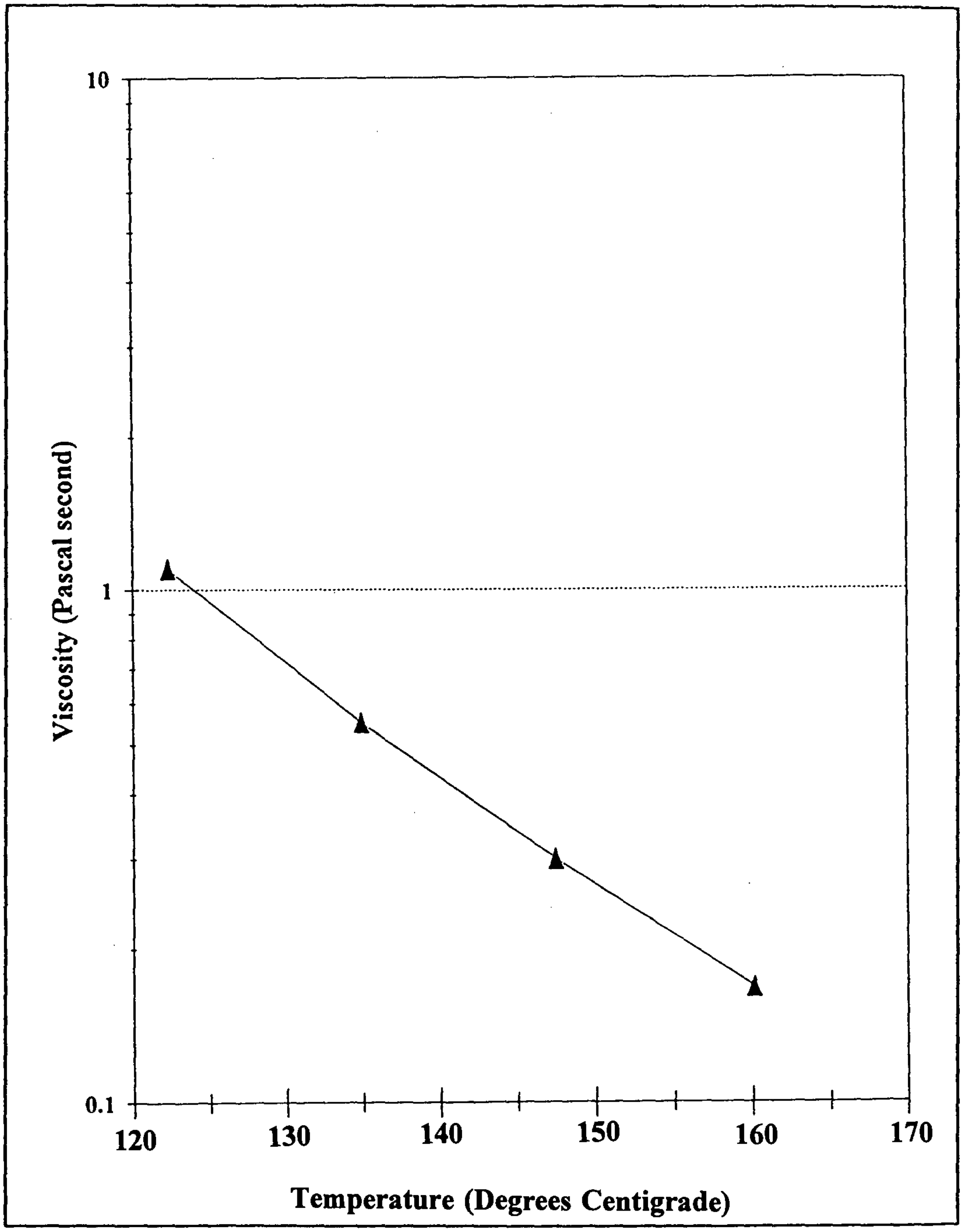


Figure 14. Viscosity versus temperature plot for the 75/25 (198:233) two-pot Sulphlex binder using the Brookfield viscometer.

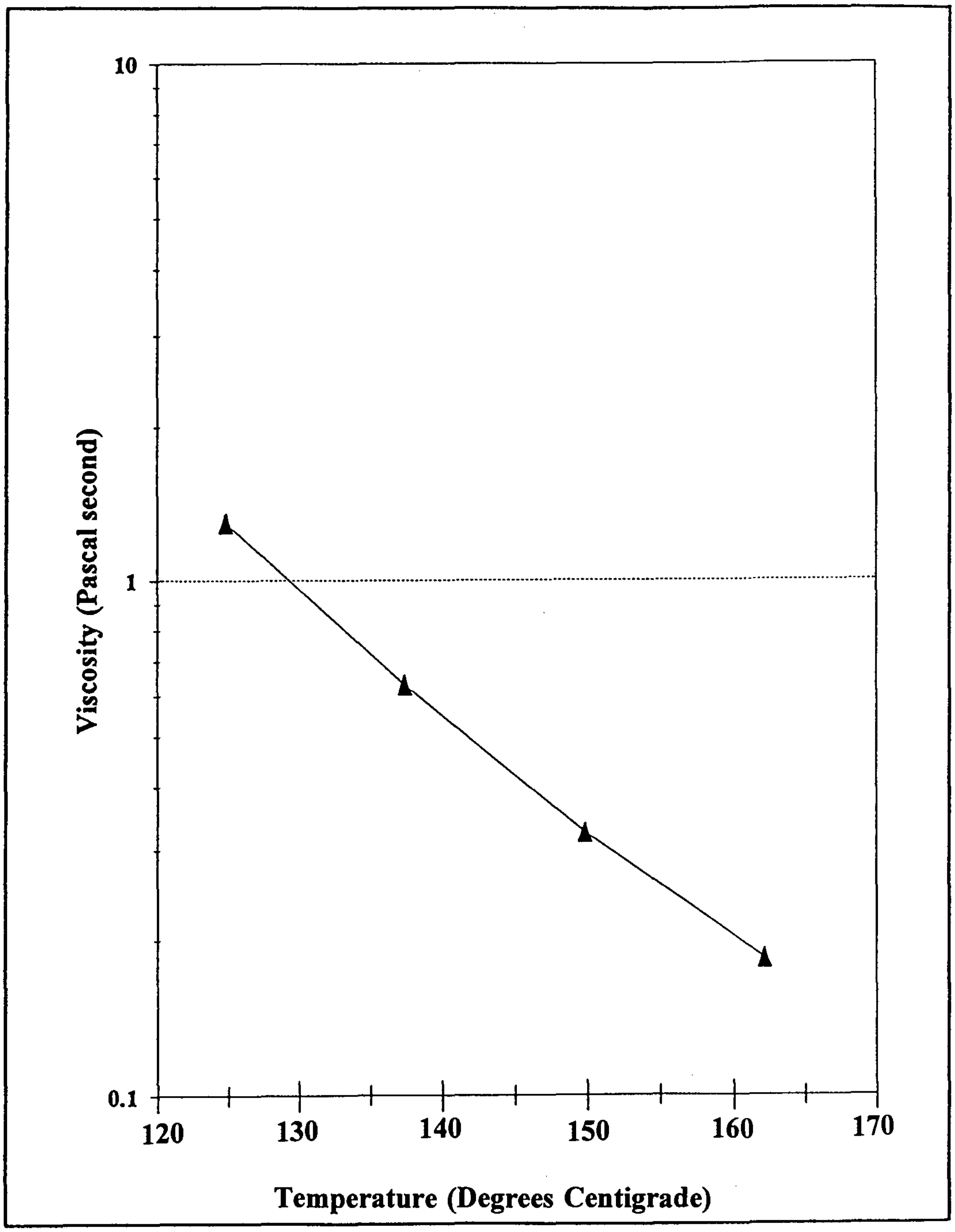


Figure 15. Viscosity versus temperature plot for the Fourth Generation Sulphlex binder using the Brookfield viscometer.

Table 14 presents the Superpave binder specifications used in this study to evaluate the performance potential of Sulphlex binders. As seen in table 14, a number of rheological measurements are used to classify the performance potential of asphalt binders. These rheological properties were selected as they are associated with specific distress mechanisms. The tests are performed at a temperature associated with the distress mechanism in question. Distress mechanisms specifically addressed by the Superpave binder specifications are:

- Rutting - a minimum value of $G^*/\sin \delta$ is required at the maximum pavement temperature for the tank asphalt.
- Rutting - a minimum value of $G^*/\sin \delta$ is required at the maximum pavement temperature for the rolling thin film oven test (RTFOT) residue.
- Thermal cracking - a maximum value of stiffness and minimum value of the slope of the log stiffness versus log time curve measured at the minimum pavement design temperature plus 10 °C (18 °F) is required (at a loading time of 60-s). These values are measured on PAV residue. The stiffness requirement is relaxed when enhanced strain to failure properties can be demonstrated.
- Fatigue - a maximum value of $G^*\sin \delta$ is required at an intermediate pavement temperature on PAV residue.

Superpave researchers selected the rheological parameter of $G^*/\sin \delta$ as the parameter by which to evaluate rutting potential. This parameter is numerically equal to the reciprocal of loss compliance, 1/J", and was used because a regression analysis demonstrated a strong relationship between 1/J" and the rate of rutting of pavements from wheel tracking tests. Since $G^*/\sin \delta$ is numerically equal to 1/J", it is used so that introduction of an additional rheological term is not necessary.

The minimum required value of $G^*/\sin \delta$ for the tank asphalt as well as for the RTFOT aged binder was added to the Superpave specification to provide protection in those cases where the RTFOT in not representative of the hardening that occurs during mixing and laydown.

The limiting stiffness criterion to avoid thermal cracking is simply an attempt to assure that the binder possesses an acceptable level of strain tolerance at low service temperatures. Although different researchers have chosen different combinations of stiffness and loading time over the years to specify the limiting stiffness temperature, a creep stiffness of 300 MPa (42,800 psi) measured after a loading time of 2 h was chosen

Table 14. Performance graded asphalt binder specifications.

PERFORMANCE GRADE	PG 46-			PG 52-							PG 58-					PG 64-					
	34	40	46	10	16	22	28	34	40	46	16	22	28	34	40	10	16	22	28	34	40
Average 7-day Maximum Pavement Design Temperature, °C[a]	<46			<52							<58					<64					
Minimum Pavement Design Temperature, °C[a]	>-34	>-40	>-46	>-10	>-16	>-22	>-28	>-34	>-40	>-46	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-40
ORIGINAL BINDER																					
Flash Point Temp, T48: Minimum °C	230																				
Viscosity, ASTM D4402:[b] Maximum, 3 Pa•s, Test Temp, °C	135																				
Dynamic Shear, TP5:[c] G*/sinδ, Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN RESIDUE (T179)																					
Mass Loss, Maximum, percent	1.00																				
Dynamic Shear, TP5: G*/sinδ, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	46			52							58					64					
PRESSURE AGING VESSEL RESIDUE (PP1)																					
PAV Aging Temperature, °C[d]	90			90							100					100					
Dynamic Shear, TP5: G*sinδ, Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	10	7	4	25	22	19	16	13	10	7	25	22	19	16	13	31	28	25	22	19	16
Physical Hardening[e]	Report																				
Creep Stiffness, TP1:[f] S, Maximum, 300 MPa, *m* - value, Minimum, 0.300 Test Temp @ 60s, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30
Direct Tension, TP3:[f] Failure Strain, Minimum, 1.0% Test Temp @ 1.0 mm/min, °C	-24	-30	-36	0	-6	-12	-18	-24	-30	-36	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	-30

[a] Pavement temperatures are estimated from air temperatures using an algorithm contained in the SUPERPAVE software program, may be provided by the specifying agency, or by following the procedures as outlined in PPX.

[b] This requirement may be waived at the discretion of the specifying agency if the supplier warrants that the asphalt binder can be adequately pumped and mixed at temperatures that meet all applicable safety standards.

[c] For quality control of unmodified asphalt cement production, measurement of the viscosity of the original asphalt cement may be substituted for dynamic shear measurements of G*/sinδ at test temperatures where the asphalt is a Newtonian fluid. Any suitable standard means of viscosity measurement may be used, including capillary or rotational viscometry (AASHTO T201 or T202).

[d] The PAV aging temperature is based on simulated climatic conditions and is one of three temperatures 90°C, 100°C or 110°C. The PAV aging temperature is 100°C for PG 64- and above, except in desert climates, where it is 110°C.

[e] Physical Hardening — TP1 is performed on a set of asphalt beams according to Section 13.1, except the conditioning time is extended to 24 hrs ± 10 minutes at 10°C above the minimum performance temperature. The 24-hour stiffness and *m*-value are reported for information purposes only.

[f] If the creep stiffness is below 300 MPa, the direct tension test is not required. If the creep stiffness is between 300 and 600 MPa the direct tension failure strain requirement can be used in lieu of the creep stiffness requirement. The *m*-value requirement must be satisfied in both cases.

Table 14. Performance graded asphalt binder specifications. (continued)

PERFORMANCE GRADE	PG 70-						PG 76-					PG 82-				
	10	16	22	28	34	40	10	16	22	28	34	10	16	22	28	34
Average 7-day Maximum Pavement Design Temp, °C^{b}	<70						<76					<82				
Minimum Pavement Design Temperature, °C^{b}	>-10	>-16	>-22	>-28	>-34	>-40	>-10	>-16	>-22	>-28	>-34	>-10	>-16	>-22	>-28	>-34
ORIGINAL BINDER																
Flash Point Temp, T48: Minimum °C	230															
Viscosity, ASTM D4402:^{b} Maximum, 3 Pa•s, Test Temp, °C	135															
Dynamic Shear, TP5:^{c} $G^*/\sin\delta$, Minimum, 1.00 kPa Test Temp @ 10 rad/s, °C	70						76					82				
ROLLING THIN FILM OVEN (T240) OR THIN FILM OVEN (T179) RESIDUE																
Mass Loss, Maximum, percent	1.00															
Dynamic Shear, TP5: $G^*/\sin\delta$, Minimum, 2.20 kPa Test Temp @ 10 rad/s, °C	70						76					82				
PRESSURE AGING VESSEL RESIDUE (PP1)																
PAV Aging Temperature, °C^{d}	100(110)						100(110)					100(110)				
Dynamic Shear, TP5: $G^* \sin\delta$, Maximum, 5000 kPa Test Temp @ 10 rad/s, °C	34	31	28	25	22	19	37	34	31	28	25	40	37	34	31	28
Physical Hardening^{e}	Report															
Creep Stiffness, TP1:^{f} S, Maximum, 300.0 MPa, *m* - value, Minimum, 0.300 Test Temp @ 60s, °C	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24
Direct Tension, TP3:^{f} Failure Strain, Minimum, 1.0% Test Temp @ 1.0 mm/min, °C	0	-6	-12	-18	-24	-30	0	-6	-12	-18	-24	0	-6	-12	-18	-24

for the Superpave asphalt binder specification. The bending beam rheometer (BBR) test is used to determine the binder stiffness at the appropriate pavement temperature. Superpave researchers determined that the stiffness after 2 h of loading (for test temperature T_{min}) is approximately equal to the stiffness after 60 s loading time at a test temperature of T_{min} + 10 °C (18 °F). This allows the specification criterion to be determined after a reasonable test time of 60 s of loading at T_{min} + 10 °C (18 °F). This relationship between testing temperature and time of loading to determine the critical stiffness is based on the analysis of data from the SHRP core asphalts and extended asphalts. These data demonstrated a very similar time-temperature equivalency or time-temperature shift factor at temperatures below the defining temperature (or glass transition temperature). This assumption may not be appropriate for Sulphlex binders.

In addition to the maximum stiffness requirement at the minimum pavement design temperature, the absolute value of the slope of the creep compliance mastercurve is also included in the Superpave binder specifications, where the slope, m, is also defined after 60 s of loading as shown in equation 9.

$$m = [d\log(S(t))/ d\log(t)] \tag{9}$$

The Superpave binder criteria require that the stiffness of the binder tested at the low pavement design temperature after 60 s of loading not exceed 300 MPa (42,800 psi) and the slope be at least 0.3. However, the maximum stiffness at the grading test temperature may be between 300 and 600 MPa (42,800 to 85,700 psi) as long as the strain to failure at the grading temperature is greater than 1 percent. No waiver is permitted for the m value.

The Superpave binder criterion for fatigue resistance is based on fatigue data obtained from the Zaca-Wigmore road study as well as other road studies. These studies verified that $G^*\sin\delta$, loss modulus, can be used as a specification criterion. The value of the loss modulus in the Superpave specifications is required to be below 5.0 MPa (713 psi) at the intermediate pavement design temperature.

In summary the Superpave performance-based specifications for asphalt binders include the following rheological parameters as tools for determining distress potential:

- Rutting - minimum value of inverse of compliance, 1/J", expressed as $G^*/\sin\delta$ at the maximum design temperature.

- Fatigue - maximum value of loss modulus, $G^*/\sin\delta$, which is the energy dissipated per load cycle.
- Thermal cracking - stiffness and absolute slope of stiffness versus time on a log-log scale measured in creep after 60 s at minimum design pavement temperature.
- Thermal cracking - strain at failure as determined in a constant rate of strain test.

The performance grade of Superpave graded asphalts is designated as PG*n*-*m*. The PG stands for performance grade binder. The *n* denotes the high temperature response of the binder while the *m* is indicative of the binder's response at the intermediate and low temperatures. Higher values of *n* and *m* represent the ability to perform under increasingly severe conditions.

In order to evaluate the Sulphlex binders in this study for susceptibility to rutting, dynamic shear rheometer (DSR) testing was performed on tank Sulphlex and RTFOT-aged Sulphlex at temperatures of 25, 40, 60, and 95 °C (77, 104, 140, and 203 °F) and at the required loading frequency of 10 rad/s. These temperatures were selected as the temperature gradient maintained within the specimen could only be reliably maintained at these temperatures with the Carri-Med CSL rheometer available during initial binder evaluation. An additional series of DSR testing was performed using a Rheometrics Model RDS II Rheometer on the same tank Sulphlex binders. This second sequence of testing was performed at 10 rad/s and over a temperature range of 25 to 95 °C (77 to 203 °F) at temperature intervals of approximately 5 °C (9 °F). The range and increments of temperatures were selected in order to more precisely determine the high temperature grade number for the binder. This high temperature range sequence of testing was performed on tank, RTFOT-aged and PAV-aged (without previous RTFOT aging). Samples subjected to PAV aging only were tested to evaluate the effect of oxidative (but not RTFOT) aging on the high temperature rheological response of these binders.

In order to evaluate the susceptibility of Sulphlex binders to fatigue cracking and thermal cracking, RTFOT and PAV aged specimens were tested using the DSR over a temperature range of 5 to 25 °C (41 to 77 °F), at 10 rad/s. In addition to the RTFOT and PAV aged samples, tank Sulphlex samples were subjected to DSR testing in order to evaluate the effects of aging within this temperature range.

Thermal cracking potential was evaluated using Superpave performance grade criteria after testing the candidate Sulphlex binders in the bending beam rheometer at temperatures of -25, -15, and -10 °C (-13, 5, and 14 °F).

Dynamic Shear Rheometer - Rutting Susceptibility

The dynamic shear rheometer (DSR) was used to assess the rheological properties of the Sulphlex binders. The test was conducted in accordance with Superpave procedures as outlined in SHRP method B-003. The test measures the dynamic shear modulus and phase angle of the binder when tested in dynamic or oscillatory shear using parallel plate test geometry. The test is applicable to binders having dynamic shear modulus values in the range of 0.1 kPa to 10 MPa (0.014 to 1,430 psi), which are typically obtained between 5 °C (41 °F) and 85 °C (185 °F).

Table 15 summarizes the $G^*/\sin\delta$ values determined in the initial phase of high temperature (25, 40, 60, and 95 °C (77, 104, 140, and 203 °F)) testing using the Carri-Med CSL rheometer to evaluate the rutting potential of the four Sulphlex and control AC-20 binders. The data are recorded for both the tank binder and the RTFOT-aged binder as required in the Superpave specifications.

According to Superpave binder specifications, a minimum value for $G^*/\sin\delta$ of an unaged or tank binder is 1.0 kPa (145 psi) to ensure acceptable rutting resistance. According to the data in table 15, the 50/50 (198:233) one-pot synthesis and the Fourth Generation Sulphlex binder meet this specification at 60 °C (140 °F), and therefore have a performance grade of at least PG 60-m. Superpave specifications require a minimum $G^*/\sin\delta$ value of 2.2 kPa (319 psi) after RTFOT-aging. Accordingly, the one-pot synthesized 50/50 (198:233) blend and the Fourth Generation Sulphlex meet this criterion at 60°C (140 °F). The two-pot 50/50 (198:233) blend almost meets this criterion at 60 °C (140 °F). However, the 75/25 (198:233) blend falls considerably short of the minimum $G^*/\sin\delta$ value of the aged residue at 60 °C (140 °F). The AC-20 control easily meets requirements for a PG60-m grade. The phase angle for all four Sulphlex binders in this temperature range was close to 90 degrees, indicating that the binder response is almost purely viscous over this temperature range. The loss tangent, which is the ratio of the viscous modulus, G", to the elastic modulus, G', was also computed. At 60 °C (140 °F), the loss tangents for the 50/50 (198:233) one-pot synthesis, and Fourth Generation binders were 96.18 and 9.93, respectively. Traditionally, a lower loss tangent at higher temperatures indicates that the binder is able to maintain a better elastic response and can better resist creep deformation. On the basis of the $G^*/\sin\delta$ value and the loss tangent value, the Fourth Generation and 50/50 (198:233) one-pot synthesized blend binders are the most favorable in terms of high temperature rut resistance. Furthermore, binders with lower loss tangents have better low-strain fatigue lives under certain conditions like a controlled-stress mode of loading.(28)

Table 16 summarizes the continuous DSR testing of tank, RTFOT-aged and PAV-aged binders. These data were collected using the Rheometerics rheometer at

Table 15. Summary of initial DSR testing (using Carri-Med CSL Rheometer) to evaluate rutting potential ($G^*/\sin\delta$) and performance grade classification of Sulphlex binders and control asphalt binder.

Designation of Binder	Test Temp., °C (°F)	25 (77)		40 (104)		60 (140)		95 (203)	
	Level of Aging	Tank	RTFOT	Tank	RTFOT	Tank	RTFOT	Tank	RTFOT
50/50 (198:233) Two-Pot Blend		-*	370,645	10,500	19,925	700	2,010	40	75
50/50 (198:233) One-Pot Synthesis		-	623,540	16,750	27,770	1,100	2,410	50	85
75/25 (196:233) Two-Pot Blend		-	161,875	10,470	10,470	----	1,335	----	60
Fourth Generation		-	207,170	15,760	15,635	1,600	2,180	100	125
AC-20 (Control)		132,075	480,400	10,030	38,405	1,330	4,490	55	150

*Value of $G^*/\sin\delta$ in each cell is reported in Pa.

Table 16. Summary of continuous DSR testing to evaluate rutting potential ($G^*/\sin\delta$) over a temperature range of 40 to 95 °C (104 to 203 °F) for Sulphlex binders and control asphalt binder.

Test Temp., °C	Level of Aging	Binder Designation				
		50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Blend	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
40	Tank	13,780*	31,915	4,050	16,260	10,030
	RTFOT	33,000	38,400	48, 290	98,230	38,405
	PAV	14,180	31,115	3,770	---	---
45	Tank	6,865	15,150	2,090	9,070	
	RTFOT	16,775	18,670	26,420	50,920	
	PAV	6,970	14,960	1,945	---	
50	Tank	3,520	7,115	1,130	5,285	
	RTFOT	9,575	9,695	10,500	26,050	
	PAV	3,569	7,595	1,045	---	
55	Tank	1,880	3,730	609	3,190	
	RTFOT	6,260	5,630	5,965	12,910	
	PAV	1,933	4,050	580	---	
60	Tank	1,045	2,005	362	1,995	1,330
	RTFOT	4,590	3,810	3,310	5,520	4,480
	PAV	1,086	2,250	340	---	
65	Tank	600	1,075	220	1,240	---
	RTFOT	3,560	2,690	1,600	2,700	2,190
	PAV	640	1,280	210	---	---
70	Tank	335	650	135	780	
	RTFOT	1,560	1,590	850	1,450	
	PAV	390	750	130	---	
95	Tank	30	70	20	75	55
	RTFOT	1,300	65	30	45	150
	PAV	40	50	20	--	

*Value of $G^*/\sin\delta$ in each cell is reported in Pa.

a testing temperature range of 25 to 95 °C (77 to 203 °F) at approximately 5 °C (9 °F) increments in temperature. From table 16 a more definitive evaluation of the PG*n-m* grade can be established as a 5 °C (9 °F) continuous grade. According to the tank binder data from table 16, the Superpave high temperature grade designation of the five binders is shown in table 17. The binders tested using the Rheometrics rheometer and whose data are summarized in table 16 were from the same batches as these tested using the Carri-Med rheometer (table 15). All samples were stored identically in tightly covered containers in a 7 °C (45 °F) room. However, the samples tested using the Rheometric rheometer were stored for a longer period of time prior to testing (approximately 5-months longer). Each sample was heated twice to a temperature of approximately 65 °C (150 °F) prior to testing.

The purpose of the PAV-aged (without previous RTFOT aging) samples presented in table 16 is to evaluate the effect of simulated long-term oxidative aging on the rheological behavior of the binders between test temperatures of 25 and 95 °C (77 to 203 °F). It should be noted that these samples were PAV-aged only and were <u>not</u> subjected to RTFOT aging prior to DSR testing. The procedure followed for all PAV aging in this study was 20 h in the pressure aging vessel at a pressure of 2,100 kPa (300 psi) at a temperature of 100 °C (212 °F). Comparisons between Sulphlex binders and PAV (only) aged Sulphlex binders demonstrated that PAV aging does not increase the shear modulus of the binder over this wide range of test temperatures. The conclusion is that oxidative aging, which is designed to occur in the PAV test for asphalt binders, does not significantly affect the Sulphlex binders. Perhaps this indicates that, unlike asphalt binders, Sulphlex binders are not susceptible to rheological changes caused by oxidative aging. Table 17 illustrates that the effect of RTFOT aging of the four Sulphlex binders at test temperatures of 60 °C (140 °F) was to increase the shear modulus by approximately 50 to 120 percent over the unaged shear modulus. Therefore, the RTFOT aging effects are significant while PAV aging effects are not.

Dynamic Shear Rheometer - Fatigue Cracking Susceptibility

A more complete evaluation of fatigue potential of the Sulphlex binders was carried out using the Rheometerics rheometer. During this testing both tank and RTFOT and PAV-aged binders were subjected to DSR testing over a temperature range of from approximately 5 to 25 °C (41 to 77 °F). These data for the RTFOT and PAV aged Sulphur samples are summarized in table 18. Superpave specifications require that the value of $G^{*}\sin\delta$ not exceed 5,000 kPa (713 psi) after the binder has been subjected to both RTFOT and PAV-aging. The test temperature at which the value of loss modulus falls below the 5,000 kPa (713 psi) mark helps define the low temperature PG *n-m* designation. This value is used in conjunction with rheological data from the bending beam rheometer to determine the full Superpave performance grade designation.

Table 17. Superpave high temperature performance grade of Sulphlex binders and control asphalt binder

Parameter Evaluated	Binder Designation				
	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
Approximate Temperature (°C) at which G*/sin δ = 1.0 kPa (Tank Binder)	60	65	55	65	60
Approximate Temperature (°C) at which G*/sin δ = 2.2 kPa (RTFOT - Aged Binder)	65	65	60	65	65
Superpave Binder High Temperature Grade PG n - m	PG 58-m	PG 64 - m	PG 52 - m	PG 64 - m	PG 64 - m

Table 18. Summary of DSR testing to evaluate fatigue cracking potential (G*sin δ) and performance grade classification of Sulphlex binders and control asphalt binder.

Test Temperature ˚C	Level of Aging	Binder Designation				
		50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesized	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
5	RTFOT and PAV	5,874*	3,939	8,425	1,464	----
8.5	RTFOT and PAV	4,596	2,012	6,205	744	----
12.5	RTFOT and PAV	3,153	826	3,066	320	----
17	RTFOT and PAV	1,811	342	1,214	139	4,800
22	RTFOT and PAV	828	146	485	63	2,610

*Value of G^*sin δ in each cell is reported in units of Pa.

Bending Beam Rheometer - Thermal Cracking Susceptibility

The bending beam rheometer (BBR) was used to assess the flexural creep stiffness of the Sulphlex binders. The test was conducted according to Superpave procedures outlined in SHRP method B-003.(14)

The test measures the properties of the binders at low temperatures. The specification test was conducted at temperatures of -25, -15, and -10 °C (-13, -5, and 13 °F). Stiffness was measured as a function of time over a 4-min period under a 100 g load. The test was conducted on beam specimens which had undergone rolling thin film oven aging (ASTM D 2872) and the pressure aging vessel (SHRP B-005). Data from bending beam rheometer (BBR) testing is summarized in table 19.

On the basis of DSR testing at the maximum and intermediate pavement temperatures and BBR testing at minimum pavement temperatures, the projected Superpave PG designations for the four Sulphlex binders evaluated in this study are as shown in table 20.

Environmental Scanning Electron Microscopy (ESEM)

Under the binder testing program, micrographs using the environmental scanning electron microscope were recorded at 5 °C (41 °F), 25 °C (77 °F), and 40 °C (104 °F) in order to visually chart the microstructural changes that occur within the binder over this temperature range. The reason for adopting this sub-study was to identify any microstructural changes that might be able to explain the anomalies noted between 25 °C (77 °F) and 40 °C (104 °F) in some mixture testing of 75/25 (198:233) Generation Sulphlex mixtures. The samples were taken from the surface and the core of the binder mass. Samples were conditioned at 25 °C (77 °F) for 7 days prior to ESEM studies. Photomicrographs were taken at a magnification of 585X. Figures 16 through 27 show the different structures of the four binders from the surface and the interior at the above mentioned temperatures.

From the micrographs, a marked difference was observed in the structure of the 50/50 (198:233) and one-pot synthesized blends (Task C) between the surface and the interior extractions. This difference was noticed in the other blends, but to a lesser degree. However, the structures of the (Task B) 50/50 (198:233) and one-pot synthesized (Task C) material differed from the (Task B) 75/25 (198:233) and Fourth Generation blends. While the former system was characterized by larger sulfur crystals, the latter system showed development of an elongated "fiberlike" structure. The scans are inconclusive with no definitive insight being provided into the anomalous behavior of the latter system.

Table 19. Summary of BBR testing to evaluate thermal cracking potential (creep stiffness (S_{BBR}) and slope (m) of stiffness versus time of loading) for Sulphlex binders and control asphalt binder.

Binder Designation	Test Temperature, °C (°F)					
	-25 (77)		-15 (5)		-10 (14)	
	S_{BBR}^*	m^{**}	S_{BBR}^*	m^{**}	S_{BBR}^*	m^{**}
50/50 (198:233) Two-Pot Blend	1341/ 1294	0.23/ 0.23	846/ 360	0.43/ 0.58	86	0.76
50/50 (198:233) One-Pot Synthesis	1347/ 971	0.24/ 0.23	937/ 517	0.38/ 0.53	139	0.73
75/25 (198:233) Two-Pot Blend	539/ 438	0.34/ 0.29	72/ 75	0.71/ 0.70	----	----
Fourth Generation	610/ 590	0.40/ 0.34	62/ 63	0.73/ 0.72	----	----
AC-20 (Control)	----	----	270	0.30	----	----

*Values reported in this cell are of the creep stiffness at 60 s and are in units of MPa.

**Values reported in this cell are of the slope of the stiffness versus time of loading plot at 60 s.

Table 20. Superpave performance grades of Sulphlex binder evaluated in binder study.

