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VALUATION OF WOOD LIGNIN AS A SUBSTITUTE R EXTENDER OF ASPHALT

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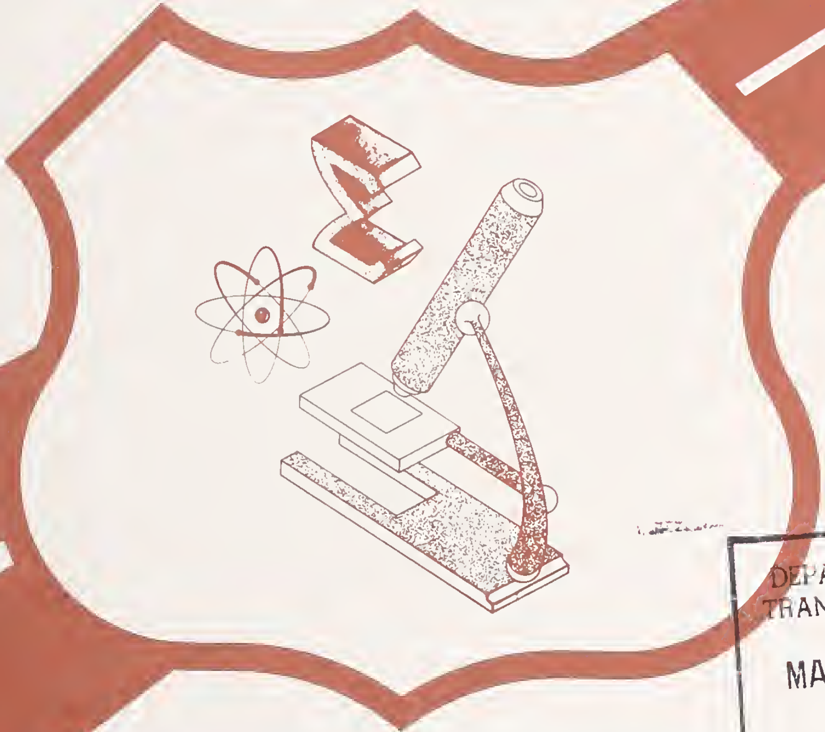
Final Report



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FOREWORD

This study presents the findings of an FHWA administrative contract research study conducted by the University of Washington. The study was concerned with the evaluation of wood lignin as a potential replacement for asphalt in highway paving mixtures. The findings will be of interest to researchers interested in identifying alternatives to asphalt in highway construction.

Types of wood lignin currently produced as byproducts of pulp and papermaking operations were screened in the laboratory as either a complete substitute or a partial replacement for asphalt in paving mixtures. Promising materials were further evaluated in detail using the binder alone and in full-scale lignin-asphalt paving mixtures. The report concludes that it is technically feasible to use wood lignins to successfully replace a portion of the asphalt in flexible paving mixtures, but that from an economic standpoint the exploitation of this technology must await higher asphalt prices.

This report is being distributed on an individual basis to interested researchers and technologists. Additional copies of the report for the public are available from the National Technical Information Service (NTIS), Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.

Charles F. Scheffey

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16. Abstract

This report covers an extensive evaluation of the feasibility of using wood lignin as a substitute or extender of asphalt in paving mixtures. The decreasing supply and escalating price of asphalt has accelerated the search for alternatives. Lignin, the cementitious material that binds wood fibers together, is a by-product of the paper manufacturing industry. The material is available on a continuing basis and in large quantities since wood is a renewable resource. Lignins are extracted from wood using chemicals in two principal processes: kraft and sulfite.

The project was aimed at evaluating the use of lignins in three possible ways: (1) alone as a substitute for asphalt, (2) as an extender for asphalt cement in hot mixtures, and (3) as an extender of emulsified asphalt in conjunction with rubber in cold mixtures. Extensive screening of many binder candidates and formulations was made on the basis of binder properties and mixing with sand to make test cylinders. The most promising materials were further evaluated using both binder and full scale lignin asphalt pavement mixtures and were compared to conventional mixtures. Additional evaluation regarding environmental exposure, expected structural performance and economic feasibility was also included as a key part of the research.

The general conclusions developed during this study are that both the technical and economic feasibilities of using wood lignin as a partial replacement for asphalt are positive. However, using lignin alone as a substitute for asphalt was not found to be possible in this study. Laboratory studies have shown that mixtures with lignin asphalt binders have similar and possibly improved engineering properties as compared to conventional paving mixtures. Although not currently economically feasible, lignin asphalt pavements will soon be a viable alternative as the cost of asphalt increases.

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PREFACE

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LIST OF TABLES

No. Title Page

2.1. Summary of binder test results for lignin alone. 15
2.2. Characteristics of prepared lignin sulfonate binders 20
2.3. Characteristics of prepared lignin sulfonate binders 21
2.4. Comparison of binder characteristics 29
3.1. Summary of lignin-asphalt binders test results 45
3.2. Phase B test results 47
3.3. Mix design data, swell test results. 50
3.4. Percent indirect tensile strength gain after swell test. 51
3.5. Physical properties of Steilacoom aggregate. 52
3.6. Physical properties of asphalt cements 54
3.7. Composition of AC-5 paving asphalt 54
3.8. Summary of binder test results 55
3.9. Viscosity and other properties of lignin binders 59
3.10. Viscosity and pellet abrasion measurements of lignin-asphalt binders, both unaged and aged under various conditions 61
3.11. Summary of various mix design data 66
3.12. Optimum binder content, percent by weight of dry aggregate . . .71
3.13. Preliminary binder properties. 74
3.14 Summary of binder test results 86
3.15. Summary of test results for calcium lignin sulfonate mixtures using granite aggregates .87
3.16. Summary of test results for calcium lignin sulfonate mixture using limestone aggregate. 88
3.17. Resilient modulus (M_R) after freeze-thaw conditioning for different binder contents .93
3.18. Percentage M_R retained after freeze and thaw conditioning. . . .94
3.19. Resilient modulus (M_R) after 60°C temperature conditioning . . .95
3.20. Resilient modulus (M_R) after weather exposure. 96
3.21. Physical properties of lignin extended asphalt binders 119
3.22. Proximate analysis of coal 122
4.1. Kraft pine lignins[a]. 129
4.2. Asphalt and emulsified asphalts. 131
4.3. Rubber latices 132
4.4. Gradations of aggregates used in lignin concrete mixes. 134
4.5. Methods of preparation and testing of concretes containing kraft lignins. 137
4.6. Properties of Ottawa sand mixes[a] with lignin-based binders . . 141
4.7. Density and unconfined compressive strength of lignin-asphalt rubber concretes 142
4.8. Density and unconfined compressive strength of dense-graded[a] mixes containing alkali lignin, asphalt and rubber 146
4.9. Cohesion of dense-graded concrete[a] with lignin-asphalt and lignin-asphalt-rubber binders. 147
4.10. Density and unconfined compressive strength of unaged and roof-aged lignin concrete briquets[a] containing polyvinyl acetate. . 149
4.11. Effect of variation in type of rubber on density and compressive strengths of lignin-asphalt-rubber bound concrete 152
4.12. Effects of water content of binder at time of compaction of briquets[a]. 153

No. Title Page

4.13. Compressive strength of lignin-asphalt-rubber concrete four inch briquets compacted in kneading compactor at binder water content of 50% . . . 154
5.1 The radiated energy in watts of Hanovia Vapor Lamp . . . 163
5.2. Composition of 4 briquet samples used in Series 1 . . . 165
5.3. Composition of 10 briquet samples used in Series 2 . . . 166
5.4. Composition of 10 briquet samples used in Series 3 . . . 167
5.5. Composition of 19 binder samples used in Series 4. Date: 10/1/77 to 10/13/77 . . . 168
5.6. Test results for Series One . . . 171
5.7. Test results for Series Two . . . 172
5.8. Results of kraft lignin binder samples in Test Series No. 3 . . . 175
5.9. Results of 100% AC-5 control binder samples in Test Series No. 3 . . . 175
5.10. Results of Test Series No. 3 for binder samples with 30 percent lignin . . . 176
5.11. Results of fourth test series binder samples exposed to U.V. radiation . . . 177
5.12. Results of fourth test series binder samples not exposed to U.V. radiation . . . 177
5.13. Lignin/AC-5 briquets exposure[a] tests at Indio, California . . . 178
6.1. Summary of final moduli for base and subgrade layers determined at two critical locations . . . 182
6.2. Summary of maximum strains at bottom of surface layer and on top of subgrade at two critical locations . . . 183
6.3. Limiting vertical strain on top of subgrade . . . 184
6.4. Summary of rut depth prediction results of various mixes with various thicknesses . . . 186
6.5. Summary of roughness prediction results of various mixes with various thicknesses . . . 186
6.6. Summary of fatigue cracking prediction results of various mixes with various thicknesses . . . 187
6.7. Summary of pavement performance prediction results of various mixes with various thicknesses . . . 187
7.1. Cost of asphalt, paving 85-100 penetration, FOB city tank cars ($ per ton) . . . 202
7.2. Total asphalt production in the United States . . . 203
7.3. Sulfite lignin production in the United States . . . 206
7.4. Kraft lignin production in the United States . . . 206
7.5. Projected pavement cost using asphalt binder or lignin-asphalt binder . . . 208

LIST OF FIGURES

No. Title Page

1.1. Structural sketch for extensively sulfonated lignin sulfonic acid. 3
1.2. Distribution of molecular weights of initial sodium lignin sulfonate sample, showing the molarities of NaCl solution used for equilibrations and elutions, respectively 3
1.3. Tentative structural features in a segment of pine kraft lignin molecule (4). 4
1.4. Geographical distribution of lignin production. 6
1.5. Changes in the sources of energy in the U.S. pulp and paper industry - 1971 through 1975. 7
2.1. Relative frequency distribution for molecular weight of lignin sulfonates. 16
2.2. Relative frequency distribution for molecular weight of lignin sulfonates. 16
2.3. Gelation of lignin sulfonates by oxidative coupling reaction. . . 25
2.4. Changes of viscosity of ammonium lignin sulfonate 25
2.5. Changes of viscosity of calcium lignin sulfonate. 26
2.6. Soaking stability for mixtures on 8% binder based on sand . . . 26
2.7. Tentative structures of lignin sulfonate binders. 29
3.1. Hypothetical asphaltene molecule. 31
3.2. Pressure reaction apparatus used for lignin-asphalt extender binders (Series 4500, Parr Instrument Co.). 32
3.3. Sectioned view of the pressure reaction apparatus shows the principal parts of the 2000 ml bomb 33
3.4. Methods of preparation of lignin-asphalt binders. 34
3.5. Schematic diagram of sliding plate microviscometer. 37
3.6. Preparation of mixtures and test specimens. 38
3.7. Cylindrical specimen showing diametral compressive load being applied and mode of failure 41
3.8. Response of chamber and specimens to programmed temperature cycles. 43
3.9. Schematic diagram of lignin-asphalt binder studies. 43
3.10. Mixing time for lignin-extended asphalt binders 48
3.11. Unit weight of lignin-extended asphalt binders, Phase B 48
3.12. Hveem stability of lignin-extended asphalt binders, Phase A . . 49
3.13. Tensile strength of lignin-extended asphalt binders 49
3.14. Gradation of Steilacoom aggregate 53
3.15. Relationship between softening point and percent lignin in asphalt 56
3.16. Relationship between penetration and percent lignin in asphalt. 56
3.17. Relationships between viscosity and percent lignin in asphalt . 57
3.18. Effect of mixing AC-5 asphalt cement with varying amounts of powdered kraft lignin 57
3.19. Mix design procedures 64
3.20. Unit weight vs. binder content. 67
3.21. Hveem stability vs. binder content. 67
3.23. Resilient modulus vs. binder content after vacuum saturation. . 68
3.24. Relative resilient modulus retained after vacuum saturation . . 68
3.25. Tensile strength vs. binder content after vacuum saturation . . 69
3.26. Voids in mixtures vs. binder content. 69

No. Title Page

3.27. Binder preparation method. 72
3.28. M_R vs. various sulfur contents binders 73
3.29. Comparison of AR-4000, AC-5, AKS and AK test data. 75
3.30. Percent of retained M_R after freeze-thaw conditioning. 78
3.31. AKS percent voids. 78
3.32. A Acid pretreatment test series. .80
B Acid pretreatment test series. .81
C Acid pretreatment test series. .82
3.33. Modifying and blending calcium lignin sulfonate with asphalt . . .84
3.34. Hveem stabilometer value vs. percent binder. 89
3.35. Initial dry resilient modulus (M_R) vs. percent binder. 89
3.36. Vacuum saturated resilient modulus (M_R)(wet M_R)vs. percent binder.90
3.37. Vacuum saturated wet indirect tensile strength vs. percent binder.90
3.38. Unit weight vs. percent binder .91
3.39. Percent voids vs. percent binder 91
3.40. Resilient modulus (M_R) after freeze-thaw conditioning. 98
3.41. Resilient modulus (M_R) after freeze-thaw conditioning vs. percent binder 98
3.42. Percent of initial resilient modulus retained after freeze-thaw conditioning 99
3.43. Resilient modulus vs. duration of 60°C conditioning. 99
3.44. Resilient modulus after 60°C conditioning vs. binder contents. . 100
3.45. Resilient modulus after weather exposure 100
3.46. Resilient modulus after weather exposure 101
3.47. Comparative Hveem stability value vs. percent binder content . . 101
3.48. Comparative vacuum saturated resilient modulus (wet M_R) vs. percent binder. 102
3.49. Comparative resilient modulus vs. percent binder content 102
3.50. Comparative indirect tensile strength vs. percent binder content 103
3.51. Comparative unit weight vs. percent binder 103
3.52. Comparative percent voids vs. percent binder 104
3.53. Flow diagram showing the hot precoating mix design precedures. . 106
3.54. Hveem value for precoated mixtures 109
3.55. Dry M_R comparison. 109
3.56. Indirect tensile strength. 110
3.57. MR retained after variable saturation. 110
3.58. M_R retained after 15 cycles freeze-thaw. 111
3.59. Comparison of the Hveem stability test results 111
3.60. Comparison of M_R dry test results. 120
3.61. Comparison of M_R after vacuum saturation 120
3.62. Comparison of %M_R retained after the freeze-thaw test. 121
3.63. Comparison of the tensile strength before and after the freeze and thaw test. 121
4.1. Viscosity at 25°C of aqueous solution of Indulin C, the sodium salt of kraft pine lignin (1). 130
4.2. Design of the lignin-asphalt-rubber mixes used in this investigation 135
4.3. Density of compacted briquets of lignin-asphalt-rubber mix as a function of the water content of the binder at the time of compaction. Data are shown for briquets immediately after compaction by double-end static compaction and after air drying to constant weight 155

No. Title Page

4.4 Unconfined compressive strength of lignin-asphalt-rubber mixes as a function of the water content of the binder at the time of compaction. Data are shown for (1) the strength of the briquets immediately after compaction, (2) the strength after drying to constant weight, and (3) strength of water saturated briquets which were dried and subsequently immersed in water for 7 days at room temperature. 155
5.1. General Electric 1F8 U.V. lamp test set-up 162
5.2. Flow chart showing testing and measurement for Series 1 and 2. . .166
5.3. Test flow chart for binder pour plate samples in Test Series 3 . .167
5.4. Flow chart of tests and measurements for Series 4. Date: 10/1/77-10/13/77 169
5.5. COD concentration vs. time for Test Series 2 in basic solution . .170
5.6. COD concentration vs. time for Test Series 2 in acid solution. . .170
6.1. Mixture characterization testing scheme for pavement analysis. . .180
6.2. Effect of temperature on resilient modulus 190
6.3. Effect of applied load on resilient modulus. 190
6.4. Effect of load duration on resilient modulus 191
6.5. Effect of load frequency on resilient modulus. 191
6.6. Effect of saturation and freeze-thaw cycles on resilient modulus .192
6.7. Effect of temperature on indirect tensile strength 192
6.8. Effect of saturation and freeze-thaw cycles on indirect tensile strength 193
6.9. Fatigue response for various mixtures. 193
6.10. Effect of repeated loading on permanent strain 194
6.11. Relationship between radial strain and stress at the bottom of surface layer. 194
6.12. Relationship between radial strain at bottom of surface layer and required surface thickness to prevent fatigue failure of various mixes at various axle loads. 195
6.13. Relationships between vertical compressive strain on top of subgrade and required surface thickness to prevent rutting of various mixes at various axle loads. 195
6.14. Fatigue responses for various mixtures 196
6.15. Layer equivalency. 196
6.16. Relationships between predicted rut depth of surface layer of 6 in. (154 mm) made with various mixes and number of years 197
6.17. Relationships between predicted rut depth of surface layer of 9.5 in. (241 mm) made with various mixes and number of years . . .197
6.18. Relationships between predicted serviceability index of surface layer of 3 in.(76.2 mm) made with various mixes and number of years. 198
6.19. Relationships between serviceability index of surface layer of 6 in. (152 mm) made of various mixes and number of years 198
6.20. Relationships between predicted serviceability index of surface layer of 9.5 in. (241 mm) made of various mixes and number of years. 199
7.1. Utilization of various paving asphalt materials in the U.S.. . . .204

ABREVIATIONS

ABS	absorbance
AC-5	asphalt cement
AK	asphalt kraft lignin (same as L/A)
AKC	AC-5/kraft lignin/coal
AKCB	AC-5/kraft lignin/carbon black
AKCT	AC-5/kraft lignin/coal tar
AKL	AC-5/kraft lignin
AKS	AC-5/30 KL/2 Sulphur
APT	acid pretreated
AR-4000	asphalt cement
ca.	circa (approximately)
CaLS	calcium lignin sulfonate
CMS	medium setting cationic emulsion
CMS-2S	medium setting cationic asphalt emulsion
COC	Cleveland open cup
COD	chemical oxygen demand
CRS	rapid setting cationic emulsion
CRS-2	rapid setting cationic asphalt emulsion
CSS-1	slow setting cationic asphalt emulsion
H.S.	hard solid
KL	kraft lignin
KL/SUL/PB	kraft lignin/sulphur/Parr Bomb
KL/4 sul	kraft lignin 4% sulphur
L/A	lignin asphalt (binder)
MC-250	medium curing cutback asphalt
M_R	resilient modulus
N	normal (chem.)
NH_4LS	ammonia lignin sulfonate
OMe	oxygen methyl
OPEC	Organization of Petroleum Exporting Countries
OV	open vessel
P	applied dynamic load
PAM	polyacrylamide
PB	Parr Bomb

pen	penetration
PSI	present servicability index
rev.	revolution
RTFC	rolling thin film oven (Calif.)
RTFO	rolling thin film oven
RT-8	road tar
S-value	Hveem stability value
SBR	styrene butadiene rubber
SG	specific gravity
S.L.	sticky liquid
Sol.	solution
S.S.	soft solid
SS-1h	slow setting anionic asphalt emulsion
SSD	saturated surface dry
SV	slope variance
t	sample thickness
UV	ultraviolet radiation
V.S.L.	very sticky liquid
V.S.S.	very soft solid

δ_h	horizontal dynamic deformation
ε_x	tensile or radial strain
ε_t	horizontal tensile strain
ε_v	vertical compressive strain
ν	Poisson's ratio
μ	Poisson's ratio
σ_d	axial deviator stress
σ_t	ultimate stress in indirect tension
σ_T	indirect tensile strength

MEASUREMENTS AND CONVERSIONS

(Source: "Metric Practice Guide", American Society for Testing and Materials, 1973)

Å	angstrom	
Btu	British thermal units	(Btu)(1.05×10^3) = J
°C	centigrade	
cm	centimetre	
cps	centipoise	(cps)(1.0×10^{-3}) = Pa·s
cst	centistokes	(cst)(1.0×10^{-6}) = m^2/s
d	day	
$/ton	dollars/ton	($/ton)(2.2) = $/kg
$\$/yd^2/in.$	dollars/yard^2/inch	($\$/yd^2/in.$)(.33) = $\$/m^2/cm$
°F	fahrenheit	(°F - 32)/(1.8) = °C
ft.	foot	(ft.)(2.073×10^{-1}) = m
gm	gram	
h	hour	
in.	inch	(in.)(2.54) = cm (in.)(25.4) = mm
J	Joule	
kg	kilogram	
Kip		(Kip)(4.44822×10^3) = N
KN	kilonewton	
KPa	kilo pascals	
lb.	pound	(lb.)(.45) = kg
mg	milligram	
min.	minute	
mm	millimetre	
MP	mega poise	(MP)(1.0×10^5) = Pa·s
MPa	mega pascal	
N	newton	
nm	nanometer	
Pa·s	pascal-second	
pbw	parts by weight	
pcf	pounds per cubic foot	(pcf)(1.601846×10) = kg/m^3
P	poise	(P)(1.0×10^{-1}) = Pa·s
psi	pounds per square inch	(psi)(6.894×10^{-3}) = MPa
tons		(tons)(9.0×10^2) = kg

TABLE OF CONTENTS

Preface ii
List of Tables iv
List of Figures vi
Abreviations ix
Measurements and Conversions xi
Table of Contents xii

I. INTRODUCTION 1
  A. Background 1
  B. The Nature of Lignin Sulphonates 1
  C. The Nature of Kraft Lignins 2
  D. Sources, Distribution and Current Uses of Wood Lignins 5
  E. Objectives 10
  F. Scope of Research 10
  G. Research Approach 10
  H. References 11

II. LIGNINS ALONE AS SUBSTITUTES FOR ASPHALT 13
  A. Preliminary Evaluation of Lignins Alone 13
  B. Lignin Sulphonate Molecular Weight Studies 14
  C. Detailed Experiments on Lignin Sulphonate 17
  D. Summary and Conclusions 24
  E. Reference 28

III. LIGNIN AS AN EXTENDER OF ASPHALT 30
  A. Binder Preparation 30
  B. Laboratory Tests on Binders 35
  C. Mixture Design Procedures 36
  D. Evaluation of Lignin as Asphalt Extenders 43
    Phase A - Preliminary Evaluation 44
    Phase B - Intermediate Evaluation 46
    Phase C - Detailed Testing and Analysis 52
  E. Evaluation of Kraft Lignin-Asphalt Binder (Phase C-1) 58
  F. Evaluation of Kraft Lignin-Sulphur-Asphalt Binder (Phase C-2) 71
  G. Evaluation of Acid Pretreated Lignin Sulphonate-Asphalt Binder (Phase C-3) 79
  H. Evaluation of Other Binder Modifications (Phase C-4) 97
    Precoating 97
    Use of Admixtures 118
    Preparation of Binders 123
    Mixture Tests 124
  I. References 126

IV. KRAFT LIGNIN IN EMULSIFIED ASPHALT BINDERS 127
  A. Introduction 127
  B. Materials and Experimental Procedures 127
  C. Test Results 138

D. Discussion 156
E. Summary 158
F. References 160

V. ENVIRONMENTAL EFFECTS ON LIGNIN BINDER
A. Introduction 161
B. Analytical Methods 163
C. Test Series 164
D. Test Results and Conclusions 169

VI. PAVEMENT DESIGN AND PERFORMANCE PREDICTIONS
A. Mixture Characterization for Pavement Analysis 179
B. Pavement Design Analysis 181
C. Development of Design Curves 181
D. Material Equivalencies 184
E. Pavement Performance Predictions 184
F. Results of Performance Prediction 185
G. References 200

VII. ECONOMIC FEASIBILITY
A. Cost and Production Trends of Asphalt 201
B. Cost and Production Trends of Wood Lignins 203
C. Lignin-Asphalt Binder 207
D. Conclusions 208

VIII. SUMMARY AND CONCLUSIONS
A. Summary 209
B. Conclusions 212

APPENDIX A. PULP AND LIGNIN PRODUCTION IN THE U.S. 215

APPENDIX B. BINDER TEST RESULTS 225

I. INTRODUCTION

A. Background

The current inflation in the cost of construction materials, primarily as a result of the recent energy crisis and aggregate shortages, has forced many engineers to seek alternative approaches other than conventional materials for pavement construction. One such promising approach is to use wood lignins as a means of reducing the dependence of the use of asphalt cement.

Lignin is a cementious material that binds fibers together in wood and lignin derivatives are a major by-product of the paper making industry. Aside from being one of the nation's more valuable renewable resources, lignin is one of the few materials which is expected to be in large supply in the future. On the other hand, though there exist some natural occurring asphalts, nearly all the asphalt used in the USA are refined and a significant portion imported.

Basically two types of wood lignins are commercially available - lignin sulfonate and kraft lignin. In the past years, highway soil stabilization has been one important use for wood lignins. In fact, from the late 1920's until the present, significant quantities of spent sulfite liquor have been sprayed on roads both for the purpose of making a hard durable surface and for dust palliation (1). In some instances, spent liquor solids have been bladed into the surface with graders. In areas of low rainfall, spent liquor treatments have produced durable roads with less tendency to form chuck holes than those surfaced by an oil treatment. Kraft lignins, and lignin sulfonates in the absence of rain, had maintained road surfaces smooth and dust-free for a long period of time. Lignins have also been used together with asphalt and road oils to produce emulsions (2). Lignin derived emulsifiers which include kraft derivatives have been used as stabilizers for asphalt emulsions (3).

B. The Nature of Lignin Sulfonates

Lignin is a natural polymer of a phenolic type which occurs in all plant tissue and makes up in wood about 25 to 32%. In wood it appears to exist as a three-dimensional network and thus is substantially insoluble in water and other solvents.

For more than one hundred years "pulp" for manufacture of paper and other products in the form of cellulose fibers have been produced from woody tissue by the "sulfite process" whereby aqueous solutions of bisulfites and sulfurous acid are used at elevated temperature to dissolve lignin and some carbohydrates and leave behind the cellulose sulfite pulp fibers.

The dissolving occurs because some chemical linkages in the three-dimensional infinite network are broken and lyophylic sulfonate groupings are added.

After the pulp fibers have been separated by filtration, the liquid remaining is called spent sulfite liquor and contains lignin sulfonates, certain sugars from the wood and also the process chemicals.

For many years attempts have been made to use spent sulfite liquor and recently, its utilization is being made in a number of cases to produce process heating as a result of evaporation and burning, and also in some cases saleable chemical products. However, considerable amounts of spent sulfite liquor remain available in several parts of the United States and appropriate uses for these materials are being sought.

Over the last several decades, many studies have been made of the properties, and the chemistry and chemical reactions of lignin sulfonates. The results and findings have been summarized by Glennie (4). The chemical structure of lignin sulfonates as found in spent sulfite liquors have been outlined by Glennie and this illustrative structure is shown in Figure 1.1 (4). This example shows finite molecular weight with solubilizing groups attached and it is no longer an infinite network by reason of the cleavage of certain linkages in the dissolving process.

As available in spent sulfur liquors, lignin sulfonates exist as molecules of widely different molecular weights. Extensive studies of the molecular weights of lignin sulfonates have been conducted by McCarthy and co-workers and an example of the distribution (in the form of an integral curve) is shown in Figure 1.2 (5).

Lignin sulfonates are prduced as calcium, magnesium, sodium or ammonium salts. They are commonly sold in the form of spray dried powder or as 40-60% solutions in water, usually containing the sugars formed in the pulping process.

C. The Nature of Kraft Lignins

Kraft lignin (or thiolignin) is the major constituent of kraft black liquor solids. It is a polymeric material of relatively low average molecular weight (< 5000) consisting of about 65% carbon, 5% hydrogen and 30% oxygen and can be recovered in a reasonable high yield by acidifying and filtering the precipitated lignin.

In many ways, kraft lignin is a more versatile raw material than are lignin sulfonates from the sulfite spent liquor. It can be easily isolated from the spent pulping liquor, is soluble in mny organic solvents, possesses thermoplastic properties, contains less sulfur and is soluble in caustic. It reacts with phenols, amines, aldehydes and sulfides. Reaction with sodium sulfite produces a series of sodium lignin sulfonates with varying amounts of sulfonic acid groups. These sulfonated kraft lignins are more expensive to produce than lignin sulfonates, but they have the advantage of being free of carbonhydrate constituents and are insoluble in water.

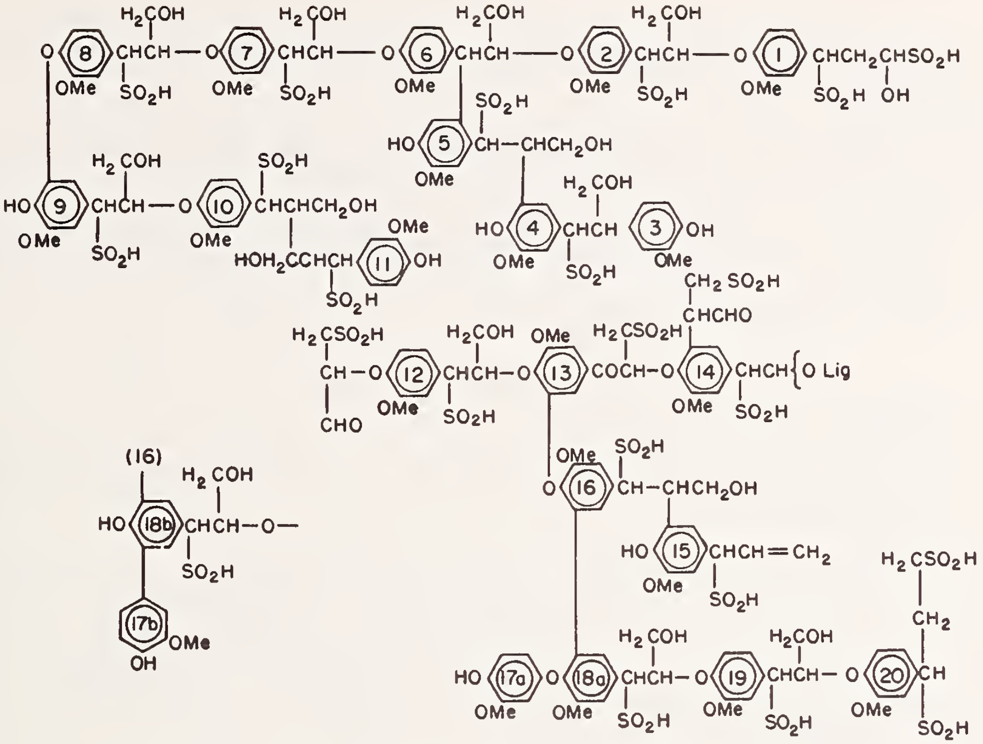


Figure 1.1. Structural sketch for extensively sulfonated lignin sulfonic acid.

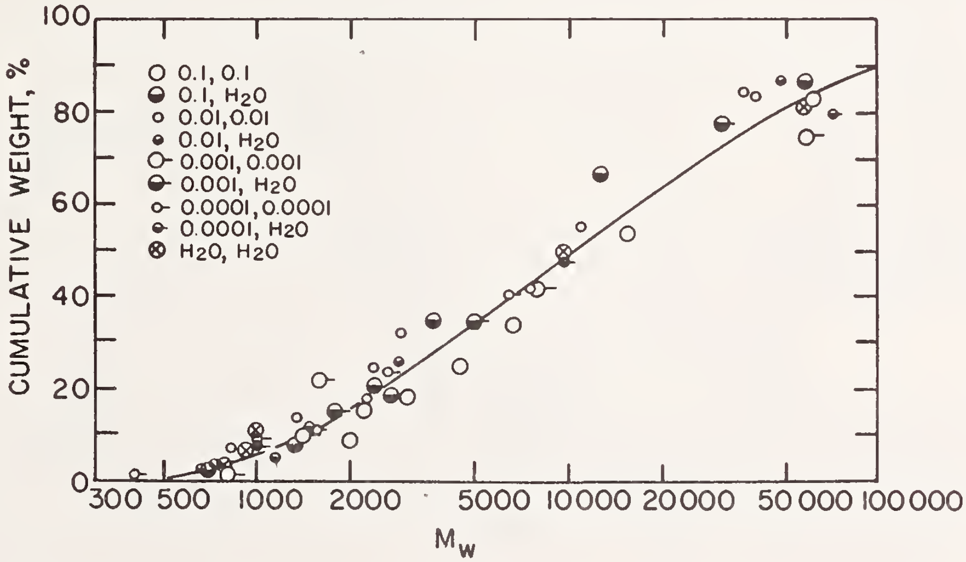


Figure 1.2. Distribution of molecular weights of initial sodium lignin sulfonate sample, showing the molarities of NaCl solution used for equilibrations and elutions, respectively.

Kraft lignin is recovered either as its sodium salt or in the form of free lignin containing very little ash. Both forms when dry are free flowing brown powders.

In the United States, the only commercially available kraft sulfate lignin, "Indulin" (Westvaco) is produced in three grades:

1. "Indulin C" is the crude sodium salt which contains some occluded black liquor solids and therefore has a relatively high ash content of about 22.5%;

2. "Indulin B" is a purified sodium salt which has a lower ash content of about 9%; and

3. "Indulin AT" represents an acidified lignin with an ash content of less than 1%.

Kraft lignins from softwoods, such as Indulin AT which is derived from pine, have methoxyl contents of about 14%. Hardwood kraft lignins, currently not commercially available, contain about 21% methoxyl. The average molecular weight for pine lignin is 1600 and for hardwood lignin is 1050. A typical structural feature in a segment of pine kraft lignin molecule is as shown in Figure 1.3.

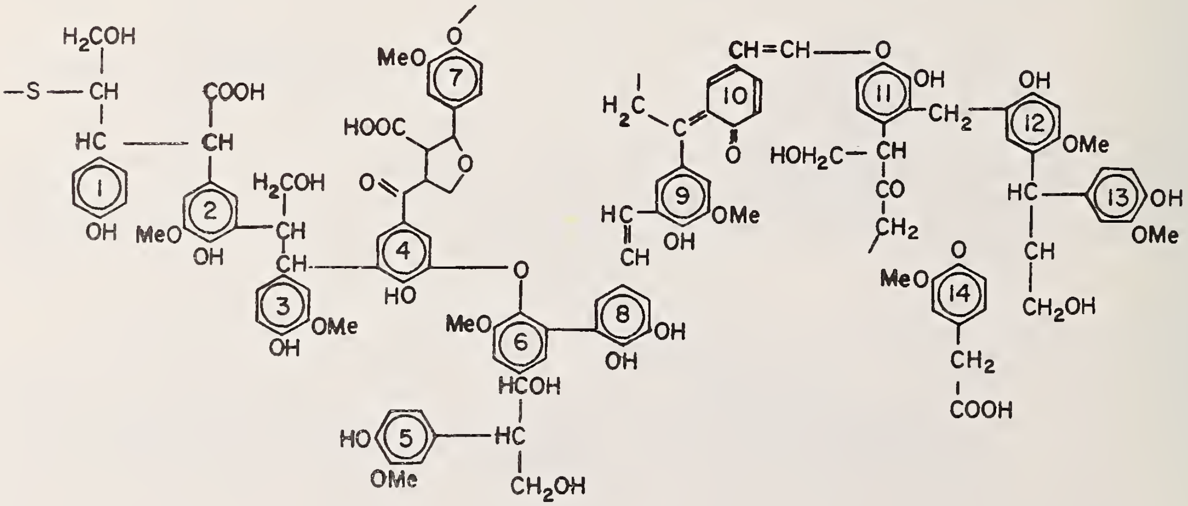


Figure 1.3. Tentative structural features in a segment of pine kraft lignin molecule (4).

D. Sources, Distribution and Current Uses of Wood Lignin

One general assumption is that wood lignins are readily available in sufficient quantities. However, a look at the paper and pulp industry is required to ascertain the nature and quantities involved. Although numerous sources have been consulted, one of the better references is Lockwood's Directory of the Paper and Allied Trades, Vance Publishing Co., New York. The 1976 edition generally includes statistical data through 1974. A common problem that exists in the industry is a lack of data on wood lignins. However, much of the recovery information can be inferred from pulp and paper figures.

The paper and allied products industry is large, having total sales in 1974 of $33 billion. This boils down to a per capita use of paper and board of 614 lbs (276 kg). In general, one can assume that for each ton (900 kg) of pulp a mill produces, approximately ½ ton (450 kg) of lignin results. In general, figures show that in the U.S. and Canada, about 1.35 million tons (1.25×10^9 kg) of sulfite spent liquor solids are produced annually. In addition, the kraft process results in about 15 million tons (1.35×10^{10}kg) of kraft lignin annually.

A relatively complete listing of pulp mills in the U.S. is shown in Appendix A. The data include by state the type of process, pulp output, and estimate of lignin based on the above formula. As a matter of interest, these production figures have been translated to a map of the U.S. shown in Figure 1.4. The individual mills are indicated by a circle for sulfite and triangle for kraft. The size of each symbol are relative to the production of the mill. Upon examination of the map, one can readily see that lignin production and potential availability are somewhat regional. The largest quantities would generally be in three areas: Pacific Northwest, Upper Midwest, and Southeast. This would imply the potential utilization for paving purposes might be on a local or regional basis, because of transportation costs.

Previous utilization of lignins has been varied. An emerging development in recent years has been the conversion of waste materials to energy as fuel for the pulp mills. Figure 1.5 shows this development on a percent change basis and compares lignins with other fuels. The use of bark and pulping liquors has increased markedly.