Binder Designation	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
Performance Grade (PG n-m)	PG 58 - 22	PG 64 - 22	PG 52 - 34	PG 64 - 28	PG 64 - 22

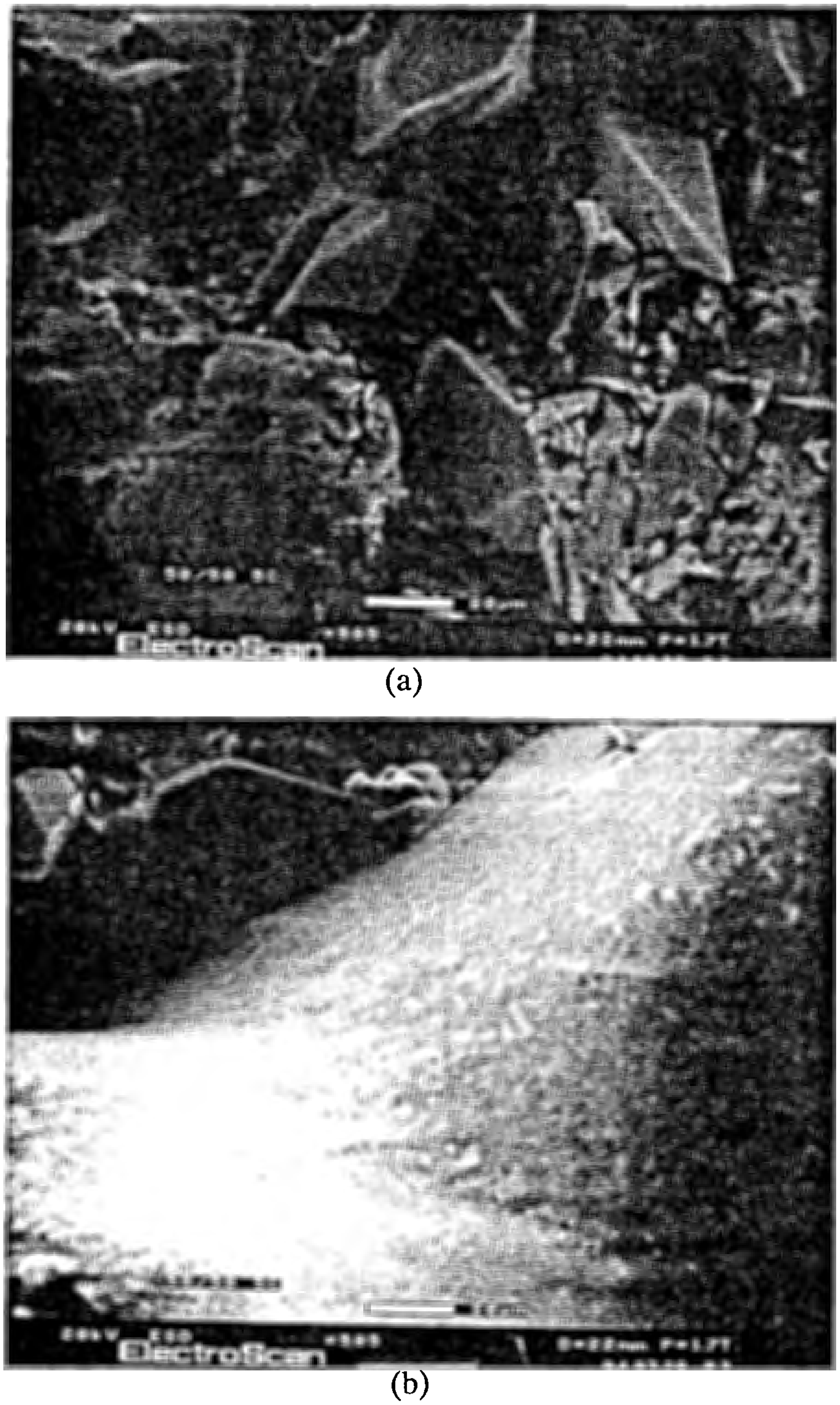
MIXTURE TESTS

Mixture Designs

The graded aggregate and Sulphlex binders were heated to 149 °C (300 °F) and thereafter mixed in 4000 g batches. The 51-mm (2-in) height by 102-mm (4-in) diameter samples were molded using the Texas gyratory compactor while the 102-mm (4-in) height by 102-mm (4-in) diameter samples were molded using the California kneading compactor (ASTM D 1561). These samples were molded (ASTM D 4013) using mix design methodologies consistent with the AAMAS procedural manual for mixture design.(12)

Acceptable mix designs for the Sulphlex and control mixtures were determined using the Marshall method (ASTM D 1559). Table 21 is a summary of the parameters and data used to arrive at the design binder content. The design criteria used are summarized in table 22.

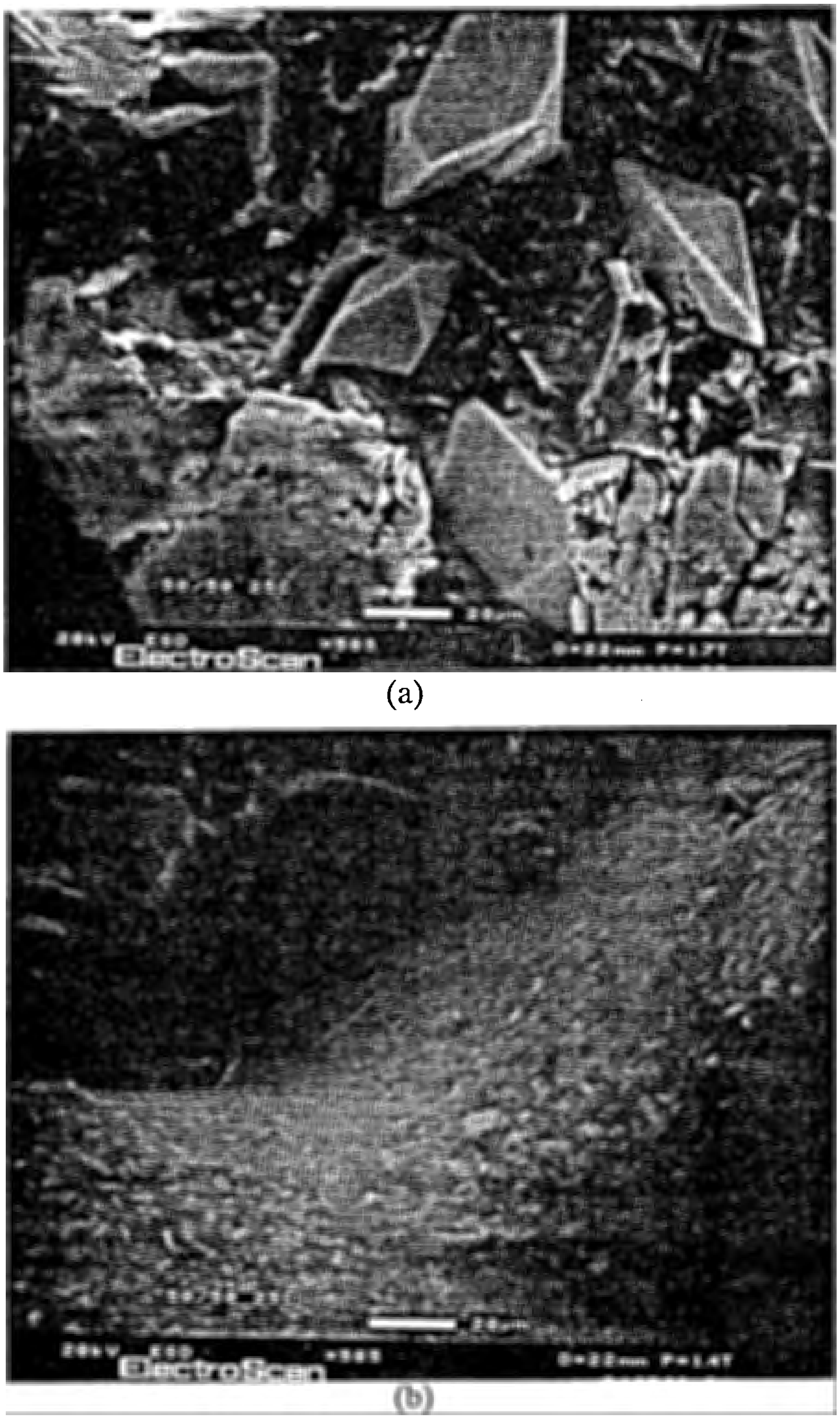
On the basis of the mixture design criteria presented in table 22, a design binder content of 7 percent by weight of the mixture was selected for all four Sulphlex mixes. After selecting 7 percent binder, three replicate samples were prepared for each of the four Sulphlex binders using the gyratory compactor and kneading compactor to verify the ability to achieve mixtures with four percent air voids (± 0.5 percent). This air void tolerance was maintained for each sample prepared.



(a)

(b)

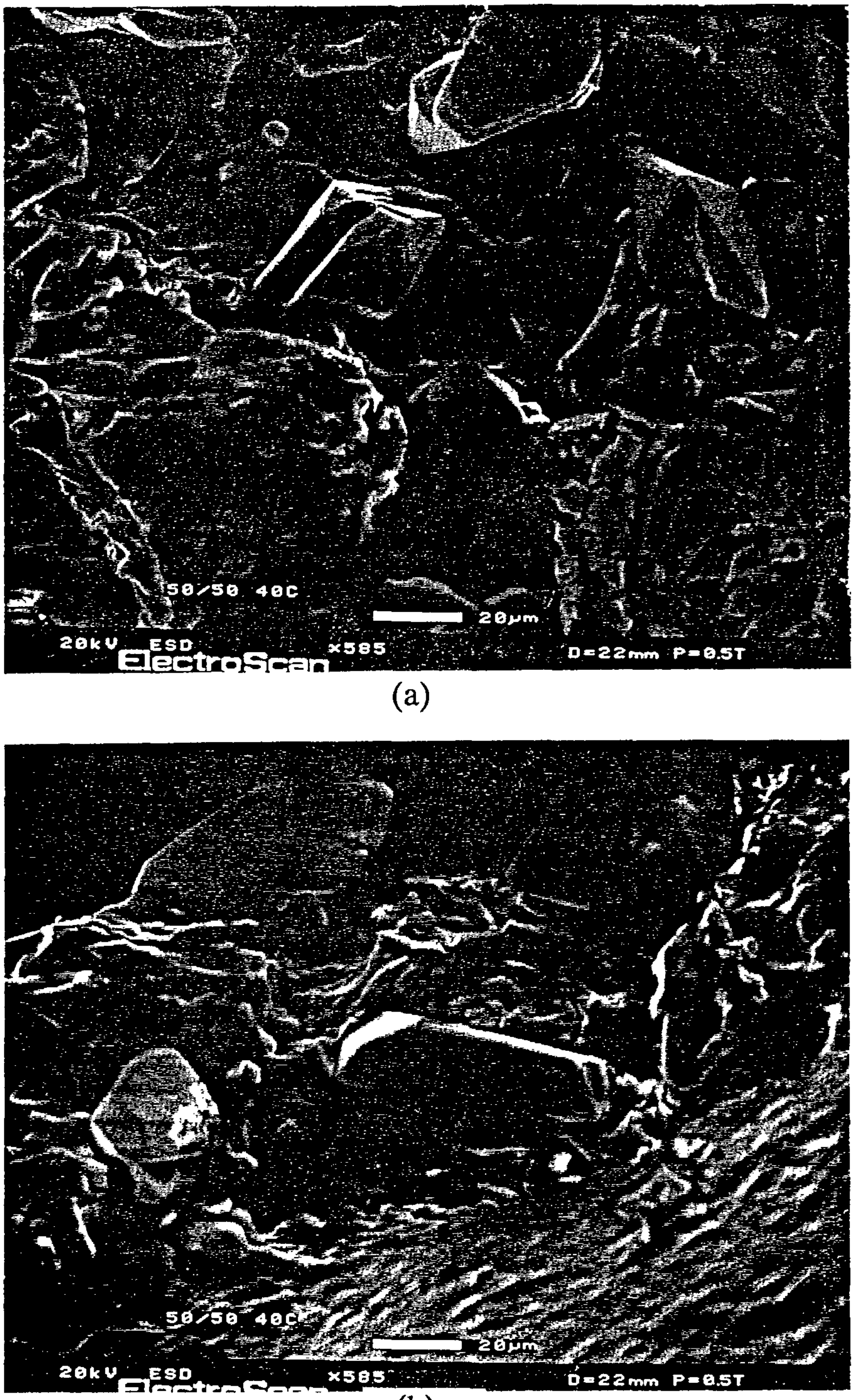
Figure 16. Scanning Electron Micrographs of the 50/50 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 5 °C (41 °F) using the ESEM.



(a)

(b)

Figure 17. Scanning Electron Micrographs of the 50/50 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 25 °C (77 °F) using the ESEM.



(a)

(b)

Figure 18. Scanning Electron Micrographs of the 50/50 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 40 °C (104) using the ESEM.

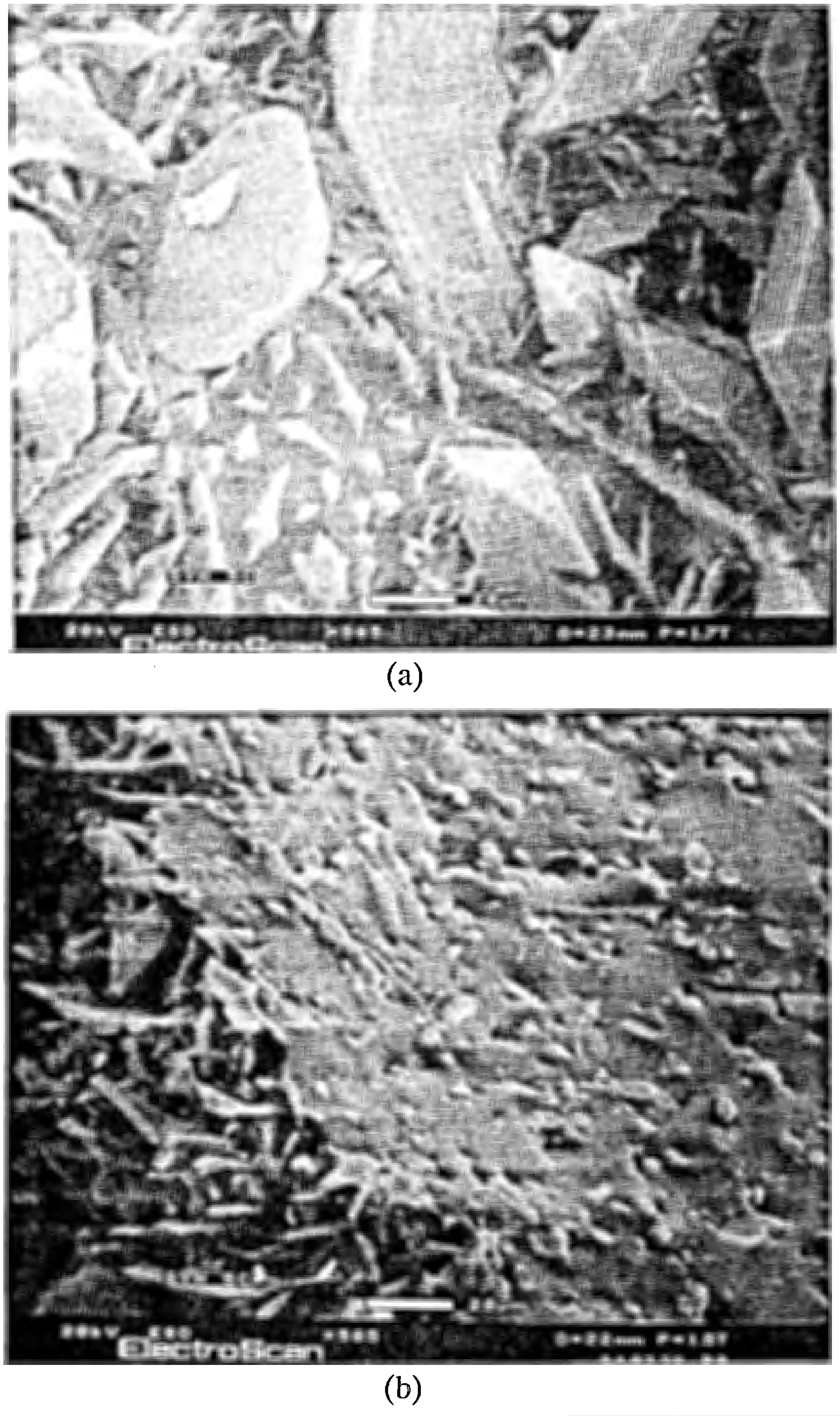


Figure 19. Scanning Electron Micrographs of the 50/50 (198:233) one-pot synthesized binder from (a) the surface, and (b) the interior at 5 °C (41 °F) using the ESEM.

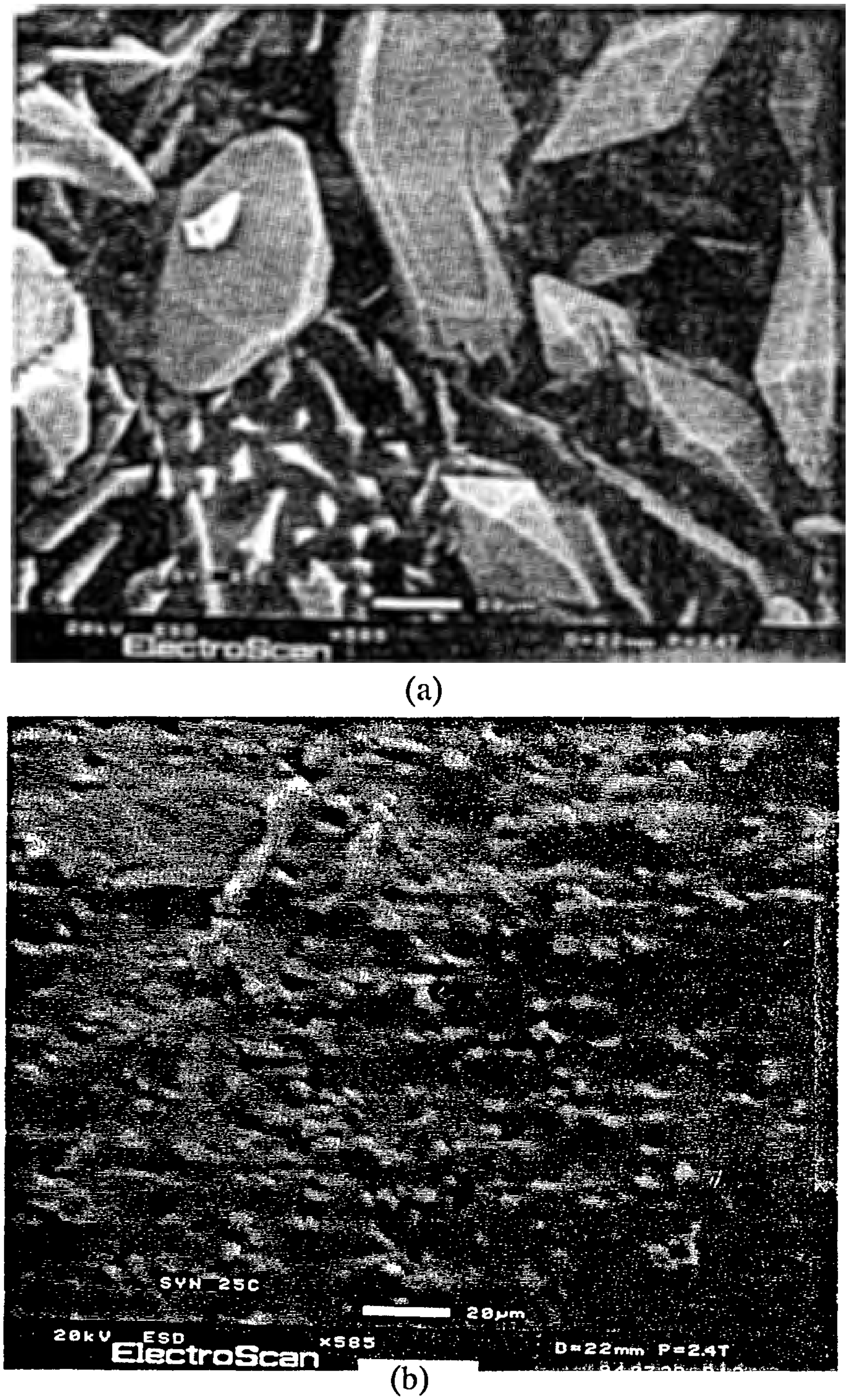
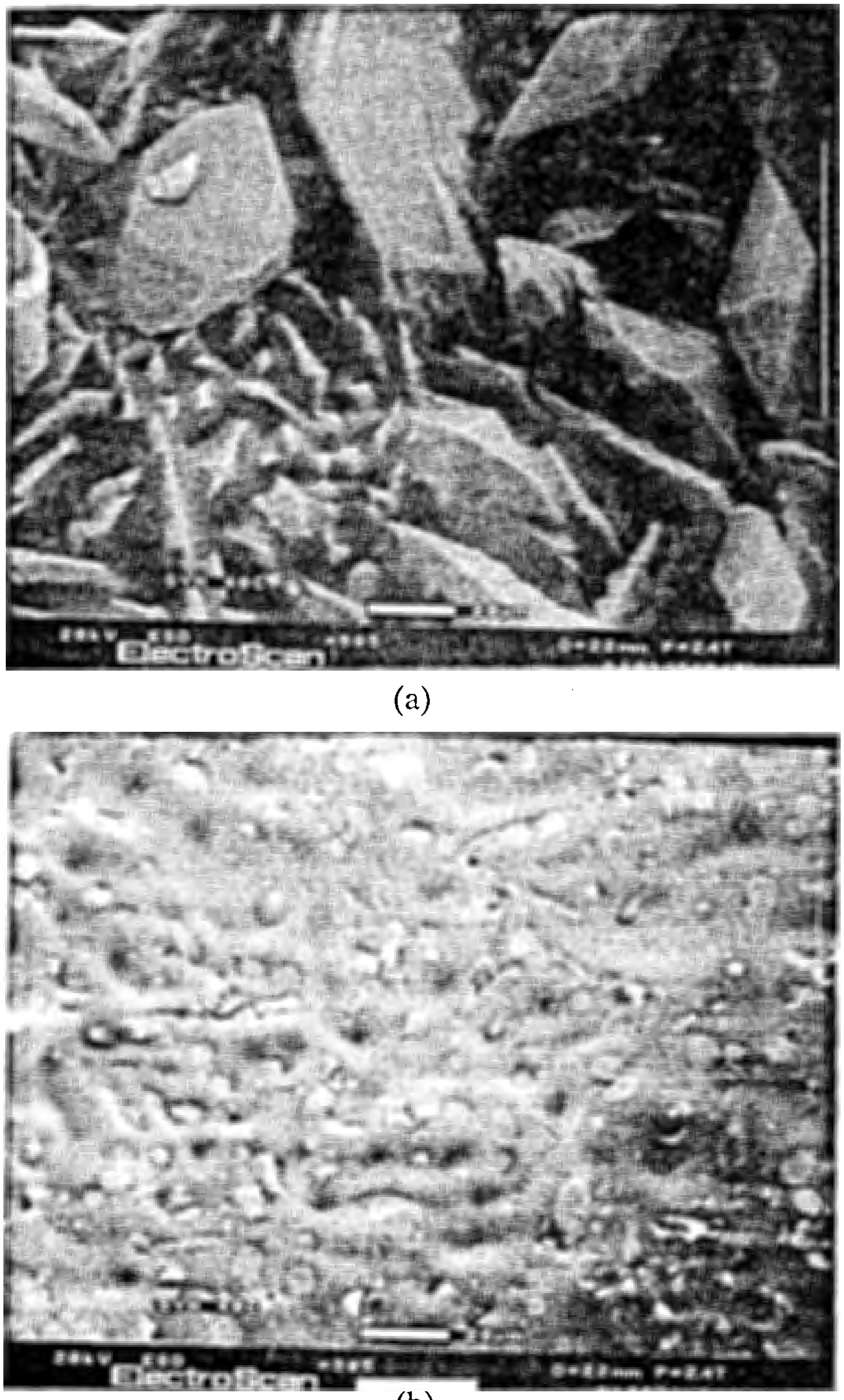


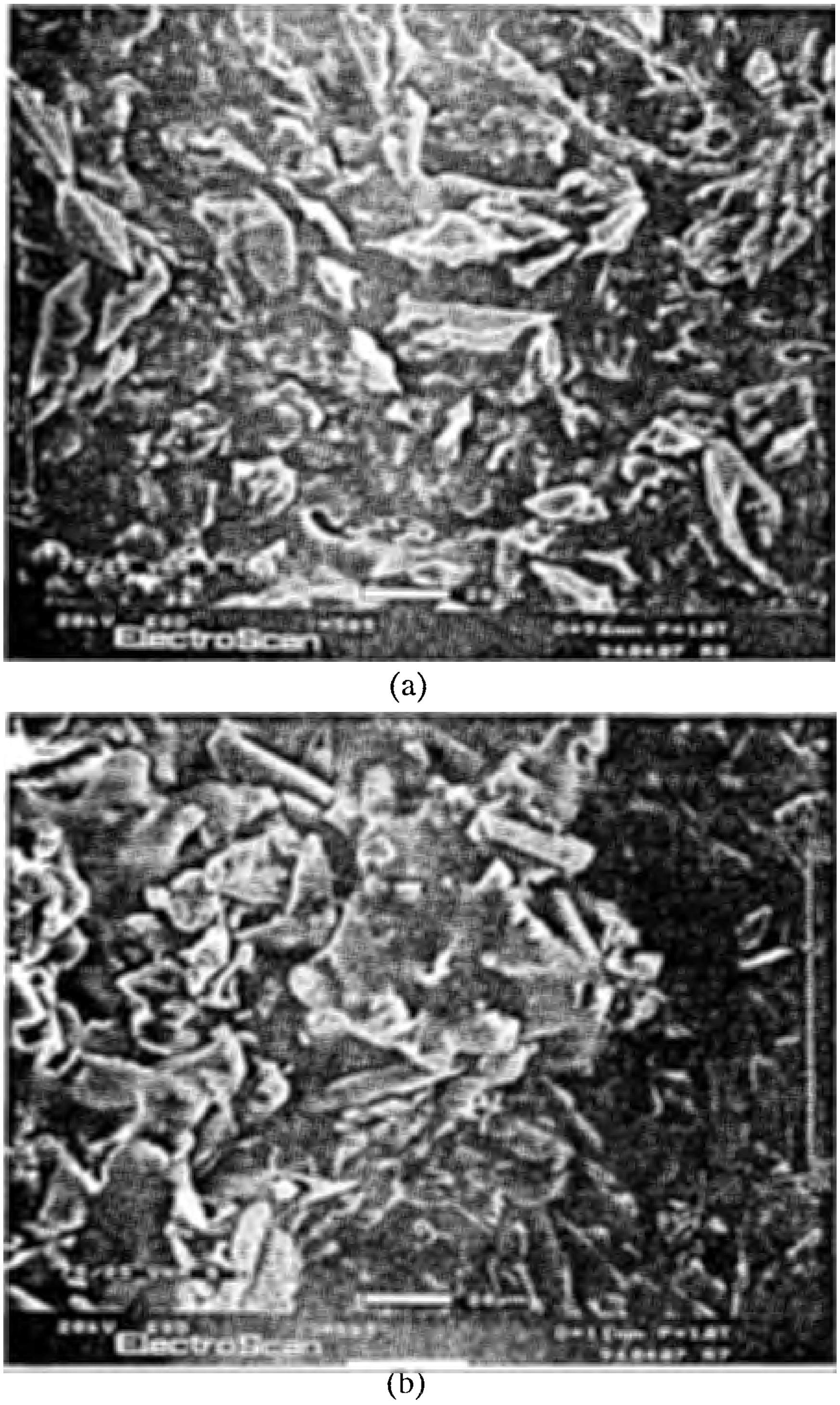
Figure 20. Scanning Electron Micrographs of the 50/50 (198:233) one-pot synthesized binder from (a) the surface, and (b) the interior at 25 °C (77 °F) using the ESEM.



(a)

(b)

Figure 21. Scanning Electron Micrographs of the 50/50 (198:233) one-pot synthesized binder from (a) the surface, and (b) the interior at 40 °C (104 °F) using the ESEM.



(a)

(b)

Figure 22. Scanning Electron Micrographs of the 75/25 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 5 °C (41 °F) using the ESEM.

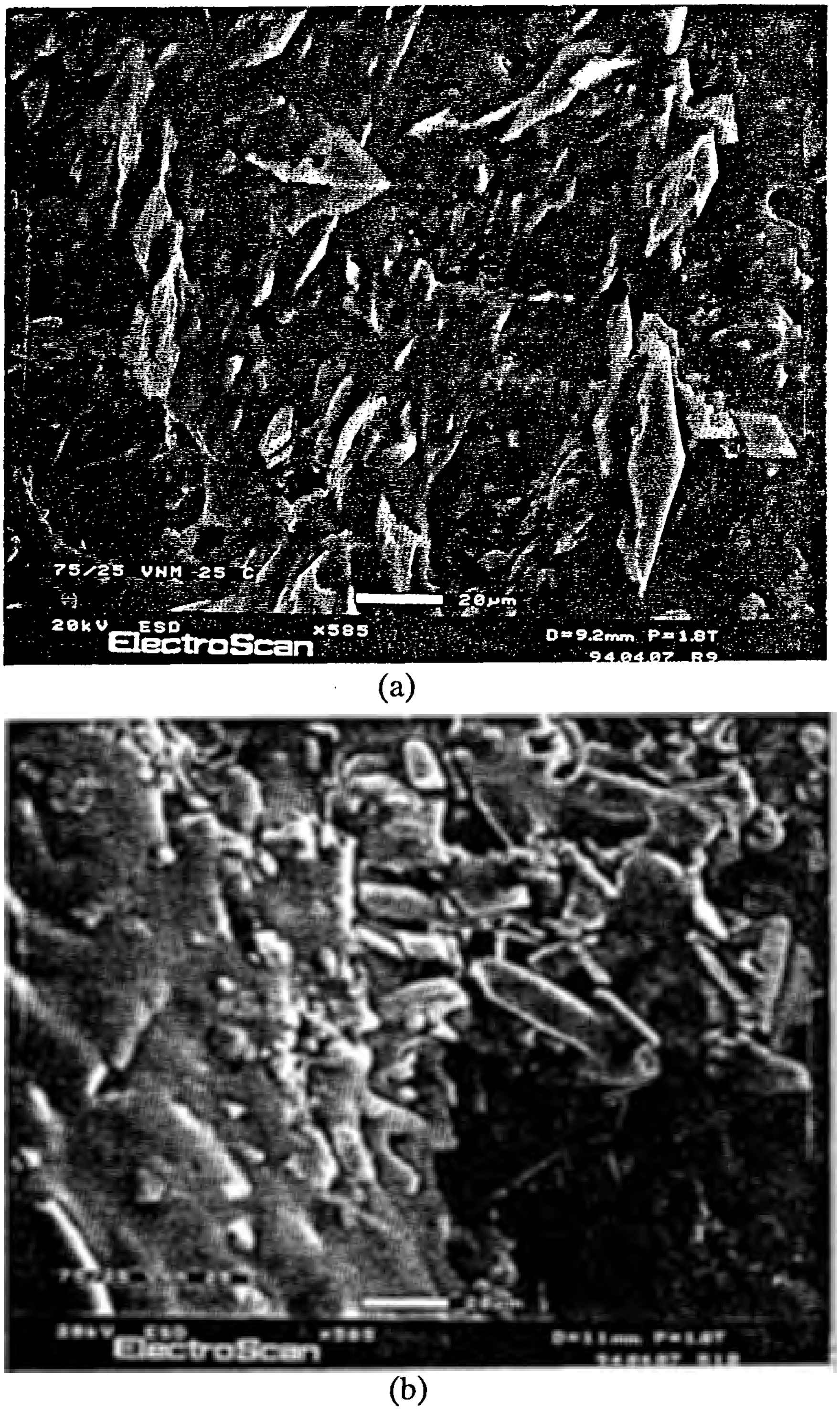
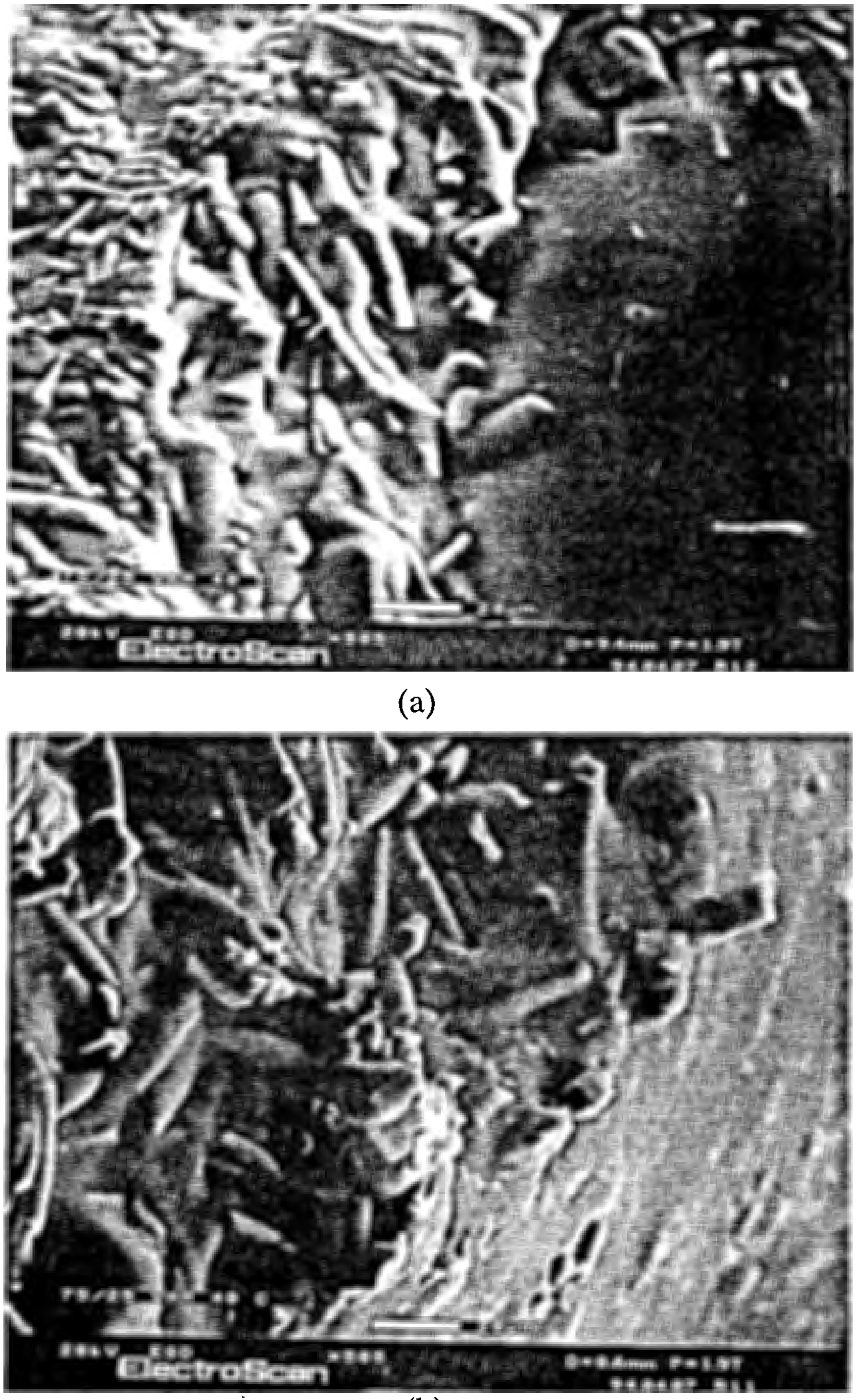


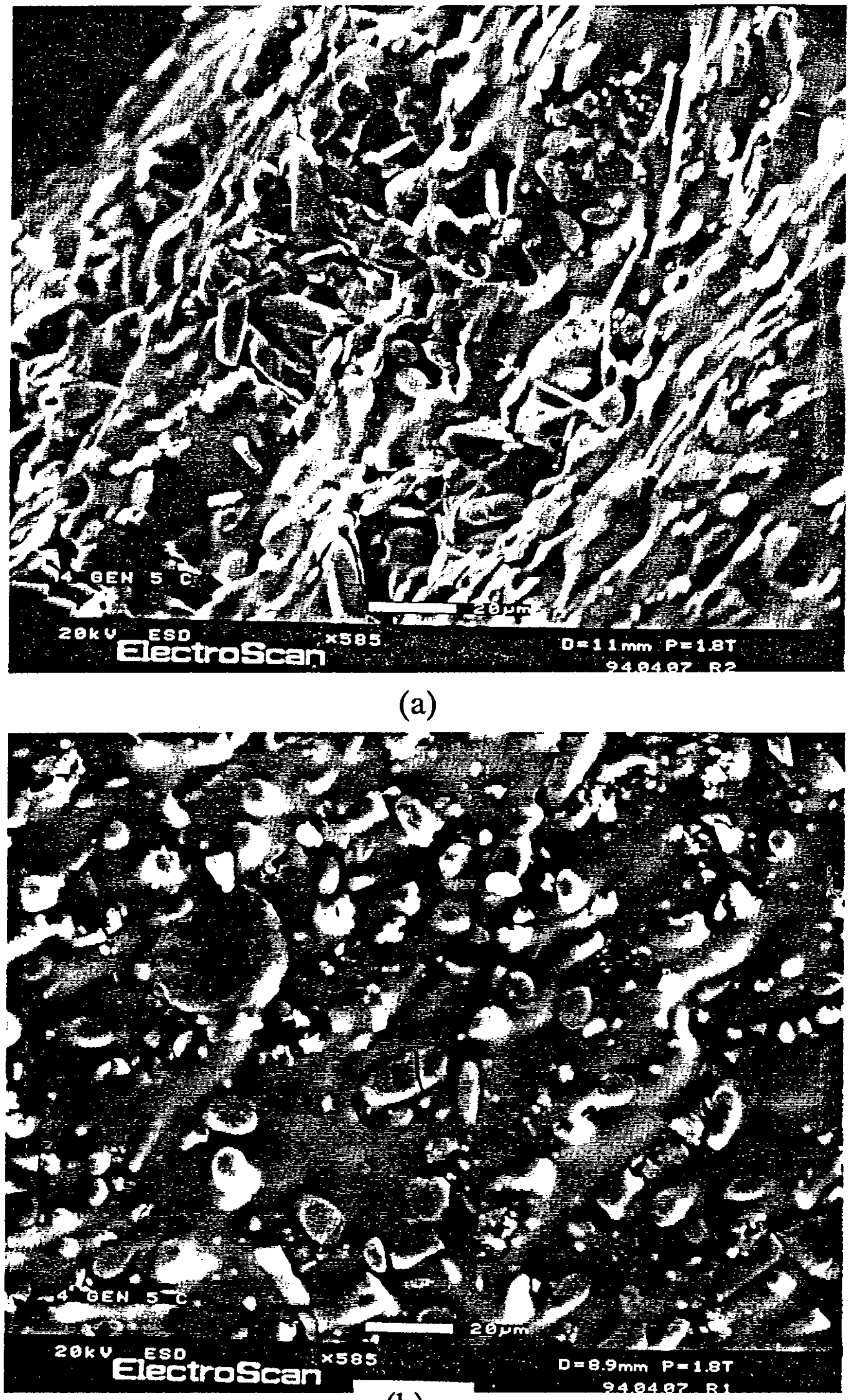
Figure 23. Scanning Electron Micrographs of the 75/25 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 25 °C (77 °F) using the ESEM.



(a)

(b)

Figure 24. Scanning Electron Micrographs of the 75/25 (198:233) two-pot blend binder from (a) the surface, and (b) the interior at 40 °C (104 °F) using the ESEM.



(a)

(b)

Figure 25. Scanning Electron Micrographs of the Fourth Generation binder from (a) the surface, and (b) the interior at 5 °C (41 °F) using the ESEM.

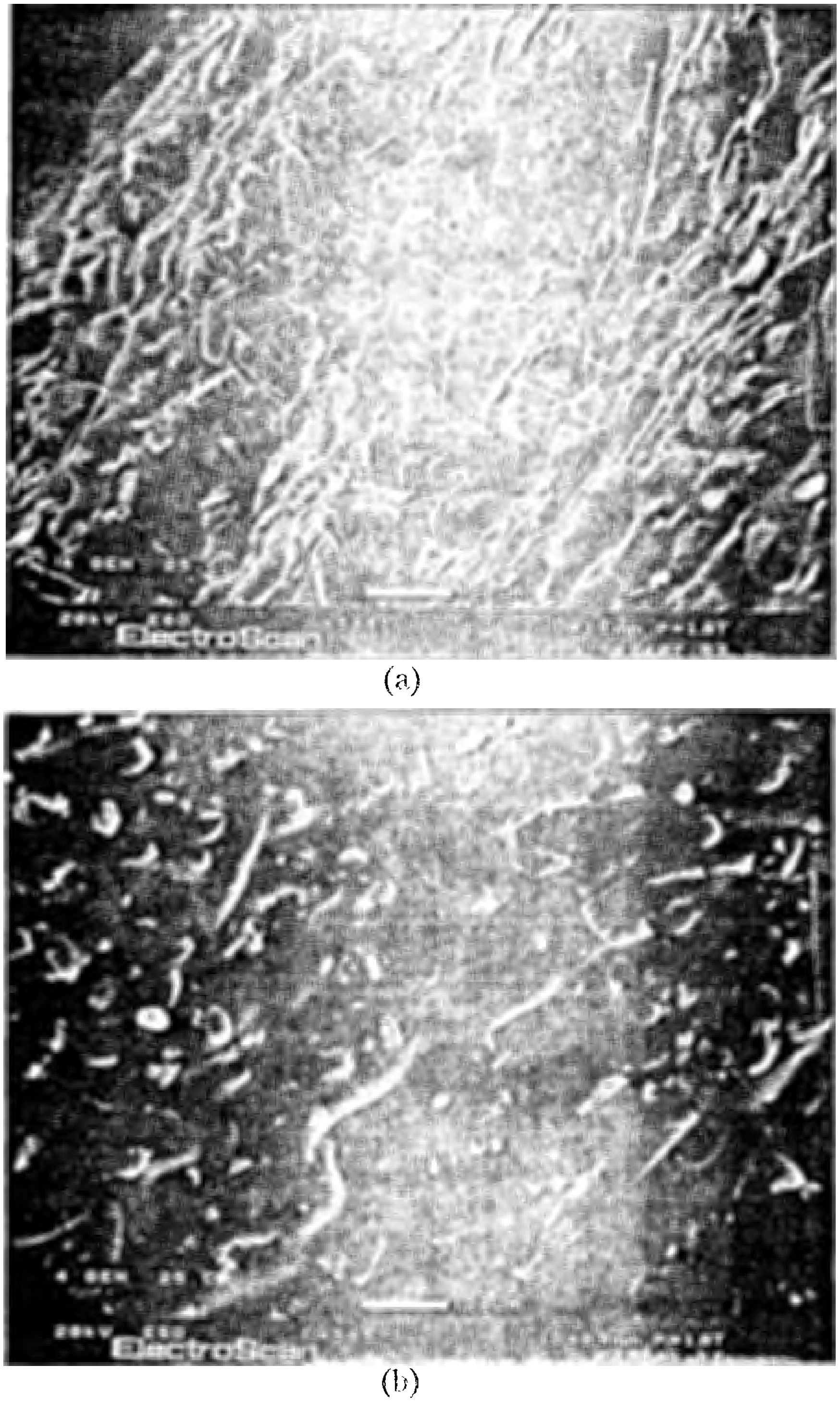


Figure 26. Scanning Electron Micrographs of the Fourth Generation binder from (a) the surface, and (b) the interior at 25 °C (77 °F) using the ESEM.

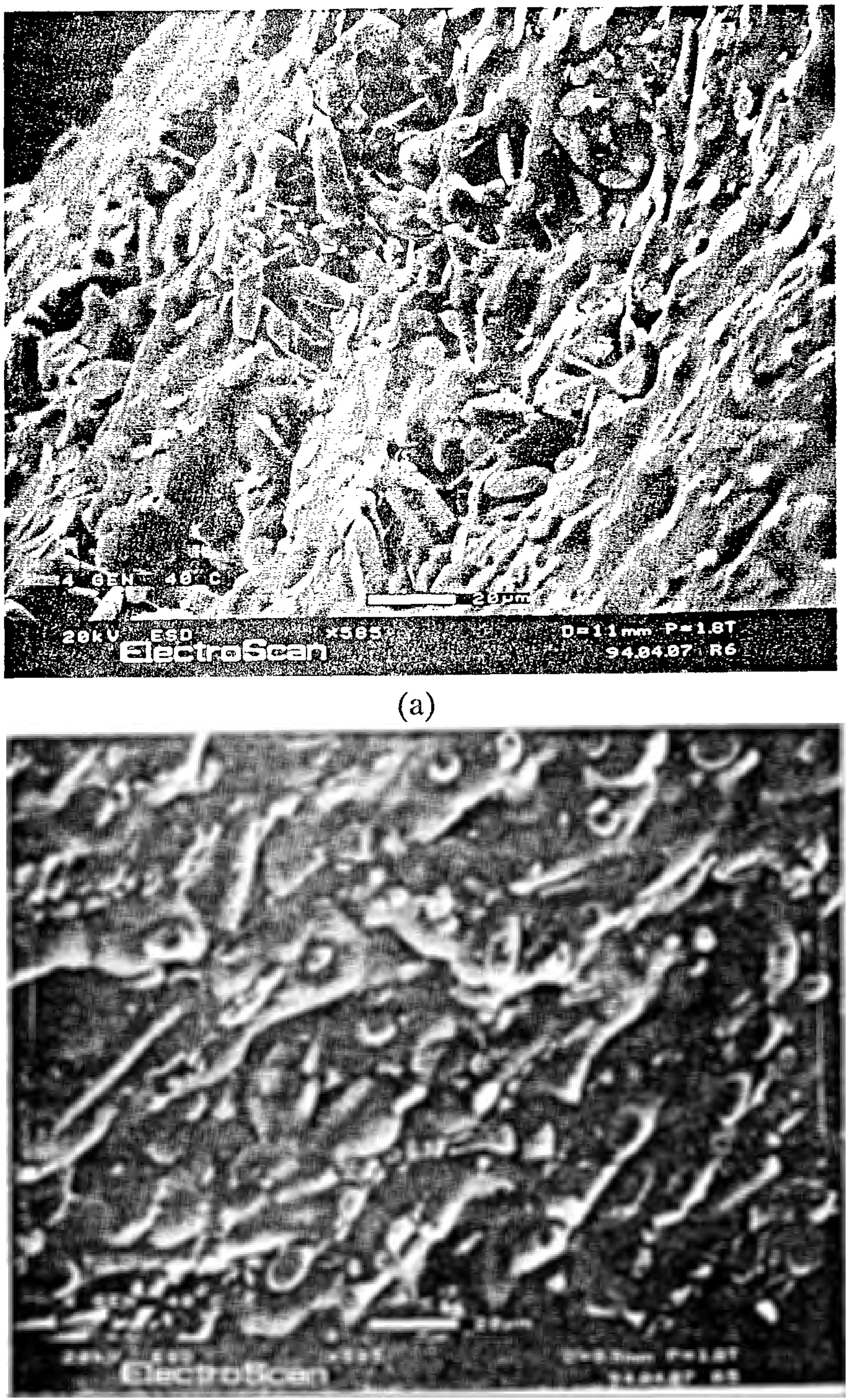


Figure 27. Scanning Electron Micrographs of the Fourth Generation binder from (a) the surface, and (b) the interior at 40 °C (104 °F) using the ESEM.

Table 21. Optimum mix design of Sulphlex binders using the Marshall criteria.

Binder Type	Percent Binder, by Weight of Total Mix	Air Voids, Percent	Voids in Mineral Aggregate (VMA), Percent	Marshall Stability, N	Marshall Flow, mm	Unit Weight, Kg/m^3	Voids Filled with Asphalt, (VFA), Percent
50/50 (198:233) Two-Pot Blend	6.5	4.7	10.4	7,708	5.33	2,478	54.7
	7.0	3.4	11.0	9,030	5.00	2,490	70.0
	7.5	1.8	11.3	9,026	5.00	2,496	83.8
	8.5	0.4	11.4	9,102	5.33	2,504	96.4
50/50 (198:233) One-Pot Synthesis	6.5	3.9	9.7	9,617	5.76	2,498	58.8
	7.0	3.7	11.2	8,690	5.70	2,510	70.0
	7.5	2.4	11.4	8,738	5.26	2,507	80.5
	8.5	0.2	11.6	9,230	5.26	2,499	98.1
Fourth Generation	6.5	3.9	10.0	9,306	5.79	2,475	63.8
	7.0	3.7	10.0	9,310	5.90	2,470	65.0
	7.5	3.5	10.0	9,386	6.32	2,490	65.8
	8.5	0.9	10.0	8,187	6.10	2,507	90.1
AC-20 (Control)	5.0	4.1	11.5	7,216	3.05	2,478	75.0

Table 22. Mixture design criteria for Sulphlex and asphalt mixtures.

Test Parameter	Criteria
Marshall Stability	6,660 N (1,500 lb)
Marshall Flow	None
Voids in Mineral Aggregate (VMA)	12 percent
Voids Filled with Binder (VFB)	70 - 80 percent
Air Voids	4 percent (Target)

Sulphlex mixes behave somewhat differently than traditional asphalt concrete mixes. The Marshall stability typically does not drop as dramatically for Sulphlex mixes as for asphalt mixes as the air void content is reduced to below about 3 percent. Therefore, Sulphlex binder contents of above 8.0 percent could have been used and, with these high binder contents, an acceptable Marshall stability could have been maintained. The decision was made to achieve 4 percent air voids. This was achieved for each mix at approximately 7.0 percent binder. The optimum binder content for the control asphalt concrete mixture was scaled down by a factor equal to the specific gravity of the Sulphlex (approximately 1.50) and rounded to 5.0 percent asphalt cement (AC-20) by total weight of the mix. Samples were prepared to verify that this mix achieved acceptable stability, air voids, etc. (See table 21.) This approach allowed the researchers to evaluate five mixes with equal binder contents by volume.

Mixtures in the Second Generation Sulphlex study incorporated higher Sulphlex binder contents (e. g., approximately 8.5 percent).(16) Those optimum binder contents were based on sample fabrication with a Marshall compaction hammer. This type of impact compaction produces mixtures with substantially higher air voids than does the gyratory compactor. Sulphlex mixtures tend to be easily compacted at typical compaction temperatures (e. g., 116 to 149 °C or 240 to 300 °F), especially with a gyratory type compaction effort. The result of fabrication using a gyratory compactor was a substantially lower Sulphlex binder content than when Marshall impact compaction was used. The low binder, thin film thickness Sulphlex mixtures produced with gyratory compaction may partly explain differences between mixture performance in the Second Generation study and this study. The lower binder content, thinner film mixtures produced in this study may help explain mixture anomalies in mixture performance that did not appear in previous studies.

Diametral Resilient Modulus, M_R

The resilient modulus test was used to help evaluate the resistance of the Sulphlex mixtures to fracture and fatigue and to evaluate their general structural attributes. The resilient modulus test was used for screening purposes for two reasons. First, it is easy to perform and nondestructive in nature, giving an indication of performance over a wide range of temperatures. Second, the relationships of temperature versus stiffness are indispensable indicators of performance. The low temperature stiffness response can be evaluated together with tensile strengths at low temperatures to predict low temperature cracking potential. At higher temperatures the resilient responses can be used to evaluate stress distribution potential (dissipation of vertical compressive stresses induced by traffic wheel loads with depth) of Sulphlex and asphalt mixtures used as pavement layers.(16)

Data presented in tables 23 and 24 were compared to similar testing with the same aggregates during testing of Second Generation Sulphlex mixtures at TTI and with data for traditional asphalt concrete mixtures using various types of densely graded mineral aggregates and various grades and sources of asphalt cement. Diametrial resilient moduli versus temperature data are plotted for all mixtures using limestone aggregate in figure 28. This figure is taken directly from NCHRP Report 338.(12) This figure is designed to plot the test results of total resilient modulus (unconditioned) versus temperature, as compared to the range of values that are appropriate for high volume roadways.(12)

Based on the results documented in tables 23 and 24, and figure 28 the following trends were observed:

1. The temperature susceptibilities of the 50/50 (198:233) two-pot blended binder, 50/50 (198:233) one-pot synthesized binder and the control asphalt are quite similar. At temperatures of 5 °C (41 °F) and above, the AC-20 control mix is stiffer than the two Sulphlex mixes. At the lowest temperature of -23 °C (-10 °F), however, the two Sulphlex mixes were consistently and substantially stiffer than the control indicating a greater thermal fracture potential for these Sulphlex binders at the low test temperature of -23 °C (-10 °F).

2. The 75/25 (198:233) two-pot blend and the Fourth Generation Sulphlex exhibit similar and very unique temperature susceptibilities. Unfortunately, these binders demonstrate high diametral resilient moduli at the lower test temperatures of -23 °C (-10 °F) and 5 °C (41 °F). These moduli values are substantially higher than the moduli at the corresponding temperatures for the

Table 23. Resilient modulus of Sulphlex blends at various temperatures using a crushed limestone aggregate. (Each value in this table is the average of three replicate tests.)

Temperature, °C (°F)	Diametral Resilient Modulus, M_R (MPa)*				
	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
40 (104)	502	602	8,190	3,920	697
25 (77)	2,191	2,548	1,904	1,568	2,849
5 (41)	8,400	7,498	11,200	8,120	9,730
-23 (-10)	25,978	29,260	54,040	44,450	20,720

*1 MPa = 145 psi

Table 24. Resilient modulus at various temperatures for the 75/25 (198:233) two-pot blend and Fourth Generation Sulphlex blends of using a river gravel as the aggregate. (Each value in this table is the average of three replicate tests.)

Temperature, °C (°F)	Diametral Resilient Modulus, M_R (MPa)*		
	75/25 (198:233)	Fourth Generation	AC-20 (Control)
40 (104)	5,950	7,280	525
25 (77)	3,640	5,110	2,350
5 (41)	7,770	12,250	8,960
-23 (-10)	33,110	35,770	20,290

*1 MPa = 145 psi

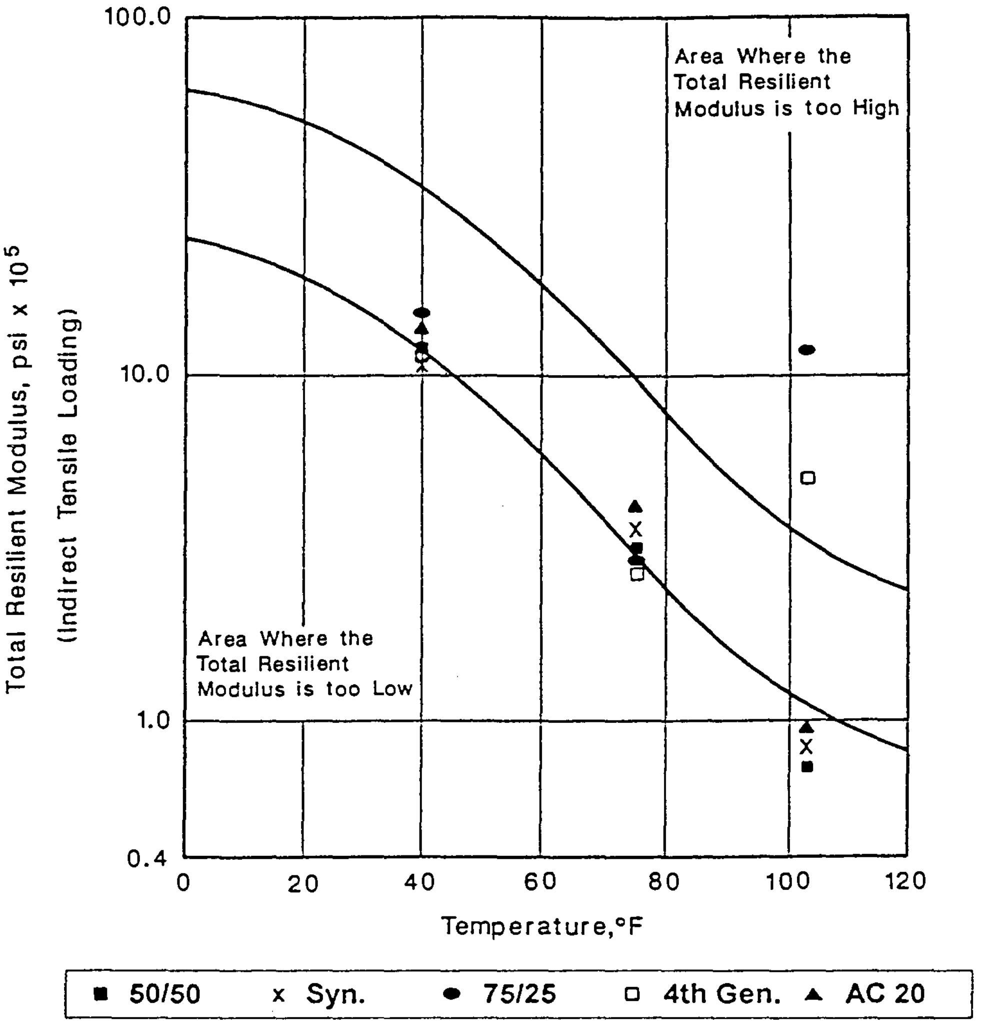


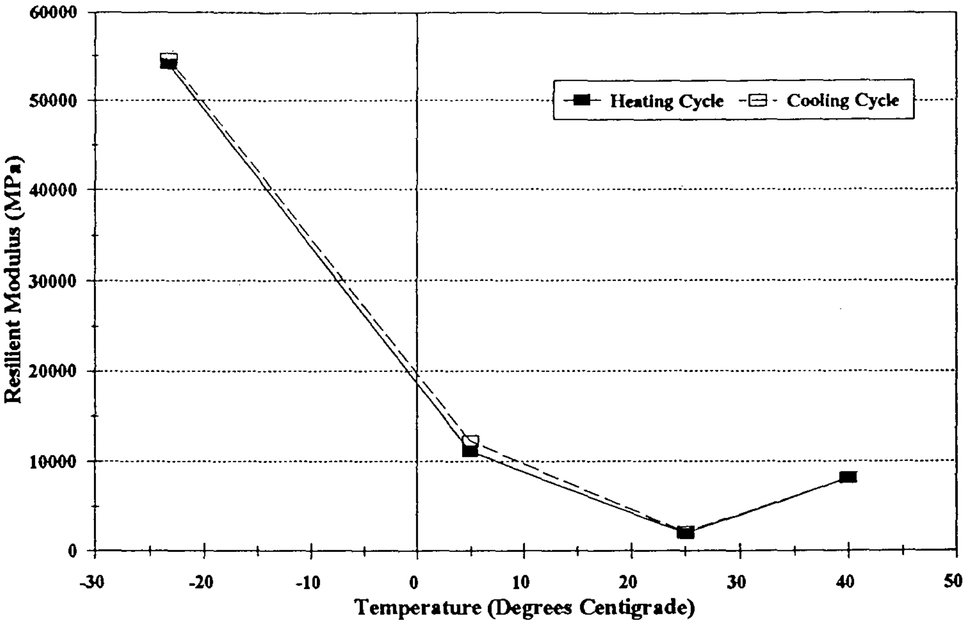
Figure 28. Diametral resilient modulus versus temperature for the binders tested under this program according to AAMAS procedures.[(12)]

50/50 (198:233) two-pot and one-pot synthesized Sulphlex binders. This would not be expected based on the Superpave Bending Beam Rheometer (BBR) test presented in the Superpave Binder Test section. The BBR results indicate superior low temperature properties of the 75/25 (198:233) and Fourth Generation binders. The low temperature diametral moduli of the Sulphlex mixes are substantially higher than for the asphalt control mix and other traditional, well-performing asphalt mixtures.

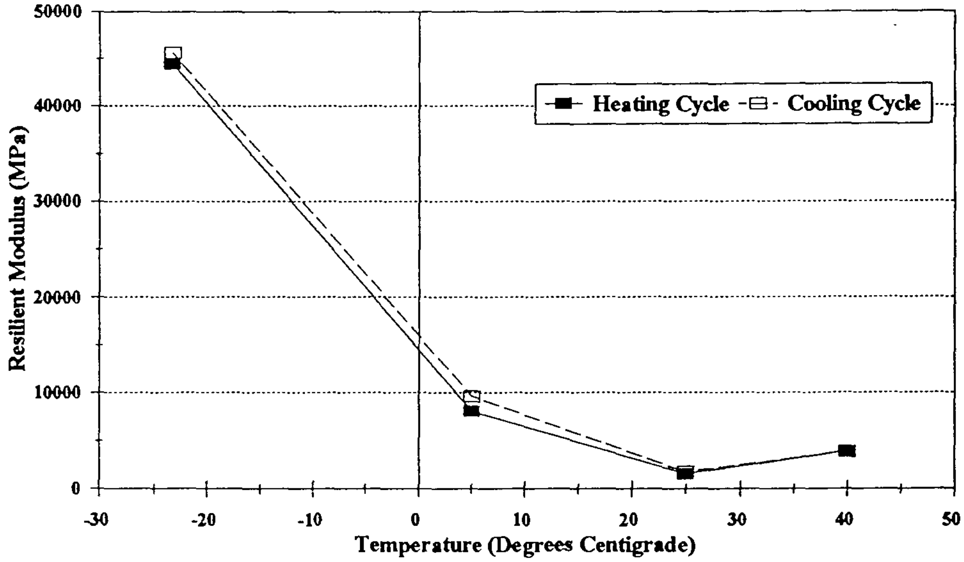
3. Surprisingly, both the 75/25 (198:233) two-pot blend and the Fourth Generation binder exhibit a greater stiffness at 40 °C (104 °F) than at 25 °C (77 °F) with the limestone aggregate. The resilient moduli values of the samples molded using a silicious river gravel aggregate instead of crushed limestone exhibit the same trends as those molded using the crushed limestone aggregate. From this it was concluded that this anomaly of increasing resilient modulus with an increase in temperature from 25 °C (77 °F) to 40 °C (104 °F) is not simply an aggregate-related effect, but is an inherent characteristic of the binder itself, at least in the mixture analyzed in this study and under the stress state in thin films induced in the mixtures during diametral resilient modulus testing.

4. The same Fourth Generation Sulphlex mixture samples which demonstrated the anomalous stiffening between 25 and 40 °C (77 and 104 °F) were stored at 25 °C (77 °F) for 7-days and subsequently reheated to 40 °C (104 °F). Resilient modulus values were then measured across a range of temperatures beginning at 40 °C (104 °F) and descending down to -23.3 °C (-10 °F). These mixtures demonstrate somewhat higher stiffnesses although not significantly higher than when originally tested (figure 29). This may indicate that the stiffening effect between 25 °C (77 °F) and 40 °C (104 °F) is not permanent. This unexpected phenomena was repeated in subsequent testing. A total of six replicate samples verified this phenomena.

5. The anomalous effect of stiffening between 25 °C (77 °F) and 40 °C (104 °F) in the 75/25 (198:233) two-pot blend and in the Fourth Generation Sulphlex, but not in the 50/50 (198:233) two-pot blend nor, in the 50/50 (198:233) one-pot synthesis, is at present not understood. The anomaly was not seen in previous Sulphlex research at TTI. However, 75/25 (198:233) blend and Fourth Generation Sulphlex binders were not evaluated in previous studies. However, the numerical values of the moduli of the 75/25 (198:233) two-pot blend and Fourth Generation are very comparable to numerical values of moduli for sulphlex mixtures determined in the Second Generation study.(16)



(a)



(b)

Figure 29. The cycling effect over a range of temperatures for (a) the 75/25 (198:233) two-pot blend, and (b) the Fourth Generation Sulphlex binder.

The diametral test data indicate that a transition in the stiffness of the 50/50 (198:233) two-pot blend and 50/50 (198:233) one-pot synthesized binder occurs between 5 °C (41 °F) and -23.3 °C (-10 °F) at which point the stiffness of the Sulphlex increases substantially over that of the AC-20 asphalt. This occurrence could be related to a phenomenon similar to a second order transition. It has been noted from previous research that the transition regions (from viscoelastic to glassy) for the Sulphlex blends are very different from that for the Sulphlex 198 alone, occurring at a much higher temperature.(16) Second Generation Sulphlex studies have also indicated that the law of mixture proportioning can be utilized to produce Sulphlex products with thermomechanical responses which are adequate to meet a variety of applications.(16) This led to the concept of the 75/25 (198:233) Sulphlex blend, in hopes of developing an improved mixture for low temperatures. This blend, however, exhibited very high stiffnesses at the lowest temperature of -23 °C (-10 °F) and surprisingly at 40 °C (104 °F).

Both the 75/25 (198:233) two-pot blend and the Fourth Generation Sulphlex have resilient modulus - stiffness characteristics over the 5 °C (41 °F) to 40 °C (104 °F) temperature range that are deemed favorable according to AAMAS criteria.(12) Although these blends exhibit an anomalous and significant stiffness increase between 25 °C (77 °F) and 40 °C (104 °F), this effect is not a major concern as the reheating effect proved to have only a minor effect on stiffness over the range of temperatures evaluated. In fact, the modulus increase from 25 °C (77 °F) to 40 °C (104 °F) is favorable as it indicates a lower susceptibility to permanent deformation. However, more careful study is needed to fully investigate the cause and ramifications of this phenomenon.