Other product oriented uses make use of unique properties. Lignin sulfonates are anionic, water soluble, surface-active derivatives of wood lignins. They have many diverse uses resulting from their dispersing, binding, and sequestering properties. Generally, very small quantities of lignins are necessary to accomplish these effects. Concentrations of two percent or less are typical. The nature of this utilization is summarized as follows:

> Dispersing - Lignins perform as dispersing agents by preventing the formation of aggregates of finely divided insoluble particles in water. They attach themselves to the individual particles and provide a negative charge to the particle. These like-charged particles repel themselves, and therefore agglomerates are prevented

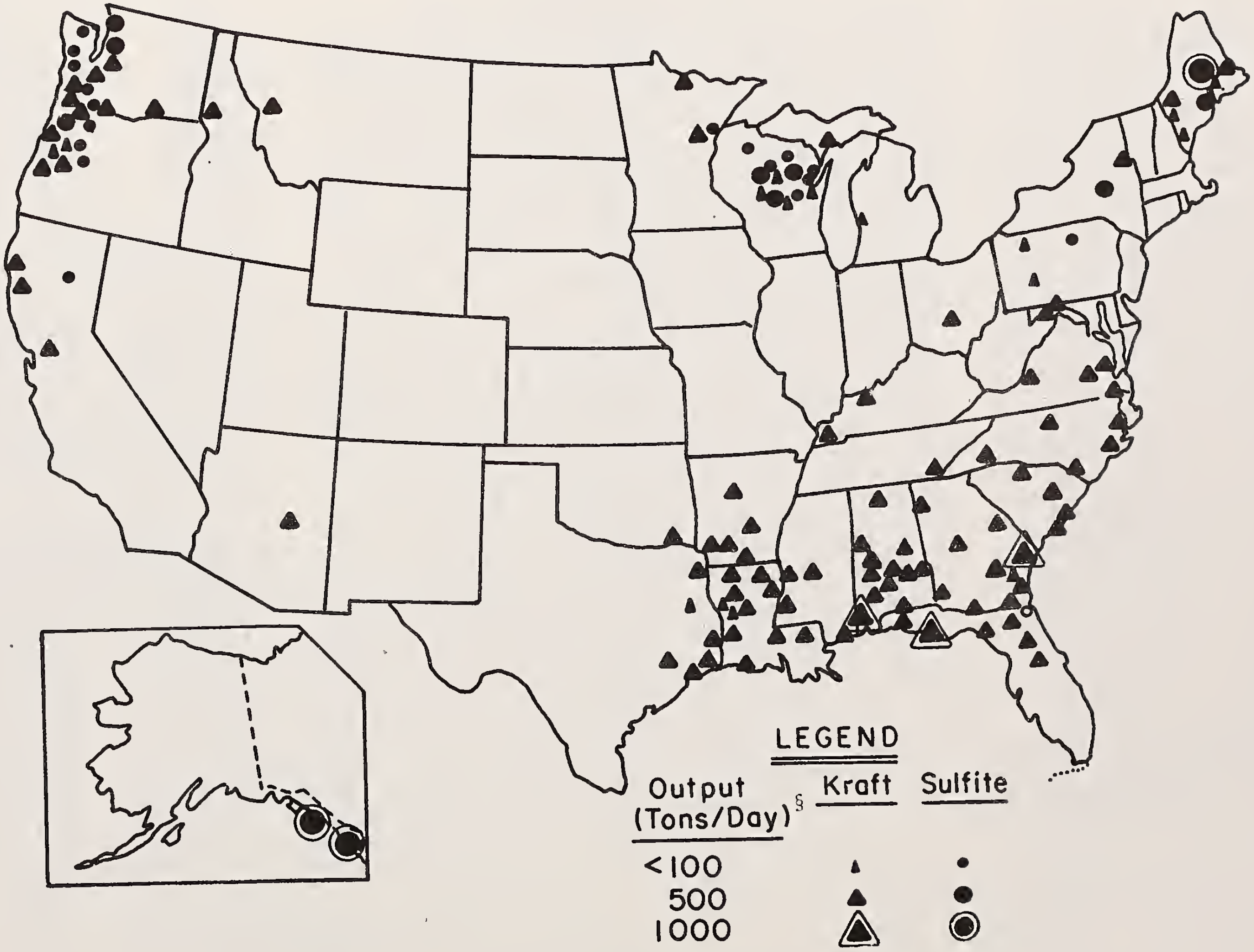


Figure 1.4. Geographical distribution of lignin production.

§To convert to kg: (tons)(2.0×10^3)(.45)

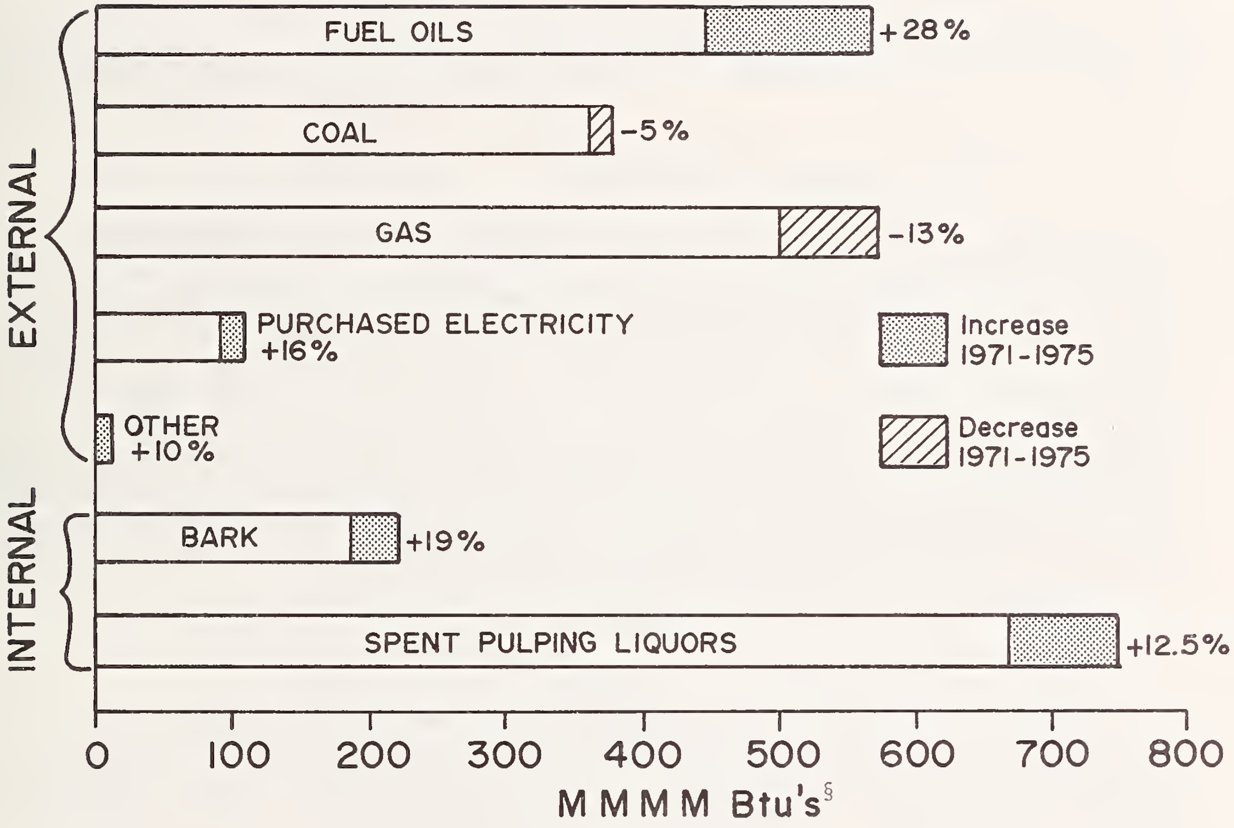


Figure 1.5. Changes in the sources of energy in the U.S. pulp and paper industry - 1971 through 1975.

§To convert to J: Btu x (1.05×10^3)

and the insolubles remain in suspension.

Binding - Lignins give quick tack and adhesiveness when moistened. Special products containing wood sugar derivatives exhibit excellent binding properties.

Sequestering - Lignins exhibit the ability to sequester, or chelate, many metallic ions. When sequestered, the metallic ions no longer undergo their normal reactions. Thus, certain metallic ions can be prevented from becoming undesirable compounds. The sequestering property of the lignin sulfonates is useful in making metals available to plants or in neutralizing undesirable metallic ions in emulsions or suspensions.

Following is a brief discussion and list of some of the current uses of lignin in construction related activities of lignin products and these include

Dust control and road stabilization

Experience has shown that roads stabilized with lignin sulfonic acids and resins have less frost heaving and spring break-up damage. Lignin stabilized bases make excellent bases for oil seal or blacktop roads. Unsurfaced roads can be freed of wet-weather mud. Used as a binder on secondary and temporary roads, lignin products have been shown to make better roads in several ways. For example, lignin binds gravel into a hard skid resistant surface, increases load bearing strength whether wet or dry, binds dust particles to the road, reduces or eliminates need for frequent grading, makes better roads with poorer quality aggregates, improves compaction at lower moisture levels, decreases the rate of water penetration into roads, increases run-off, reduces mud condition, and improves the engineering properties of many soils.

Oil well drilling muds

Modified lignin sulfonates, chrome and ferrachrome lignin sulfonates have been found, which are very effective in attaining the necessary properties of good drilling muds. In drilling oil wells, water disperants are constantly fed into the hole to form drilling mud. The drilling mud serves many purposes. It cools and lubricates the drill, hydraulically cuts and removes cuttings, transports cuttings to the surface, cements and seals the wall of the drill hole, holds cuttings in suspension during drilling, and forms a hydrostatic head which serves as a means of controlling high pressure gas, oil and water flows.

Concrete admixtures

The dispersive action of certain lignins is useful in mixing and placing portland cement concrete. As admixtures in concrete, lignins can reduce water requirements, retard setting time, increase strength and workability, provide optimum air entrainment for good freeze-thaw characteristics, and the bond strength of concrete to reinforcing steel is also increased in lignin treated concrete.

Grinding aid for portland cement

Lignins are used in the grinding of the clinker and to a small extent in the wet initial grinding. Their function is to reduce the agglomeration of ground particles and keep the surfaces of the grinding media clean. They also make the cement flow more readily by reducing inter-particle attraction, which reduces "pack set" during storage and transportation.

Grout fluidifier

Improved workability and greater strength at lower costs are obtained in cement grouting using lignin products. Their addition increases fluidity of the grout without any increase in water content thus yielding possibilities for stronger and denser grout.

Gypsum board production

Lignin sulfonates, when added to gypsum mixes (0.1%) are enough to disperse most stuccos. Dispersion of stucco reduces the amount of water required to fluidize the slurries fed to the forming rollls of gypsum board machines resulting in higher quality boards at lower cost.

Ceramics

Lignin sulfonates are used as clay deflocculants in the manufacture of brick, tile, refractories, pottery and porcelain ware. Lignin sulfonates act, as in grout mixtures, to reduce the water required for a given fluidity, increasing the green and dry strength.

Other uses of lignin products include:

ore flotation reagent
electrolytic refining
resin ingredients and extender
rubber additives
treating stomach ulcers
flame retardant
tanning agents
crystal growth inhibitor
briquetting coal and animal feed binder
fertilizer and chelating micronutrients
linoleum paste base
dyestuff pastes
scale and foam inhibitor for boiler water
industrial cleaners
foam stabilization
asphalt emulsifier and stabilizer
polyvinyl alcohol (PVA) adhesive extender

E. Objectives

The primary objective of this project was to evaluate wood lignins as substitutes for asphalt. More specifically, the objectives were:

1. To evaluate the utilization of lignins alone and/or with chemicals as substitutes for asphalt cement,
2. To evaluate the utilization of lignins as extenders for asphalt cement, and
3. To evaluate the utilization of rubber modified kraft lignin in pavements.

F. Scope of Research

The scope and funding of this project provided for the processing and development of systematic procedures for evaluating wood lignins and to look into the feasibility of utilizing wood lignins as substitutes or extenders for asphalt. The research included identifying the potential lignins or modified-lignin candidates, formulation and testing of various lignin binders, development of mix design procedures, and evaluation of the technical and economic feasibility of utilizing wood lignins in pavements.

To futher enhance the potential usefulness of wood lignins as paving mixtures, theoretical pavement design and field performance data of lignin-asphalt pavements were also compared with conventional asphalt concretes.

General information is also presented as guidelines to prospective users of wood lignins as paving materials.

G. Research Approach

The research approach to this study deals primarily with the laboratory preparation and evaluation of binders and paving mixtures. The study is divided into three main project areas as follows:

1. Evaluation of lignins as substitutes for asphalt;
2. Evaluation of lignins as extenders for asphalt; and
3. Evaluation of rubber modified lignins.

Each project area involves several tasks including:

1. Development of binders
    (a) Selection of binder preparation method, materials and tests

    - (b) Processing of binders and tests
    - (c) Evaluation of test results

2. Development of paving mixtures
    - (a) Selection of materials, method of preparation of mixtures and specimens, and mixture composition criteria.
    - (b) Processing of mixtures and fabrication of specimens
3. Development of mix design data
    - (a) Select test method
    - (b) Tests of paving mixtures
    - (c) Evaluation of test results

In addition, limited analysis of the performance of selected mixtures were made including:

4. Development of pavement design data
    - (a) Select analysis method and required tests
    - (b) Material characterization
    - (c) Select hypothetical design problems and input
    - (d) Analysis and evaluation of results
5. Prediction of pavement performance
    - (a) Select analysis method
    - (b) Select design problems and input variables
    - (c) Analysis and evaluation of results

H. References

1. Anon., Paper Industry, Patent 21,638, 1939.

2. Freeman, H., Canadian Patent 535,849, 1957.

3. Borgfeldt, M.J., U.S. Patent 3,123,569, 1964.

4. Sarkanen, K.W. and Ludwig, C.H., Lignins, Wiley-Interscience, New York, 1971.

5. McCarthy, Joseph P., Macromolecules 1:236-244, 1968.

II. LIGNINS ALONE AS SUBSTITUTES FOR ASPHALT

In a number of experiments conducted in the United States and overseas, industrial waste lignins have been used experimentally as binders for roads. In some cases, this utilization has been reasonably effective and the practice is continuing.

However, one basic difficulty is the fact that lignin sulfonates in spent liquors are soluble in water and thus, when a dried road surface or base becomes wet with rain, the lignin sulfonates dissolve and lose their utility as a road binder.

Thus, in the present approach toward use of lignin sulfonates as substitutes for asphalt, it is desirable to bring about insolubility or limited solubility in the lignin sulfonates and thereby avoid the problems created by water.

Therefore, one of the objectives of this investigation was to try to find ways to develop a new asphalt-like binder from lignin sulfonates having less water solubility. Preferably, the method developed would include two steps.

The first desirable step would be to convert lignin sulfonates to high molecular weight materials which would still retain solubility but would require only a small degree of reaction to become insoluble - this change might be accomplished by preliminary industrial processing of lignin sulfonates. The second step would be the conversion of lignin sulfonates to an entirely insoluble form as a result of appropriate applications of heating, chemicals and pressure.

Accordingly, lignin sulfonate molecular weight studies were pursued with two main objectives:

1. To estimate the molecular weight distribution of lignin sulfonates from a number of sources and to identify, if possible, the most promising beginning material for use as substitutes for asphalt.
2. To estimate the molecular weight distributions of partly condensed or reacted lignin sulfonates in order to ascertain what degree of condensation remains to be completed by reactions in the field compared to those conducted in a pre-processing step.

A. Preliminary Evaluation of Lignins Alone

The preliminary formulation of lignin type of pavement binder was both intriguing and frustrating. From the outset, it was assumed that using lignins alone and/or chemically modified would be difficult.

However, several binder formulations using lignin sulfonates and kraft lignin were made and tests performed.

A summary of the laboratory tests, has been condensed from Appendix B and is shown in Table 2.1. As a preliminary criterion, strength of the molded specimens was considered a reasonably reliable approach. However, a certain level of strength also should be retained after soaking in water. Perusal of Table 2.1 readily indicates that very little strength of soaked samples was indicated. Many of the straight lignin solutions, for example No. CE001, a calcium lignin sulfonate, developed good strength when cured (dried). In this example, 116 psi (5.6 MPa) in a 2 in. (50.8 mm) diameter by 4 in. (101.6 mm) high cylinder was a very hard, dense mixture. When placed in a beaker of water, however, it disintegrated in a few minutes.

For most of the lignin trials, the above results became common place. Other factors also became evident. For example, some chemical combinations produced gas upon curing and resulted in expansion of the compacted mixture, often extruding from the mold more than 0.5 inch (12.7 mm). Other chemical modifications produced stiff rubbery materials that, although interesting, were not suitable for paving mixtures.

B. Lignin Sulfonate Molecular Weight Studies

The identification and description of the lignin sulfonate preparations investigated are included in Appendix B. These samples include spent sulfite liquors from several sources, including some which have been fractionated.

The procedures used for estimation of the molecular weight distributions may be summarized as follows: A laboratory scale chromatographic column was packed with a Sephadex porous gel using an aqueous eluant stream. The sample to be analyzed, which contained the several component lignin sulfonate molecules, was added to the top of the column and then the lignin sulfonates were eluted using very dilute aqueous solution of sodium chloride. The elution was monitored with ultraviolet radiation absorption measurements which are reflective of the concentration of lignin sulfonates present.

The elution curves obtained are shown in Figures 2.1 and 2.2 where the ordinate represents the concentration of lignin sulfonates and the abscissa represents the volume of eluant. These are "frequency" or "differential" distribution curves for molecular weights whereas Figure 1.2 gives a "cumulative" or "integrative" distribution curve which is roughly Poisson rather than Gaussian type.

The type of chromatographic column used has the characteristics of giving rise to elution of the higher molecular weight lignin sulfonate molecules early in the elution curve and progressively decreasing molecular weight substances in the latter part of the curve. This effect is indicated by the relative molecular weight ranges which are also given in the abscissa of Figures 2.1 and 2.2.

Table 2.1. Summary of binder test results for lignin alone.

Laboratory Number	Unconfined Compressive Strength		Solution Color*	Degradation **
	Dry (psi)[§]	Soaked (24 hrs)		
CE 001	116	0	7	Severe
002	191	0	7	Severe
003	420	0	6	Moderate
008	81	0	7	Severe
011	2	0	7	Severe
033	89	0	7	Severe
035	65	0	7	Severe
036	100	0	7	Severe
037	154	0	7	Severe
038	110	0	7	Severe
039	16	0	5	Severe
042	57	0	6	Severe
043	38	0	6	Severe
046	67	0	6	Severe
047	32	0	6	Severe
050	5	0	4	Severe
051	12	0	5	Severe
055	8	0	6	Severe
058	8	0	6	Severe
059	24	0	6	Severe
084	142	73	4	Slight
090	40	0	7	Severe
098	-	86	6	Severe
099	-	25	5	Severe

Notes:

- Samples failed during extruding process because they were still wet and adhered to mold surface: (CE 004, 5, 6, 13, 17, 18, 44, 86)
- Mixes were too stiff to mix: (CE 012, 23, 27, 28, 29, 30, 31, 32, 70, 71, 72)
- Not tested: (CE 019, 020)
- Samples expanded during curing: (CE 045, 54, 73, 85, 91, 92)

* An arbitrary scale from 0-7 (0-clear to 7-nearly black) was developed by mixing various concentrations of lignin in water. The soaking water in the above tests were then compared to these "standard" samples.

** Degradation was a subjective evaluation of the appearance of cylindrical specimens after soaking.

[§] To convert to MPa: psi x 6.894 x 10^{-3}

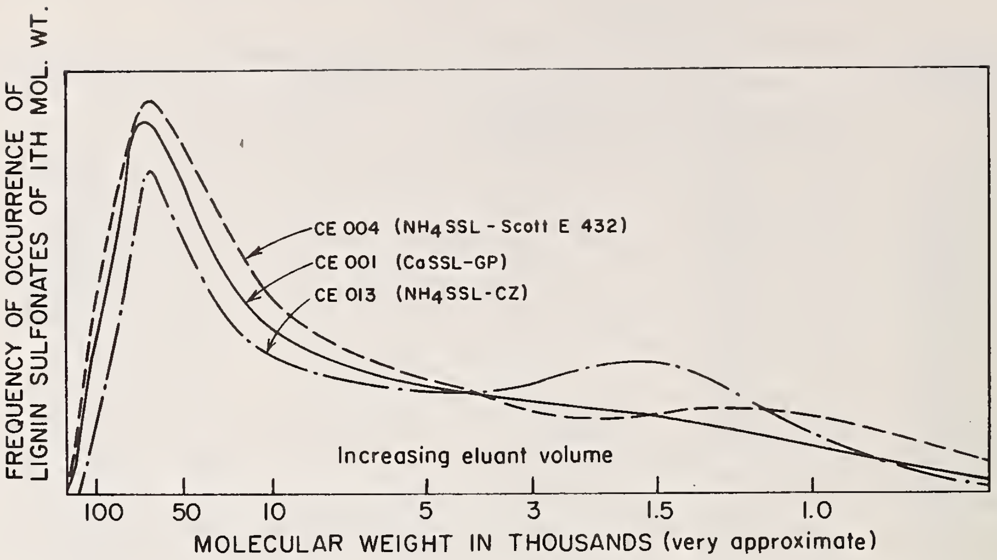


Figure 2.1. Relative frequency distribution for molecular weight of lignin sulfonates.

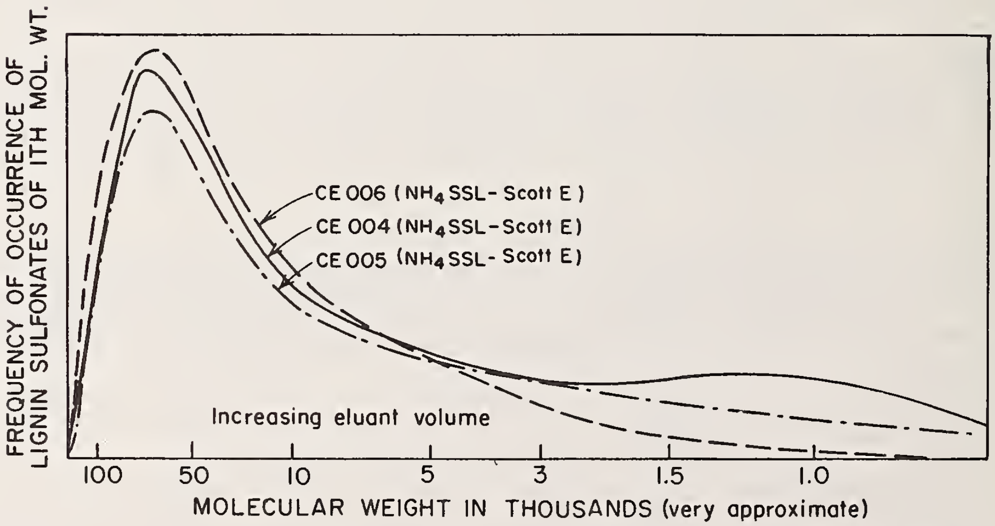


Figure 2.2. Relative frequency distribution for molecular weight of lignin sulfonates.

The eluant volumes associated with particular values of lignin molecular weights can be roughly estimated using data published by Gupta and McCarthy (1) where absolute molecular weights were established by use of ultracentrifuge sedimentation equilibrium measurements.

Generally, one observes in Figures 2.1 and 2.2 that all the lignin sulfonate molecular distribution curves are somewhat similar. However, differences are evident in the average molecular weights and in the differing proportions of lower to higher molecular weight materials present in certain samples.

For Figures 2.1 and 2.2 one should visualize a full spectrum of molecular weights ranging from a few hundred up to 100,000 or more. Thus the low, medium and high ranges may be interpreted as something like 200-1,000; 1,000-10,000; and 10,000-100,000+, respectively.

The molecular weight distributions of the lignin sulfonates present in spent sulfite liquors from three different sources are indicated in Figure 2.1. Of these, CE 013 (NH_4SSL-CZ) appears to contain the largest proportion of low molecular weight polymers, CE 004 (NH_4SSL-Scott E 432) has a smaller proportion, and CE 001 (CaSSL-GP) the smallest proportion.

In Figure 2.2 there is shown again the result for CE 004 but here along with results for two samples obtained by fractionation of this material. The data indicate that CE 005 (NH_4SSL-Scott E 435) and CE 006 (NH_4SSL-Scott 441) contain progressively lesser proportions of lower molecular weight lignin sulfonates than CE 006.

For purposes of the present project it appears that the samples containing the lesser low molecular weight lignin sulfonates may be preferred since other things being equal, these may be convertible in higher yields to insoluble lignin sulfonates.

C. Detailed Experiments on Lignin Sulfonates

As a result of the molecular weight studies, a series of experiments were conducted with the higher molecular weight lignin sulfonates. The materials used, the binders prepared, tests of binders, the results obtained and conclusions reached are presented as follows:

Materials

Commercial concentrated spent sulfite liquors (50% solid concentration) as below were used without any purification.

Scott Paper Co., TREX-LTA LIGNIN LIQUOR (main component: ammonium lignin sulfonate, NH_4LS)

Georgia Pacific, LIGNOSITE (main component: calcium lignin sulfonate, CaLS).

Test of Binders

The various binders were screened for suitability and general evaluation. Test specimens were prepared by mixing binders with sand (Ottawa sand No. 60) in the range of 8 to 12% based on sand weight, compacting in a small mold (2 in. [50.8 mm] diameter and 4 in. [101.6 mm] height), and curing at 122°F (50°C) overnight, then 221°F (105°C) overnight. Following extrusion from the mold, specimens were tested for unconfined compressive strength, solubility and swelling. In some cases, binders were preheated before mixing with sand at 221°F (105°C) for 15 min. in order to reduce viscosity to a point where mixing could be accomplished. Only the binders prepared by method (d) were cured at 248 to 302°F (120 to 150°C) for the final curing stage.

Because of the characteristics of less thermal softening of the binders from method (c) and (d), quite different methods were also adopted. Sand was mixed with NH_4-LS and other chemicals in a glass bottle at 122°F (50°C) for 2 hrs. Then, the mixtures were compacted and cured in the same way as described above.

Preparation of Polymerized Lignin Sulfonate That are Less Water Soluble

Properties of asphalt as a road binder are generally discussed in terms of (1) viscoelasticity, (2) thermal setting, (3) hydrophobicity, and (4) inertness. Similar information is probably also applicable for the discussion of the new asphalt-like lignin sulfonate binders. Among them, hydrophobicity has been the most important characteristic to be improved, because lignin sulfonate binders have high water solubility or swelling property.

The water solubility of lignin sulfonate has been considered to be mainly dependent on the amount of sulfonic group and molecular weight. The usual way of decreasing solubility is to increase the molecular weight by polymerization reactions, and by partial defulfonation.

Polymerization reactions also have effects on viscoelastic and thermal setting behavior of the lignin sulfonate binder because of changes in molecular weight and cross-linking density.

Heat Treatment with or without Acid

250 ml of Ca LS or NH_4 LS were enclosed in a stainless steel reaction vessel (volume 400 ml) with or without some amount of hydrochloric acid, then heated in a rocking autoclave. Treatment conditions were as follows:

	Ca LS	NH_4 LS
Lignin Sulfonate*	48.5%	50%
Hydrochloric Acid*	0.35-3.5%	0%
Temperature	212-347°F (100-175°C)	284-338°F (140-170°C)
Time	2 hrs	1-2 hrs

* based on total weight of mixture

Characteristics of lignin sulfonate binders prepared by these methods are shown in Tables 2.2 and 2.3. It is clear that softness and solubility in water of these binders are dependent on the treatment conditions, such as heating temperture, heating time, amount of acid added and origin of lignin sulfonate.

There was a remarkable difference in the reactivities of CaLS and NH_4LS. In the case of CaLS, some amount of acid was essential to prepare water insoluble lingin sulfonate under the conditions adopted in this study; on the other hand, NH_4 LS easily changed to water insoluble rubber-like materials only by heating without acid. The reason for these different reactivities was not clear, but might be attributed to the stabilities of sulfonate groups.

The binders can be classified into three groups based on solubility in water:

1. Easily soluble lignin sulfonate: These binders are characterized by S.L. (sticky liquid) with solubility index +++ to ++ in Tables 2.2 and 2.3, and obviously cannot be used as a road binder.

2. Less soluble lignin sulfonate: These binders are noted under conditions a to f in Tables 2.2 and 2.3, and characterized by V.S.L. (very sticky liquid) or V.S.S. (very soft solid) with solubility index +. From the standpoint of applicability, these binders were expected to become water insoluble with a small additional reaction which might correspond to the curing stage. However, all binders of this class still have some solubility and high swelling property in water even after the curing stage. Furthermore, they become very brittle following curing and did not retain sufficient cohesiveness to sand particles.

3. Insoluble lignin sulfonate: These binders were characterized by S.S. (soft solid) or H.S. (hard solid) with solubility index ± or -. These binders became almost water insoluble after curing but turned out to be too hard to mix with sand even at elevated temperature.

From these results, it can be concluded that simple heat treatments of lignin sulfonates with or without acid were not successful methods to prepare road paving materials.

Oxidative Coupling with Hydrogen Peroxide-Potassium Ferricyanide Catalyst

100 ml of CaLS or NH_4LS was mixed thoroughly with 10 ml of $K_3Fe(CN)_6$ aqueous solution containing 0.8 to 3 g $K_3Fe(CN)_6$, and then mixed with 8 to 30 ml of H_2O_2 (30% concentration). A small amount of NaOH was also added to maintain a pH at about 4.5. The reaction was continued at room temperature until the mixtures changed to very sticky rubber-like materials. The time required for the above reaction was called "Gelation Time" and measured as an indication of reactivity. One of the possible ways of

Table 2.2. Characteristics of prepared lignin sulfonate binders.

Acid (HCL)	Temperature							
	212°F(100°C)		257°F(125°C)		302°F(150°C)		347°F(175°C)	
	Solubility	Appearance	Solubility	Appearance	Solubility	Appearance	Solubility	Appearance
0.35%	+++	S.L.	+++	S.L.	+++	S.L.	++	S.L.
1.05%	+++	S.L.	++	S.L.	+(a)	V.S.L.^{1}	+(c)	V.S.S.
1.40%	+++	S.L.			+(b)	V.S.L.^{2}	-	S.S.
1.80%	+++	S.L.	+(d)	V.S.L.	-	S.S.	-	H.S.

Notes: S.L.: sticky liquor
V.S.L.: very sticky liquor
V.S.S.: very soft solid
S.S.: soft solid
H.S.: hard solid

+++: very soluble
++: soluble
+: somewhat soluble
±: slightly soluble
-: insoluble

(a),(b),(c),(d): preparation methods
Lignin sulfonate: 48.5%
Time: 2 hours
1: CE036
2: CE038

Table 2.3. Characteristics of prepared lignin sulfonate binders.

Temperature	Heating Period					
	1 hour		1.5 hours		2 hours	
	Solubility	Appearance	Solubility	Appearance	Solubility	Appearance
284°F(140°C)	†††	S.L.	†††	S.L.	††	S.L.
304°F(150°C)	†††	S.L.	†	V.S.S.(e)	‡	S.S.
320°F(160°C)	†	V.S.S.(f)	‡	S.S.	-	S.S.
338°F(170°C)	-	S.S.	-	H.S.	-	H.S.

Notes: S.L.: sticky liquor
V.S.S.: very soft solid
S.S.: soft solid
H.S.: hard solid

†††: very soluble
††: soluble
†: somewhat soluble
‡: slightly soluble
-: insoluble

(e),(f): preparation methods
Lignin sulfonate: 50%
Acid: 0%

converting lignin sulfonate to a water insoluble form is oxidative coupling. To date, polymerization of lignin products by oxidative coupling is not well known, but it has been recently shown to be a promising method in adhesives technology. It is also known that lignin sulfonates can be converted to an insoluble gel by oxidative treatment with chromic acid and corresponding preparations have found application as stabilizing agents for soils. However, in the latter case, complexing with chromium ions adds to the effect of oxidative coupling and the product, after curing, becomes hard and brittle.

It appears desirable to determine to what degree oxidative coupling could be used as a polymerization method for the production of water insoluble lignin sulfonate binders. For this purpose, an exploratory series of polymerizations have been made using hydrogen peroxide with potassium ferricyanide catalyst. Two kinds of lignin sulfonates showed quite different reactivities (Fig. 2.3). CaLS easily changed to a rubber-like gel in 10 to 20 min. reaction time; on the other hand, NH_4LS took at least several hours under the same dosage of oxidative agents. These quite different reactivities of two lignin sulfonates are presumably coincident with the different temperatures of materials during reaction, namely 95 to 102°F (35 to 39°C) for NH_4LS and 72 to 77°F (22 to 25°C) for CaLS. However, resulting rubber-like gels from the two lignin sulfonates showed similar appearances. The low reactivity of NH_4LS might be due to some sort of side reaction which consumed oxidative agents.

Rubber-like gels were almost insoluble in water, but showed high swelling properties probably because of the increased numbers of hydrophylic functional groups and many small air bubbles in the gel. The gel, once formed, did not become soft enough to mix with sand even at the elevated temperature. Therefore, some oxidative coupling reaction was applied after mixing with sand. The mixture after compacting in the mold and curing however, also showed a high swelling property and turned out to be inapplicable as a road binder.

Co-Polymerization With Urea-Formaldehyde Resin

NH_4LS was preheated in a stainless steel reaction vessel at 302 to 320°F (150 to 160°C) for 2 hrs., and then mixed with partially polymerized urea-formaldehyde resin (20 to 25% based on NH_4LS solid), and heated in a glass bottle at 122°F (50°C), pH 4.1 for 2 hrs.

Partially polymerized urea-formaldehyde resin was prepared by heating the mixture of urea and formaldehyde (molar ratio: urea/formaldehyde - 1/1 - 1/4) at pH 9, 245°F (120°C) for 1 hr.

As discussed earlier, reduction of swelling in water is very important in order to maintain sufficient strength after soaking. As a means of reducing swelling, addition of synthetic resins can be visualized. For this application, the resin must be inexpensive and readily available. Urea-formaldehyde resin is probably one of the most suitable resins from these standpoints. Furthermore, under moderate polymerization conditions, the lignin sulfonate-urea formaldehyde polymerization product can be expected to maintain some flexibility because of its presumably loose three dimensional network structure.

The best result was obtained by mixing sand with urea-formaldehyde resin (molar ratio: urea/formaldehyde - 1/4) and prepolymerized NH_4-LSA, 2.5% and 10% based on sand. respectively. The samples extruded from the mold did not show any more swelling tendency and kept some strength even after soaking overnight. The unconfined compression strength was about 75 to 95 psi (.52 to .65 MPa). These characteristics may be acceptable for some kinds of road binders.

However, from the standpoint of practical applicability as a road binder, there are still some large problems to be solved, namely less flexibility, expansion during curing, amount of urea-formaldehyde resin required and strong formaldehyde odor.

Co-Polymerization With Phenol-Formaldehyde Resin

NH_4LS or CaLS was mixed with varying amounts of phenol (or bark phenol), formaldehyde and hydrochloric acid, and then heated in a glass bottle at 122°F (50°C) for 2 hrs.

Amounts of chemicals added were as follows:

	Concentration*
phenol or bark phenol	1.0 - 5.0%
formaldehyde	1.0 - 3.0%
hydrochloric acid	0.35 - 3.5%

*based on total weight of mixture

Phenol-formaldehyde resin is also one of the inexpensive and readily available resins, Application of bark phenon-formaldehyde resin is desirable from the standpoint of forest products utilization. However, co-polymerization products of lignin sulfonate, phenol (or bark phenol) and formaldehyde could not be applied successfully because of the excessive brittleness and lack of cohesiveness with sand particles.

Condensation With Polyacryamide

250 ml of NH_4LS was mixed with 2 to 6g of commercial polyacrylamide powder (Accostrength 86, American Cyanamid Co.), and then heated at 304°F (150°C) for 0.5 to 2 hrs. in a stainless steel reaction vessel.

It was found that the insolubilization of NH_4LS was remarkably accelerated by a small amount of urea. The mechanism of this reaction is not yet clear, but may be attributed to the condensation reaction between the amino group in urea and the benzyl-alcohol and carbonyl groups in lignin sulfonate. Although the insolubilized NH_4LS with urea was still inapplicable as a road binder because of its swelling property, it was suggestive of the application of polymers which have similar type amino groups.

Polyacrylamide is a long, linear chain vinyl polymer with pendant amide groups. Therefore, if condensation with lignin sulfonate happened at the amide group of this polymer, it would be very effective in binding lignin sulfonate molecules together with some flexibility and restraining the swelling property during soaking in water. Figs. 2.4 and 2.5 show the viscosities of the binder solution. Although the viscosity of NH_4LS without polyacrylamide increased during the heat treatment, the effect of the polyacrylamide was considerable. In the case of CaLS the effect was more apparent, because CaLS itself did not change so much in terms of viscosity by heat treatment alone. Under these conditions, the viscosity of the polyacrylamide solution itself apparently did not change. Therefore, it is reasonable to conclude that these large viscosity increases are due to the same kinds of reactions between lignin sulfonate and polyacrylamide. The extremely high viscosity of polyacrylamide and formaldehyde treated NH_4LS is presumably attributed to the introduction of methylol groups by the reaction of formaldehyde. These methylol groups are probably highly reactive towards polyacrylamide.

The best binder by this procedure was obtained by adding 5g polyacrylamide to 250 ml NH_4-LS and heating at 302°F (150°C) for 1.5 hrs. This binder could be mixed successfully with sand after softening by short pretreatment at 221°F (105°C) for 15 min. This binder also showed considerable stability after soaking which was nearly comparable to that of the urea-formaldehyde copolymerized samples (Fig. 2.6).

D. Summary and Conclusions

Although there are many interesting characteristics of lignin sulfonates binders as a road paving material, the current applications are limited only to secondary or temporary road paving, mainly because of their low durabilities. Therefore, the most important purpose of this study was to develop new procedures for the lignin sulfonate binders which fulfilled four important points, that is, (1) water insolubility, (2) low swelling property, (3) low brittleness, and (4) sufficient strength. These properties of binders are essentially dependent on the molecular weight, amount of hydrophylic groups (mainly sulfonic acid group) and density of the three dimensional network.

In this study, five procedures were tested to change these lignin sulfonate characteristics and to prepare better binders for paving. However, it turned out to be very difficult to adequately fulfill all the requirements. A water insoluble lignin sulfonate binder having less swelling was usually very brittle and did not retain sufficient cohesive strength especially after curing. Table 2.4 shows the comparison of the five procedures in terms of (1) swelling, (2) brittleness and (3) reactivity.

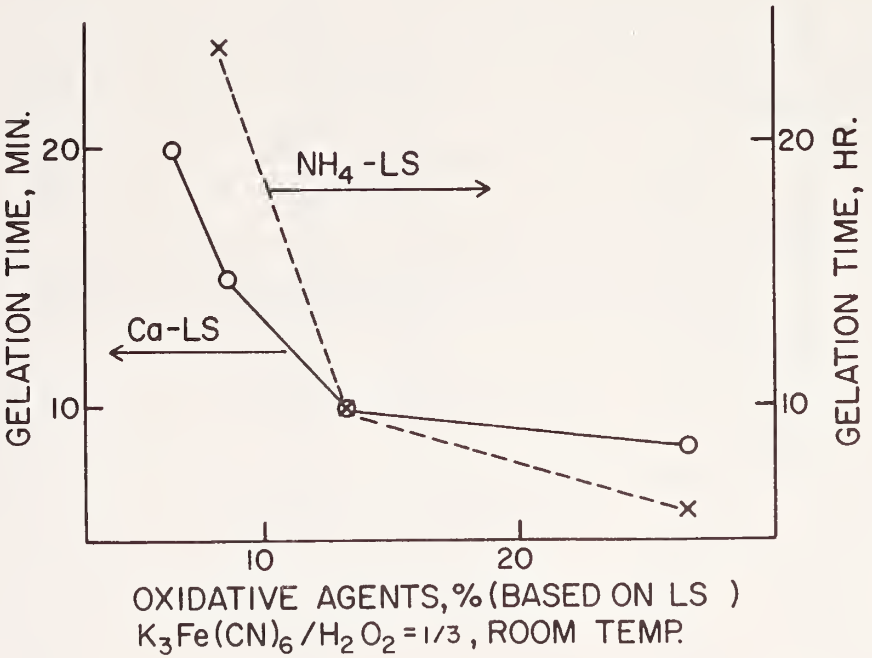


Figure 2.3 Gelation of ligninsulfonates by oxidative coupling reaction.