It should be noted that at temperatures below -17.8 °C (0 °F), the diametral resilient modulus test is a very imprecise test due to the low strains to failure induced over the temperature range which are very difficult to precisely measure using traditional techniques.

Indirect Tensile Testing - (IDT)

Indirect tensile testing was performed at the same temperatures as the resilient modulus testing; that is, 40, 25, 5, and -23.3 °C (104, 77, 41, and -10 °F.) The results are summarized in tables 25 and 26. As in low temperature resilient modulus testing, failure strains were difficult to measure at the very low temperatures with the precision necessary for the differentiation among the binders.

The locus of IDT failure strain (table 25) and the diametral resilient modulus (table 23) at the same temperature are plotted in figure 30. This figure allows one to evaluate long-term fatigue cracking potential compared to a good quality densely graded hot mix. A brief description of the applicability of this figure is appropriate.

Table 25. Indirect tension test results for the Sulphlex binders tested with the standard limestone aggregate. (Each value in this table is the average of three replicate tests.)

Temp., °C (°F)	Parameter	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20
40 (104)	S_t, kPa	242*	360	889	1470	218
	ϵ_t, %	1.9	1.2	0.11	0.14	1.7
25 (77)	S_t, kPa	685	879	832	1082	759
	ϵ_t, %	1.4	0.88	0.26	0.45	0.93
5 (41)	S_t, kPa	1869	2135	2024	2240	2010
	ϵ_t, %	0.79	0.68	0.17	0.40	0.74
-23.3 (-10)	S_t, kPa	3451	4648	4333	6580	3675
	ϵ_t, %	0.11	0.09	0.02	0.05	0.51

*1 kPa = 0.145 psi

Table 26. IDT test results for the 75/25 (198:233) two-pot blend and Fourth Generation Sulphlex binder with a river gravel aggregate. (Each value in this table is the average of three replicate tests.)

Temp., °C (°F)	Parameter	75/25 (198:233) Two-Pot Blend	Fourth Generation
40 (104)	S_t, kPa*	315	588
	ϵ_t, percent	0.27	0.39
25 (77)	S_t, kPa	714	1351
	ϵ_t, percent	0.42	0.64
5 (41)	S_t, kPa	399	924
	ϵ_t, mil/in	0.83	0.55
-23.3 (-10)	S_t kPa	3619	4060
	ϵ_t, percent	0.02	0.03

*1 kPa = 0.145 psi

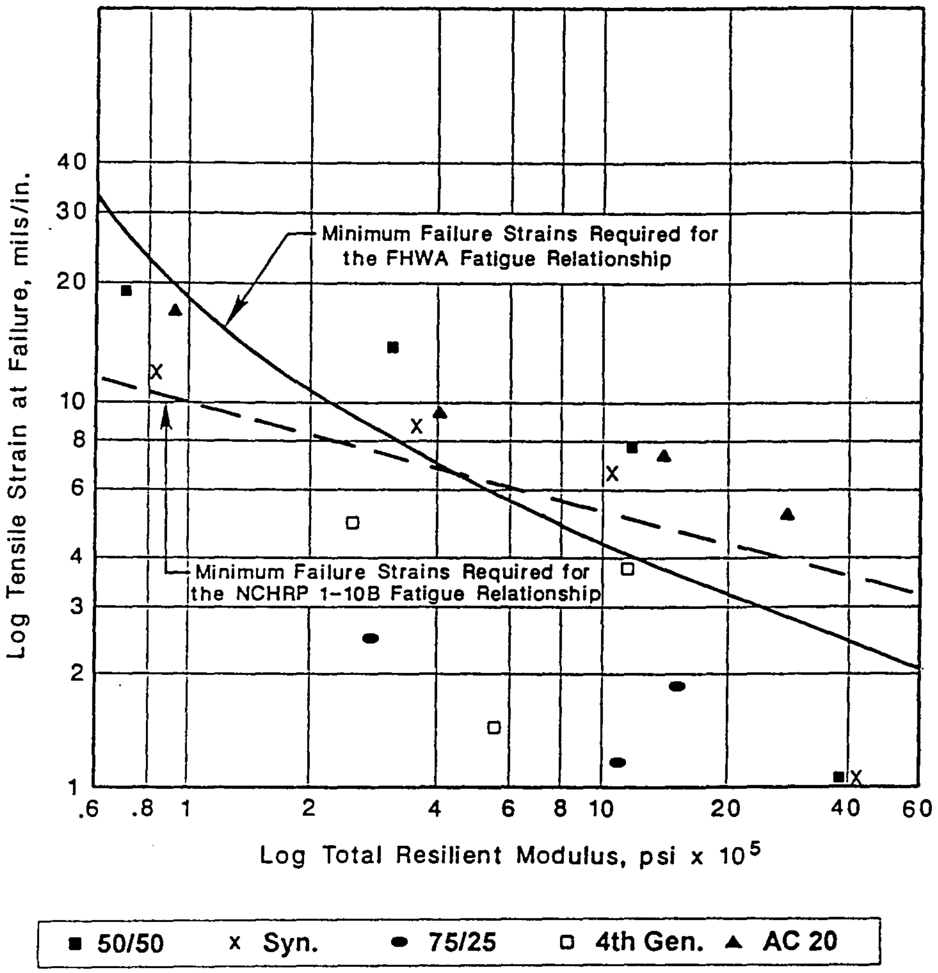


Figure 30. Tensile strain at failure versus total resilient modulus for the binders tested and evaluated according to AAMAS methodology to evaluate fatigue cracking potential.(12)

Figure 30 is based on the widely used fatigue relationship:

$$N = f_1 \, (\epsilon_t)^{-f_2} \, (E_R)^{-f_3} \tag{9}$$

where N is number of allowable wheel load applications to failure, ϵ_t is the tensile strain at the bottom of the asphalt concrete layer and f_1, f_2, and f_3 are fatigue regression constants developed from correlation between field and laboratory data.

One method for evaluating the suitability of an asphalt concrete mix to resist fatigue is to ensure that the mix meets or exceeds the fatigue properties of a good, acceptable mix. For the purposes of AAMAS, the "standard mix" is the densely - graded AASHTO Road test hot mix. The curve plotted on figure 30 represents the relationship between tensile failure strain and total resilient modulus for the "standard mix" when N = 1 load application. Thus, if the loci of total diametral resilient modulus and diametral failure strain at a selected temperature plot above the standard curve (FHWA relationship is recommended), it is assumed that the mixture under evaluation is more fatigue resistant than the "standard mix." If the locus falls below the standard curve, the mix is inferior in terms of long-term fatigue.

From the indirect tensile strength test the following trends were observed:

1. It is apparent that the IDT strengths and strains at failure follow the same temperature susceptibility pattern observed in the resilient modulus data, figure 28.

2. The magnitudes of the IDT strengths and strains at failure, table 25, for the 50/50 (198:233) two-pot blend and the 50/50 (198:233) one-pot synthesized blends closely follow those of the AC-20 binder within variations of experimental error except at the lowest test temperature of -23 °C (-10 °F) where the failure strains of the Sulphlex mixes are only approximately 20 percent of the AC-20 control mix.

3. The Fourth Generation Sulphlex and the 75/25 (198:233) two-pot blend showed very high strengths and very low strains at 40 °C (104 °F). The anomalous increase in modulus (increase in tensile strength and decrease in IDT failure strain) between 25 °C (77 °F) and 40 °C (104 °F) substantiates the validity of the stiffening effect recognized during resilient modulus testing.

4. From figure 30, it can be concluded that mixtures fabricated with the 50/50 (198:233) two-pot blend and 50/50 (198:233) one-pot synthesized binders meet the NCHRP fatigue criteria along with mixtures fabricated with AC-20 at temperatures above 5 °C (41 °F) while mixtures fabricated with the other blends fail to meet the criteria at any temperature. The Fourth Generation mixtures exhibit failure strains of an order of magnitude less than the other binders at temperatures above 25 °C (77 °F). These data are consistent with data previously recorded and documented in the Second Generation Sulphlex Final Report on other Sulphlex mixtures.(16)

5. Using AAMAS fatigue criteria, figure 30, all Sulphlex mixtures demonstrate essentially the same level of fatigue resistance below 5 °C (41 °F), which is poor. The control mix exhibits good fatigue behavior.

6. If a general conclusion can be drawn from this data, it is in favor of the 50/50 (198:233) two-pot blend whose loci of IDT strength and diametral resilient modulus for a specific temperature consistently lie above the rest of the Sulphlex mixes over the temperature range. These mixture results are not consistent with binder test results ($G^{*}\sin \delta$, table 18) which indicate that all Sulphlex mixtures are fatigue resistant. Neither Superpave binder criteria nor AAMAS mixture criteria can be adopted and/or applied to Sulphlex binders and/or mixes without more careful evaluation. However, these are perhaps the best available criteria for evaluating the potential performance of Sulphlex binders and mixes. It would certainly also hold true that Superpave binder evaluation procedures may not be applicable to Sulphlex binders based on the currently used asphalt specifications.

7. The anomalous modulus increase which occurs between 25 °C (77 °F) and 40 °C (104 °F), first noticed as an unexpected increase in resilient modulus, is also apparent based on the IDT data in table 25 for mixtures fabricated with limestone aggregate. As with resilient modulus data, the anomaly only occurs with the 75/25 (198:233) two-pot blend and Fourth Generation Sulphlex and not with the 50/50 (198:233) two-pot blend nor 50/50 (198:233) one-pot synthesized binder. In order to evaluate whether or not the anomaly was related to binder-aggregate interaction, IDT strength and stress at failure were also determined for the 75/25 (198:233) blend and Fourth Generation Sulphlex mixtures using a silicious river gravel aggregate in lieu of the limestone aggregate. These data, summarized in table 26, but do not substantiate the trends of increasing tensile strength between 25 °C (77 °F) and 40 °C (104 °F) demonstrated in 75/25 (198:233) two-pot blend and Fourth Generation Sulphlex mixtures with limestone aggregate.

Indirect Tensile Creep

Indirect tensile creep testing was carried out according to AAMAS procedures at 5 °C (41 °F).(12) The indirect tensile creep modulus was determined as a function of time at a stress level of between 5 and 20 percent of the indirect tensile failure stress, and the slope of the creep strain versus time of loading plot was computed between 1000 and 3600 s. The results of the indirect tensile creep test are summarized in table 27 and figures 31 through 35. Table 27 presents creep moduli at 100, 1,000 and 3,600 s, the arithmetic slope of the IDT test and recovery efficiency. Recovery efficiency is defined as the ratio of recovered strain during the rebound period (1 h) to total IDT strain recovered during the creep test.

Table 27. Indirect tensile creep results at 5 °C (41 °F) for four Sulphlex and control mixtures. (Each data point is the average of three replicate tests.)

Creep Modulus (kPa)*					
Time	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
100 s	50,176	73,094	61,208	84,315	144,445
1000 s	9,842	18,277	18,116	31,717	45,507
3600 s	6,678	10,913	12,530	28,686	33,383
Slope ϵ_p/time	$2.59*10^{-6}$	$1.83*10^{-6}$	$3.46*10^{-4}$	$1.07*10^{-4}$	$0.53*10^{-6}$
Recovery Efficiency	0.40	0.24	0.70	0.81	0.24

*1 kPa = 0.145 psi

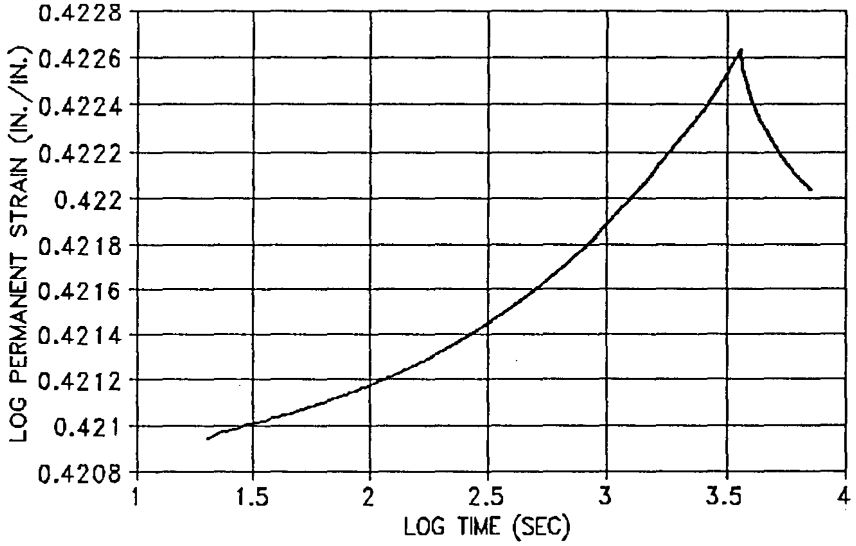


Figure 31. Example plot of IDT permanent creep strain versus time for the 50/50 (198:233) two-pot blend binder at 5 °C (41 °F).

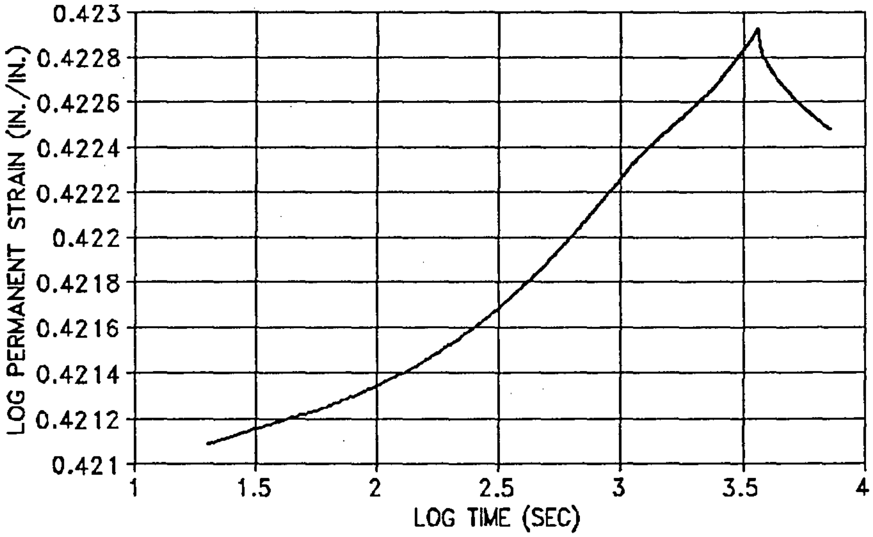


Figure 32. Example of IDT permanent creep strain versus time for the 50/50 (198:233) one-pot synthesized binder at 5 °C (41 °F).

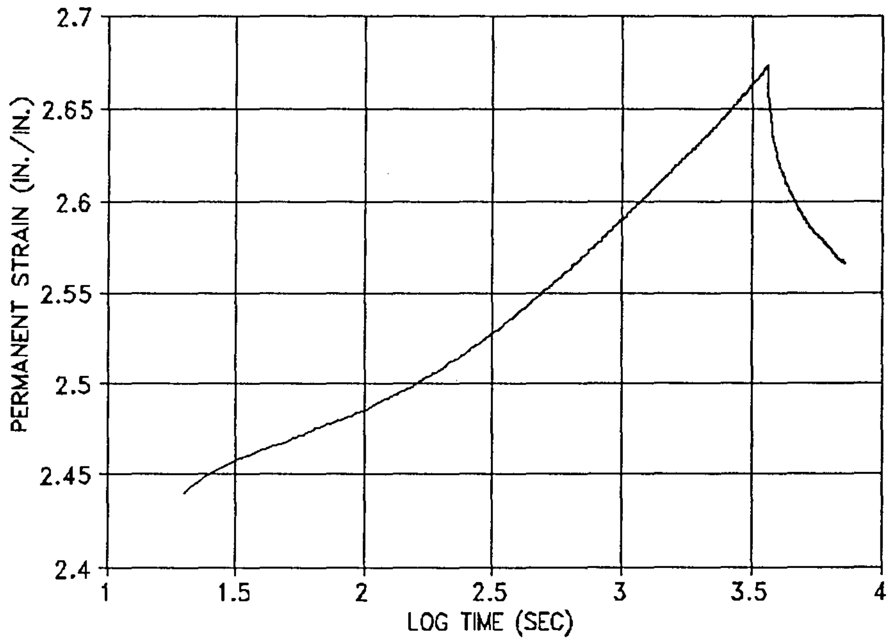


Figure 33. Example of IDT permanent creep strain versus time for the 75/25 (198:233) two-pot blend binder at 5 °C (41 °F).

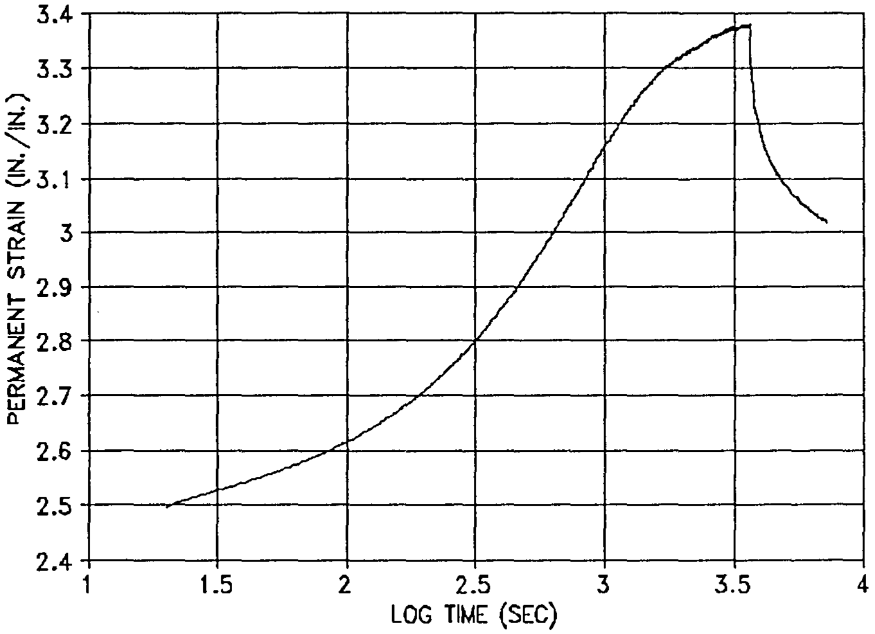


Figure 34. Example of IDT permanent creep strain versus time for the Fourth Generation Sulphlex binder at 5 °C (41 °F).

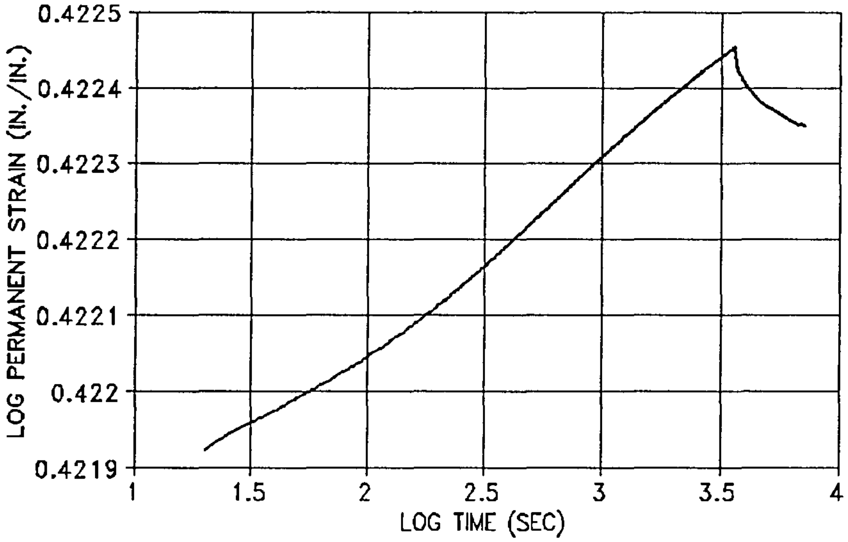


Figure 35. Example of IDT permanent creep strain versus time for the AC-20 control binder at 5 °C (41 °F).

The first procedure suggested by AAMAS by which to assess the thermal cracking potential of the mixture, is to calculate the tensile stress induced in the pavement at a specific temperature, $\sigma(T_i)$, caused by a drop in temperature, ΔT, and considering that the mix has a thermal coefficient of expansion of contraction, α_A, between approximately $1*10^{-5}$ and $1.8*10^{-5}$ in/in/°F.(5) The relationship is expressed in equation 10 as follows.

$$\sigma(T_i) = \alpha_A\,(\Delta T_i)\,\Delta E_{ct} \tag{10}$$

The creep modulus, E_{ct} (where the subscript "ct" stands for creep-tensile), used in low temperature cracking evaluations was estimated from the creep modulus determined at 3600 s. The loading rate adopted was 1.27 mm/min (0.05 in/min). Assuming that the thermal coefficient of the asphalt concrete and the Sulphlex mixtures is approximately the same, the only material property affecting the thermal stress induced in the pavement is the tensile creep stiffness, E_{ct}.

A tensile creep value at a loading time of 3,600 s provides an indication of the thermal fracture potential of the mixtures evaluated. Historically, tensile loading times of between 3,600 and 20,000 s have been used to evaluate creep stiffness related to pavement thermal cracking as these times correlate to the loading periods induced in the field due to thermal fluctuations.(12) Thus, a relative approximation of low temperature thermal fracture potential can be made by comparing the tensile creep stiffness values (table 27) at 3,600 s. Accordingly, the relative rank from least to greatest thermal fracture or thermal fatigue potential among the mixtures evaluated is: 50/50 (198:233) two-pot blend, 50/50 (198:233) one-pot synthesis, 75/25 (198:233) two-pot blend, Fourth Generation, and AC-20 (Control).

The second approach suggested by AAMAS to investigate thermal cracking potential is based on the assumption that the stiffness and strength of asphalt or Sulphlex concrete mixtures vary with both, temperature and time of loading. The decrease in thermal stress due to stress relaxation was approximated by the relationship as shown in equation 11 below.

$$\sigma(T_i) = \alpha_A\,(\Delta T)\,E_o(T_i)\,(t_r)^{-n_c} \tag{11}$$

where n_c is the slope of the indirect tensile creep versus time of loading curve at temperature, T_i; $E_o(T_i)$ is the intercept of the indirect tensile creep curve at temperature T_i, in psi; t_r is the relaxation time, and is assumed in this case as 3600 s; and ΔT is the critical temperature change at which cracking is expected to occur, measured in °C or °F. Based on the above relationship, mixtures possessing a higher slope, n_c, tend to dissipate thermal stresses more rapidly. Based on this criterion, the relative susceptibility of the mixtures to thermal cracking is ranked as shown in table 28.

The critical temperature change at which cracking occurs can be estimated from the following relationship as shown in equation 12.(12)

$$\Delta T = [E_{ct}(T_i)/E_o]^{1/n_t}\ [t_r^{n_c}/\alpha_A E_o(T_i)] \tag{12}$$

where $E_{ct}(T_i)$ is the indirect tensile creep modulus measured at temperature T_i which in this case was 5 °C (41 °F); E_o is a regression constant developed from the laboratory test data, and n_t is the slope of the relationship between indirect tensile strength and resilient modulus of the mixture measured at temperatures (5, 25, and 40 °C) of (41, 77, and 104 °F). The value α_A is the thermal coefficient of contraction. The value n_c defines the slope of the tensile creep versus time of creep loading (t_r). Thus, three tensile-creep related parameters are included in the AAMAS procedure for the evaluation of thermal fracture potential of asphalt mixes: n_c, n_t, and E_{ct}.

The values of n_c relate to the susceptibility of the indirect tensile creep stiffness to temperature changes. The most desirable situation is for n_c to be low indicating relatively low temperature susceptibility of the tensile creep modulus to the temperature at which the creep modulus is determined. The n_c values recorded in table 28 indicate a similar sensitivity for AC-20 and the 50/50 (198:233) one-pot synthesized binder and a similar n_t grouping for the 50/50 and 75/25 (198:233) two-pot blends and Fourth Generation Sulphlex. Based on n_t, the synthesized blend and the AC-20 control are less temperature sensitive than the 50/50, 75/25 (198:233) blends and Fourth Generation Sulphlex.

The researchers believe that the relative fracture potential of the mixes should be based most heavily on E_{ct} and n_c, (table 28), as these values are directly related to fracture potential as shown in equation 13.(12) In addition, Lytton et. al., have shown that n_c is directly related to the rate of crack growth in the Paris-Erdogren basic fracture law.(9)

$$\frac{dc}{dN} = A\ (\Delta k)^n \tag{13}$$

where dc/dN is the rate of crack growth per cycle, Δk is the change in stress intensity at the crack tip per load cycle and A and n are material properties. Figures 31 through 35 present the log permanent strain versus time of loading tensile creep relationships for the mixtures evaluated.

The summary of E_{ct} and n_c data presented in table 28 result in a different order of ranking of thermal fracture potential. The researchers believe that the results should be weighted more heavily in terms of the n_c parameter.

The two AAMAS procedures used to evaluate the potential of the mixture to resist thermal fracture indicate that the Sulphlex mixes are better suited to resist thermally induced fracture than is the AC-20 control asphalt at the test temperature of 5 °C (40 °F). The creep results are, hence, generally consistent with the results of the diametral resilient modulus test at 5 °C (41 °F) except for the 75/25 (198:233) two-pot blend.

Results from previous research on second generation Sulphlex binders used fracture mechanics and a direct tensile cyclic test to prove that a 50/50 blend of Sulphlex 198 and 233 could produce a mixture that had a thermal fracture resistance very close to that of an AC-20 asphalt at temperatures between 10 and 25°C (50 °F and 77 °F) which is substantiated by this work.(16) However, neither of the Sulphlex mixes showed promise in effectively resisting thermal fracture below 5 °C (41 °F).

Table 28. Comparison of relative thermal stress relaxation based on tensile creep (E_{ct}) and rate of relaxation (n_c) for Sulphlex and control binders.

Mixture Identification	Slope of Tensile Creep (E_{ct}) v. Loading Time, n_c	Rank Order of Fracture Susceptibility Based on n_c (from least susceptible, 1 to most susceptible, 5)	Tensile Creep Stiffness (E_{ct}) at 3,600 s	Rank Order of Fracture Susceptibility Based on E_{ct} (from least susceptible, 1 to most susceptible, 5)
50/50 (198:233) Two-Pot Blend	2.59×10^{-6}	3	6,678 kPa	1
50/50 (198:233) One-Pot Synthesis	1.83×10^{-6}	4	10,913 kPa	2
75/25 (198:233) Two-Pot Blend	3.46×10^{-4}	1	12,530 kPa	3
Fourth Generation	1.04×10^{-4}	2	28,686 kPa	4
AC-20 (Control)	0.53×10^{-6}	5	33,383 kPa	5

Uniaxial Compressive Creep

Uniaxial Compressive Creep testing was performed at two stress levels: 103 kPa (15 psi) and 414 kPa (60 psi) on 102 mm (4 in) high by 102 mm (4 in) in diameter samples. These samples were fabricated using the kneading compactor in accordance with AAMAS procedures. The two stress levels were selected as representative of a low stress level within the linear viscoelastic region of response (103 kPa, 15 psi) and a high stress (414 kPa, 60 psi) realistic of field loading conditions.

The uniaxial compressive creep modulus is an excellent indicator of rutting potential. The stiffness of asphalt concrete mixtures has often been used to predict the level of rutting or permanent deformation expected in the wheel path. One popular equation which relates the rate of rutting RR, to laboratory tests of asphalt mixes is (equation 14)

$$RR = AN^{m} \tag{14}$$

where RR is the rutting rate (or change in sample height per load application); N is the number of load applications and A and m are constants developed from field calibrated laboratory testing. The integral form of the rate of rutting, RR, equation over the total number of traffic applications is the expected rut depth. A related approach is to model rut depth in terms of permanent strain, ϵ_p, which yields the following relationship in log-form as shown in equation 15.

$$\log \epsilon_p = \log A + m \log N \tag{15}$$

The constants A and m in this equation can be estimated from static creep tests such as those required by AAMAS.(12)

$$A = a(t_{\alpha})^{m_c} - \epsilon_{rt}$$

and

$$m = \frac{\log a + 3.5563\, m_c + \log (1 - x) - \log [a\,(0.1)^{m} - t_{rt}]}{4.5563}$$

where m_c is the slope of the static creep-time curve in the steady state region, a is the intercept of the creep-time curve on the axial creep strain axis at time equal to 1 s; t_α is time of loading in seconds; ϵ_{rt} is total resilient or recovered strain from the repeated load test and x is percent recoverable creep or the recovery efficiency from static loads.

Using this approach, the total change in height within the asphalt concrete pavement sublayers can be predicted as shown in equation 16.

$$\Delta h = \sum_{i=1}^{N_n} \epsilon_{pi} h_i \tag{16}$$

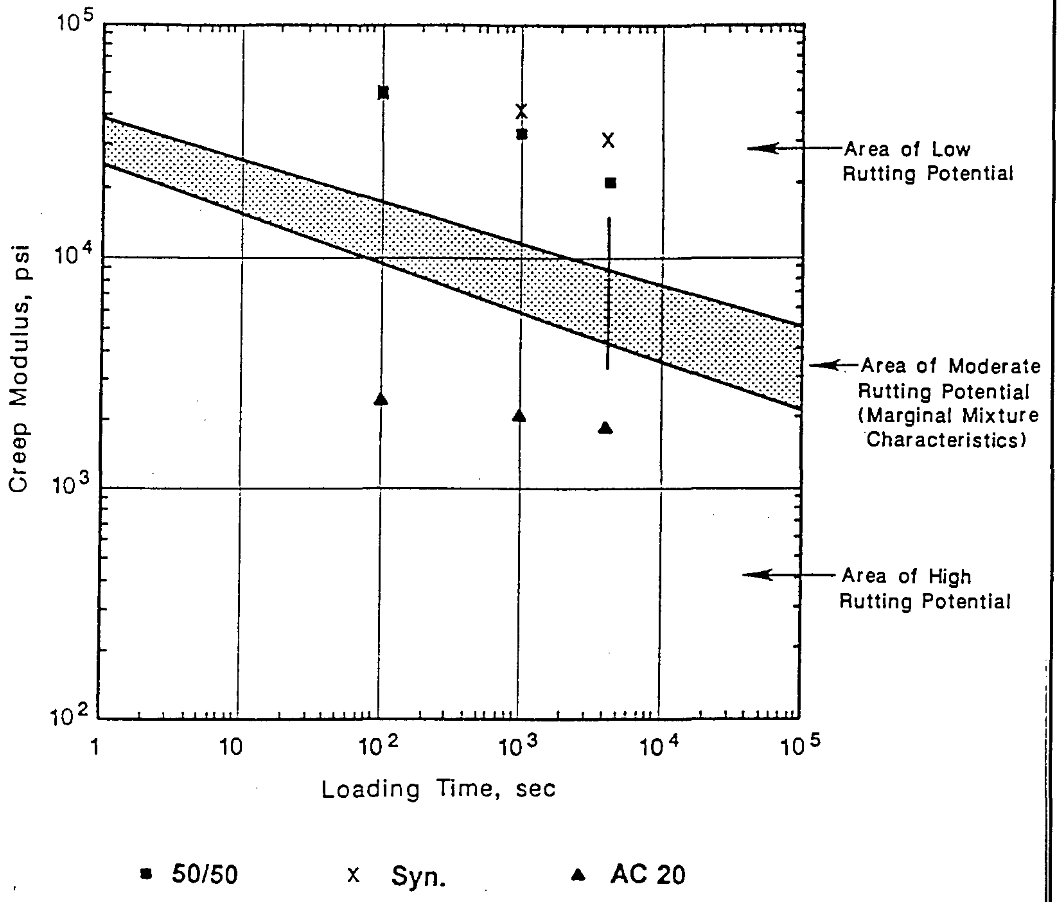
where h_i is the height of each sublayer, ϵ_{pi} is the permanent strain within each sublayer, N_n is the number of discrete, pavement lifts and Δh is the total change in asphalt concrete pavement thickness.

AAMAS adopted a graphical evaluation of compressive creep data to evaluate rutting potential.(12) This technique illustrated by figures 36 and 37 presents three regions on a plot of creep stiffness versus time of loading. The three regions are: high rutting potential, moderate rutting potential and low rutting potential. The judgement of rutting potential based on uniaxial compressive creep data is affected by the slope, m_c, and the value of creep stiffness, E_c, at a particular time of loading.