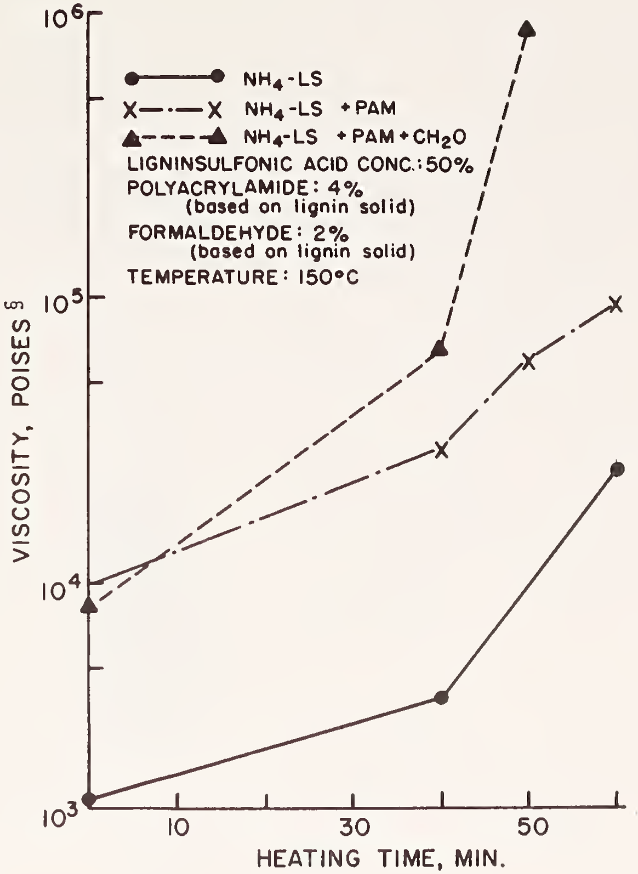


Figure 2.4. Changes of viscosity of ammonium ligninsulfonate.

§To convert to Pa·s: Poises x 1.0 x 10^{-1}

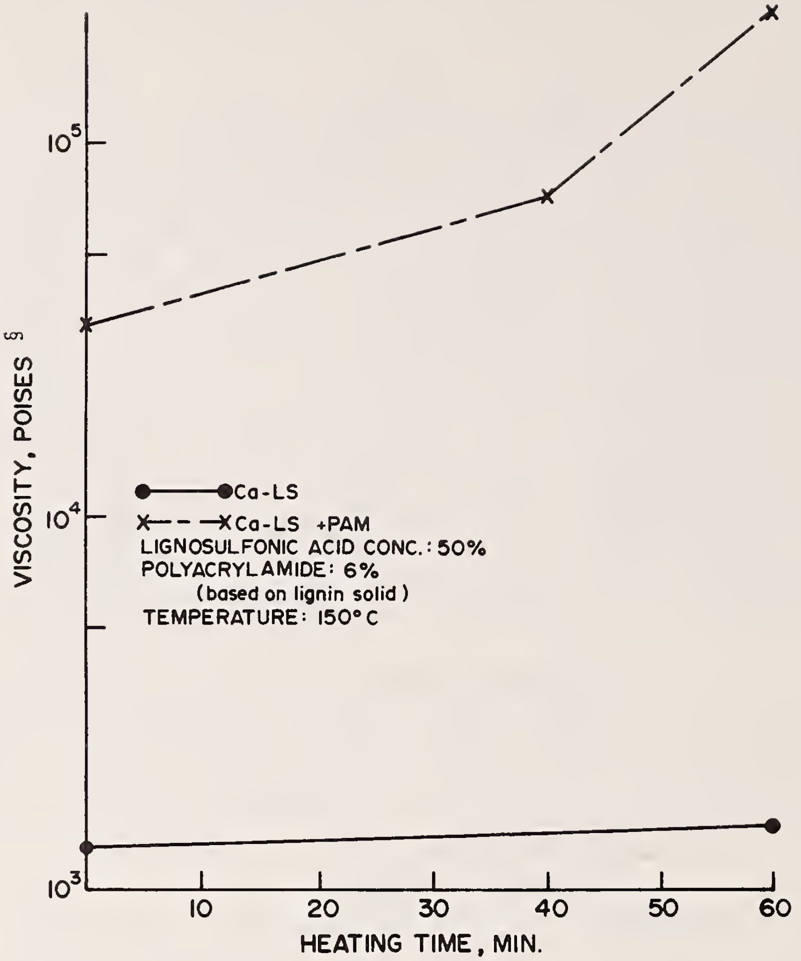


Figure 2.5. Changes of viscosity of calcium ligninsulfonate.

§To convert to Pa·s: psi x 1.0 x 10^{-1}

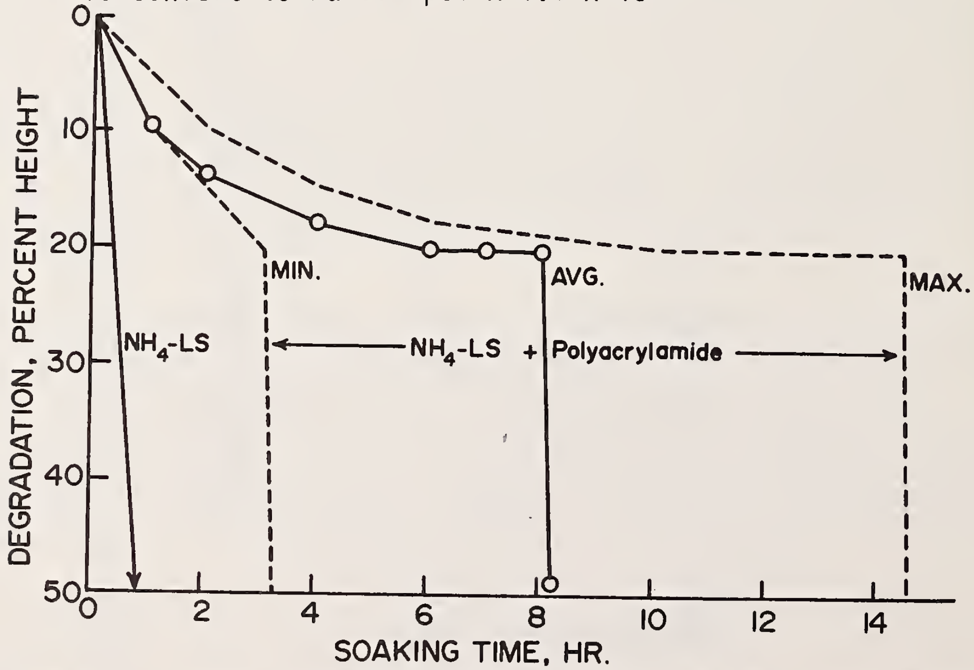


Figure 2.6. Soaking stability for mixtures on 8% binder based on sand.

Table 2.4. Comparison of binder characteristics.

	Procedure	Water Swelling	Brittleness	Reactivity
1:	Heat treatment with or without acid	high	high	Ca-LS <NH_4-LS
2:	Oxidative coupling by hydrogen-potassium ferri-cyamide catalyst	high	high	Ca-LS >NH_4-LS
3:	Co-polymerization with urea-formaldehyde resin	low	high	Ca-LS =NH_4-LS
4:	Co-polymerization with phenol(or bark phenol)-formaldehyde resin	low	high	Ca-LS =NH_4-LS
5:	Condensation with polyacrylamide	low	low	Ca-LS =NH_4-LS

It is clear that among these procedures, only the condensation of lignin sulfonate with polyacrylamide might be feasible to be the procedure for the lignin sulfonate binder preparation. The coupling reaction with hydrogen peroxide-ferricyamide might be a feasible procedure if the extremely high swelling property of the resulting binder were reduced. This procedure is desirable because it is simple and doesn't require a heating system.

The low water swelling and low brittleness of the polyacrylamide condensation product must be dependent on its three dimensional structure (Fig. 2.7). The swelling property might be restricted by the polyacrylamide-lignin sulfonate network which still leaves some room to make the binder somewhat flexible. In the case of the other procedures, the situations are probably quite different. The lignin sulfonate molecules are kept in the rather rigid three dimensional networks of polymerized lignin sulfonate or other resins. Therefore, binders cannot develop sufficient flexibility.

Although the lignin sulfonate-polyacrylamide condensation product is not good enough for highway paving, this binder can provide a better road surface for secondary and temporary roads than the stright application of sulfite waste liquor. Furthermore, application of the other polymers with pendant amino groups, such as chitin, chitosan and acrylamide vinyl copolymer, may be useful for the improvement of the binder.

E. Reference

1. Gupta, P. R., and J. McCarthy. Macromolecules 1, 236, (1968).

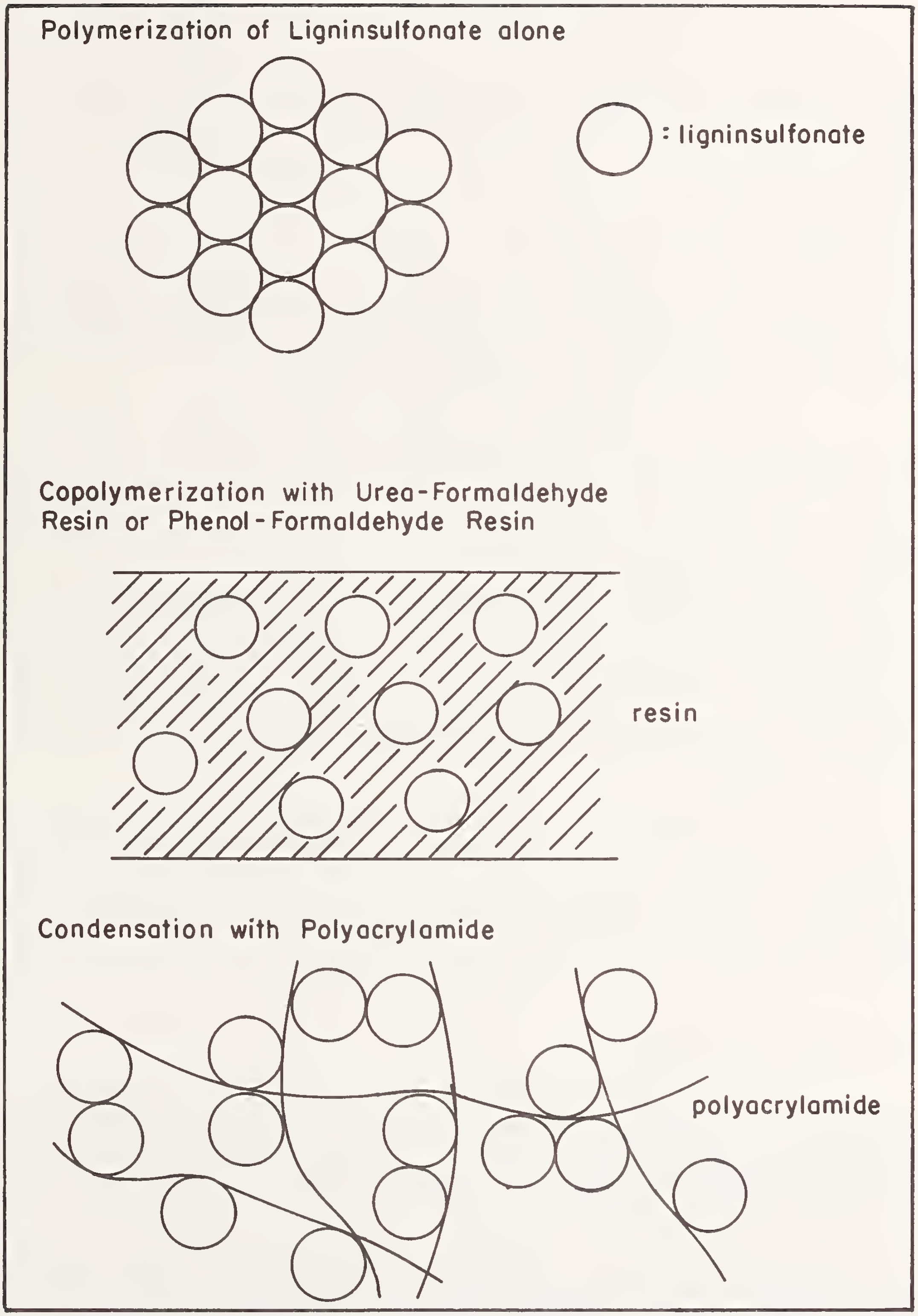


Figure 2.7. Tentative structures of lignin sulfonate binders.

III. LIGNIN AS AN EXTENDER OF ASPHALT

Asphalt is a semi-solid blend of hydrocarbon molecules ranging in molecular weight from approximately 300 through 5,000. Structurally asphalt contains aliphatic hydrocarbons, aromatics and naphthenic structures with or without aliphatic side chains. Asphalt constituents are frequently classified into three groups on the basis of carbon to hydrogen ratio: asphaltenes, $C/H > 0.8$; resins, $C/H < 0.8$ and > 0.6; and oils, $C/H < 0.6$. In addition to carbon and hydrogen, asphalts typically contain 0-1% nitrogen, 1-7% sulfur and 0-5% oxygen. The sulfur and nitrogen in asphalts are usually bound in the aromatic ring structures as pyridines, pyrroles, or thiophenes, while the oxygen are usually present as ketones or phenols. Asphalts are soluble in light hydrocarbons and are water insoluble. A representative asphaltene molecule is shown in Figure 3.1(1).

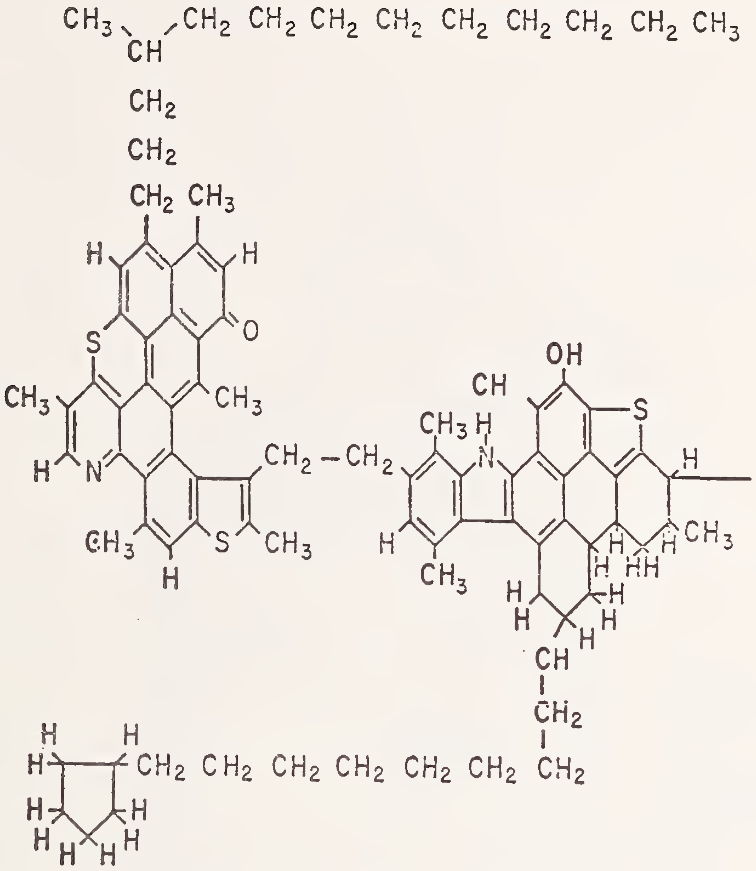
In contrast lignin is a three dimensional polymer of coniferyl, sinapyl, and p-coumaryl alcohols. As discussed earlier, two broad classes of modified lignin are commercially available: kraft lignin and lignin sulfonates. Kraft lignin, whose partial structure was shown in Figure 1.3, are polydisperse (wide molecular weight distribution) with an average molecular weight of 3,000-3,500. Representative unit formulas for kraft lignins are: hardwood $Ca\ H_{7.2}O_{1.8}S_{0.1}\ (OMe)_{1.5}$; softwood $Ca\ H_{7.9}O_{2.1}S_{0.1}(OMe)_{0.82}$. The average molecule of kraft lignin contains 15-20 of these units. Kraft lignins have a much higher carbon to hydrogen ratio (≃ 1.2) than asphalts. Oxygen in kraft lignins is bound in alkyl and aryl ether structures and as methoxy and phenol units. Sulfur is typically present as a thiol. While water and hydrocarbon are insoluble, kraft lignin is soluble in aqueous bases and organic compounds such as dioxane.

Lignin sulfonates, as typified by Figure 1.1, contain anionic sulfonate groups and a cation corresponding to the base of the pulping liquor. The presence of the sulfonate group makes lignin sulfonates water soluble. Softwood lignin sulfonates may be represented by the formula $CaH_{7.7}O_{2.0}(SO_3^-)_{0.30}(OMe)_{1.0}(Cation)_{0.30}$. While their average molecular weight is 10-11,000, molecular weights in a single sample may range from 400 to 150,000.

A. Binder Preparation

In order to utilize lignin and asphalt together in pavements, a reasonable and convenient method is required to blend the asphalt and lignin to form a coherent binder. Several methods of preparing lignin-asphalt binder have been developed and evaluated. Basically, two approaches are used - Parr reactor and Open Vessel.

The Parr reactor is an impeller stirred pressure vessel equipped with a variac controlled external electrical heater. Reaction temperatures can be read with a dial thermometer and could be varied from 77 to 662°F (25 to 350°C). The reactor can be operated at pressures up to 2,000 psig (13.79 MPa). Figures 3.2 and 3.3 show the pressure reactor used in this study.



$[C_{89}\ H_{104}\ S_3\ N_2\ O_2]_2$

Mol Wt = 1328x2
C/H Ratio = .86
% Sulfur =7.1
% Oxygen =2.4
% Nitrogen=1.8

Figure 3.1. Hypothetical asphaltene molecule. (1).

The "open vessel" method is simply a normal open vessel such as a mixing bowl used in the laboratory for material preparations.

Figure 3.4 shows the various methods for preparing lignin-asphalt binders by the Parr reactor and open vessel. These are briefly described as follows:

1. Blend lignin and asphalt in a Parr reactor. The elevated temperature and pressure in the Parr reactor is believed to promote reaction between the two materials.

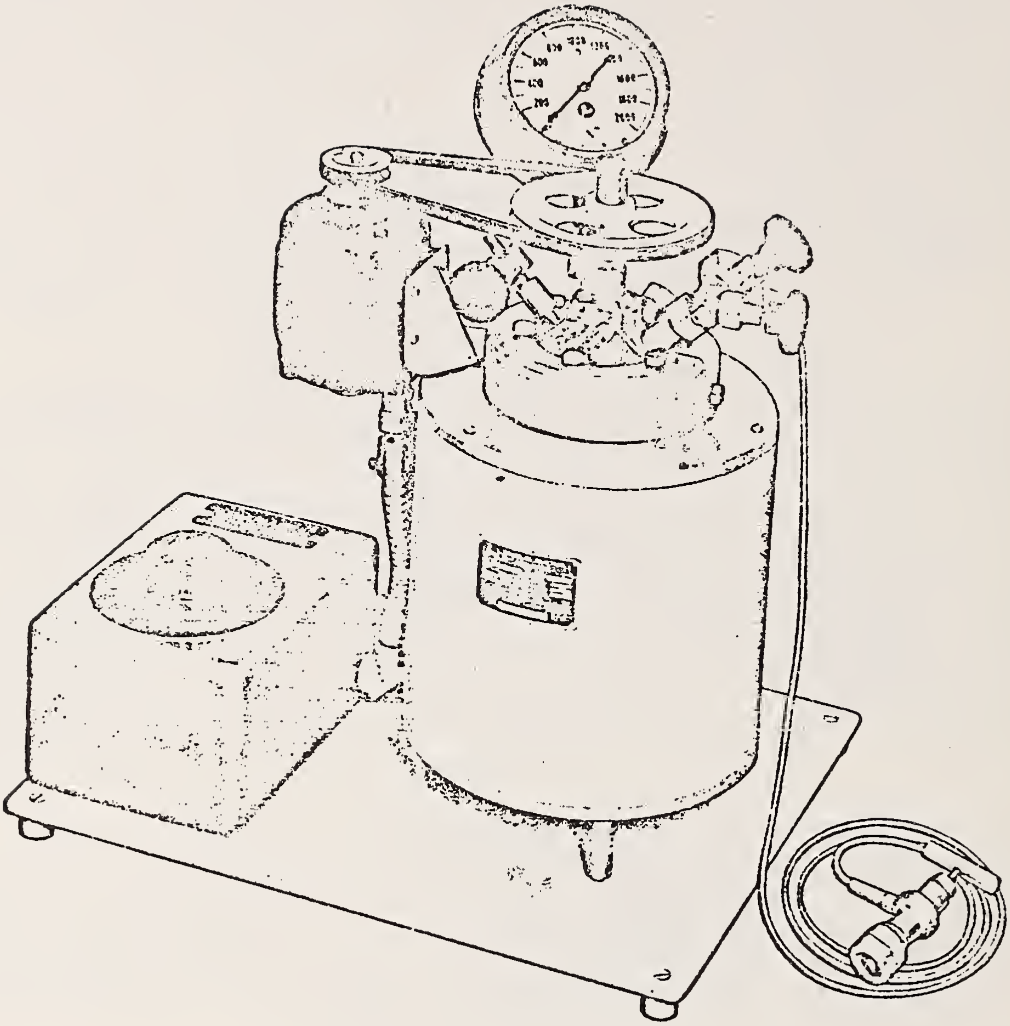


Figure 3.2. Pressure reaction apparatus used for lignin-asphalt extender binders (Series 4500, Parr Instrument Co.).

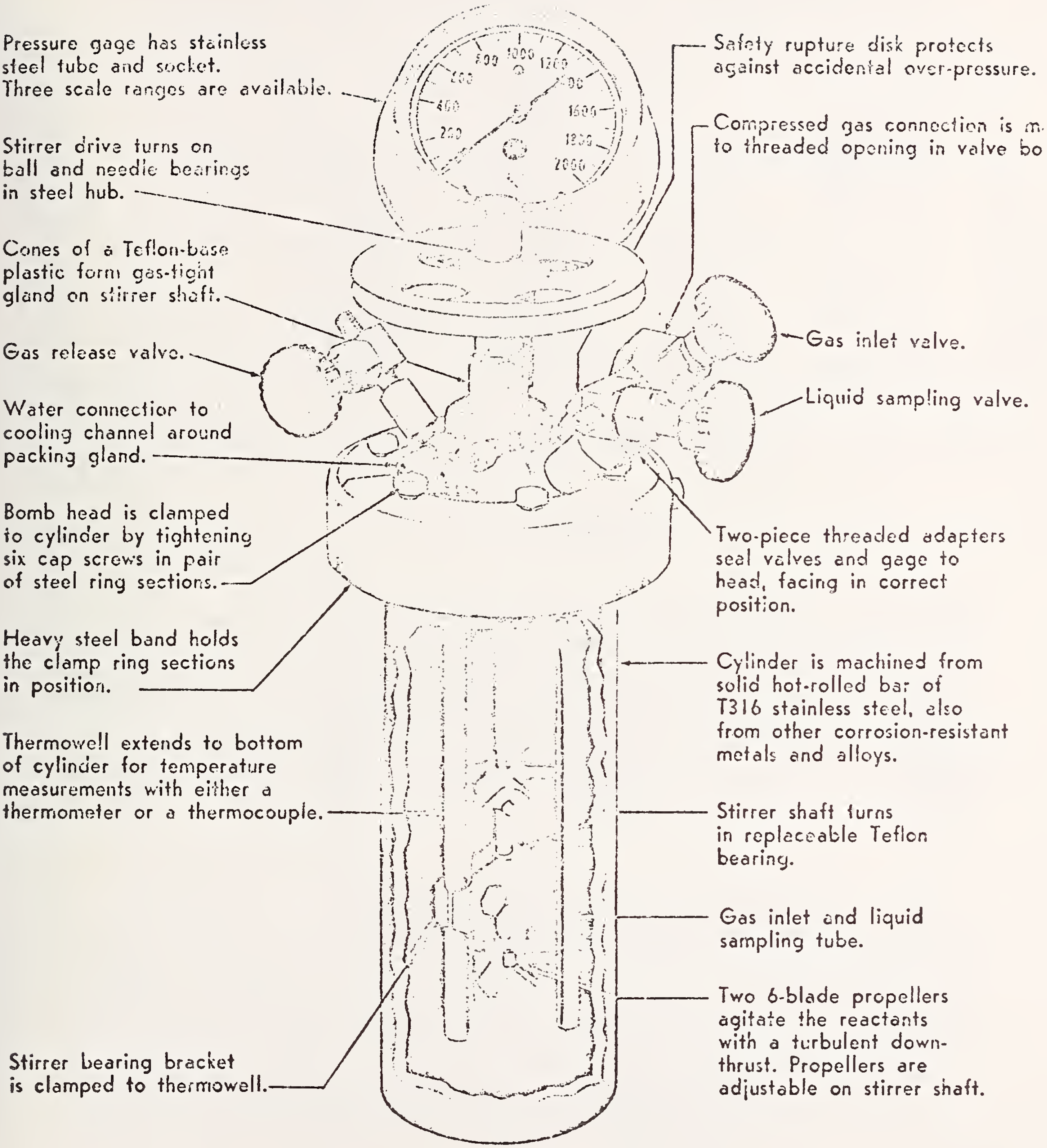


Figure 3.3. Sectioned view of the pressure reaction apparatus shows the principal parts of the 2000 ml. bomb.

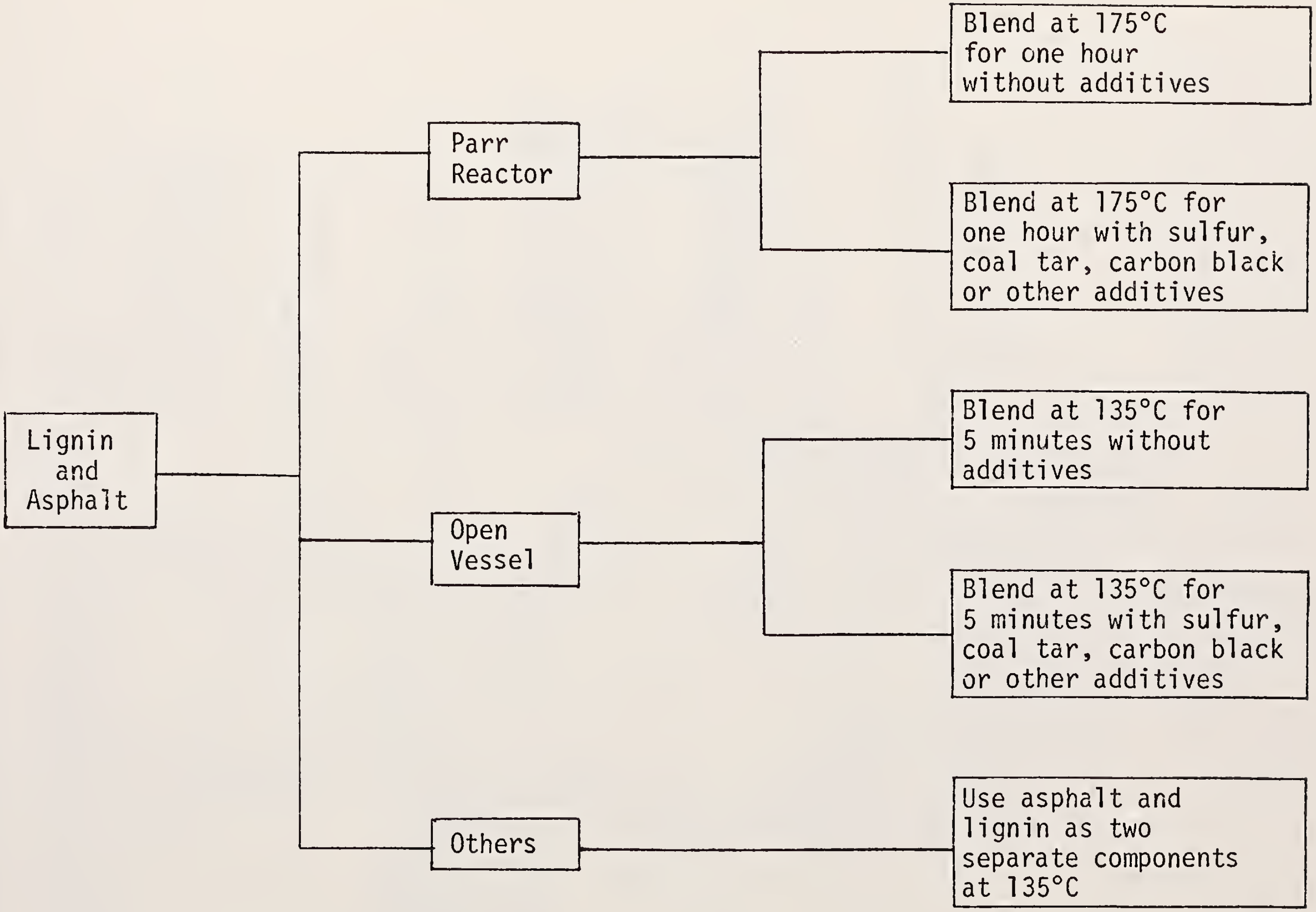


Figure 3.4. Methods of preparation of lignin-asphalt binders.

2. Blend lignin and asphalt in Parr reactor with small amounts of sulfur or other additives. The sulfur is believed to improve reactions between the two materials and make the binders more workable.

3. Blend lignin and asphalt in open vessel.

4. Blend lignin and asphalt with sulfur, coal, tar, carbon black or other additive, in an open vessel to make preparations more practical and simple.

5. Blend modified lignin and asphalt in open vessel.

B. Laboratory Tests on Binders

Tests such as specific gravity, penetration, ring and ball softening point and viscosity that are normally used to evaluate asphalt materials were performed according to ASTM procedures to determine the basic properties of the new binders. In the preliminary studies, solubility and degradation tests were also performed on each binder.

A summary of the test methods is as follows.

Penetration Test

The penetration test determines the relative hardness or consistency of the binder by measuring the distance that a standard needle will penetrate vertically into the sample under specified conditions of time, temperature and loading. Standard penetration, which is implied unless other conditions are stated, is for a load of 100 g applied for 5 seconds at a temperature of 77°F (25°C) (ASTM Test D5). Softer materials have higher penetration values. Other test conditions used are 32°F (0°C) 200g, 60 secs. and 115°F (46°C) 50g, 5 secs.

Softening Point Test

Different grade asphalts soften at different temperatures. The softening point is usually determined by the ring and ball test method (ASTM Test D36). The softening point indicates the temperature at which the binder changes from solid to liquid. In this test, the binder is poured into a brass ring of specified dimensions. The sample thus prepared is suspended in a water bath and a steel ball of specified dimensions and weight is placed in the center of the sample. The bath is heated at a controlled rate and the temperature at the instant the steel ball reaches the bottom of the glass vessel or steel plate is recorded. This temperature is termed the softening point.

Specific Gravity Test

The specific gravity of a material is the ratio of the weight of a given volume of the material to the weight of an equal volume of water at a given temperature, usually 77°F (25°C). For asphalt cements, the test is usually performed with a pycnometer bottle. By filling the bottle only partially full of asphalt or the binder, the asphalt or binder volume can be determined by the difference between the total volume of the bottle and the volume of water required to complete the filling. This test was conducted in accordance with ASTM Test Method D70.

Viscosity Test

The viscosity of each binder was measured in absolute units poises (Pa.s) with the sliding plate microviscometer (Fig. 3.5). The principal of the microviscometer is based on the measurement of the shear rate of a sample placed between parallel plates subject to a constant shear stress.

In this test, the viscometer with binder sample is first placed in the water bath at the desired test temperature. A recorder is used for measuring the displacement of the plates. A load is applied by placing a weight on the weight hanger and allowing it to remain while the pen traces a movement on the chart. The size of the weight is written on the chart immediately adjacent to the trace. An additional weight is then added or a portion removed from the weight hanger for viscosity measurement at a different shear rate.

After measurements at three or four shear rates, the chart is removed, and with a straight edge, a line is drawn through the trace for each separate load, and data from each line used in calculating viscosity.

Solubility Test

In this project, solubility is defined as the color of the water after soaking the specimen. The solubility test is an empirical test in which the color of the water after soaking of each specimen is compared to a range of standard solutions. The standard solutions were prepared by adding small amounts of lignin solids to water. A clear solution of water without lignin solids was number 0. The darkest solution containing the greatest quantity of lignin solids was numbered 7.

C. Mixture Design Procedures

Test specimens were prepared in accordance with the Hveem Method of mix design. The specimens consist of mixtures of binder candidates with Steilacoom quarry aggregate meeting Class B Washington State dense gradation. In the preliminary screening of binders, No. 60 Ottawa sand aggregate was used. The steps in the preparation of mixtures are as shown in Figure 3.6 and are presented below.

Proportioning of Materials

Materials are proportioned by weight and the binder is based on the dry weight of the aggregate.

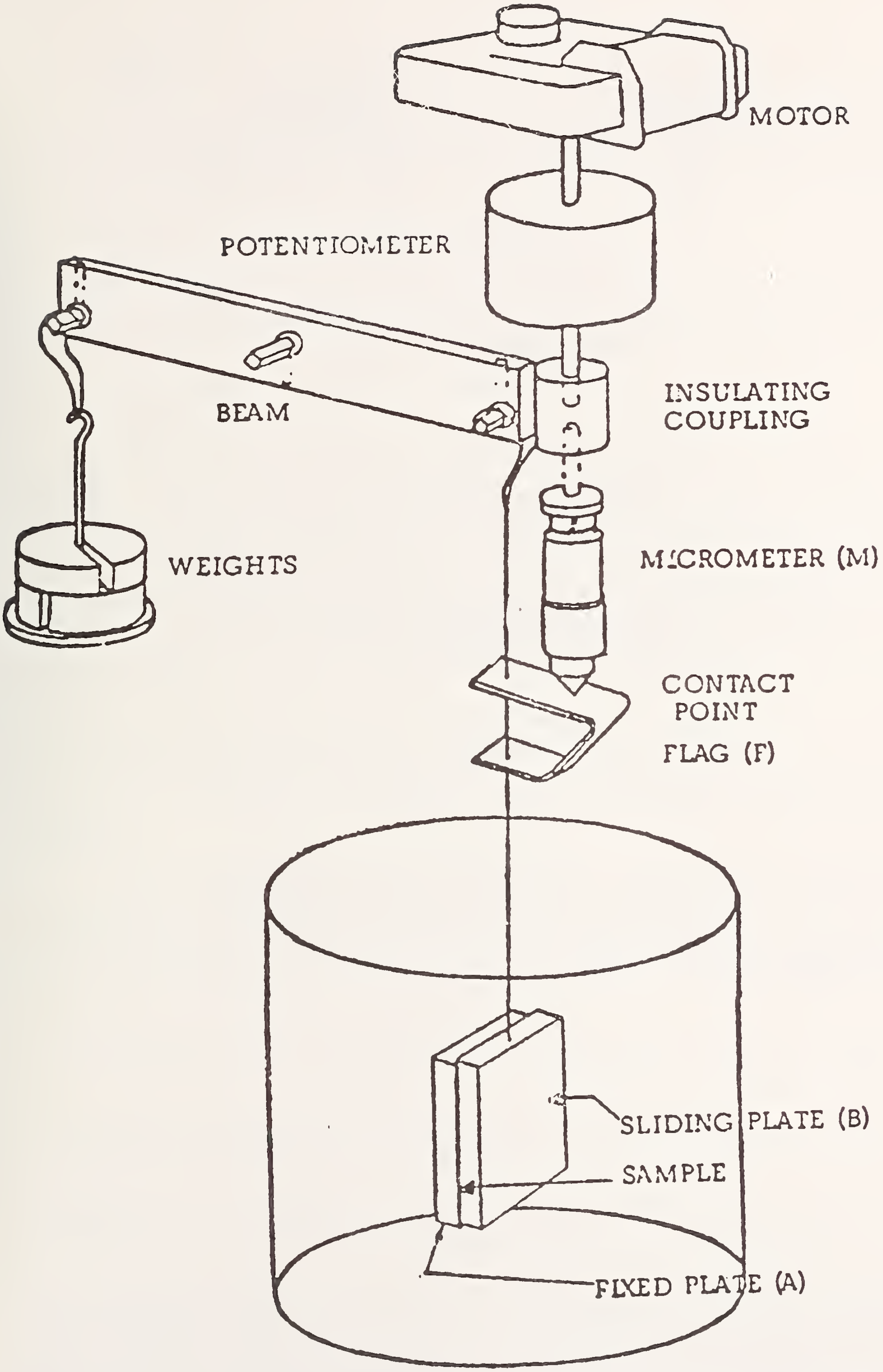


Figure 3.5. Schematic diagram of sliding plate microviscometer.

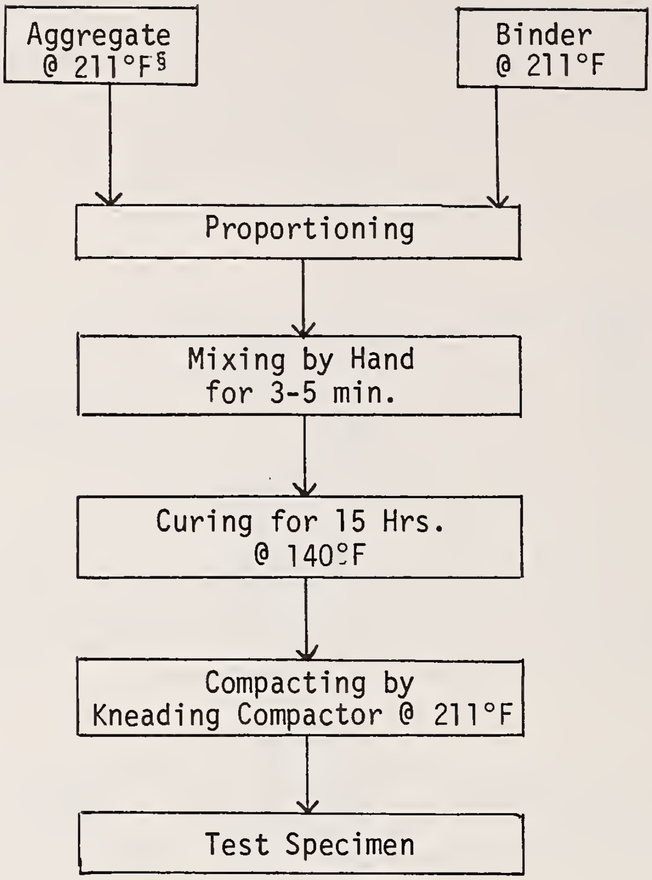


Figure 3.6. Preparation of mixtures and test specimens.

[§]To convert °C: $\frac{9}{5}$ °C - 32

Mixing

Prior to mixing, the aggregate is preheated for 24 hours and the binder preheated for one hour at 275°F (135°C). The binder is mixed with the aggregate manually. Mixing times range from three to five minutes.

Curing

Once prepared, the mixtures are placed in an oven at 140°F (60°C) for a 15 hour curing period. Following this period, the mixtures are placed in the oven and preheated at 230°F (110°C) in preparation for compaction.