The results of the compressive creep tests are summarized in table 29. From these results the following trends are identified:

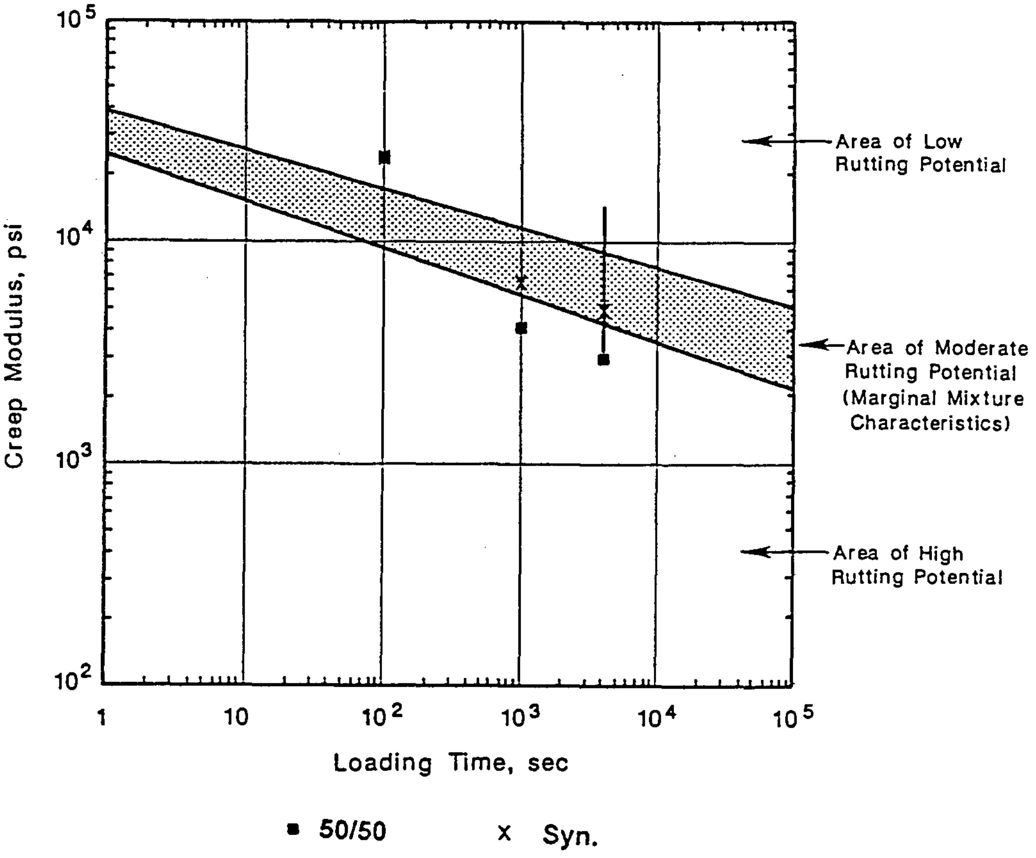
1. At the stress level of 103 kPa (15 psi) and at a temperature of 40 °C (104 °F) the 50/50 (198:233) two-pot blend and the 50/50 (198:233) one-pot synthesized binders showed high creep moduli. At this low stress level, the 75/25 (198:233) blend and the Fourth Generation Sulphlex were so rigid that strain was not measurable. At the more realistic pavement stress level of 414 kPa (60 psi) all Sulphlex mixtures are more resistant to creep deformation than is the AC-20 control mixture. The AC-20 control binder failed and could not sustain a stress of more than 138 kPa (20 psi) while the 50/50 (198:233) two-pot blend and one-pot synthesized binders performed marginally according to AAMAS criteria under the 103 kPa (15 psi) level of stress.(12)

2. The 75/25 (198:233) two-pot blend and the Fourth Generation Sulphlex also demonstrated very high moduli at the stress level of 414 kPa (60 psi.) At this elevated temperature of 40 °C (104 °F), mixtures prepared with both the 75/25 (198:233) blend and the Fourth Generation Sulphlex binder were extremely



The Creep Moduli for the 75/25 and 4th generation blends could not be determined at this low a stress level

Figure 36. Creep modulus versus time of loading for the Sulphlex and control mixtures tested according to AAMAS at 40 °C (104 °F) and at a stress of 103 kPa (15 psi).(12)



The Creep Moduli for the 75/25 and 4th generation blends were too high to be incorporated into this figure

Figure 37. Creep modulus versus time of loading for the Sulphlex and control mixtures tested according to AAMAS at 40 °C (104 °F) and at a stress of 414 kPa (60 psi).(12)

Table 29. Uniaxial compressive creep results at 40 °C (104 °F) for the binders tested under this study using limestone aggregate. (Each data point is the average of three replicate tests.)

Stress (kPa)	Time (s)	Uniaxial Creep Modulus, (MPa)*				
		50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Two-Pot Blend	Fourth Generation	AC-20 (Control)
103	100	350	350	N/O**	N/O	16
	1000	231	301	N/O	N/O	14
	3600	140	210	N/O	N/O	13
Recovery Efficiency		0.27	0.25	N/O	N/O	0.36
414	100	168	168	1,729	1,274	Failed
	1000	28	47	1,421	1,015	Failed
	3600	21	35	1,197	889	Failed
Recovery Efficiency		0.04	0.44	0.82	0.74	Failed

*1 MPa = 145 psi

**N/O indicates that no measurable strain was recorded (no observed).

stiff. The moduli were approximately 20 times greater than that of other Sulphlex mixes.

3. The 75/25 (198:233) blends and the Fourth Generation Sulphlex binders easily meet the minimum criterion stipulated by AAMAS to be able to resist rutting as seen in figures 36 and 37. Figures 38 through 45 summarize the results of the creep test. The emphasis of these tests was not on the absolute value of the creep stiffness or the slope of the creep curve but the relative performances of the binders being tested. From these results, it is evident that the Sulphlex mixtures have a substantially greater potential to resist deformation than the AC-20 control mixture. This resistance to permanent deformation at 40 °C (104 °F) is substantially aided by the anomalous stiffening effect between 25 °C (77 °F) and 40 °C (104 °F) for mixtures using 75/25 (198:233) blends and the Fourth Generation Sulphlex binders.

4. If one compares the shapes of the compressive creep curves in figures 38 through 45, it is clear that the shapes of the curves for the Sulphlex mixes are very different from the shape of the curves for the AC-20 mix. The control mixes have a shape characteristic of most asphalt concrete mixes where a clearly defined primary and secondary (steady state) region is evident. The Sulphlex mixes, however, even though much more rut resistant in terms of total permanent strain and creep stiffness, all demonstrate a clearly defined on-set of tertiary creep. The on-set of tertiary creep is quicker at higher stress levels (figures 39, 41, 43, and 45). This difference in characteristic shape of the compressive creep curves may represent a substantially different creep mechanism in Sulphlex mixes compared to asphalt concrete mixes.

Unconfined Compressive Strength

The unconfined compressive strength of the binders was evaluated at a temperature of 40 °C (104 °F) and a strain rate of 3.8 mm/min (0.15 in/min). The procedure followed was ASTM D 1074-80.(22) Table 30 summarizes the results of the unconfined compressive strength test.

From table 30, it can be observed that the Sulphlex mixtures have substantially higher unconfined compressive strengths than the AC-20 control asphalt. The failure strains, however, are not very different and do not show any significant variance. The total resilient strains, ϵ_{rt}, for all mixtures are of approximately the same magnitude.

The potential of the mixtures to deform was evaluated using the strain softening criterion developed by Von Quintus et al., and verified by Little et al.(12,29) This criterion establishes that the potential for an asphalt mixture to strain soften occurs when the total strain induced within the mixture exceeds one-half of the strain level at shear

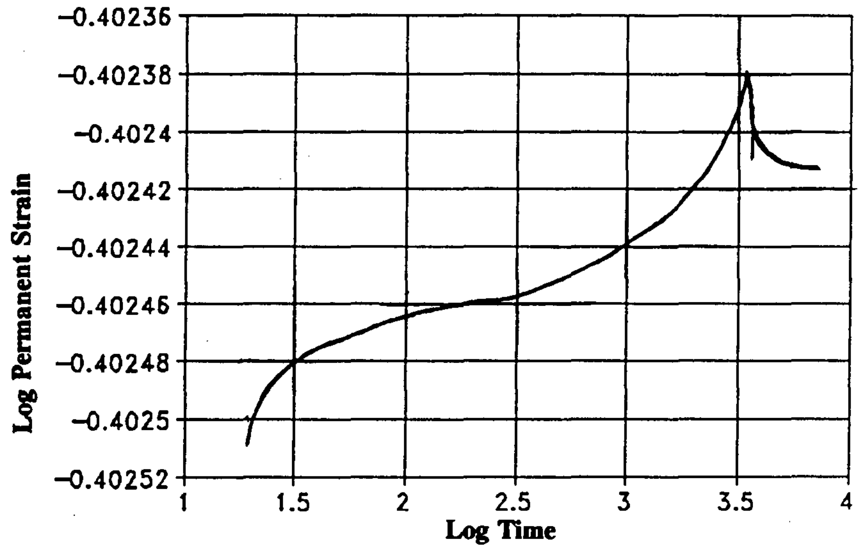


Figure 38. Uniaxial compressive creep strain versus time for the 50/50 (198:233) two-pot blend Sulphlex binder at a stress of 103 kPa (15 psi) and a temperature of 40 °C (104 °F).

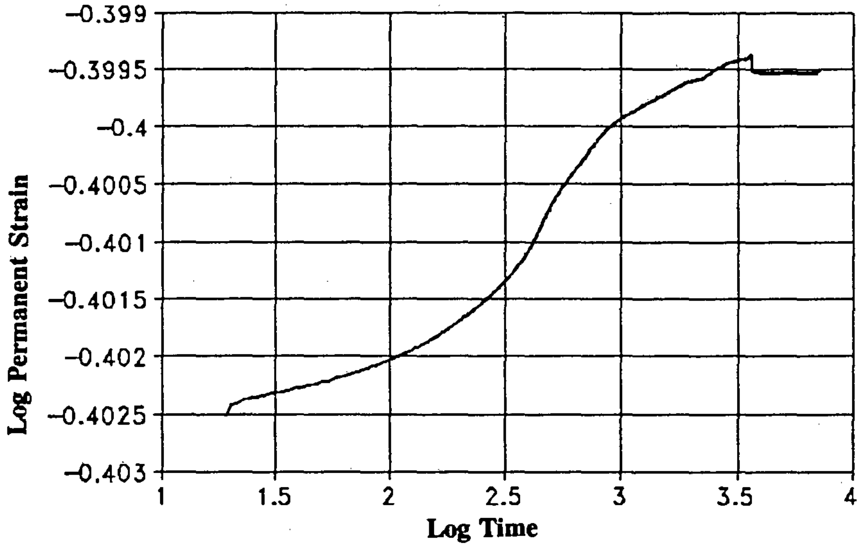


Figure 39. Uniaxial compressive creep strain versus time for the 50/50 (198:233) two-pot blend Sulphlex binder at a stress of 414 kPa (60 psi) and a temperature of 40 °C (104 °F).

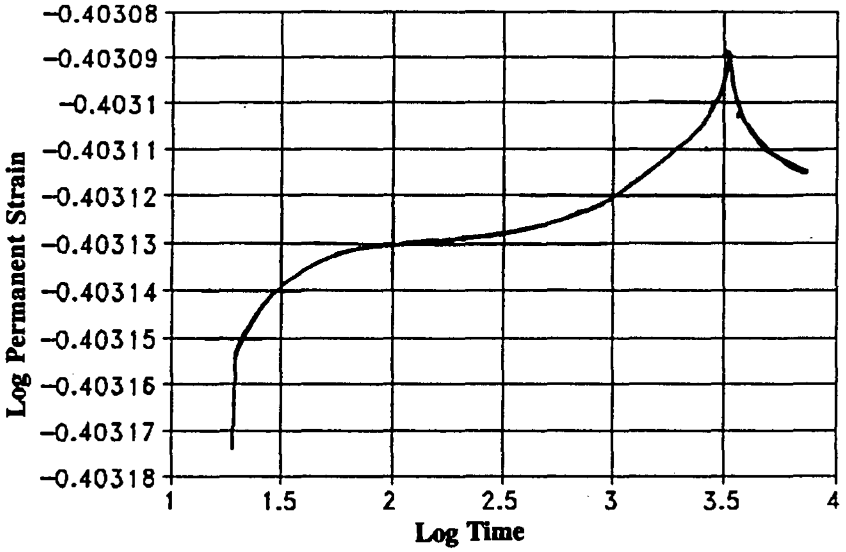


Figure 40. Uniaxial compressive creep strain versus time for the 50/50 (198:233) one-pot synthesized Sulphlex binder at a stress of 103 kPa (15 psi) and a temperature of 40 °C (104 °F).

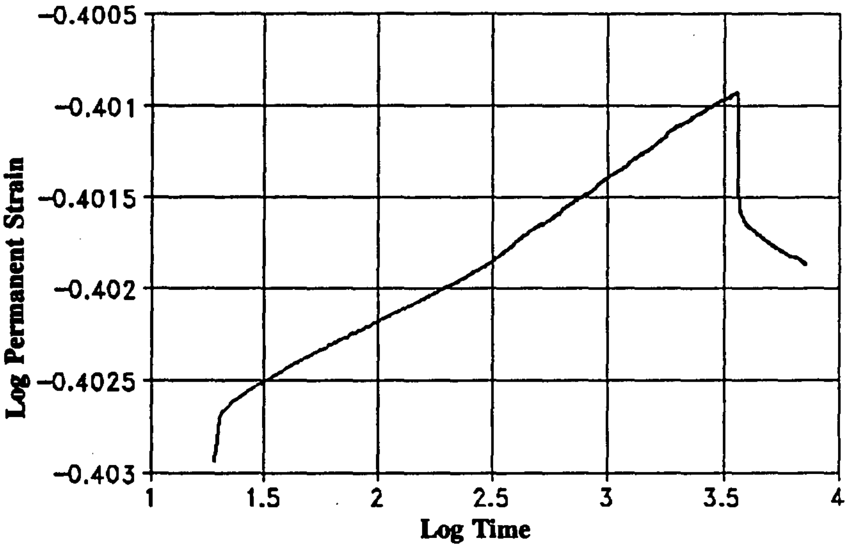


Figure 41. Uniaxial compressive creep strain versus time for the 50/50 (198:233) one-pot synthesized Sulphlex binder at a stress of 414 kPa (60 psi) and a temperature of 40 °C (104 °F).

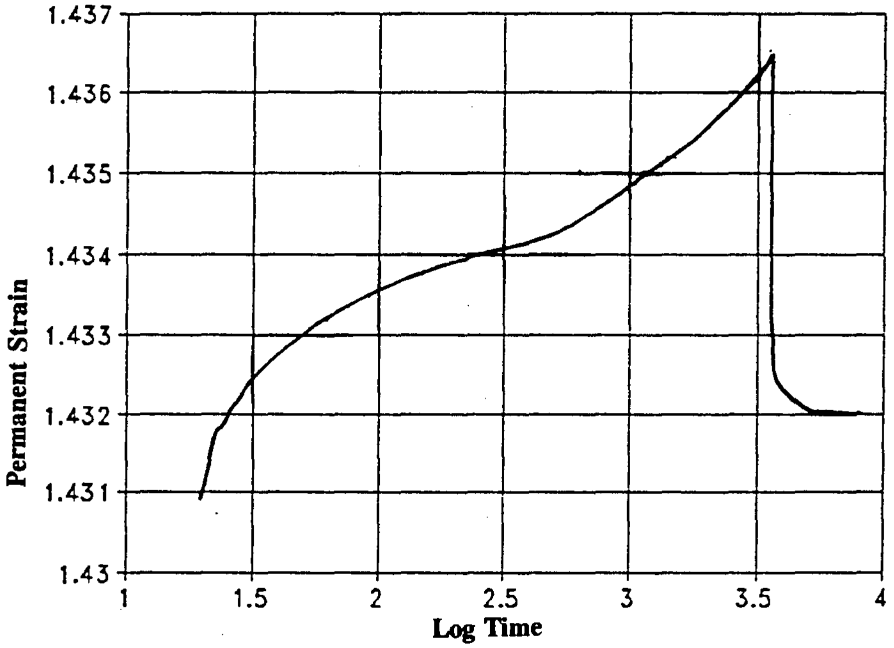


Figure 42. Uniaxial compressive creep strain versus time for the 75/25 (198:233) blend Sulphlex binder at a stress of 414 kPa (60 psi) and a temperature of 40 °C (104 °F).

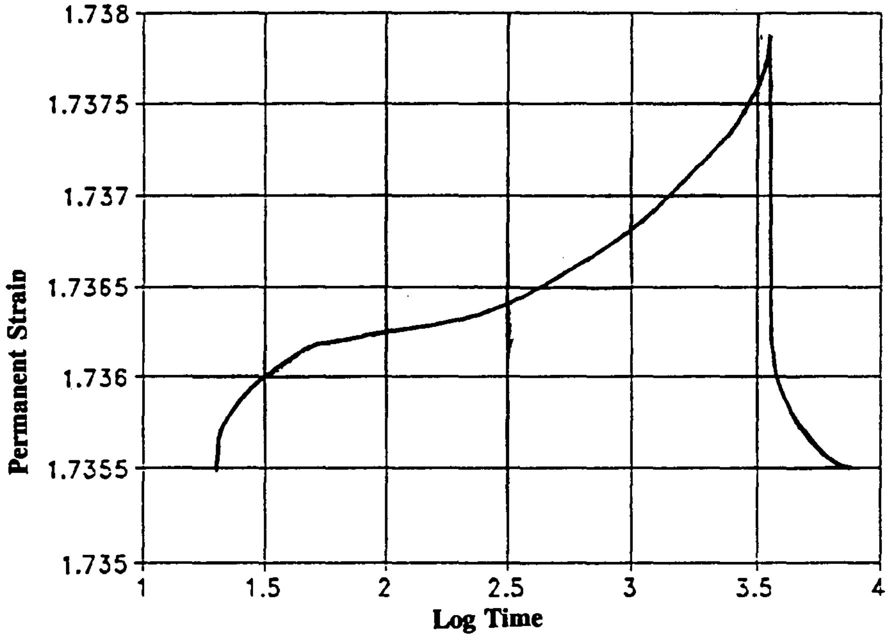


Figure 43. Uniaxial compressive creep strain versus time for the Fourth Generation Sulphlex binder at a stress of 414 kPa (60 psi) and a temperature of 40 °C (104 °F).

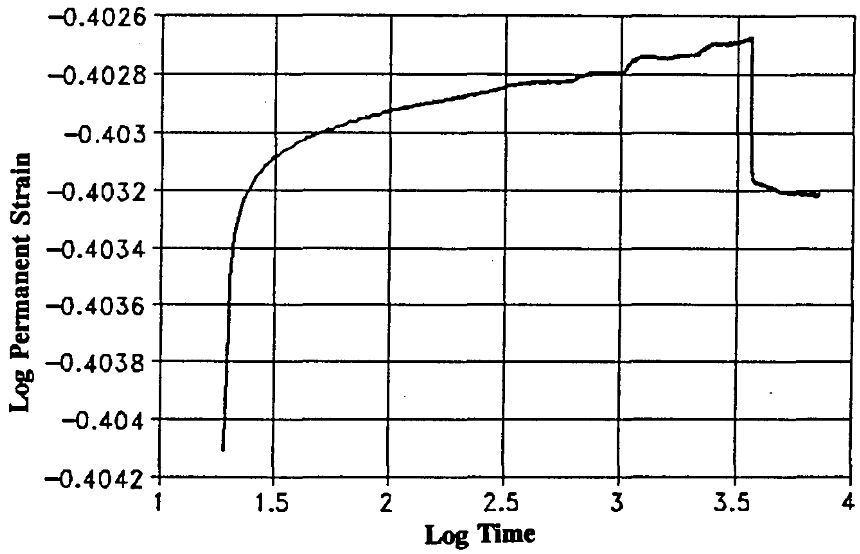


Figure 44. Uniaxial compressive creep strain versus time for the AC-20 control asphalt at a stress of 103 kPa (15 psi) and a temperature of 40 °C (104 °F).

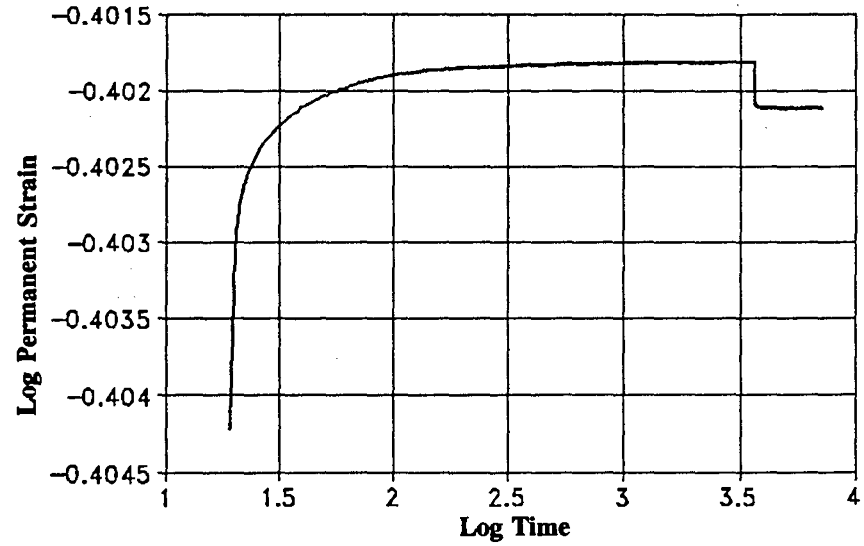


Figure 45. Uniaxial compressive creep strain versus time for the AC-20 control asphalt at a stress of 138 kPa (20 psi) and a temperature of 40 °C (104 °F).

Table 30. Unconfined compressive failure stress and failure strain at failure for the Sulphlex and control mixtures tested at 40 °C (104 °F) and a strain rate of 0.15 in/min.

	Binder Used in Mixture				
Parameter	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Blend	Fourth Generation	AC-20 Control
Stress (kPa)*	3,311	2,758	3,339	4,347	1,022
Strain, ϵ_{qu} $(10^{-3} \frac{mm}{mm})$	16	24	33	18	19

*1 kPa = 0.145 psi

failure in an unconfined compressive mode of loading. Thus Von Quintus et. al., stipulate that the sum of the total resilient strain measured in the dynamic modulus test and the total strain at the end of 3600 s of loading in the uniaxial creep test should be less than 0.5 ϵ_{qu}. This is represented mathematically as shown in equation 16.

$$\epsilon_p + \epsilon_{rt} < 0.5\ \epsilon_{qu} \tag{16}$$

A factor of safety (F.S.) against strain softening can then be defined as shown in equation 17.

$$\text{F.S.} = (0.5\ \epsilon_{qu}) / (\epsilon_p + \epsilon_{rt}) \tag{17}$$

Table 31 summarizes the values of the strain softening factors of safety. It is evident that all the Sulphlex binders demonstrate superior deformation resistance than does the control AC-20 mixture when evaluated against this criterion.

VESYS Repeated Load Permanent Deformation

The repeated load permanent deformation test was conducted in accordance with VESYS procedures. Table 32 summarizes the results of the test which measures the

Table 31. Strain softening factors of safety for the Sulphlex and control mixtures tested under this program.

Mixture	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Blend	Fourth Generation	AC-20 Control
Factor of Safety	1.96	4.29	4.18	3.76	< 1.0

Table 32. VESYS repeated load permanent deformation results for the Sulphlex and control binders tested at 40 °C (104 °F).

Cycle Number, N	Accumulated Deformation, strain $\left(\frac{mm}{mm}\right) x 10^{-6}$				
	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	75/25 (198:233) Synthesis	Fourth Generation	AC-20 Control
1	0.3	0.4	4.4	2.7	34.0
10	1.4	1.7	4.4	4.5	141.5
100	10.6	5.4	8.0	5.5	378.6
200	13.3	7.4	10.3	6.9	487.2
1000	16.3	12.1	11.9	7.1	1157.9
10000	75.2	17.6	12.0	7.4	5671.5
Dynamic Resilient Modulus, MPa*	10,220	16,100	15,050	17,290	1,715

*1MPa = 145 psi

accumulated deformation, the dynamic resilient modulus and the total permanent deformation after 10,000 cycles and a 15-min recovery.

From the above data, it is evident that the Sulphlex mixtures are highly-resistant to permanent deformation while the asphalt mixture are quite susceptible to the same.

Aging at 25 °C (77 °F)

The aging study was based on the resilient modulus and the indirect tensile stress and strain at failure at the end of the aging period. The results of the aging study are presented in table 33 and figure 46.

Table 33. Indirect tensile stress and strain at failure before and after aging (30-days at 25 °C (77 °F)) on the 50/50 (198:233) two-pot and one-pot synthesized blends of Sulphlex.

Temp. °C (°F)	Parameter	After Curing		After Curing & Aging	
		50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis	50/50 (198:233) Two-Pot Blend	50/50 (198:233) One-Pot Synthesis
25°C (77°F)	S_t, kPa	686	882	2,429	2,849
	ϵ_t, $\frac{mm}{mm} x 10^{-3}$	14	8.8	6.8	9.8

From figure 46 it is observed that the Sulphlex mixtures develop most of their stiffness within only about a week of aging. The stiffnesses remain relatively constant during the remaining aging period. This can be attributed to the initial crystallization which occurs rapidly. Further, these data substantiate the fact that after the initial phase of hardening the resilient modulus still maintains approximately the same level of temperature sensitivity as it possessed prior to aging. This phenomenon indicates a retention of viscous or viscoelastic behavior during or following periods of aging although at a completely different level of stiffness.

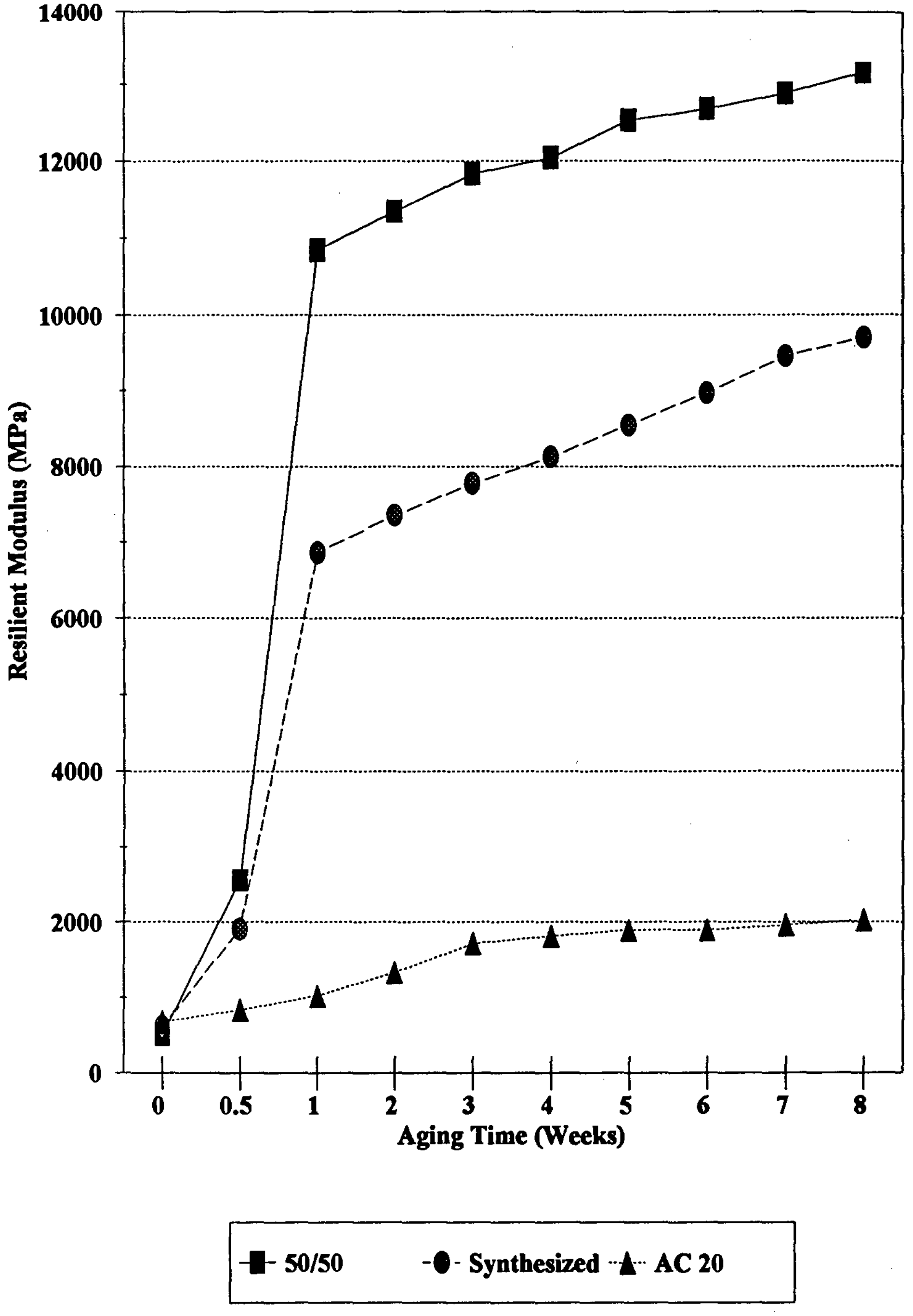


Figure 46. Results of the aging test conducted at 25 °C (77 °F) on the 50/50 (198:233) two-pot blend and one-pot synthesized Sulphlex binders.

STATISTICAL EVALUATION

Three replicate samples were tested for each test procedure (each test type and each temperature). The repeatability and validity of all the test data collected was checked using the "*t* statistic." The *t* statistic can be applied when the variance, σ, is unknown, no matter what the sample size.

The null hypothesis was that the difference between each test value and the mean value of the replicate set is <u>not</u> statistically significant.

A confidence level of 95 percent was selected and the t statistic was calculated for each replicate set of samples. The researchers observed that null hypothesis is true and that test values within each replicate set were not statistically different from the mean value of the set at a 95 percent level of confidence.

CHAPTER 6. MANUFACTURING PROCEDURES FOR FOURTH GENERATION SULPHLEX BINDERS (TASK F)

GENERAL

This chapter will present procedures for the manufacture, handling, storage and safety/environmental monitoring of Sulphlex binders. Additional consideration is given to QC/QA assessment and transporting these binders to an hypothetical test road site. The amount of Sulphlex binder to be generated for this project was that required to construct a two-lane road, 152.4-m (500-ft) long, 3.66-mm (12-ft) per lane wide and 12.7 mm (5 in) thick. The quantity of Sulphlex to be produced allows additional material to be prepared for start-up and waste.