Compaction

Laboratory specimens are compacted in accordance with Washington State Highway Department Test Method 702A utilizing the Triaxial Kneading Compactor. This method for preparation is similar to ASTM Test D-1561. The Kneading Compactor Foot pressure is reduced to 350 psi (2.41 MPa) to minimize crushing the aggregate during compaction and to achieve a desirable range of void content in the specimen. The mixtures are placed in the mold during the first 25 blows of the compactor foot. The specimens are then subjected to an additional 150 blows of compaction. A leveling load of 12,650 pounds (56.3 KN) is applied using a single plunger for a period of one minute.

Test for Specimens

For each phase of the study, specific laboratory mixture tests were performed. A summary of the test conducted during the project is as follows:

Density, air voids. After compaction, specimens are extruded from the molds and allowed to cool down to ambient temperature. The height or thickness of each sample is then measured. Two centerlines on each face of the sample are also drawn to facilitate centering the specimen in the resilient modulus testing device.

By measuring the weight of each sample in the air and in the water, specific gravity is calculated.

Percent air voids in each specimen is calculated from the laboratory determined maximum and bulk densities.

After the density determination, specimens are placed in the oven at 140°F (60°C) for two hours in preparation for the Hveem test.

Hveem stability. Some state agencies utilize the Hveem method of mix design and control rather than the commonly used Marshall method. This test has been standardized as ASTM D1560, Resistance to Deformation and Cohesion of Bituminous Mixutres by means of Hveem Apparatus. A specimen of 4 in. (101.6 mm) diameter by about 2.5 in. (63.5 mm) height is placed in the Hveem stabilometer and subjected to a gradually increasing vertical load.

As the vertical load increases, the specimen attempts to deform laterally. This results in the generation of pressures within a liquid (such as oil) which is separated from the test specimen by use of a diaphram. The lateral pressure is read at selected vertical loads. The Hveem stability is calculated by an established formula and is a measure of the resistance to lateral deformation due to vertical load. The value derived from this test is relative in nature but displays a very high correlation to pavement performance (5).

Indirect Tensile Strength

Indirect tensile strength is an indication of the fracture strength of the mixtures. It was measured by loading the specimens with compressive loads which act parallel to and along the vertical diametral plane, as shown in Figure 3.7.

Though many mix variables influence the maximum tensile strength, this strength is especially dependent on the rate of loading and temperature. In order to control these conditions, the tests are conducted at 77°F (25°C) after the specimens had been cured overnight at this temperature. The tests were performed using a 60,000 lb (27,000 kg) Baldwin Hydraulic Testing Machine at a rate of loading of 2 in. (50.8 mm) per min. (ASTM Test C-496).

Resilient Modulus

The resilient modulus, M_R, is a dymanic response defined as the ratio of the repeated axial deviator stress, σ_d, to the recoverable axial strain, ε_x.

$$M_R = \frac{\sigma_d}{\varepsilon_x}$$

With the addition of two transducers, one mounted on each side of the specimen's horizontal axis, the deformations are measured by the transducers, amplified and recorded on a strip chart recorder.

By knowing the dynamic load and calculating the deformation, M_R can be determined. For an applied dynamic load, P, in which the resulting horizontal dynamic deformation is δ_h, the M_R value is:

$$M_R = \frac{P(\mu + 0.2734)}{t\delta_h}$$

where μ is the Poisson's ratio (estimated to be 0.31 from limited tests)
t is the thickness of the sample in inches
δ_h is the deformation calculated from the amplitude of the graph ½ produced by the strip chart recorder.

A load of P = 100 lbs (45 kg) was used for all the M_R tests. Repetitive loads applied at 30 per min. were used with a 0.1 second duration (followed by

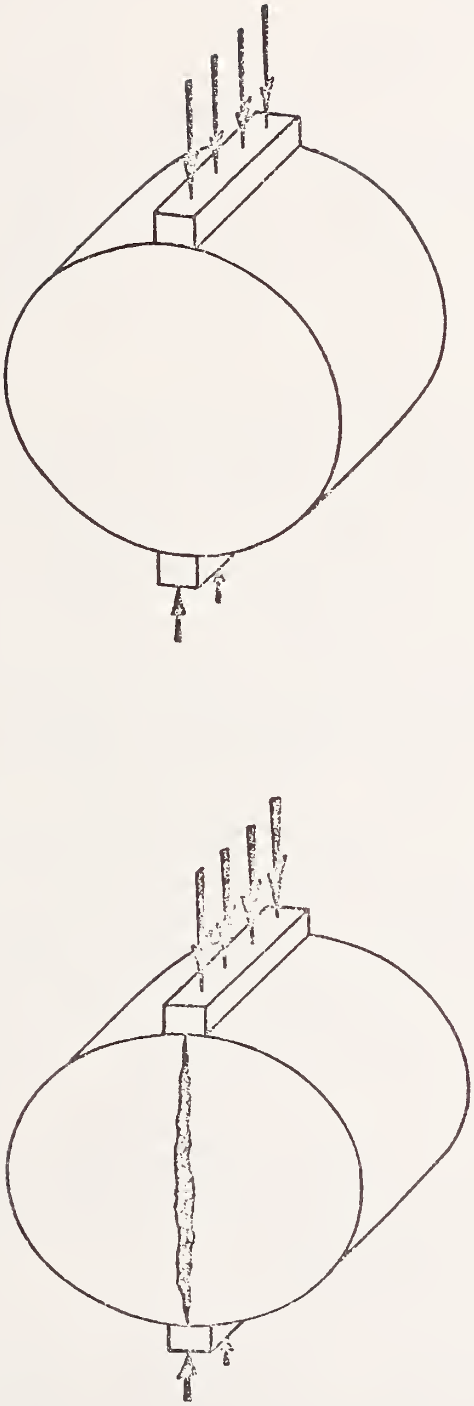


Figure 3.7. Cylindrical specimen showing diametral compressive load being applied and mode of failure.

1.9 seconds swell). Before the M_R tests, the samples were placed in a dry temperature chamber or water bath at 77°F (25°C) for a minimum of 4 hrs. Each specimen was tested twice by rotating the sample 90° and at room temperature and these results averaged.

Vacuum-Saturated and Soaked M_R

The vacuum-saturated and soaked M_R test was performed and calculated in the same way as the dry M_R, except that the specimens were submerged in water in a dessicator and subjected to a vacuum of about 25 in. (635 mm) of mercury for 15 min. After vacuum saturation, the specimens were soaked at atmospheric pressure overnight in a water bth at 77°F (25°C). The specimens were removed the next day and quickly tested in the surface moist condition.

Freeze-Thaw Cycle Conditioning

For the freeze-thaw cycle conditioning tests, the specimens were first tested in the vacuum-saturated and soaked condition as described earlier. Following the vacuum saturation and soaked M_R test, the specimens were returned to the water bath for a short soaking period. The specimens were then immediately wrapped in plastic and placed in the cyclic air chamber. The conditioning procedure followed was developed by Lottman at the University of Idaho (1). For this procedure, specimens were left surface moist and each covered separately and tightly with two layers of clear polyethylene wrap which was taped to each specimen. Each specimen was then placed in a plastic bag containing approximately 10 ml of water, and the bag was sealed. The wrapped specimens were then placed flat on the shelves of the cyclic air temperature chamber and the temperature cycling started. Temperature cycling consisted of 15 cycles (8 hrs. per cycle). Lottman determined that if the number of cycles is increased from 12 to 18 cycles about 10% more damage occurred and that 18 cycle damage produced about the maximum damage when considering matching to wheel-lane cores. In these tests, however, the number of freeze-thaw cycles were reduced from 18 to 15 since the overall effect on conditioning was not considered significant. The chamber air temperature was set for a cycle ranging from 0°F to 120°F and back to 0°F (-18° to 49° to -18°C) and is timed for eight hrs.; four hrs. per half cycle. The response of the chamber and the specimens to the programmed temperature cycles is shown in Figure 3.8 (2). At the end of selected time intervals (3, 9, 15 cycles) the wrapped specimens were remvoed from the cycle air temperature and prepared for M_R testing by soaking in the 77°F (25°C) water bath for a minimum of 4 hrs. before testing in the surface moist condition. The objective of moisture conditioning was to saturate the specimens to bring out their lowest mechanical properties caused by moisture damage and compare the various binder qualities in reducing this moisture damage.

Accelerated Conditioning at 140°F

The 140°F (60°C) accelerated conditioning test was conducted to study the physio-chemical aging phenomen and stripping potential of binder-aggregate mixtures and its effect on the resilient modulus properties of the specimens with various binders. For this test, after the specimens were fabricated they were placed in an oven at 140°F (60°C) and held at this temperature for

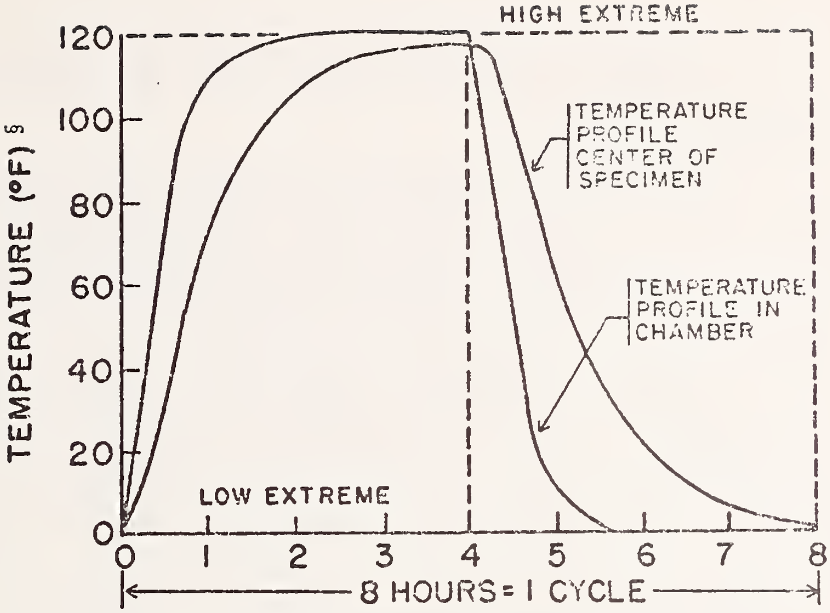


Figure 3.8. Response of chamber and specimens to programmed temperature cycles.

§To convert to °C: $\frac{5}{9}$(°F - 32)

selected time intervals. Before testing, the specimens were stored at 77°F (25°C) for a minimum of 4 hrs. The time spent cooling at 77°F (25°C) and being tested was not counted in the accumulation of 140°F (60°C) condition time. The M_R of the specimens were tested after 24, 72, 120 and 240 hours.

D. Evaluation of Lignin as Asphalt Extenders

To utilize lignins as asphalt extenders, the tasks were divided into three phases: Phase A, Phase B and Phase C. Each subsequent phase required a more thorough investigation of the possibility of using lignin-asphalt binders in pavements. Figure 3.9 is a schematic diagram of the evaluation phases of lignin-asphalt binders. The tasks and results involved in each phase of the study is described as follows:

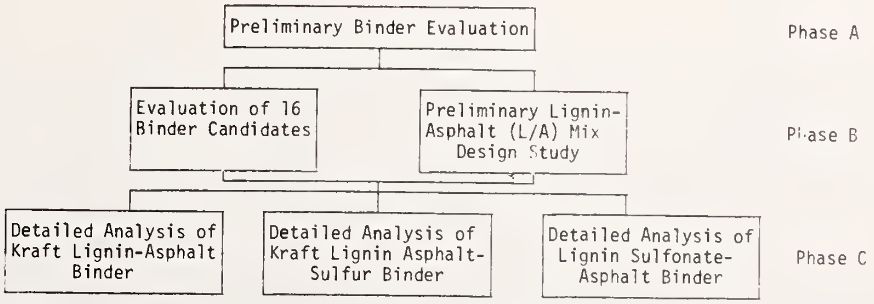


Figure 3.9. Schematic diagram of lignin-asphalt binder studies.

Phase A - Preliminary Evaluation

The task for this phase was to modify the lignins so that they would be compatable with asphalt. Three major lignin property changes were required; water insolubility , hydrocarbon solubility, and molecular weight reduction. The study involved the screening of many variables including fabrication and testing of more than one hundred binder specimens.

While the literature contained no examples of lignin-asphalt reactions, the study showed that there were a wide variety of lignin modification reactions. Previous work by Enkvist as reported in McMonagle (3) had demonstrated that kraft lignin molecules could be thermally cracked. Exploratory experiments in the laboratory (3) also demonstrated that water insolubles were formed during thermal phenolysis of lignin sulfonates. Extension of this method of pressure heating to lignin-asphalt systems was therefore attempted. Elemental sulfur was added in some cases to the reactants. To protect the asphalt from oxidation, an inert atmosphere was selectively employed.

The results of these experiments are shown in Appendix B. A general outline of the experimental technique follows.

Equipment

All pressure reactions were accomplished in a Parr model 4501 reactor (Parr Instrument Co., 211-53rd St., Moline, IL 61265) as shown in Figures 3.2 and 3.3.

Materials

Paving grade asphalt cement (AR-2000, Chevron Asphalt Co., Richmond Beach, Washington), dried lignin sulfonates and kraft lignin (see Table B-1 Appendix B), phenolic bark fraction (Silvacon 490, Weyerhaeuser Co., Tacoma, Washington), and sulfur (Stauffer Chemical Co., New York 10017) were used throughout.

Method

Samples (quantities shown in Appendix B) of dried lignins, bark fractions and/or sulfur were blended into molten asphalt [58°F (70°C)] until a uniform mixture was obtained. In selected cases the mixture was split into two portions, one of which was oven heated [194°F (90°C)] in an open pan for 1.5 hrs. the Remaining (or the entire) mixture was sealed into the pressure reactor. Where applicable, the sealed reaction vessel was thrice evacuated and purged with an inert gas (He or N_2). After insertion into the heating mantel, the reactor was heated to the specified reaction temperature. The time required to reach the reaction temperature typically was 4 hours. After reaction for a specified time (usually 1 hour) the reactor was removed from the heater and allowed to cool to 158-176°F (70-80°C). Gaseous reaction products were vented into a fume hood, the reactor was opened, and the product was poured from the reactor.

The results of this preparation method are included in Appendix B and a summary of preliminary test results are shown in Table 3.1.

Table 3.1. Summary of lignin-asphalt binders test results.

NUMBER	UNCONF. COMP. STR. PSI [§]		SOLUTION COLOR	DEGRADATION
	DRY	SOAKED		
CE 009	13	22	0	None
010	16	30	2	Slight
014	14	12	6	Moderate
015	13	17	6	Moderate
021		25	0	None*
022	14	24	6	None
024	166	0	7	Severe
034	153	5	4	Slight
040	25	0	7	Severe
041	66	51	7	Severe
048	18	7	4	None
049	89	120	2	None
052	10	8	3	Slight
053	86	80	1	None
056	14	8	3	None
057	13	16	1	None
060	15	13	6	Slight
061	25	30	2	None
062	18	8	4	None
063	79	101	4	Slight
064	51	141	1	None
065	50	169	0	None
066	35	88	1	None
067	251	506	0	None
068	48	53	1	None
069	302	385	0	None
087	146	172	1	None
088	81	78	1	None
093	56	72	2	None
094	253	64	1	Slight
095	355	166	3	Slight
096	108	210	0	None
097	86	89	4	Slight

Notes
- Mixes were stiff to mix: CE 016
- Samples failed during extruding process because they were still wet and/or too much adhesion between the material and inside surface of mold: CE 025, 026

* Not enough binder

[§] To convert to MPa: psi x 6.894×10^{-3}

Phase B - Intermediate Investigation

This phase consisted of further testing of sixteen different binders screened from those which were developed in Phase A (Tab. 3.2). Tests were performed on the binders themselves and on dense graded compacted briquettes to determine binder and mixture properties.

An investigation into the mix design properties of lignin extended asphalt was also made by using 10, 20, 30, 40 and 50% lignin blended with AC-5 asphalt cement. Figures 3.10 to 3.13 show the test results of this investigation.

The mixing time required to coat the specimens increased as the percentage of lignin in the lignin-asphalt binder increased; however, mixtures with up to 30% lignin were prepared without apparent difficulty (Fig. 3.10).

The unit weight of the specimens prepared with 10 and 20% lignin were very close to the unit weight of the specimens prepared with AC-5 alone. The mixture with 30% lignin in the binder appeared to be in a transition phase, whereas those with 40 and 50% lignin were considerably lower than all the other specimens (Fig. 3.11) (3).

Most of the specimens also displayed increased stability values on the dry side of the stability curves (Fig. 3.12). Since lignin binders were varied in one percent increments, it was difficult to estimate an optimum binder content for each mix design. However, all the mixtures with lignin binders had stability values above the minimum value of 35 as designated in the Washington State Highway Department Standard Specifications for Roads (4).

Figure 3.13 summarizes the results of the indirect tensile test. Mixtures with 30% lignin displayed tensile strengths higher than those achieved with AC-5 alone. In addition, the indirect tensile strength curves intersect at the 5% binder content showing that at this point there is sufficient binder in the mixture to impart increased tensile strength. Mixtures below this level of binder content may be susceptible to extensive raveling. The mixtures with 40 and 50% lignin binders displayed tensile strengths substantially lower than the strengths of the other specimens. This lower tensile strength appears to be a result of insufficient coating of the aggregate by the lignin-asphalt binder.

Swell test results (Tab. 3.3) showed that none of the specimens were adversely affected (specifications generally allow 0.30 in. (.763 mm) (5). This indicated that the lignin extended asphalt binders effectively waterproof the mixtures.

Indirect tensile strength tests conducted on all specimens subjected to swell test showed that these specimens gained strength as compared to the indirect tensile strengths for specimens which were subjected to Hveem stability tests but not to swell tests. A summary of this percent

Table 3.2. Phase B test results.