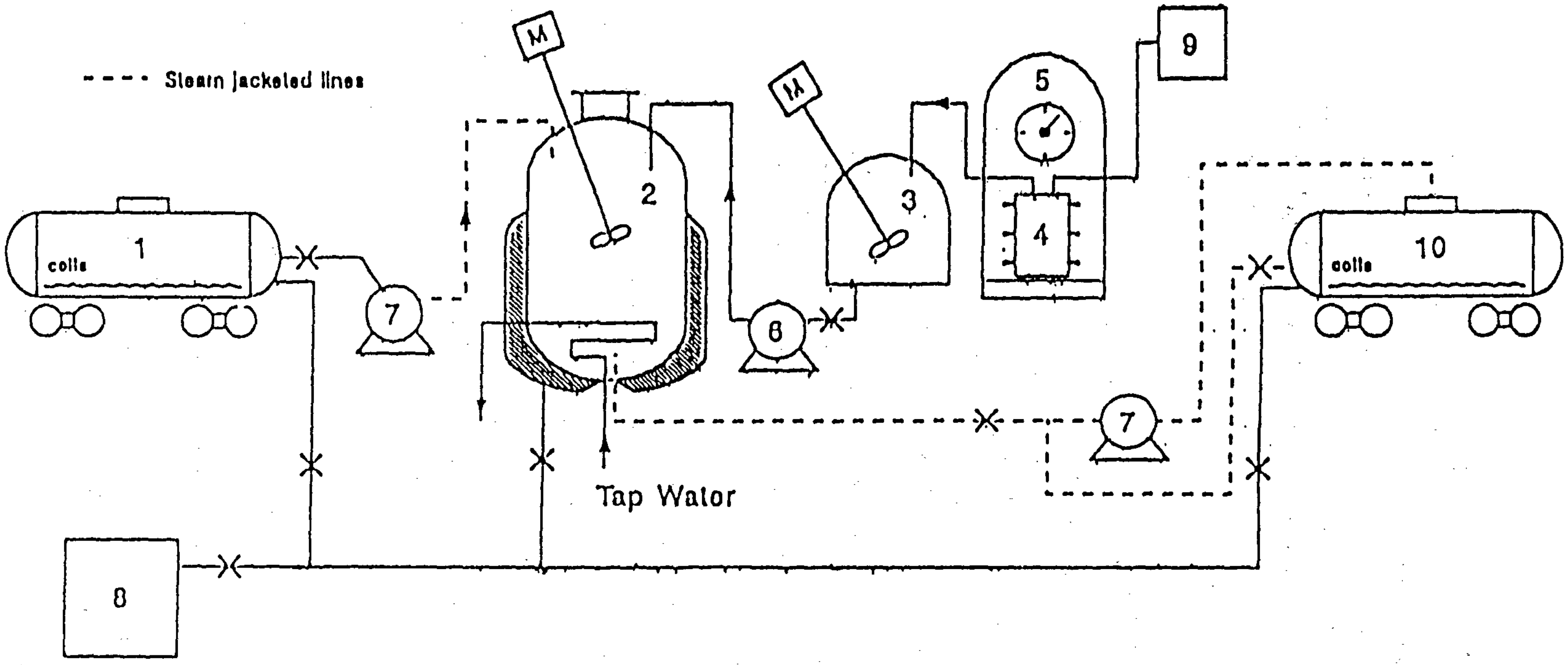
A mixture containing 8 percent Sulphlex binder and a dense graded aggregate similar to that specified for an Asphalt Institute Type VI mixture is proposed. Under these conditions, 32 tons of Fourth Generation Sulphlex is to be processed. This allows 20 percent or 6.4 tons for waste and start up.

BINDER PRODUCTION

For this treatment, the assumption will be made that binder production will be carried out in 8-ton batches within a 24-h period using the production plant shown schematically in figure 47. The raw material breakdown for each batch of Fourth Generation Sulphlex is shown in table 34.

Table 34. Fourth Generation Sulphlex raw material requirements per 8-ton batch.

Ingredients	Specific Gravity	Weight Percent	8-Ton Batch Amount Pounds	8-Ton Batch Amount Gallons
Sulfur (Liquid)	1.79/@ 135 °C (275 °F)	70	11,200	750
Dicyclopentadiene	0.97 @ 15.6 °C (60 °F)	15	2,400	300
Oligomer of Cyclopentadiene	0.84 @ 15.6 °C (60 °F)	7.5	1,200	170
Neodene C_{11} - C_{12}	0.76 @ 15.6 °C (60 °F)	7.5	1,200	190
Totals		100	16,000	1410



1) 3000 gallon sulphur transport trailer (same as item 10)
2) 1500 gallon sealed jacketed chemical reactor (stainless steel) with agitator
3) 800 gallon stainless steel chemical pre-mix tank with agitator
4) 55 gallon chemical additive supply drum(s)
5) 1000 pound platform scale
6) 25 gpm chemical pump
7) 100 gpm steam jacketed positive displacement pump
8) 7 horsepower steam generator
9) 3 horsepower air compressor
10) 3000 gallon Sulphlex storage tank

Figure 47. Batch-type Sulphlex production plant.

For this project, it is recommended that the sulfur be shipped in liquid form at temperatures between 120 to 135 °C (248 to 275 °F) in standard 14,383 l (3,800 gal) transport trailers (item 1) designed specifically for hauling sulfur. Sulfur is not classified by the Department of Transportation (DOT) as a dangerous product. Specifications which apply for sulfur handling include: American Association of Railroads (AAR) 203-W, DOT 103-W, DOT 111A 100-W-1 and DOT 111A 100-W-3. Trucking must conform in weight and dimensions to the legal requirements of the States in which they are used. For additional specifications for DOT transportation of molten sulfur, see appendix A-1.

There are numerous advantages to consumers in shipping sulfur in the liquid state rather than as a solid; not the least of these is the elimination of dust explosions. A similar trailer (item 10), as was used for shipping the sulfur (item 1), can be used for storing the processed Sulphlex binder. A steam generator (item 8) is used to supply superheated steam to the heating coils in each trailer to keep the sulfur and Sulphlex in the liquid, "ready-to-use" condition. Sulfur storage containers are commonly made of steel provided the sulfur is kept hot enough to prevent accumulation of free moisture.

Sulfur can be discharged from the trailer into the reactor either by gravity or through a steam jacketed pump (item 7). A similar pump is used to remove processed Sulphlex from the reactor (item 2). All piping for handling hot sulfur or Sulphlex, including valves, should be steam-jacketed and well insulated.

Chemicals and raw materials for Sulphlex processing can be delivered to the plant in 208 L (55 gal) drums (item 4) from appropriate suppliers and proportioned by weight into the chemical pre-mix tank (item 3) using a 454-kg (1000-lb) capacity platform scale (item 5). The chemicals are charged into the pre-mix tank (item 3) from their respective drums using compressed air generated by an air compressor (item 9). A pressure regulator value is used to control the flow rate. The chemical pre-mix tank can be filled simultaneously with the reactor. Chemicals are pumped (item 6) from this tank into the reactor (item 2) at a rate of approximately 20 gal/min. The time required for charging the reactor is approximately 35 min.

The reactor is heated and maintained at 150 ± 2 °C (302 ± 5 °F) using a thermocouple mounted on the side of the reactor. The temperature will rise from the initial 135 °C (275 °F) as the exothermic reaction proceeds. If the temperature exceeds the upper limit, ambient cooling water should be circulated to reduce the temperature. The reaction should be continued for approximately 5.5 additional h or until the desired viscosity is achieved. During this period, binder samples should be periodically taken at various depths inside the reactor using a thief tube for quality control measurement. After the reaction is complete, the Sulphlex is pumped (item 7) into the storage tank where it can be maintained molten or allowed to solidify depending on the length of time before it will be used. If desired, the material can be circulated in the tank at reduced temperature [approximately 115 °C (221 °F)] to maintain homogeneity. The storage tank (item 10) will hold approximately three batches of Sulphlex from the 8-ton reactor. The Sulphlex can be transported directly to a paving site or allowed to solidify for use at a future date.

Target product specifications for Fourth Generation Sulphlex are given below.

Specific Gravity @ 25 °C (77 °F)	1.53
@ 135 °C (270 °F)	<1.70
Solubility in $CHCl_3$	95-100 percent
Viscosity at 135 °C (275 °F)	325 cSt
Penetration @ 77 °C (170.6 °F) (100 g, 5 s)	240
Stability @ 100 °C (212 °F)	48 h (minimum)

After manufacturing, proper temperature control of the Sulphlex is necessary so as not to induce any changes in properties due to long-term storage. Recommended temperature for long-term storage is between 125 and 130 °C (252 and 266 °F). If storage is carried out at an elevated temperature; i. e., above 132 °C (or 270 °F) the material should be used within 2 days after preparation. If this time limit is expected to be exceeded, the temperature should be reduced to ambient to prevent loss of volatiles.

HANDLING SULPHLEX AND ITS RAW MATERIALS

Safety precautions associated with handling and transporting liquid and solid Sulphlex are similar to that for liquid and solid sulfur.(31,32) Important safety precautions specific to each of the raw materials used for processing the Fourth Generation Sulphlex are discussed below. For additional information the reader is referred to appendix A, Material Safety Data Sheets (MSDS) for each raw material and "Dangerous Properties of Industrial Materials," by N.I. Sax.(33,34,35)

Production of Sulphlex materials involves precautions and practices similar to those encountered in paving operations with hot-mixed asphaltic concrete. Normal precautions for handling hot fluid materials must be observed, such as workers wearing proper protective clothing, safety glasses, goggles or face shields, gloves, and hard hats. Practices for safe handling of both solid and liquid sulfur have been established by the National Safety Council, and these practices should also be observed in preparing and handling Sulphlex.(31,32)

All hydrocarbon raw materials are flammable and toxic in varying degrees. Personnel working with the raw materials should read the MSDS information on each ingredient from the supplier. A copy of the MSDS for each raw material accompanies this report. (See appendix A-1 through A-6.) There currently is no MSDS sheet on Sulphlex.

Precautions for personnel involved in the preparation and use of Sulphlex raw materials are as follows:

1. Obtain and read the MSDS sheet for each of the raw materials.
2. Have a fire extinguisher readily available in the work area.
3. No smoking in the work area.
4. Wear nonspark protective clothing.
5. Maintain temperature below a maximum of 155 °C (311 °F) to prevent possible SO_2 or H_2S generation.
6. Isolate the work area and provide ventilation and fire protection.
7. Post signs in the work area, such as "Hazardous," "Flammable," "Toxic," and "No Smoking."
8. Provide explosion-proof ventilation to control vapor concentration.

SAFETY CONSIDERATIONS FOR SULPHLEX RAW MATERIALS

Particularly important safety precautions specific to each of the raw materials are discussed below and in their respective MSDS sheets appended to this report.

Sulfur from MSDS (Appendix A-1) and Reference 35

Toxicity is low; however, chronic inhalation can cause irritation of the mucous membranes. There is a slight fire hazard when sulfur is exposed to heat or flame or to chemical reaction with oxidizers. Sulfur is dangerous when heated, and it burns and emits highly toxic fumes of SO_2 or H_2S. Additional data on the safety aspects of SO_2, H_2S and particulate sulfur was given in chapter 4.

Dicyclopentadiene from MSDS (Appendix A-2) and Reference 35

DCPD has a flashpoint of 2.22 °C (36 °F), and is a dangerously flammable liquid.

Conditions and specific materials to avoid:

1. Avoid temperatures above 155 °C (311 °F), as DCPD will decompose to two moles of cyclopentadiene, which can results in a rapid rise in pressure.
2. Avoid acids, oxidizing material, polymerization catalysts, (e. g., boron or aluminum trichlorides.)
3. Toxicity is moderate to high via oral ingestion and inhalation and moderate via dermal routes (SAX).

Exposure guidelines:

1. The American Conference of Governmental and Industrial Hygienist (ACGIH) and the Occupational Safety and Health Association (OSHA) recommends a maximum allowable concentration (MAC) of 5 ppm (27 mg/m^3) for DCPD.
2. It is advisable in areas of high concentrations to wear organic vapor respirators, chemically-resistant rubber gloves and safety glasses.

Dicyclopentadiene Oligomer (OREPREP RI-300)

The DCPD oligomer is a dangerously flammable liquid with a flashpoint of 10 °C (50 °F). The safety requirements for this chemical are the same as those for DCPD, given above. In high concentrations, it is advisable to wear organic vapor respirators, rubber gloves, and chemical goggles or safety glasses with side shields. Ventilation should be good with exhaust at the source. For additional information, the reader is referred to appendix A-3.

Neodene C_{11} - C_{12} - Internal Olefins from MSDS (Appendix A-4)

Neodene is a moderately hazardous chemical with a flashpoint of 70 °C (158 °F). It is minimally irritating to the eyes and slightly irritating to the skin. However, prolonged or repeated liquid contact can result in defatting and drying of the skin. It has a low order of acute inhalation toxicity and is slightly toxic on ingestion. Avoid contact of Neodene with oxidizing agents. Personnel working with this chemical should wear respiratory protection, protective clothing, and safety glasses.

Safety practices recommended by the manufacturers of other raw chemicals should be carefully observed. Dicyclopentadiene, Neodene, and Oligomer of dicyclopentadiene are all flammable liquids, and extreme care should be provided to prevent fire. Adequate ventilation should be provided to control airborne levels below the exposure guidelines. Currently published guidelines exist only for dicyclopentadiene, which is 5 ppm threshold level value.(34) Monitoring for total organic levels may be done with commercially available instruments and is recommended at the weighing sight.

Sulphlex

When using Sulphlex as a construction material, its limitations and its advantages must be recognized. Sulphlex, like wood or plastic materials, will ignite on exposure to a direct flame source. If it is exposed to temperatures above 96 °C (205 °F), it will begin to soften and lose strength. This effect tends to be reversible with recooling. The melting points for Sulphlex appear to be around 115 °C (248 °F). Also, Sulphlex should be used in applications consistent with its strength and thermoplastic properties, primarily paving.

When Sulphlex mixtures are produced in the recommended mixing temperature range of 127 to 155 °C (260 to 311 °F), gaseous emissions of sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) will be considerable below the allowable threshold limit values, and sulfur vapor emissions will be minimized. Threshold values established for SO_2 are 5 ppm for short-term exposure and 2 ppm for time-weighted average concentration for an 8 h exposure. Corresponding values for H_2S are 15 ppm and 10 ppm respectively.(33)

Monitoring and measuring of SO_2 and H_2S may be done with commercially available instruments. Monitoring of sulfur emission for Sulphlex production with portable instruments is recommended at the sulfur and Sulphlex storage areas and in the reactor area.

Sulphlex vapor crystallizes, on cooling, into fine dust-like particles and is non-toxic. Sulphlex dust may cause eye irritation which can be minimized by requiring goggles in areas where sulfur vapors or dust may be emitted.

AUXILIARY EQUIPMENT FOR A SULPHLEX PRODUCTION FACILITY

Personnel Protective Equipment(31,32)

Personnel handling liquid Sulphlex should wear a safety hat, safety glasses with side shields and a face-shield. (In some cases, a full hood is used.) They also need a long sleeved shirt; fabric or heat-resistant gloves - without gauntlets in order to minimize burns from trapped Sulphlex, but long enough to overlap the shirt cuffs; laced, high-top, safety shoes or boots; and trousers long enough to cover the shoe tops. Galoshes with buckle or zipper closures are also adequate. In no case should open-top boots, low-cut shoes, sandals, sneakers, or perforated shoes be worn.

Routine handling of liquid Sulphlex in adequately ventilated premises does not require respiratory protective equipment, but it should be available nearby. If personnel must enter an area where the air is contaminated with hydrogen sulfide, or sulfur dioxide as in the case of a fire, they should be equipped with air line respirator, or self-contained breathing apparatus. The face-piece must protect the eyes. They should also be provided with a safety belt and life line; and other employees should stand by to haul them out if necessary. Anyone who might have to use respiratory protective equipment should be thoroughly trained and regularly checked for proficiency. For toxicity and system information on sulfur, hydrogen sulfide and sulfur dioxide, the reader is referred to the discussions in chapter 4.

Electrical Equipment(31)

It has been the experience of the sulfur industry that electrical equipment meeting the requirements for installation in Class II, Group G locations, according to the *National Electrical Code*, is satisfactory.

Waste Disposal(32)

Small amounts of Sulphlex can best be disposed by burning, if this can be done without hazard to personnel and without violating air pollution regulations. Sulphlex exposed to the weather or buried at moderate depths may slowly generate sulfuric acid or leachates containing by-products of the chemical reactants. If the resulting acidity is objectionable, the Sulphlex can be mixed with four times its weight of crushed limestone, marble, or shell, and then buried.

Sulphlex Quality Control and Analysis

The binder production activity conducted under this contract as well as previous Sulphlex programs has shown that Sulphlex having substantially different properties can be prepared from a single formulation of raw materials by changing process conditions.(9,10,16) Thus, tight quality control must be maintained, not only on the raw materials that are being used, but also on the preparation conditions.

The Fourth Generation Sulphlex binder is a new material, and specifications need to be developed with limits on the variations allowed in each property. Fourth Generation Sulphlex has the composition shown in table 35.

Table 35. Composition of Fourth Generation Sulphlex.

Ingredient	Weight Percent
Sulfur	70
Dicyclopentadiene	15
Oligomer of Cyclopentadiene	7.5
Neodene (C_{11} C_{12}) Internal Olefin	7.5
Total	100

After being reacted at 150 °C (302 °F) for 6.5 h, this material was found to have the following properties shown in table 36.

Table 36. Properties of Fourth Generation Sulphlex binder.

Viscosity at 135 °C (275 °F)	325 cSt
Penetration at 25 °C (77 °F) (100 g, 5 s)	240
Specific gravity at 25 °C (77 °F)	1.53
Solubility in chloroform	95 - 100%

A series of Quality Control-type tests, analyses, and properties are suggested for use to ensure reproducible quality from one batch to the next. The properties and tests that appear to be most pertinent to establish product quality assurance are discussed below in the following categories:

PRIMARY TESTS

- Chemical properties.
- Rheological properties.
- Stability to heat and aging.

AUXILIARY TESTS

- Low-temperature properties.
- Moisture susceptibility.

These properties where chosen because they all appear to have significance in assessing the subsequent performance of Sulphlex as a binder and are tentatively suggested for use in characterizing this type of binder. The tests for generating these properties are listed in table 37 and discussed in following subsections. The types of tests have been categorized as primary or auxiliary wherein the former are recommended for continuous sampling throughout the reaction. The latter are suggested to satisfy specific end-use conditions such as low-temperature or moisture susceptibility.

Chemical Properties

Uniformity and Purity of Raw Materials: Essential to the manufacture of homogeneous chemical products such as plasticized sulfur binder is the uniformity of the raw materials that are used. Specifications should be set on all raw materials, and each lot used should be tested to ensure that the manufacturing and job specifications are met. This testing can be done principally by gas chromatography.

Elemental Analysis: As the Fourth Generation Sulphlex is the reaction product of sulfur and hydrocarbons, it contains only three elements, i.e., sulfur, carbon, and hydrogen. Analysis for these elements will indicate the correctness of the original charge ratios or the possibility of loss of volatiles from unreacted hydrocarbons. If all three elements are determined, the analyses will be a check of their accuracy as the results for the three elements should total 100 percent.

Table 37. Tests for controlling the quality of Sulphlex.

PRIMARY TESTS	TEST METHOD
Chemical Properties:	
● Raw materials purity	Gas Chromatography(36,37)
● Carbon, hydrogen, and sulfur contents	ASTM E 191-64
● Free sulfur	Thin Layer Chromatography (TLC)(37)
● Specific gravity	ASTM D 70-82
● Solubility in $CHCl_3$	AASHTO T 4-78 and ASTM D 2042-81
Rheological Properties:	
● Penetration at 25 °C (77 °F)	ASTM D 5-73
● Viscosity at 60 °C (140 °F)	ASTM D 2171-81
● Viscosity at 135 °C (275 °F)	ASTM D 2170-82
Stability Characteristics:	
● Rolling thin film oven test at 135 °C (275 °F); measure weight loss and viscosity ● Exposure at 100 °C (212 °F) in small tins; measure weight loss and penetration ● Exposure at RT in small tins; measure penetration and possibly perform DSC	ASTM D 2872-74 Caltrans Test 346 (1978) and AASHTO T-240-78 (Modified)
AUXILIARY TESTS	
● Molecular weight distribution	Size Exclusion Chromatography(38)
● Thermogravimetric analysis (TGA)	Ref 39
● Differential scanning calorimetry (DSC)	Ref 37

Total sulfur can be determined by a variety of standard oxygen flask combustion methods. Because of the high sulfur content of Sulphlex, some difficulties may be encountered, but the results can be expected to be within a 1-percent error.

Carbon and hydrogen are usually determined together by a combustion method. These analyses are usually accurate to within a tenth of a percent (ASTM E 191-64, Apparatus for Microdetermination of Carbon and Hydrogen in Organic and Organo-metallic Compounds).

Free Sulfur: The level of unreacted free sulfur in a plasticized sulfur affects the rate at which the plasticized sulfur can harden due to its crystallization and ultimately the level of crystallization. Sulfur has a limited solubility in the sulfur/hydrocarbon reaction product which is a function of the plasticizer. Two methods have been found useful in the analysis for free sulfur, i.e., thin layer chromatography (TLC) and gel permeation chromatography (GPC).

Solubility of Sulphlex: Differences have been observed in the solubility of different batches of the same type of Sulphlex. The same type of Sulphlex should have the same batch to batch solubility in solvents. AASHTO Test Method T 44-78 can be used with chloroform for quality control purposes. This procedure has been slightly modified to use filter paper instead of a Gooch crucible for filtering. Due to the high sensitivity of Sulphlex solubility to temperature, temperature control at least to ± 5 °C (± 9 °F), is particularly important in determining solubility of this property.

Molecular Weight and Molecular Weight Distribution

Molecular weight and molecular weight distribution are generally important characteristics of polymeric materials, even for low molecular weight materials. They are often used for quality control in polymerization. Number Average Molecular Weights can be obtained through the use of vapor pressure osmometers; however, Number Average Molecular Weight tends to emphasize the low molecular weight species in a mixture.

Volatiles Determination

The volatiles content, as determined by thin film oven (TFO) and rolling thin film oven (RTFO) tests, have been found to vary among different batches of Sulphlex. The volatiles content appears to be characteristic of a given batch of Sulphlex and can be used as a quality control test. The loss value should be low and its limit should be set for a given test condition. The volatiles loss of a product on heating is a reflection of the purity of the reactants, as well as the thermal stability of the product.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

Thermogravimetric analysis (TGA)[38] is also useful for assessing the thermal stability of batches of plasticized sulfur by showing loss of volatiles. TGA can also supply a characteristic curve for a given Sulphlex batch made of specific materials and under specific conditions.

Differential scanning calorimetry (DSC) using ASTM on a newly prepared batch of plasticized sulfur can be used to determine its second order transition temperature, T_g, which appears to be related to its low temperature behavior in aggregate mixtures. DSC performed on samples aged at ambient temperature also indicates allotropic changes in the material. The glass transition temperatures can also be determined diametrically by following the linear thermal expansion of a cylindrical specimen with temperature as described in ASTM D 696.

RHEOLOGICAL PROPERTIES

Penetration and viscosity values are important practical characteristics of binders, particularly with respect to paving operations and roadway performance. Changes of these properties with time and temperature are quite important in characterizing and defining a plasticized sulfur. Standard AASHTO asphalt penetration and viscosity tests can be used with plasticized sulfur to set specifications. Of particular importance are viscosity at 135 °C (275 °F), viscosity at 60 °C (140 °F), and penetration at 25 °C (77 °F) .

STABILITY TESTS

Changes in properties of a plasticized sulfur binder during storage, mixing, paving, and service need to be assessed. These changes can be monitored with penetration and viscosity tests. Plasticized sulfur not only experiences increases in viscosity with age but also can crystallize, both of which result in stiffening. Aging a Sulphlex at 100 °C (212 °F) and at room temperature can be used to assess the tendency to degrade. Also, the rolling thin film test can be used to accelerate the effects of high temperature exposure. The crystallization which can take place at room temperature can be monitored by penetration tests and by DSC.

Stability can also be measured with the TGA by holding the temperature constant and observing loss in weight of the test specimen with time.

Standard Tests

The standard tests recommended for the measurement of several of these properties are listed in table 38.

Table 38. Standard test methods used in testing of Sulphlex.

Property	Test Identification Number or Reference	Test Method
Penetration at 25 °C (77 °F)	ASTM D 5-73 (AASHTO T 49-78)	Standard test method for penetration of bituminous materials
Rolling Thin Film Oven (Thermal Stability) at 135 °C (275 °F)	Caltrans Test 346, 1978 (ASTM D 2872-74) (AASHTO T 240-78 modified)	Method of test for determining the effect of heat and air on a moving film of asphalt (Rolling Thin Film Oven Test)
Specific Gravity	ASTM D 70-82 (AASHTO T 228-78)	Standard test method for specific gravity of standard bituminous materials
Viscosity at 60 °C (140 °F)	ASTM D 2171-81 (AASHTO T 202-77)	Standard test method for absolute viscosity of asphalts by vacuum capillary viscometer
Viscosity at 135 °C (275 °F)	ASTM D 2170-82 (AASHTO T 201-76)	Standard test method for kinematic viscosity of asphalts (bitumens)
Viscosity (sliding plate) at 25 °C (77 °F)	Caltrans Test 348, 1978	Method of test for determining the viscosity of bituminous materials by means of the sliding plate viscometer
Solubility in $CHCl_3$	AASHTO T 44-78 (modified to use filter paper instead of Gooch crucible) (ASTM D 2042-81)	Solubility of bituminous materials in organic solvents
Purity and Uniformity	Refs 36 and 37	Gas Permeation Chromatography (GPC)
Composition	ASTM E 191-64	Apparatus for Microdetermination of Carbon and Hydrogen in organic and organo-metallic compounds
	Thin Layer Chromatography(37)	Free Sulfur
Coefficient of linear thermal expansion and T_g	ASTM D 696 (Dilatometer) and ASTM D 3418 (DSC)	Test methods for coefficient of linear thermal expansion of plastics
Thermal stability	ASTM E 1131 and TGA (Ref 38)	Thermogravimetric analysis

SULPHLEX RAW MATERIALS QUALITY CONTROL

The raw material specification for the various chemical additives used in the preparation of the Fourth Generation Sulphlex formulations are given in tables 39 through 42.

Table 39. Material specification for Dicyclopentadiene for Fourth Generation Sulphlex.

Dicyclopentadiene (DCPD), Polyester Grade	
Composition	Weight Percent
Dicyclopentadiene (DCPD)	82 - 85
Codimers - B Butadiene/cyclopentadiene codimer (CPDCD) Isoprene/CPDCD Methyl-CPD dimer	Balance
Benzene	0.09 (max)
Light hydrocarbons (C_6 and higher)	0.05 (max)
Total	100.0
Physical Data	
Boiling Point	170 °C (338 °F)
Vapor pressure at 20 °C (68 °F)	36.5 mm Hg
Vapor Density	4.6
Specific gravity @ 15.6 °C (60 °F)	0.96
Flash point by COC* method	4 - 32 °C (40 - 90 °F)
Manufacturer	Dow Chemical Freeport, Texas 409-238-2011

*Cleveland Open Cup.

Table 40. Material specification for Cyclopentadiene Oligomer.

Cyclopentadiene (CPD) Oligomer - Hydrocarbon Resin Oil Product name: OREPREP RI - 300	
Composition	Percent
Hydrocarbon polymer	35.0
C_5 Hydrocarbons	1 - 2
C_{10} Hydrocarbons	35.0
C_{15} Hydrocarbons	20.0
C_{20} Hydrocarbons	8.0
Total	100.00
Physical Data	
Boiling Point	160 °C (320 °F)
Vapor pressure at 20 °C (68 °F)	50 mm Hg
Specific gravity	.0920 - 0.953
Flash point - PMOC*	26.7 °C (80 °F)
Manufacturer	Techmark Industries Galena Park, Texas 713-455-1206

*Pensky Martin Open Cup.

Table 41. Material specification for Neodene C_{11} - C_{12} internal olefins for Fourth Generation Sulphlex.

Neodene C_{11} - C_{12} Internal Olefins	
Composition	Percent
C_{10} and below	< 1
C_{11}	47 - 59
C_{12}	40 - 52
C_{13} and above	< 1.1
Total	100.0
Physical Data	
Boiling Point	689 to 212.2 ˚C (365 to 414 ˚F)
Vapor pressure at 20 ˚C (68 ˚F)	(0.9 mm Hg at 37.8 ˚C (100 ˚F)
Specific gravity	15.6/15.6 ˚C 0.76 (60/60 ˚F)
Flash point	70 ˚C (158 ˚F) by Setaflash
Manufacturer	Shell Oil Company Houston, Texas 713-544-4199

Table 42. Material specification for Sulphur for Fourth Generation Sulphlex.

Sulfur	
Purity	> 99.9%
Physical Data	
Melting Point Rhombic, S_α Monoclinci, S_β	 95.1 ˚C (203.5 ˚F) 119.1 ˚C (246.1 ˚F)
Specific Gravity	Liquid 2.00 Solid 1.79
Manufacturer	Martin Chemical Corp. Odessa, Texas 915-381-2321

RECORDS TO BE MAINTAINED OF PROCESS PARAMETERS

- In process controls and recording: temperature, time, viscosity.
- Temperature - Control to 150 °C (302 °F) ± 2 °C (± 3.6 °F) by operator.
- Reactor Charging Schedule, e. g., loading rates of addition: sulfur, to reactor - blend of hydrocarbons, record rate.
- Viscosity - record versus time to dca. 375 kl/centistokes at 150 °C (302 °F).
- Rate of reaction - duplicate viscosity/time and temperature/time curves from one batch to the next.
- Weighing: determine yield - weight additions - to assure correct weighing and no losses from one batch to the next.
- Obtain samples of Sulphlex at each hour and at midpoint in delivery of processed binder to the storage tanker for Product Specification Tests and to monitor the process of the reaction.

FOURTH GENERATION SULPHLEX PRODUCT SPECIFICATION

The target values for processed Fourth Generation Sulphlex binders are listed in table 43.

Table 43. Production specification for Fourth Generation Sulphlex.

Specific Gravity at 25 °C (77 °F)	1.53 ± 5
Solubility in $CHCl_3$	95 - 100%
Viscosity at 135 °C (275 °F)	325 cSt ± 15
Penetration at 77 °C (170.6 °F) (100 g, 5 s)	240 dmm ± 10
Stability at 100 °C (212 °F)	48 h (minimum)

SUMMARY

The manufacturing plan discussed above provides the general requirement of a plant and its facilities to produce 32 tons of Fourth Generation Sulphlex binder for an hypothetical road construction project. Much of the handling, transportation, and safety considerations were drawn from standardized procedures for solid and liquid sulfur, which is the primary component in Sulphlex formulations. For safe handling of the other chemical raw materials, the reader is referred to the safety and handling procedures recommended by the suppliers in the Material Safety Data Sheets.

Post-construction evaluation of the hypothetical test road treated in this chapter should be accompanied by suitable monitoring of leachate and ground water for environmental impact assessment.

CHAPTER 7. CONCLUSIONS

On the basis of the research activity accomplished under this program, the following conclusions are documented:

1. The development of the Fourth Generation of Sulphlex binders involved a comprehensive binder and mixture characterization program, under which four Sulphlex binders and a control asphalt were tested. The program was built upon recommendations of the previous research activity in this area.

2. The glass transition temperature, T_g, results for all the early generations of Sulphlex binders as measured in the DSC (2nd scan) were in the range of -11.7 to -18.7 °C (-13 to -35 °F). It was observed that Sulphlex 198 had a lower T_g than Sulphlex 233, and hence better low-temperature cracking resistance is predicted. The 50/50 and 75/25 blends of Sulphlex 198 and 233 also demonstrated lower T_g's than Sulphlex 233. The T_g for the Fourth Generation Sulphlex had the lowest of all materials tested indicating an additional enhancement of low-temperature fracture resistance. The T_g values determined using the dilatometer at slower rates of temperature change were lower than those determined using the differential scanning calorimeter. The effect of the size of the test container did not seem to significantly alter the test results. All Sulphlex T_g values were lower than those measured in the AC-20 control.

3. The Brookfield viscometer data indicated that the Fourth Generation Sulphlex binder was the most temperature susceptible while the (Task B) 50/50 (198:233) blend showed the least temperature susceptibility over the range of temperatures evaluated. The (Task B) 75/25 (198:233) blend was most similar to the Fourth Generation Sulphlex with the one-pot (Task C) synthesized binder much like the (Task B) 50/50 (198:233) blend. The viscosities of the Fourth Generation Sulphlex and 75/25 (198:233) blend were appreciably higher than the other two, with an increase of over 100 percent at the higher temperatures. However, all the binders fell below 3 Pa·s as prescribed by Superpave at a temperature of 135 °C (275 °F.) Since the Sulphlex binders exhibit a temperature susceptibility much like that of asphalt, Sulphlex paving mixtures should be engineered to consider the effects of temperature sensitivity.

4. Based on dynamic shear rheometer testing the (Task B) two-pot 50/50 blend of 198 and 233 binders and the two-pot 75/25 blend of 198 and 233 binders were the most rut susceptible. These binders graded as PG 58- and PG 52-, respectively. The one-pot (Task C) 50/50 blend of 198 and 233 binders and the Fourth Generation blend both graded as PG 64-. A closer evaluation of dynamic shear rheometer data revealed that the Fourth Generation Sulphlex binder had a

lower loss tangent at high test temperatures than the one-pot 50/50 blend. This indicates that a greater percentage of the total deformation of the Fourth Generation blend is elastic at higher test temperatures, compared to the 75/25 two-pot blend. Hence, of the four binders tested, the Fourth Generation blend was the best based on dynamic shear rheometer test values.

5. Low temperature fracture potential of binders is based primarily on the results of the Bending Beam Rheometer in the Superpave binder specifications. The creep stiffness and the slope of the stiffness versus time relationship at a loading time of 60 s, are the criteria. Based on these criteria, the 75/25 blend of 233 and 198 and the Fourth Generation blend are more resistant to low temperature fracture than are either the one-pot or the two-pot 50/50 blends of 233 and 198 or the AC-20 control binder. This is based on the fact that the 75/25 blend and the Fourth Generation blend maintain a stiffness of below 300 Mpa and a slope of below 0.30 at lower temperatures than do either of the other Sulphlex binders or the control binder. Previous research on Sulphlex binders identified low temperature fracture as a major shortcoming. The 75/25 two-pot 233/198 blend and the Fourth Generation blend are positive steps in addressing this shortcoming.

6. The environmental scanning electron microscope (ESEM) scans showed that the properties of the Sulphlex binder did not deteriorate in the temperature range between 25 °C (77 °F) and 40 °C (104 °F). This temperature range was selected because of the mixture anomalies demonstrated for the 75/25 (198:233) blend and the Fourth Generation blend in mixture testing. The crystallinity of sulfur remained unaffected by temperature in this range. In the case of the 50/50 (198:233) and one-pot synthesized blends, there was a difference in the structures of the material cored from the surface and the interior with a marked increase in the crystal size at the surface. Further, the structures of the 50/50 (198:233) blended and one-pot synthesized material were different from that of the 75/25 (198:233) blended and Fourth Generation Sulphlex binders with the former systems having larger crystals than the latter systems. The ESEM scans were inconclusive in themselves and did not provide an insight into the unusual behavior of the 75/25 (198:233) blended and Fourth Generation Sulphlex mixtures, in the above mentioned temperature range.

7. The Sulphlex mixtures showed a similar sensitivity to fabrication variables like mixing temperature, compactive effort, compaction temperature etc., as asphalt. Hence, the Sulphlex mixtures were produced using the same procedures and standards used for asphalt. The optimum binder contents were determined to be 7 percent as against 5 to 5.5 percent traditionally used for asphalts. These were equal percentages considered on a volume basis.

8. The air void requirement of 3 to 5 percent required for asphalt mixtures was required to ensure acceptable durability in Sulphlex mixtures. On the basis of the Marshall mixture design procedure it was observed that the Sulphlex mixtures had very high stabilities and concomitant flows.

9. The resilient moduli determined over the range of temperatures, indicated that the 50/50 (198:233) and one-pot synthesized blends fell in the same range as the control asphalt, although stiffer at the lower temperatures. The 75/25 (198:233) blended and Fourth Generation Sulphlex binders, however, showed much higher stiffnesses all along the temperature range. An anomalous increase in the resilient modulus at 40 °C (104 °F) compared to the resilient modulus at 25 °C (77 °F) was also observed. The 75/25 (198:233) blend and Fourth Generation Sulphlex binders proved to be superior at 40 °C (104 °F) by falling within the typical modulus range prescribed by AAMAS (figure 28, page 90) while the other blends failed to meet the AAMAS requirement at the same temperature. At 40, 25, 5, and -23.3 °C (77, 41, and -10 °F) the values were in the same range and met the AAMAS criteria. The greater temperature susceptibility of the 75/25 (198:233) blend and Fourth Generation Sulphlex binders observed in the Brookfield viscometer results was substantiated by these results. The results of thermal cycling of the 75/25 (198:233) blends and Fourth Generation Sulphlex binders, did not show appreciable increases in the resilient moduli values after one cycle of heating. This proved that the blends would not exhibit drastic increases in stiffness as a result of the anomalous stiffness increase between 25 °C (77 °F) and 40 °C (104 °F).

10. From the results of the indirect tensile stress and strain at failure tests, it was observed that the ultimate strengths of the 75/25 (198:233) blends and Fourth Generation Sulphlex binders were appreciably higher than the other blends. However, the failure strains were an order of magnitude lower for these two blends than for the 50/50 (198:233) blended, one-pot synthesized Sulphlex binders, and the control asphalt. The 50/50 (198:233) blended and one-pot synthesized Sulphlex binders met the NCHRP minimum failure strain fatigue criteria all along the temperature range, while the 75/25 (198:233) blends and Fourth Generation Sulphlex binders fell short of meeting the requirements. From this it was concluded that the 75/25 (198:233) blends and Fourth Generation Sulphlex mixtures were relatively more brittle than the other mixtures at the lower temperatures. This cannot be assumed as a contradiction to the earlier conclusions using the bending beam rheometer, since the accuracy of the results at these low temperatures is highly questionable and since AAMAS criteria for evaluation of texture potential based on IDT and resilient modulus data do not extend below 5 °C (41 °F).

11. Based on the results of the indirect tensile creep test it was concluded that the 75/25 (198:233) blends and Fourth Generation Sulphlex binders had a greater potential to dissipate thermal stresses rapidly. The AAMAS procedures used to evaluate the potential of the mixture to resist thermal fracture indicated that the Sulphlex mixes were better suited to resist thermally induced fracture than was the AC-20 control asphalt. This is in agreement with the changes in m-value with temperature as presented in table 19, page 72.

12. The results of the uniaxial compressive creep test at 40 °C (104 °F) indicated that all the Sulphlex mixtures were adequately equipped to resist rutting at the high and more realistic stress level of 0.414 MPa (60 psi.) The 75/25 (198:233) blends and Fourth Generation Sulphlex binders had very high creep moduli at this high stress level, with the values being an order of magnitude higher than the other Sulphlex and asphalt binders. The asphalt control binder fell below AAMAS specifications at 0.103 MPa (15 psi) and failed at 0.414 MPa (60 psi.) The recovery efficiencies for the 75/25 (198:233) and Fourth Generation binders were also very high.

13. The unconfined compressive strengths of the Sulphlex binders were much higher than for the AC-20 control asphalt. The strains were however in the same range. The Fourth Generation Sulphlex binder exhibited the highest strength, a measure of its resistance to high temperature rutting. The 75/25 (198:233) blends, one-pot synthesized and Fourth Generation Sulphlex binders exhibited high factors of safety against strain softening. The AC-20 asphalt failed under the same conditions.

14. All the Sulphlex binders showed very minimal permanent deformations on being subjected to the VESYS repeated load permanent deformation test. This indicated that the Sulphlex binders are highly resistant to permanent deformation at the high temperatures.

15. The aging of Sulphlex at normal ambient temperatures was found to be very different from that for the AC-20 control asphalt. The aging process in Sulphlex was mainly due to crystallization and the loss of volatiles from the plasticizers. The process was hence more rapid and occurred within the first week unlike the asphalt which aged more slowly. The increase of temperature from 25 to 40 °C (77 to 104 °F) seemed to have a more profound stiffening effect on the Sulphlex mixture than did aging at 25 °C (77 °F.) It has been documented that the viscosity of liquid sulfur changes dramatically with temperature. The viscosity decreases gradually with increasing temperature up to 160 °C (320 °F) above which the viscosity undergoes a very large and abrupt increase with temperature. At 188 °C (370 °F), it has been documented that the viscosity reaches a tremendously high maximum which practically prevents it from flowing.(30)

Although the stiffening effect seemed to be occurring at a lower temperature in mixtures, the effect of increasing viscosity with increasing temperature cannot be ruled out. Goodrich in his paper has documented that at temperatures above 50 °C (122 °F), the effect of the aggregate reflected more on the properties of the mixture than the binder itself.(28) This provides us with some insight into this abnormal behavior, but no concrete conclusions can be drawn.

16. Sulphlex is a complex chemical compound. Rheological properties of the Sulphlex blends are apparently very different from asphalt binders and Superpave PG Specifications may not be appropriate for grade selection and performance predicting of Sulphlex binders.

17. Sulphlex mixtures respond considerably differently than can be predicted from Superpave, rheologically-related binder properties. This may be related to thin-film mixture and binder-aggregate interaction effects which may not be adequately evaluated based on tests on the binder in mass.

18. A generic manufacturing plant, production plant, safety considerations and raw material specifications were prepared for the delivery of Fourth Generation Sulphlex in sufficient quantity to construct a hypothetical roadway test section. Current costs of sulfur and chemical additives tend to make Sulphlex binders a reasonable alternative to asphalt in flexible pavement mixtures.

The results of this study indicate that the Fourth Generation represents an improvement in low-temperature fracture resistance over the First, Second and Third Generations of Sulphlex binders. The use of Sulphlex binders in roadway construction will ultimately depend on the relative economics and availability of asphalt. Although laboratory tests indicate that the Fourth Generation Sulphlex binder should perform well these results need to be verified under actual field conditions.

APPENDIX A
Material Safety Data Sheets (MSDS)

A-1	Sulfur
A-2	Dicyclopentadiene
A-3	OREPREP (CPD Oligomer)
A-4	Neodene C_{11}-C_{12} Internal Olefin
A-5	Dipentene (Limonene)

June 30, 1992

USA and WORLDWIDE

APPENDIX A-1
SULFUR

Material Safety Data Sheet

SULFUR (Liquid)

PHILLIPS 66 COMPANY
A Division of Phillips Petroleum Company
Bartlesville, Oklahoma 74004

PHONE NUMBERS	
Emergency:	(918) 661-8118
Technical Services:	(918) 661-9091
For Additional MSDSs:	(918) 661-7297

A. Product Identification

Synonyms: Brimstone, Molten sulfur
Chemical Name: Sulfur
Chemical Family: Sulfur
Chemical Formula: S
CAS Reg. No.: 7704-34-9
Product No.: CC5500

Product and/or Components Entered on EPA's TSCA Inventory: YES

This product is in U.S. commerce, and is listed in the Toxic Substances Control Act (TSCA) Inventory of Chemicals; hence, it may be subject to applicable TSCA provisions and restrictions.

B. Components

Ingredients	CAS Number	% By Wt.	OSHA PEL	ACGIH TLV
Sulfur	7704-34-9	99 (Min)	NE	NE

See Section F, Recommended Exposure Limits.

NA - Not Applicable NE - Not Established

C. Personal Protection Information

Ventilation: Provide ventilation sufficient to control levels of sulfur dioxide and hydrogen sulfide to within acceptable limits. (See Section F.)

Respiratory Protection: Not generally required unless needed to prevent respiratory irritation. When entering areas of unknown concentrations, use NIOSH/MSHA self-contained breathing apparatus.

Eye Protection: Use safety glasses with side shields. For splash protection, use chemical goggles with face shield.

Skin Protection: Use heat resistant gloves and clothing when handling molten sulfur.

NOTE: Personal protection information shown in Section C is based upon general information as to normal uses and conditions. Where special or unusual uses or conditions exist, it is suggested that the expert assistance of an industrial hygienist or other qualified professional be sought.

D. Handling and Storage Precautions

Do not get in eyes, on skin or on clothing. Do not breathe vapor, mist, fume or dust. May be harmful. Proper personal protective equipment must be used when handling this chemical. Immediately remove and launder contaminated clothing before reuse. Wash thoroughly after handling. Use only with adequate ventilation.

Store in a well-ventilated area. Store in a closed container.

E. Reactivity Data

Stability: Stable
Conditions to Avoid: Not Applicable
Incompatibility (Materials to Avoid): Oxygen and oxidizing agents

Hazardous Polymerization: Will Not Occur
Conditions to Avoid: Not Applicable
Hazardous Decomposition Products: Toxic sulfur dioxide and hydrogen sulfide gases. These gases may accumulate in storage container.

F. Health Hazard Data

Recommended Exposure Limits:

The components of vapors and fumes may include:

Ingredients	OSHA PEL	ACGIH TLV
Sulfur dioxide	2 ppm	2 ppm
Hydrogen sulfide	10 ppm	10 ppm

APPENDIX A-1
SULFUR (continued)

Acute Effects of Overexposure:

Eye: Fumes can cause severe irritation, conjunctivitis, keratitis, tearing, photophobia and the liquid can result in thermal burns.

Skin: Fumes can cause severe irritation to the skin and the liquid can result in thermal burns.

Inhalation: Toxic by this route of exposure. Fumes are extremely irritating to the mucous membranes of the nose, throat, and upper respiratory tract. Overexposure may produce a cough, reflex broncho constriction, choking, runny nose, pulmonary edema, unconsciousness, convulsions, respiratory paralysis, and death.

Ingestion: Not Applicable

Subchronic and Chronic Effects of Overexposure:

No known applicable information.

Other Health Effects:

SO2 has been postulated to be a promoter of carcinogens in animals if exposure to SO2 is chronic. The significance of this study to man has not been determined.

The odor of hydrogen sulfide may not be recognized after prolonged inhalation due to paralysis of the sense of smell. Effects from inhaling the fume may lead to chronic bronchitis, respiratory irritation, increased loss of pulmonary function, and tearing of the eyes.

Health Hazard Categories:

	Animal	Human		Animal	Human
Known Carcinogen	___	___	Toxic	_X_	_X_
Suspect Carcinogen	___	___	Corrosive	___	___
Mutagen	___	___	Irritant	_X_	_X_
Teratogen	___	___	Target Organ Toxin	_X_	_X_
Allergic Sensitizer	___	___	Specify - Lung - Irritant;		
Highly Toxic	___	___	Eye and Skin Hazard - Thermal burns		

First Aid and Emergency Procedures:

NOTE: For thermal burns, cool quickly with water and seek immediate medical attention.

Eye: Immediately flush eyes with running water for at least fifteen minutes. If irritation or adverse symptoms develop, seek medical attention.

Skin: Immediately wash skin with soap and water for at least fifteen minutes. If irritation or adverse symptoms develop, seek medical attention.

Inhalation: Immediately remove from exposure. If breathing is difficult, give oxygen. If breathing ceases, administer artificial respiration followed by oxygen. Seek immediate medical attention.

Ingestion: Give two glasses of water and induce vomiting, only if subject is conscious. Seek medical attention.

G. Physical Data

Appearance:	Yellow to dark yellow liquid
Odor:	Pungent; oily and/or rotten egg
Boiling Point:	832F (444C)
Vapor Pressure:	0.11 psia @ 284F (140C)
Vapor Density (Air = 1):	>1
Solubility in Water:	Negligible
Specific Gravity (H20 = 1):	1.79 @ 60/60F (15.6/15.6C)
Percent Volatile by Volume:	Negligible
Evaporation Rate (Butyl Acetate = 1):	<1
Viscosity:	Not Established

H. Fire and Explosion Data

Flash Point (Method Used):	335-370F (168-188C) (COC, ASTM D92)
Flammable Limits (% by Volume in Air):	LEL - Not Established UEL - Not Established
Fire Extinguishing Media:	Sand, carbon dioxide (CO2), water fog
Special Fire Fighting Procedures:	Sand or carbon dioxide may be used to smother small fires. Water fog should be used to control large sulfur fires. Solid streams of water should not be used. For large fires or fires in a confined area, self-contained breathing apparatus should be worn.
Fire and Explosion Hazards:	Sulfur dioxide and hydrogen sulfide may be released.

I. Spill, Leak and Disposal Procedures

Precautions Required if Material is Released or Spilled:
Confine spill. Allow to cool. Shovel into disposal drums. Wear protective equipment and/or garments described in Section C if exposure conditions warrant.

Waste Disposal (Insure Conformity with all Applicable Disposal Regulations):
Burn under controlled conditions or place in other RCRA permitted waste disposal facility.

J. DOT Transportation

Shipping Name: Sulfur, molten
Hazard Class: 9 (Misc. hazardous materials)
ID Number: NA 2448
Packing Group: III
Marking: Non-bulk packages: Sulfur, molten, NA 2448
Bulk packages; Molten Sulfur, 2448
Label: Class 9
Placard: Class 9/2448
Hazardous Substance/RQ: Not Applicable
Shipping Description: Sulfur, molten, 9 (Misc. hazardous material), NA 2448, PG III
Packaging References: 49 CFR 173.213, 173.247

NOTE: Above information is applicable for domestic shipments only. International shipments of molten sulfur must be classified as Division 4.1 (Flammable Solid) materials.

K. RCRA Classification - Unadulterated Product as a Waste

Prior to disposal, consult your environmental contact to determine if TCLP (Toxicity Characteristic Leaching Procedure, EPA Test Method 1311) is required. Reference 40 CFR Part 261.

L. Protection Required for Work on Contaminated Equipment

Contact immediate supervisor for specific instructions before work is initiated. Wear protective equipment and/or garments described in Section C if exposure conditions warrant.

M. Hazard Classification

☒ This product meets the following hazard definition(s) as defined by the Occupational Safety and Health Hazard Communication Standard (29 CFR Section 1910.1200):

☐ Combustible Liquid
☐ Compressed Gas
☐ Flammable Gas
☐ Flammable Liquid
☐ Flammable Solid
☐ Flammable Aerosol
☐ Explosive
☒ Health Hazard (Section F)
☐ Organic Peroxide
☐ Oxidizer
☐ Pyrophoric
☐ Unstable
☐ Water Reactive

☐ Based on information presently available, this product does not meet any of the hazard definitions of 29 CFR Section 1910.1200.

N. *Additional Comments*

SARA 313

As of the preparation date, this product did not contain a chemical or chemicals subject to the reporting requirements of Section 313 of Title III of the Superfund Amendments and Reauthorization Act of 1986 and 40 CFR Part 372.

APPENDIX A-2
Dicyclopentadiene

EXXON CHEMICAL

MATERIAL SAFETY DATA SHEET

EXXON CHEMICAL AMERICAS, P.O. BOX 3272, HOUSTON, TEXAS 77001
A Division of EXXON CHEMICAL COMPANY, A Division of EXXON CORPORATION

DICYCLOPENTADIENE 97/DCPD-97

PAGE: 1
DATE PREPARED: JAN 3, 1995
MSDS NO.: 96220000

SECTION 1 PRODUCT IDENTIFICATION & EMERGENCY INFORMATION

PRODUCT NAME: Dicyclopentadiene 97/DCPD-97

CHEMICAL NAME:
4,7-methano-1H-indene,3A,4,7,7A-tetrahydro CAS 77-73-6

CHEMICAL FAMILY:
Aliphatic diolefin

PRODUCT DESCRIPTION:
Colorless liquid or white to colorless crystalline solid

EMERGENCY TELEPHONE NUMBERS:	**EXXON CHEMICAL AMERICAS**	**800-726-2015**
	CHEMTREC	**800-424-9300**

SECTION 2 HAZARDOUS INGREDIENT INFORMATION

This product is hazardous as defined in 29 CFR1910.1200.

OSHA HAZARD
Flammable
May cause lung, kidney,
and/or liver damage
Toxic if ingested
TLV
Eye irritant

For additional information see Section 3.

SECTION 3 HEALTH INFORMATION & PROTECTION

NATURE OF HAZARD

EYE CONTACT:
Irritating, but does not injure eye tissue.

SKIN CONTACT:
Low order of toxicity.
Irritating.

INHALATION:

Vapor concentrations above recommended exposure levels are irritating to the eyes and the respiratory tract, may cause headaches and dizziness, are anesthetic and may have other central nervous system effects.

May cause breathing disorders and/or lung damage.

INGESTION:

Small amounts of the liquid aspirated into the respiratory system during ingestion, or from vomiting, may cause bronchiopneumonia or pulmonary edema.

Moderately toxic.

FIRST AID

EYE CONTACT:

Flush eyes with large amounts of water until irritation subsides. If irritation persists, get medical attention.

SKIN CONTACT:

Immediately flush with large amounts of water; use soap if available. Remove contaminated clothing, including shoes, after flushing has begun. If irritation persists, seek medical attention.

INHALATION:

Using proper respiratory protection, immediately remove the affected victim from exposure. Administer artificial respiration if breathing is stopped. Keep at rest. Call for prompt medical attention.

INGESTION:

If swallowed, DO NOT induce vomiting. Keep at rest. Get prompt medical attention.

ACUTE TOXICITY DATA IS AVAILABLE UPON REQUEST.

WORKPLACE EXPOSURE LIMITS

OSHA REGULATION 29CFR1910.1000 REQUIRES THE FOLLOWING PERMISSIBLE EXPOSURE LIMITS:

A TWA of 5 ppm (30 mg/m3) for Dicyclopentadiene.

The recommended permissible exposure levels indicated above reflect the levels revised by OSHA in 1989 or in subsequent regulatory activity. Although the 1989 levels have since been vacated by the 11th Circuit Court of Appeals, Exxon Chemical recommends that the lower exposure levels be observed as reasonable worker protection.

THE ACGIH RECOMMENDS THE FOLLOWING THRESHOLD LIMIT VALUES:

a TWA of 5 ppm (27 mg/m3) for Dicyclopentadiene.

MATERIAL SAFETY DATA SHEET

EXXON CHEMICAL
EXXON CHEMICAL AMERICAS, P.O. BOX 3272, HOUSTON, TEXAS 77001
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PRECAUTIONS

PERSONAL PROTECTION:

For open systems where contact is likely, wear safety glasses with side shields, long sleeves, and chemical resistant gloves.
Where contact may occur, wear long sleeves and safety glasses with side shields.
Where concentrations in air may exceed the limits given in this Section and engineering, work practice or other means of exposure reduction are not adequate, NIOSH/MSHA approved respirators may be necessary to prevent overexposure by inhalation.

VENTILATION:

The use of local exhaust ventilation is recommended to control process emissions near the source. Laboratory samples should be stored and handled in a lab hood. Provide mechanical ventilation of confined spaces.
See respiratory protection recommendations.
Use explosion-proof ventilation equipment.

SECTION 4 FIRE & EXPLOSION HAZARD

FLASHPOINT: 36 Deg F. METHOD: TCC NOTE: Minimum
FLAMMABLE LIMITS: LEL: 1.0 UEL: 10.0 NOTE: (Approximate)
AUTOIGNITION TEMPERATURE: NOTE: Not Available

GENERAL HAZARD:

Flammable Liquid, can release vapors that form flammable mixtures at temperatures at or above the flashpoint.
Unstable, material will vigorously polymerize, decompose, condense or will become self-reactive under conditions of shocks of pressure or temperature.
Static Discharge, material can accumulate static charges which can cause an incendiary electrical discharge .
"Empty" containers retain product residue (liquid and/or vapor) and can be dangerous. DO NOT PRESSURIZE, CUT, WELD, BRAZE, SOLDER, DRILL, GRIND, OR EXPOSE SUCH CONTAINERS TO HEAT, FLAME, SPARKS, STATIC ELECTRICITY, OR OTHER SOURCES OF IGNITION; THEY MAY EXPLODE AND CAUSE INJURY OR DEATH.
Empty drums should be completely drained, properly bunged and promptly returned to a drum reconditioner, or properly disposed of.

DICYCLOPENTADIENE 97/DCPD-97

FIRE FIGHTING:

Use water spray to cool fire exposed surfaces and to protect personnel. Shut off "fuel" to fire. If a leak or spill has not ignited, use water spray to disperse the vapors.
Either allow fire to burn under controlled conditions or extinguish with foam or dry chemical. Try to cover liquid spills with foam.
Avoid spraying water directly into storage containers due to danger of boilover.

HAZARDOUS COMBUSTION PRODUCTS:

No unusual

SECTION 5 SPILL CONTROL PROCEDURE

LAND SPILL:

Eliminate sources of ignition. Prevent additional discharge of material, if possible to do so without hazard. For small spills implement cleanup procedures; for large spills implement cleanup procedures and, if in public area, keep public away and advise authorities. Also, if this product is subject to CERCLA reporting (see Section 7) notify the National Response Center.
Prevent liquid from entering sewers, watercourses, or low areas. Contain spilled liquid with sand or earth. Do not use combustible materials such as sawdust.
Recover by pumping (use an explosion proof or hand pump) or with a suitable absorbent.
Consult an expert on disposal of recovered material and ensure conformity to local disposal regulations.

WATER SPILL:

Eliminate sources of ignition. Warn occupants and shipping in surrounding and downwind areas of fire and explosion hazard and request all to stay clear.
Consult an expert on disposal of recovered material and ensure conformity to local disposal regulations.

SECTION 6 NOTES

HAZARD RATING SYSTEMS:

This information is for people trained in:
National Paint & Coatings Association's (NPCA)
Hazardous Materials Identification System (HMIS)
National Fire Protection Association (NFPA 704)
Identification of the Fire Hazards of Materials

	NPCA-HMIS	NFPA 704
HEALTH	2	1
FLAMMABILITY	3	3
REACTIVITY	3	1

KEY
4 = Severe
3 = Serious
2 = Moderate
1 = Slight
0 = Minimal

SECTION 7 REGULATORY INFORMATION

DEPARTMENT OF TRANSPORTATION (DOT):
DOT SHIPPING DESCRIPTION: FLAMMABLE LIQUID, N.O.S., (DICYCLOPENTADIENE), 3, UN 1993, II

FLASHPOINT: 36 Deg F. METHOD: TCC NOTE: Minimum

TSCA:
This product is listed on the TSCA Inventory at CAS Registry Number 77-73-6

CERCLA:
If this product is accidentally spilled, it is not subject to any special reporting under the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). We recommend you contact local authorities to determine if there may be other local reporting requirements.

SARA TITLE III:
Under the provisions of Title III, Sections 311/312 of the Superfund Amendments and Reauthorization Act, this product is classified into the following hazard categories: Immediate health, Delayed Health, Fire, Reactive.
This information may be subject to the provisions of the Community Right-to-Know Reporting Requirements (40 CFR 370) if threshold quantity criteria are met.
This product contains the following Section 313 Reportable Ingredients:

COMPONENT	CAS NO.	MAXIMUM %
Dicyclopentadiene	77-73-6	98.0

EXXON
CHEMICAL

MATERIAL SAFETY DATA SHEET

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A Division of EXXON CHEMICAL COMPANY, A Division of EXXON CORPORATION

DICYCLOPENTADIENE 97/DCPD-97

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SECTION 8 TYPICAL PHYSICAL & CHEMICAL PROPERTIES

SPECIFIC GRAVITY:
0.97 at 60

SOLUBILITY IN WATER, WT. % AT °F:
Insoluble

SP. GRAV. OF VAPOR, at 1 atm (Air=1):
4.60

EVAPORATION RATE, n-Bu Acetate=1:
Not Available

VAPOR PRESSURE, mmHg at °F:
502 at 100 Aproximate
117 at 131 Aproximate

VISCOSITY OF LIQUID, CST AT °F:
2.2 at 100

FREEZING/MELTING POINT, °F:
50 to 90

BOILING POINT, °F:
120 to 340

SECTION 9 REACTIVITY DATA

STABILITY:
Unstable

CONDITIONS TO AVOID INSTABILITY:
Temperatures above 150 Deg. F
Lack of inhibitor. Distillation to dryness - peroxide might form.

HAZARDOUS POLYMERIZATION:
Will occur

CONDITIONS TO AVOID:
Lack of inhibitor or temps. above 150 Deg. F

MATERIALS AND CONDITIONS TO AVOID INCOMPATIBILITY:
Oxidizing agents, mineral acids, formic acids.

HAZARDOUS DECOMPOSITION PRODUCTS:
None

SECTION 10 STORAGE AND HANDLING

ELECTROSTATIC ACCUMULATION HAZARD:
Yes, use proper grounding procedure

STORAGE TEMPERATURE, °F:
130 Maximum

STORAGE/TRANSPORT PRESSURE, mmHg:
Atmospheric

LOADING/UNLOADING TEMPERATURE, °F:
120 Maximum

VISC. AT LOADING/UNLOADING TEMP., cST:
2.2

APPENDIX A-2
Dicyclopentadiene
(continued)

EXXON
CHEMICAL

MATERIAL SAFETY DATA SHEET

EXXON CHEMICAL AMERICAS, P.O. BOX 3272, HOUSTON, TEXAS 77001
A Division of EXXON CHEMICAL COMPANY, A Division of EXXON CORPORATION

DICYCLOPENTADIENE 97/DCPD-97

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REVISION SUMMARY:
Since NOVEMBER 19, 1993 this MSDS has been revised in Section(s):
7

REFERENCE NUMBER:	DATE PREPARED:	SUPERSEDES ISSUE DATE:
HDHA-C-50008	January 3, 1995	November 19, 1993

FOR ADDITIONAL PRODUCT INFORMATION, CONTACT YOUR TECHNICAL SALES REPRESENTATIVE
FOR ADDITIONAL HEALTH/SAFETY INFORMATION, CALL 713-870-6884

APPENDIX A-3
OREPREP CPD Oligomer

MATERIAL SAFETY DATA SHEET

Printed 02-18-1997

OREPREP DCPD

CAUTION CODE 3-3-0

MSDS ID: DCPD

1 - SECTION I - IDENTITY

OREPREP
A Division of Baker Performance
Chemicals Incorporated
A Baker Hughes Company
3900 ESSEX LANE, P.O. BOX 27714
HOUSTON, TX 77227-7714

EMERGENCY TELEPHONE NUMBERS:
CHEMTREC: 1-800-424-9300
BPCI: 1-800-231-3606
TELEPHONE NUMBER FOR INFORMATION:
713-599-7400

CHEMICAL NAME: Chemical Identity Is A Trade Secret

CHEMICAL FAMILY: Unsaturated Cyclic Hydrocarbon

2 - SECTION II - REGULATORY CLASSIFICATION

ENVIRONMENTAL	OCCUPATIONAL	TRANSPORTATION
RQ= 125 Gallons (Benzene)	OSHA Non-Hazardous: NA	Not Regulated: NA
TPQ= None	OSHA Hazardous: Yes	Regulated: Yes
	X Acute	Flammable Liquid,
SARA S313: Yes	X Chronic	N.O.S., (Contains
Benzene <1%	X Fire	Dicyclopentadiene,
	NA Pressure	Benzene), 3, UN 1993,
	NA Reactive	III

The components of this product are listed on the TSCA inventory.

3 - SECTION III - HAZARDOUS INGREDIENTS

HAZARDOUS COMPONENT	CAS #	PEL(OSHA)* TWA	STEL	A/L	TLV(ACGIH)* TWA	STEL	MFG* REC, TWA
Dicyclopentadiene (Proprietary)	77-73-6				5		
Benzene (<1%)	71-43-2	1	5	0.5	10		

*ppm unless otherwise indicated; (C) denotes ceiling limit

4 - SECTION IV - PHYSICAL & CHEMICAL PROPERTIES

Specific Gravity @77F: 0.9602 (H2O=1)

pH:
5% of Product: 7.6 @ 75F

Density (lbs/gallon): 7.989

Viscosity (Method): 6cps (Brookfield)

Vapor Density (Air=1): > 1

Appearance and Odor: Colorless liquid with camphor-like odor.

Solubility: Insoluble in water

Stability: Stable

Freezing Point: Not Determined

Pour Point: <-60F

Flash Point (Method): 84F (PMCC)

Percent Organic Compounds: 100%

4 - SECTION IV - PHYSICAL & CHEMICAL PROPERTIES (continued)

Boiling Point: Not Determined

Conditions to Avoid: Oxidizers; heat sparks, or open flame

Vapor Pressure: 0.807 (Reid)

Haz. Decomp. Prod: Carbon monoxide; oxides of nitrogen; oxides of sulfur

Hazardous Polymerization: Will occur at temperatures above 338F - De-dimerizes

FIRE CONTROL PROCEDURES: Use foam, dry chemical, CO2, water fog or spray. Do not enter a fire area without proper protective equipment, including NIOSH/MSHA approved, self-contained breathing apparatus. Cool exposed containers with water spray. Avoid vapors.

FIRE HAZARDS:
Flammable Liquid. Can release vapors that form explosive mixtures at temperatures at or above the flash point.
Vapors can travel to source of ignition and flash back.
Never use welding or cutting torch on or near drums, even when empty.
Explosion may result.

5 - SECTION V - HEALTH HAZARDS

EFFECTS OF OVEREXPOSURE:
INHALATION: Inhalation of high levels of vapors or mists or inhalation for prolonged periods of time may cause central nervous system (CNS) effects; lightheadedness, headaches or unconsciousness.
EYE CONTACT: Eye contact may cause irritation and redness.
SKIN CONTACT: Prolonged or repeated contact with skin may cause irritation or contact dermatitis.
INGESTION: May be harmful if ingested.

OTHER INFORMATION:

Dicyclopentadiene vapors are irritating to the mucous membranes, upper respiratory tract and skin. Inhalation of concentrated vapors may cause headaches, nausea, vomiting and dizziness.

Dicyclopentadiene Toxicity Data:
Orl - Rat - LD50 = 353 mg/kg
Inh - Rat - LCLo = 500 ppm/4H
Orl - Mus - LD50 = 1041 mg/kg
Skn - Rat - LD50 = 5080 mg/kg
Skn - Rbt - LD50 = 5080 mg/kg
Irritation Data:
Skn - Rbt = 10 mg/24H - open - Severe
Skn - Rbt = 9300 ug/24H - open Severe
Eye - Rbt = 500 mg/24H - Modereate

Benzene is a contaminant of the petroleum distillate. Exposure to high concentrations of benzene may cause breathlessness, irritability, euphorea, giddiness, eye, nose, and respiratory tract irritation. Severe exposuree may lead to convulsions and loss of consciousness. Repeated or prolonged exposure at low concentrations may result in various blood disorders, ranging from anemia to leukemia. Benzene is recognized by OSHA, NTP, and IARC as a human carcinogen, and regulated under 29 CFR 1910.1028. For further information regarding the hazards and control of benzene, please see the appendices of the aforementioned regulation.

Benzene is known to the State of California to cause cancer. Benzene is regulated in California under the Safe Drinking Water & Toxic Enforcement Act of 1986 (Proposition 65).

TARGET ORGANS (29 CFR 1910.1200-APPENDIX A):

Eye Hazard
Cutaneous Hazard (Skin)

MATERIAL SAFETY DATA SHEET

Printed 02-18-1997

OREPREP DCPD

CAUTION CODE 3-3-0
MSDS ID: DCPD

5 - SECTION V - HEALTH HAZARDS (continued)

Pulmonary Agent (Lungs)
Hepatotoxin (Liver)

6 - SECTION VI - EMERGENCY & FIRST AID PROCEDURES

EYE CONTACT: Flush eyes immediately with large amounts of water for at least 15 minutes. Call a physician if irritation persists.
INHALATION: Remove to fresh air. If not breathing, give artificial respiration. If breathing is labored, administer oxygen. If irritation or adverse symptoms develop, seek medical attention.
SKIN CONTACT: Remove contaminated clothes. Wash skin thoroughly with mild soap and water. Launder clothes before reuse.
INGESTION: If swallowed, seek medical attention. ONLY induce vomiting at the instructions of medical personnel. Never give anything by mouth to an unconscious person.

7 - SECTION VII - PROTECTIVE EQUIPMENT RECOMMENDATIONS

VENTILATION: The use of mechanical ventilation is recommended whenever this product is used in a confined space, is heated above ambient temperatures, or is agitated. Where engineering controls are not feasible, assure use is in an area where there is natural air movement.

Under normal operating conditions, no excursions above the regulated (recommended) exposure levels should occur. However, if used at elevated temperatures, lower atmospheric pressure (high altitudes) or any other physical conditions that may increase the inhalation exposure, respiratory protective equipment as described below, should be worn. Also, due to individual susceptibility and sensitivity, before respirators are used, a full medical evaluation should be performed per 29 CFR 1910.134(b)(10).

RESPIRATORY	CHEMICAL RESISTANT APPAREL	EYE/FACE
X As Needed	X Gloves	X Goggles
Air Supplied (SCBA)	Clothing	Full Face Shield
X Air Purifying	Boots	
X Full Face Piece		
Half Face Piece		
X Cartridge or Cannister		
Acid Gas		
X Organic Vapor		
Ammonia		

A thorough review of the job task (job safety analysis) by a competent safety professional should be conducted to determine the appropriate level of protection. See 29 CFR 1910, Subpart I and 29 CFR 1910.133 for further information.

8 - SECTION VIII - SPILL & LEAK PROCEDURES

Don appropriate protective clothing and respiratory protection prior to entering a spill/leak area. Eliminate ignition sources. Approach area upwind if possible. Shut off leak if it can be done safely. Dike and pump large spills into salvage containers. Soak up residue and small spills with absorbent clay, sand, or dirt and place in salvage containers. If RQ (reportable quantity) is exceeded, report to National Spill Response Office 1-800-424-8802. Also, in some jurisdictions, spills or leaks of any hazardous materials are reportable--consult local lead agencies for further information. Continue to observe precautions.

WASTE DISPOSAL METHOD(S): Re-evaluation of the product may be required by the user at the time of disposal, since the product uses, transformations, mixtures and processes may change the classification to non-hazardous, or hazardous for reasons other than, or in addition to product characteristics. Dispose of all waste and/or containers in accordance with federal, state and local regulations.

REQUIREMENTS FOR TRANSPORTATION, HANDLING AND STORAGE: Transport, handle and store in accordance with OSHA Regulation 1910.106 and applicable DOT regulations.
Avoid inhalation of vapors or mists. Do not get in eyes,on skin or on clothing Keep container closed when not in use. Wear suitable protection for eyes and skin when handling. Use with adequate ventilation. Avoid contact with oxidizers. Store in well-ventilated area. Store in cool, dry area.
Control ignition source; keep away from heat, sparks and open flame. Use properly grounded electrical equipment when working with this product.
CAUTION: THIS PRODUCT CONTAINS A CANCER HAZARD

NOTE: The information on this MSDS is based on data which is considered to be accurate. Baker Performance Chemicals Incorporated, however makes no guarantees or warranty, either expressed or implied of the accuracy or completeness of this information.

The conditions or methods of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of this product.

This MSDS was prepared and is to be used only for this product. If the product is used as a component in another product, this MSDS information may not be applicable.

By: Anita Wright Date: 4/6/93 Supercedes: New
Regulatory Information Technician

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

Shell

MSDS NUMBER ▶ 7,157-6

97368 (4-85)

24 HOUR EMERGENCY ASSISTANCE				**GENERAL MSDS ASSISTANCE**
SHELL: 713-473-9461 CHEMTREC: 800-424-9300				SHELL: 713-241-4819
ACUTE HEALTH * 1	FIRE 2	REACTIVITY 0	HAZARD RATING ▶	LEAST - 0 SLIGHT - 1 MODERATE - 2 HIGH - 3 EXTREME - 4

*For acute and chronic health effects refer to the discussion in Section III

BE SAFE
READ OUR PRODUCT SAFETY INFORMATION
... AND
PASS IT ON
(PRODUCT LIABILITY LAW REQUIRES IT)

SECTION I NAME

PRODUCT ▶	NEODENE(R) 1112 INTERNAL OLEFIN
CHEMICAL NAME ▶	INTERNAL OLEFIN BLEND
CHEMICAL FAMILY ▶	OLEFIN
SHELL CODE ▶	31904

SECTION II-A PRODUCT/INGREDIENT

NO.	COMPOSITION	CAS NUMBER	PERCENT
P	NEODENE 1112 INTERNAL OLEFIN	MIXTURE	100
1	ALKENES, C10-16	68991-52-6	>99
2	OTHER RANGE OLEFINS	MIXTURE	<1

SECTION II-B ACUTE TOXICITY DATA

NO.	ACUTE ORAL LD50	ACUTE DERMAL LD50	ACUTE INHALATION LC50
P	NONE ESTABLISHED		

SECTION III HEALTH INFORMATION

THE HEALTH EFFECTS NOTED BELOW ARE CONSISTENT WITH REQUIREMENTS UNDER THE OSHA HAZARD COMMUNICATION STANDARD (29 CFR 1910.1200).

EYE CONTACT
PRODUCT IS IRRITATING TO THE EYES.

SKIN CONTACT
PRODUCT IS IRRITATING TO THE SKIN. PROLONGED OR REPEATED LIQUID CONTACT CAN RESULT IN DEFATTING AND DRYING OF THE SKIN WHICH MAY RESULT IN SKIN IRRITATION AND DERMATITIS.

INHALATION
THIS PRODUCT IS PRESUMED TO HAVE A LOW ORDER OF ACUTE INHALATION TOXICITY.

INGESTION
BASED ON ESSENTIALLY SIMILAR PRODUCT TESTING, PRODUCT IS SLIGHTLY TOXIC, BUT INGESTION MAY RESULT IN VOMITING; ASPIRATION (BREATHING) OF VOMITUS INTO THE LUNGS MUST BE AVOIDED AS EVEN SMALL QUANTITIES MAY RESULT IN ASPIRATION PNEUMONITIS.

SIGNS AND SYMPTOMS
IRRITATION AS NOTED ABOVE. ASPIRATION PNEUMONITIS MAY BE EVIDENCED BY COUGHING, LABORED BREATHING AND CYANOSIS (BLUISH SKIN); IN SEVERE CASES DEATH MAY OCCUR.

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

PRODUCT NAME: NEODENE(R) 1112 INTERNAL OLEFIN **MSDS 7,157-6**

AGGRAVATED MEDICAL CONDITIONS
PREEXISTING SKIN AND EYE DISORDERS MAY BE AGGRAVATED BY EXPOSURE TO THIS PRODUCT.

SECTION IV OCCUPATIONAL EXPOSURE LIMITS

	OSHA		ACGIH		OTHER
NO.	**PEL/TWA**	**PEL/CEILING**	**TLV/TWA**	**TLV/STEL**	

NONE ESTABLISHED.

SECTION V EMERGENCY AND FIRST AID PROCEDURES

EYE CONTACT
FLUSH EYES WITH PLENTY OF WATER FOR 15 MINUTES WHILE HOLDING EYELIDS OPEN.

SKIN CONTACT
REMOVE CONTAMINATED CLOTHING/SHOES AND WIPE EXCESS FROM SKIN. FLUSH SKIN WITH WATER. FOLLOW BY WASHING WITH SOAP AND WATER. IF IRRITATION OCCURS, GET MEDICAL ATTENTION. DO NOT RESUE CLOTHING UNTIL CLEANED.

INHALATION
REMOVE VICTIM TO FRESH AIR AND PROVIDE OXYGEN IF BREATHING IS DIFFICULT. GET MEDICAL ATTENTION.

INGESTION
DO NOT INDUCE VOMITING. IF VOMITING OCCURS SPONTANEOUSLY, KEEP HEAD BELOW HIPS TO PREVENT ASPIRATION OF LIQUID INTO THE LUNGS. GET MEDICAL ATTENTION.*

NOTE TO PHYSICIAN
*IF MORE THAN 2.0 ML PER KG HAS BEEN INGESTED AND VOMITING HAS NOT OCCURRED, EMESIS SHOULD BE INDUCED WITH SUPERVISION. KEEP VICTIM'S HEAD BELOW HIPS TO PREVENT ASPIRATION. IF SYMPTOMS SUCH AS LOSS OF GAG REFLEX, CONVULSIONS OR UNCONSCIOUSNESS OCCUR BEFORE EMESIS, GASTRIC LAVAGE USING A CUFFED ENDOTRACHEAL TUBE SHOULD BE CONSIDERED.

SECTION VI SUPPLEMENTAL HEALTH INFORMATION

NONE IDENTIFIED.

SECTION VII PHYSICAL DATA

BOILING POINT: 365-414 (DEG F)	SPECIFIC GRAVITY: .76 @ 60/60 DEG F (H2O=1)	VAPOR PRESSURE: 0.9@100 DEG. F (MM HG)
MELTING POINT: NOT AVAILABLE (DEG F)	SOLUBILITY: VERY SLIGHT (IN WATER)	VAPOR DENSITY: APX. 5.6 (AIR=1)

EVAPORATION RATE (N-BUTYL ACETATE = 1):

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

PRODUCT NAME: NEODENE(R) 1112 INTERNAL OLEFIN **MSDS 7,157-6**

APPEARANCE AND ODOR:
COLORLESS LIQUID. MILD HYDROCARBON ODOR.

SECTION VIII FIRE AND EXPLOSION HAZARDS

FLASH POINT AND METHOD:	**FLAMMABLE LIMITS /% VOLUME IN AIR**
158 DEG F SETAFLASH	LOWER: N/AV UPPER: N/AV

EXTINGUISHING MEDIA
USE WATER FOG, FOAM, DRY CHEMICAL OF CO2. DO NOT USE A DIRECT STREAM OF WATER. PRODUCT WILL FL AND CAN BE REIGNITED ON SURFACE WATER.

SPECIAL FIRE FIGHTING PROCEDURES AND PRECAUTIONS
CAUTION. COMBUSTIBLE. DO NOT ENTER CONFINED FIRE SPACE WITHOUT FULL BUNKER GEAR (HELMET WITH FACE SHIELD, BUNKER COATS, GLOVES AND RUBBER BOOTS), INCLUDING A POSITIVE PRESSURE NIOSH APPROVED SELF-CONTAINED BREATHING APPARATUS. COOL FIRE EXPOSED CONTAINERS WITH WATER.

UNUSUAL FIRE AND EXPLOSION HAZARDS
CONTAINERS EXPOSED TO INTENSE HEAT FROM FIRES SHOULD BE COOLED WITH WATER TO PREVENT VAPOR PRESSUR BUILDUP WHICH COULD RESULT IN CONTAINER RUPTURE. CONTAINER AREAS EXPOSED TO DIRECT FLAME CONTAC SHOULD BE COOLED WITH LARGE QUANTITIES OF WATER AS NEEDED TO PREVENT WEAKENING OF CONTAINER STRUCTURE.

SECTION IX REACTIVITY

STABILITY: STABLE HAZARDOUS POLYMERIZATION: WILL NOT OCCUR

CONDITIONS AND MATERIALS TO AVOID:
AVOID CONTACT WITH OXIDIZING AGENTS.

HAZARDOUS DECOMPOSITION PRODUCTS
CARBON MONOXIDE AND UNIDENTIFIED ORGANIC COMPOUNDS MAY BE FORMED DURING COMBUSTION.

SECTION X EMPLOYEE PROTECTION

RESPIRATORY PROTECTION
IF EXPOSURE MAY OR DOES EXCEED OCCUPATIONAL EXPOSURE LIMITS (SEC. IV) USE A NIOSH-APPROVED RESPIRATOR TO PREVENT OVEREXPOSURE. IN ACCORD WITH 29 CFR 1910.134 USE EITHER AN ATMOSPHERE-SUPPLYING RESPIRATOR OR AN AIR-PURIFYING RESPIRATOR FOR ORGANIC VAPORS.

PROTECTIVE CLOTHING
AVOID CONTACT WITH EYES. WEAR SAFETY GLASSES OR GOGGLES AS APPROPRIATE. AVOID PROLONGED OR REPEATED CONTACT WITH SKIN. WEAR CHEMICAL RESISTANT GLOVES AND OTHER CLOTHING AS REQUIRED TO MINIMIZE CONTACT.

ADDITIONAL PROTECTIVE MEASURES
USE EXPLOSION-PROOF VENTILATION AS REQUIRED TO CONTROL VAPOR CONCENTRATIONS.

SECTION XI ENVIRONMENTAL PROTECTION

SPILL OR LEAK PROCEDURES
CAUTION. COMBUSTIBLE. SPILLED MATERIAL IS SLIPPERY. *** LARGE SPILLS *** ELIMINATE POTENTIAL SOURCES OF IGNITION. WEAR APPROPRIATE RESPIRATOR AND OTHER PROTECTIVE CLOTHING. SHUT OFF SOURCE OF LEAK ONLY IF SAFE TO DO SO. DIKE AND CONTAIN. REMOVE WITH VACUUM TRUCKS OR PUMP TO STORAGE/SALVAGE VESSELS. SOAK UP RESIDUE WITH AN ABSORBENT SUCH AS CLAY, SAND, OR OTHER SUITABLE MATERIAL; PLACE IN NON-LEAKING CONTAINERS AND SEAL TIGHTLY FOR PROPER DISPOSAL. FLUSH AREA WITH WATER TO REMOVE TRACE RESIDUE; DISPOSE OF FLUSH SOLUTION AS ABOVE. *** SMALL SPILLS *** TAKE UP WITH AN ABSORBENT MATERIAL AND PLACE IN NON-LEAKING CONTAINERS FOR PROPER DISPOSAL.

PRODUCT NAME: NEODENE(R) 1112 INTERNAL OLEFIN **MSDS 7,157-6**

SECTION XII SPECIAL PRECAUTIONS

KEEP LIQUID AND VAPOR AWAY FROM HEAT, SPARKS AND FLAME. SURFACES THAT ARE SUFFICIENTLY HOT MAY IGNITE EVEN LIQUID PRODUCT IN THE ABSENCE OF SPARKS OR FLAME. EXTINGUISH PILOT LIGHTS, CIGARETTES AND TURN OFF OTHER SOURCES OF IGNITION PRIOR TO USE AND UNTIL ALL VAPORS ARE GONE.

WASH WITH SOAP AND WATER BEFORE EATING, DRINKING, SMOKING OR USING TOILET FACILITIES. LAUNDER CONTAMINATED CLOTHING BEFORE REUSE.

SECTION XIII TRANSPORTATION REQUIREMENTS

DEPARTMENT OF TRANSPORTATION CLASSIFICATION:
COMBUSTIBLE LIQUID, III

D.O.T. PROPER SHIPPING NAME:
COMBUSTIBLE LIQUID, N.O.S. (CONTAINS 1-UNDECENE, 1-DODECENE)

OTHER REQUIREMENTS:
NA1993, GUIDE 128. NOT REGULATED BY D.O.T. IF IN A CONTAINER OF 119 GALLON CAPACITY OR LESS.

SECTION XIV OTHER REGULATORY CONTROLS

THIS PRODUCT IS LISTED ON THE EPA/TSCA INVENTORY OF CHEMICAL SUBSTANCES.

PROTECTION OF STRATOSPHERIC OZONE (PURSUANT TO SECTION 611 OF THE CLEAN AIR ACT AMENDMENTS OF 1990): PER 40 CFR PART 82, THIS PRODUCT DOES NOT CONTAIN NOR WAS IT DIRECTLY MANUFACTURED WITH ANY CLASS I OR CLASS II OZONE DEPLETING SUBSTANCES.

IN ACCORDANCE WITH SARA TITLE III, SECTION 313, THE ENVIRONMENTAL DATA SHEET (EDS) SHOULD ALWAYS BE COPIED AND SENT WITH THE MSDS.

SECTION XV STATE REGULATORY INFORMATION

BASED ON INFORMATION AVAILABLE TO SHELL, THIS PRODUCT DOES NOT CONTAIN ANY CHEMICAL SUBSTANCE REGULATED BY A SPECIFIC STATE LIST.

SECTION XVI SPECIAL NOTES

THIS MSDS REVISION HAS CHANGES IN SECTION XIII.

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

PRODUCT NAME: NEODENE(R) 1112 INTERNAL OLEFIN **MSDS 7 157-6**

DATE PREPARED: JUNE 15, 1993

J. C. WILLETT

BE SAFE

READ OUR PRODUCT
SAFETY INFORMATION ...AND PASS IT ON
(PRODUCT LIABILITY LAW
REQUIRES IT)

SHELL OIL COMPANY
PRODUCT SAFETY AND COMPLIANCE
P. O. BOX 4320
HOUSTON, TX 77210

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

Shell

ENVIRONMENTAL DATA SHEET

EDS NUMBER ▶ 7,157-1

97449 (9-87)

PRODUCT ▶	NEODENE(R) 1112 INTERNAL OLEFIN
PRODUCT CODE ▶	31904

SECTION I PRODUCT/COMPOSITION

NO.	COMPONENT	CAS NUMBER	PERCENT
P	NEODENE 1112 INTERNAL OLEFIN	MIXTURE	100
1	ALKENES, C10-16	68991-52-6	>99
2	OTHER CARBON RANGE OLEFINS	MIXTURE	<1

SECTION II SARA TITLE III INFORMATION

NO.	EHS RQ (LBS) (*1)	EHS TPQ (LBS) (*2)	SEC 313 (*3)	313 CATEGORY (*4)	311/312 CATEGORIES (*5)
P					H-1, P-3

FOOTNOTES

*1 = REPORTABLE QUANTITY OF EXTREMELY HAZARDOUS SUBSTANCE, SEC.302
*2 = THRESHOLD PLANNING QUANTITY, EXTREMELY HAZARDOUS SUBSTANCE, SEC 302
*3 = TOXIC CHEMICAL, SEC 313
*4 = CATEGORY AS REQUIRED BY SEC 313 (40 CFR 372.65 C), MUST BE USED ON TOXIC RELEASE INVENTORY FORM
*5 = HAZARD CATEGORY FOR SARA SEC. 311/312 REPORTING
HEALTH H-1 = IMMEDIATE (ACUTE) HEALTH HAZARD H-2 = DELAYED (CHRONIC) HEALTH HAZARD
PHYSICAL P-3 = FIRE HAZARD P-4 = SUDDEN RELEASE OF PRESSURE HAZARD
P-5 = REACTIVE HAZARD

SECTION III ENVIRONMENTAL RELEASE INFORMATION

SECTION IV RCRA INFORMATION

PLACE IN AN APPROPRIATE DISPOSAL FACILITY IN COMPLIANCE WITH LOCAL REGULATIONS.

APPENDIX A-4
NEODENE C_{11}-C_{12} INTERNAL OLEFIN

PRODUCT NAME: NEODENE(R) 1112 INTERNAL OLEFIN EDS 7,157-1

DATE PREPARED: OCTOBER 19, 1992

SHELL OIL COMPANY
CORPORATE ENVIRONMENTAL AFFAIRS
P. O. BOX 4320
HOUSTON, TX 77210

FOR ADDITIONAL INFORMATION ON THIS ENVIRONMENTAL DATA PLEASE CALL
(713) 241-2252

FOR EMERGENCY ASSISTANCE PLEASE CALL
SHELL: (713) 473-9461
CHEMTREC: (800) 424-9300

APPENDIX A-5
DI PENTENE (LIMONENE)

Material Safety Data Sheet

Section 1: CHEMICAL IDENTIFICATION

Name: **Limonene**. (CAS #: 0138-86-3) RTECS # 098100000	Chemical Family: Terpene Molecular Formula: $C_{10}H_{16}$ Molecular Weight: 136.24

Synonyms: Acintene DP * Acintene DP Dipentene * Cajeputene * Cinene * Dipanol * Dipentene (DOT) * Eulimen * Flavor orange * Inactive Limonene * Kautschin * Limonene * Dl-Limonene * P-Mentha-1,8-Diene, Dl- * 1,8(9)-P-menthadiene * P-Menthane * 1-Methyl-4-Isopropenyl-1-Cyclohexene * Nesol * Orange Flavor * Delta-1,8-Terpodiene * UN2052 (DOT) * Unitene

Section 2: COMPOSITION/INFORMATION ON INGREDIENTS

Limonene, CAS # 0138; Percent: 100% Other Contaminants: None	CERLA Ratings (Scale 0-3): Health=1; Fire=2; Reactivity=0; Persistence=1 NFPA Ratings (Scale 0-4): Health=0; Fire=2; Reactivity=0 No Occupational limits established by OSHA, ACGIH, or NIOSH

Section 3: HAZARDS IDENTIFICATION

Label Precautionary Statements: Combustible (USA); Flammable (EU); Harmful
Harmful by inhalation, in contact with skin and if swallowed.
Irritating to eyes, respiratory system and skin.
May cause sensitization by inhalation and skin contact.
In case of accident or if you feel unwell seek medical advice immediately (show the label where possible).
In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
Take off immediately all contaminated clothing.
Wear suitable protective clothing, gloves and eye/face protection.

Section 4: FIRST-AID MEASURES

In case of contact, immediately flush eyes or skin with copious amounts of water for at least 15 minutes while removing contaminated clothing and shoes. If inhaled, remove to fresh air. If not breathing give artificial respiration. If breathing is difficult, give oxygen. If swallowed, wash out mouth with water provided person is conscious. Call a physician. Remove and wash contaminated clothing promptly.

Section 5: FIRE FIGHTING MEASURES

Extinguishing media: Carbon Dioxide, Dry chemical powder or appropriate foam.
Special Firefighting Procedures: Wear self-contained breathing apparatus and protective clothing to prevent contact with skin and eyes. Use water spray to cool fire-exposed containers. Combustible liquid.
Unusual Fire and explosions Hazards: Vapor may travel considerable distance to source of ignition and flash back. Container explosion may occur under fire conditions. Forms explosive mixtures in air.

Section 6: ACCIDENTAL RELEASE MEASURES

Evacuate area. Shut off all sources of ignition. Wear self-contained breathing apparatus, rubber boots and heavy rubber gloves. Cover with and activated carbon adsorbent, take up and place in closed containers. Transport outdoors. Ventilate area and wash spill site after material pickup is complete.

Section 7: HANDLING AND STORAGE (Also, Refer to section 8)

Spill/Leak: Notify safety personnel. Eliminate sources of ignition, and institute cleanup procedures. Pump or vacuum spilled limonene into suitable containers for disposal. Alternatively soak up spilled limonene with an absorbent such as vermiculite or sawdust and place it into appropriate containers for disposal. Cleanup personnel should wear protective gloves and aprons to prevent this material from contacting skin or eyes.

APPENDIX A-5
DI PENTENE (LIMONENE)

Section 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

Chemical safety goggles. Rubber gloves. Safety shower and eye bath. Mechanical exhaust required. NIOSH/MSHA-approved respirator. Do not breathe vapor. Avoid contact with eyes, skin and clothing. Avoid prolonged or repeated exposure. Wash thoroughly after handling. Irritant. Harmful liquid and fumes. Sensitizer. Keep tightly closed. Keep away from heat and open flame. Store in a cool dry place.

Section 9: PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	colorless liquid	Autoignition Temperature:	458 F
Odor:	Pleasant lemon-like	Vapor Pressure:	1 mm 20 C
Physical Properties:		Specific Gravity:	0.856
Boiling Point:	170 C to 180 C	Vapor Density:	>4.7 @ 80 C
Flashpoint:	110 F/43 C	Melting point:	-96 C
Explosion Limits in Air:	Upper 6.1% 150 C	Evaporation Rate:	Not Available
	Lower 0.7% 150 C	Solubility in water:	Slightly soluble
		Solvents:	Alcohol, Ether

Section 10: STABILITY AND REACTIVITY

Stability: Limonene is stable in closed containers during routine operations at room temperature.
Incompatibilities: Limonene can react dangerously with a mixture of Iodine Pentafluoride and tetra floro ethylene. Not compatible with oxidizing agents.
Conditions to avoid: Do not accidentally heat Limonene. Prevent its contact with skin or eyes because it is a skin irritant.
Hazardous Combustion or Decomposition Products: Thermal oxidative degeneration of Limonene can produce toxic gases such as Carbon Monoxide and Carbon Dioxide

Section 11: TOXICOLOGICAL INFORMATION

Acute effects: Harmful if inhaled or swallowed. Vapor or mist is irritating to the eyes, mucous membranes and upper respiratory tract. Causes skin irritation. May cause allergic respiratory and skin reactions.
RTECS #: 058100000
P-Mentha-1,8-Diene
Irritation Data: SKN-RBT 500 mg/24H MDD FCTXAV 12,703,74
Toxicity Data
ORL-MUS LD50:5550 μl/kg (ZYZAEU 24,700,89) IVN-MUS LD50:1010 μl/kg (ZYZAEU 24,700,89)
Only selected registry of toxic effects of chemical substances (RTECS) data is presented here. See actual entry in RTECS for complete information.

Section 12: ECOLOGICAL INFORMATION

Data not yet available.

Section 13: DISPOSAL CONSIDERATIONS

This combustible material may be burned in a chemical incinerator equipped with an after burner and scrubber. Observe all federal, State and Local Environmental Regulations.

Section 14: TRANSPORT INFORMATION

Contact chemical company for transportation information.

Section 16: OTHER INFORMATION

The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide.

APPENDIX A-6
VINYL TOLUENE

------------------ IDENTIFICATION -------------------

PRODUCT #: 30898-6

NAME: 3(4)-METHYLSTYRENE, 98%, MIXTURE OF ISOMERS

CAS #: 39294-88-7

MF: C9H10

SYNONYMS

METHYLSTYRENE * NCI-C56406 * TOLUENE, VINYL- (MIXED ISOMERS) * UN 2618 (DOT) * VINYLTOLUENE * VINYL TOLUENE (ACGIH,OSHA) * VINYL TOLUENES (MIXED ISOMERS), INHIBITED (DOT) *

------------------ TOXICITY HAZARDS -------------------

RTECS NO: WL5075000

STYRENE, METHYL-

IRRITATION DATA

SKN-RBT 100% MOD	AMIHAB 14,387,56
EYE-RBT 90 MG MLD	AMIHAB 14,387,56

TOXICITY DATA

ORL-RAT LD50:4 GM/KG	AMIHAB 14,387,56
ORL-MUS LD50:3160 MG/KG	HYSAAV 34(7-9),334,69
IHL-MUS LC50:3020 MG/M3	HYSAAV 34(7-9),334,69

APPENDIX A-6
VINYL TOLUENE (continued)

REVIEWS, STANDARDS, AND REGULATIONS

ACGIH TLV-TWA 50 PPM; STEL 100 PPM 85INA8 5,630,86

MSHA STANDARD-AIR:TWA 100 PPM (480 MG/M3) DTLVS* 3,278,71

OSHAPEL:8H TWA 100 PPM (480 MG/M3) FEREAC 54,2923,89

OSHAPEL FINAL:8H TWA 100 PPM (480 MG/M3) FEREAC 54,2923,89

EPA TSCA CHEMICAL INVENTORY, 1986

EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JANUARY 1989

NIOSH ANALYTICAL METHODS: SEE HYDROCARBONS, AROMATIC, 1501

NTP CARCINOGENESIS STUDIES;TEST COMPLETED (PEER REVIEW), FEBRUARY 1989

MEETS CRITERIA FOR PROPOSED OSHA MEDICAL RECORDS RULE FEREAC 47,30420 82

TARGET ORGAN DATA

SENSE ORGANS AND SPECIAL SENSES (OTHER OLFACTION EFFECTS)

SENSE ORGANS AND SPECIAL SENSES (OTHER EYE EFFECTS)

ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

APPENDIX A-6
VINYL TOLUENE (continued)

------------------ HEALTH HAZARD DATA -----------------

ACUTE EFFECTS

MAY BE HARMFUL BY INHALATION, INGESTION, OR SKIN ABSORPTION.

VAPOR OR MIST IS IRRITATING TO THE EYES, MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.

CAUSES SKIN IRRITATION.

TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.

FIRST AID

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.

IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.

CALL A PHYSICIAN.

WASH CONTAMINATED CLOTHING BEFORE REUSE.

APPENDIX A-6
VINYL TOLUENE (continued)

-------------------- PHYSICAL DATA --------------------

SPECIFIC GRAVITY: 0.896

APPEARANCE AND ODOR

COLORLESS LIQUID

------------ FIRE AND EXPLOSION HAZARD DATA -----------

FLASHPOINT: 119 F BY:

EXTINGUISHING MEDIA

WATER SPRAY.

CARBON DIOXIDE, DRY CHEMICAL POWDER, ALCOHOL OR POLYMER FOAM.

SPECIAL FIREFIGHTING PROCEDURES

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.

COMBUSTIBLE LIQUID.

UNUSUAL FIRE AND EXPLOSIONS HAZARDS

EMITS TOXIC FUMES UNDER FIRE CONDITIONS.

------------------- REACTIVITY DATA -------------------

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

APPENDIX A-6
VINYL TOLUENE (continued)

TOXIC FUMES OF:

CARBON MONOXIDE AND CARBON DIOXIDE

--------------- SPILL OR LEAK PROCEDURES --------------

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

WEAR RESPIRATOR, CHEMICAL SAFETY GOGGLES, RUBBER BOOTS AND HEAVY RUBBER GLOVES.

COVER WITH DRY LIME OR SODA ASH, PICK UP, KEEP IN A CLOSED CONTAINER AND HOLD FOR WASTE DISPOSAL.

VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

WASTE DISPOSAL METHOD

THIS COMBUSTIBLE MATERIAL MAY BE BURNED IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER.

OBSERVE ALL FEDERAL, STATE, AND LOCAL LAWS.

--- PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE ---

CHEMICAL SAFETY GOGGLES.

COMPATIBLE CHEMICAL RESISTANT GLOVES.

NIOSH/MSHA-APPROVED RESPIRATOR.

SAFETY SHOWER AND EYE BATH.

MECHANICAL EXHAUST REQUIRED.

DO NOT BREATHE VAPOR.

AVOID CONTACT WITH EYES, SKIN AND CLOTHING.

WASH THOROUGHLY AFTER HANDLING.

IRRITANT.

HARMFUL VAPOR.

KEEP TIGHTLY CLOSED.

KEEP AWAY FROM HEAT AND OPEN FLAME.

STORE IN A COOL DRY PLACE.

--------- ADDITIONAL PRECAUTIONS AND COMMENTS ---------

SECTION 9 FOOTNOTES

STABILIZED WITH 50 PPM 4-TERT-BUTYLPYROCATECHOL.

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. SIGMA-ALDRICH SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE

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