BINDER DESCRIPTION	BINDER PROPERTIES			BINDER-AGGREGATE PROPERTIES (DENSE GRADATION)					
	VISC. POISES x 10^6	PEN. dmm.	SOFT. PT. C°	% BINDER	HVEEM STAB.	DRY M_R	WET M_R	TEN. STR.	WATER SOL.
1. AR-4000	1.9	40	42	6	49	277	308	55	None
2. AC-5	0.25	81	36	5	38	178	130	28	None
3. AC5/30KL OV	3.9	50	44	8	39	201	163	33	None
4. AC5/30KL PB	3.8	40	44	8	na	167	167	44	None
5. AC5/30KL/4Sul OV	5.2	48	45	8	28	165	157	36	None
6. AC5/30KL/4Sul PB	2.6	32.5	46	8	36	290	326	50	None
7. AC5/5Sul OV	2.6	85	33.5	5	33	164	169	49	None
8. AC5/5Sul PB	1.1	85	35	5	48	212	282	35	None
9. AC5/30NH_4LS OV	1.4	55	41	8	50	161	168	38	Severe
10. AC5/30NH_4LS PB	1.9	44	49	8	46	330	328	70	Severe
11. AC5/26NH_4LS/4Sul PB	2.9	42	47	7	47	332	224	56	Slight
12. AC5/30 APT NH_4LS OV	5.1	50	46	8	40-50	256	240	51	Slight
13. AC5/30CaLS OV	2.1	55	47	8	50	201	240	39	Severe
14. AC5/20CaLS PB	1.6	43	47	8	41	270	276	51	Moderate
15. AC5/26CaLS/4Sul PB	8.4	33	49	8	38	318	199	47	Slight
16. AC5/30 APT CaLS OV	3.9	50	44	8	47	364	321	71	Slight

APT = Acid Pretreated
CaLS = Calicum Lignin Sulfonate
KL = Kraft Lignin

NH_4LS = Ammonia Lignin Sulfonate
OV = Open Vessel
PB = Parr Bomb

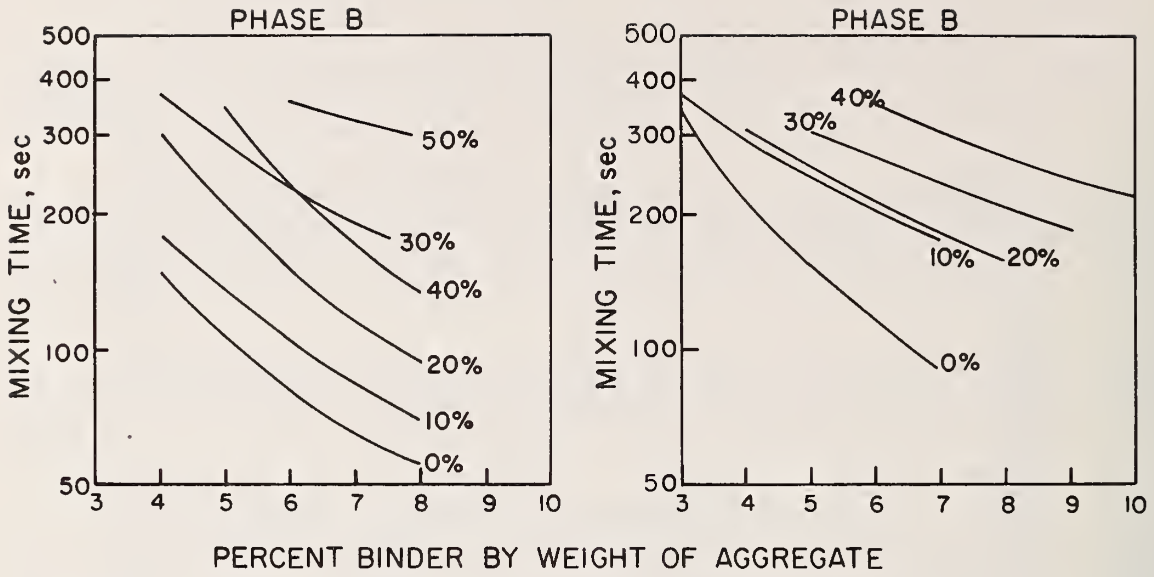


Figure 3.10. Mixing time for lignin-extended asphalt binders.

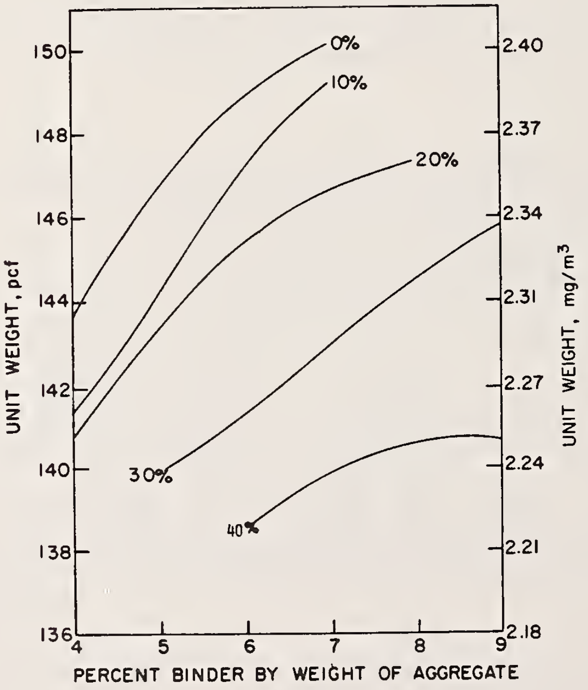


Figure 3.11. Unit weight of lignin-extended asphalt binders, Phase B.

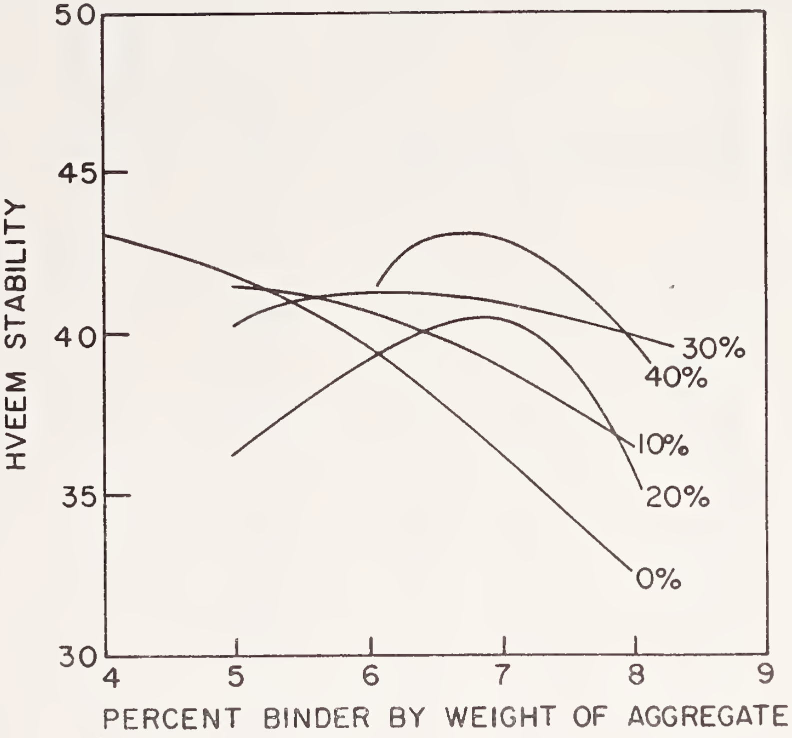


Figure 3.12. Hveem stability of lignin-extended asphalt binders, Phase A.

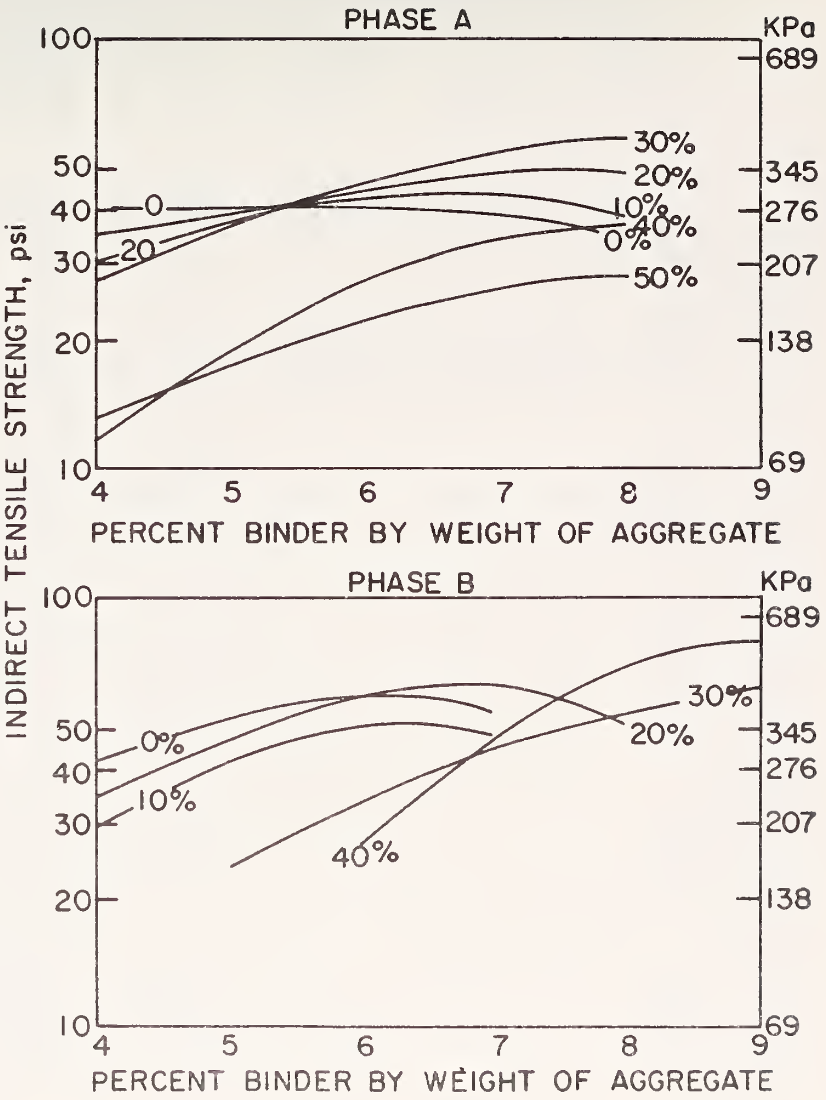


Figure 3.13. Tensile strength of lignin-extended asphalt binders.

[§] To convert to MPa: psi x 6.894 x 10^{-3}

Table 3.3. Mix design data, swell test results.

SPEC. NO.	BINDER TYPE	BINDER %	APPEARANCE	MIXING TIME sec.	HEIGHT in. (cm)	SWELL in. (cm)	SPLIT TENSION psi(KPa)
A					2.50	.000	104.0
B					2.50	.000	104.9
AVG	AR-4000	5	Normal	150	2.50	.000	104.5
					(6.35)	(.00)	(720)
A	AC-5				2.50	.009	48.3
B	0%				2.50	.002	49.3
AVG	Lignin	5	Normal	90	2.50	.005	48.8
					(6.35)	(.01)	(336)
A	AC-5				2.50	.002	50.8
B	10%				2.50	.001	56.8
AVG	Lignin	5	Normal	135	2.50	.0015	53.8
					(6.35)	(.00)	(371)
A	AC-5				2.50	.004	47.7
B	20%				2.50	.007	52.8
AVG	Lignin	5	Dry-Normal	180	2.50	.006	50.2
					(6.35)	(.02)	(346)
A	AC-5				2.50	.000	47.0
B	30%				2.50	.001	63.0
AVG	Lignin	6	Dry-Normal	210	2.50	.0005	55.0
					(6.35)	(.00)	(379)
A	AC-5				2.63	.001	41.7
B	40%				2.63	.001	53.8
AVG	Lignin	7	Dry	180	2.63	.0025	47.8
					(6.70)	(.01)	(330)
A	AC-5				2.63	.000	45.4
B	50%				2.75	.003	29.5
AVG	Lignin	7	Dry	360	2.69	.0015	37.5
					(6.80)	(.00)	(258)

Table 3.4. Percent indirect tensile strength gain after swell test.

BINDER	STRENGTH GAIN (%)*
AR-4000	17
AC-5	28
AC-5, 10% Lignin	39
AC-5, 20% Lignin	42
AC-5, 30% Lignin	61
AC-5, 40% Lignin	35
AC-5, 50% Lignin	26

* Expressed as percentage gain in strength compared to indirect tensile results of specimens after Hveem stability test.

gain in strength is presented in Table 3.4. The gain in strength is highest for the mixture with 30% lignin extended asphalt binder.

From the results of this investigation, certain conclusions were made as follows:

1. Lignin-asphalt binders containing up to 30% lignin perform adequately in hot mixes with dense graded aggregate for the range of binder contents normally associated with a paving grade asphalt. The performance of these binders correlates closely with the performance of AC-5 without lignin.

2. Lignin-asphalt binders containing more than 40% lignin are extremely viscous and have physical characteristics that are markedly different from paving grade asphalts and binders containing lesser amounts of lignin.

The success of the above binders was directly related to the predrying of the lignin before mixing with asphalt. This factor cannot be over emphasized.

From the foregoing results, three lignin-asphalt binders each containing 30% of lignin were identified as most promising binders, and were used for more extensive studies. There binders are:

1. AC-5/30 KL	OV
2. AC-5/30 KL/4 Sul.	PB
3. AC-5/30 APT CaLS.	OV

Phase C - Detailed Testing and Analysis

In this phase, a thorough evaluation of the three binders

1. AC-5/30 KL
2. AC-5/30 KL/4 Sul
3. AC-5/30 APT CaLS

which were chosen in Phase B was made.

Materials

Aggregate

A crushed granite aggregate from the Steilacoom quarry was used. The physical properties of this aggregate determined in the laboratory are presented in Table 3.5.

Table 3.5. Physical properties of Steilacoom aggregate.

	Fine Aggregate	Coarse Aggregate
Bulk Specific Gravity	2.43	2.64
Bulk Specific Gravity (SSD)	2.59	2.69
Apparent Specific Gravity	2.88	2.72
Absorption	5.49	1.12
	Aggregate	Specification
LA Abrasion (%)	15	30 max
Sand Equivalent (%)	87	45 min

Uniform aggregate gradation in all mixtures was achieved by sieving the aggregate into respective sizes and recombining by weight to the dense gradation presented as in Figure 3.14 to conform with the State of Washington Standard Specifications for Class B Asphalt Concrete (4).

Asphalt

Paving grade asphalt cements AR-4000 and AC-5 were used for the analysis. The physical properties of AR-4000 and AC-5 are as shown in Table 3.6. While control specimens were made from both asphalt cements, AC-5 was used as part of the lignin-asphalt binder in the study. The composition of AC-5 paving asphalt is as shown in Table 3.7.

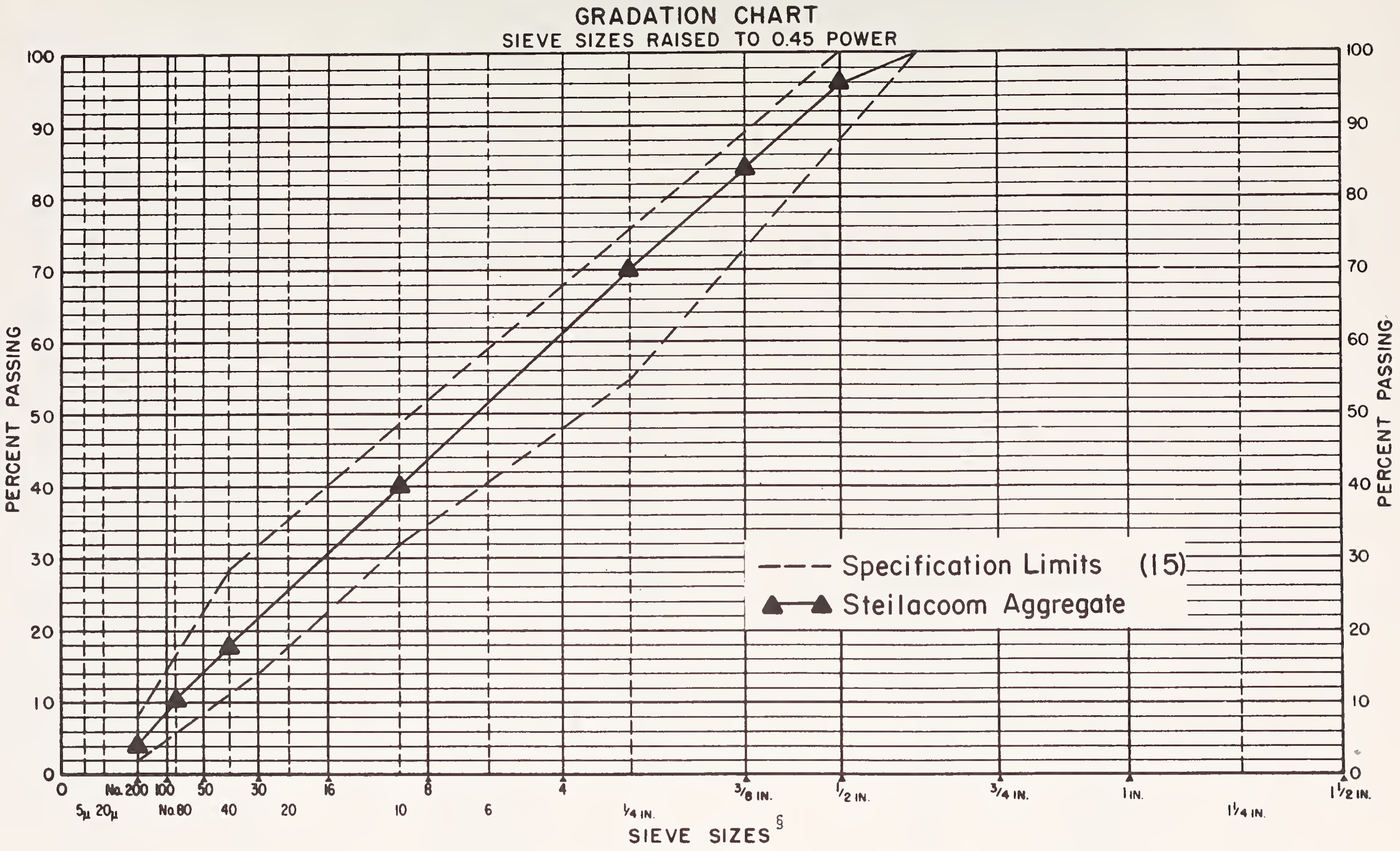


Figure 3.14. Gradation of steilacoom aggregate.

[§] To convert to mm: in. x 45.4

Table 3.6. Physical properties of asphalt cements.

Physical Properties[§]	AR-4000*	AC-5**
Flash Point by COC, °F	440	550
Penetration @ 77°F, .1 mm	25	183
Viscosity @ 275°F, centistokes	275	205
Viscosity @ 140°F, Poise	3000-5000	553
Ductility @ 77°F, cm	75	125+
Penetration retained after RTFO @ 77°F, %	45	47.5
Solubility in Trichlorethylene, %	99+	99+

* Specification from AASHTO M226

** Results of laboratory test by Chevron Asphalt Company

[§] To convert: 5/9(°F-32) = °C
Poise x 1.0 x 10^{-1} = Pa·s

Table 3.7. Composition of AC-5 paving asphalt.

Compositions	AC-5*
Asphaltenes, %	19.9
Nitrogen Bases, %	24.0
First Acidaffins, %	18.1
Second Acidaffins, %	26.9
Paraffins, %	11.1 (waxy)

* As determined by Matrecon, Inc.

Lignins

Two types of lignins, dried lignin sulfonate and kraft lignin were used for this study.

Sulfur

Sulfur was used as part of the binder in one study, to act as a plasticizer and as an inexpensive catalyst in chemically combining the lignin and asphalt.

Precoating Agents

Precoating agents such as asphalt emulsions, cutback asphalts, kraft liquor, lime, cement, etc., were used to precoat the aggregate prior to mixing with the intent to reduce the lignin-asphalt binder content and to improve the workability and coatability of the mix.

Binder Test Results

Results of tests of binders are summarized in Table 3.8.

Table 3.8. Summary of binder test results.

Binder Description	Penetration @ 39°F,§ .1 mm	Softening Point, °F§	Viscosity @ 77°F§ Poise 10^5	Specific Gravity
AC-5	81	95	2.5	1.011
AC-5 with 10% Lignin	73	99	4.5	1.001
AC-5 with 20% Lignin	65	102	9.1	0.999
AC-5 with 30% Lignin	50	111	39	0.997
AC-5 with 40% Lignin	47	136	52	0.992
AC-5 with 50% Lignin	32	212+	*	0.989

*Could not make a film of binder for testing.
§To convert to °C: 5/9(°F - 32).

The specific gravity of the lignin extended asphalt binders were all about 1.0. The addition of various percents of lignin to AC-5 did not change the specific gravity of the asphalt. This is because lignin and asphalt have about the same specific gravity.

A change in softening point, penetration, and viscosity occurred with increasing lignin content as shown in Figures 3.15, 3.16 and 3.17, respectively. The lignin appeared to increase the softening point, viscosity and decrease the penetration of the AC-5. In other words, it tends to stiffen the asphalt. These variables can be compared directly in Figure 3.18.

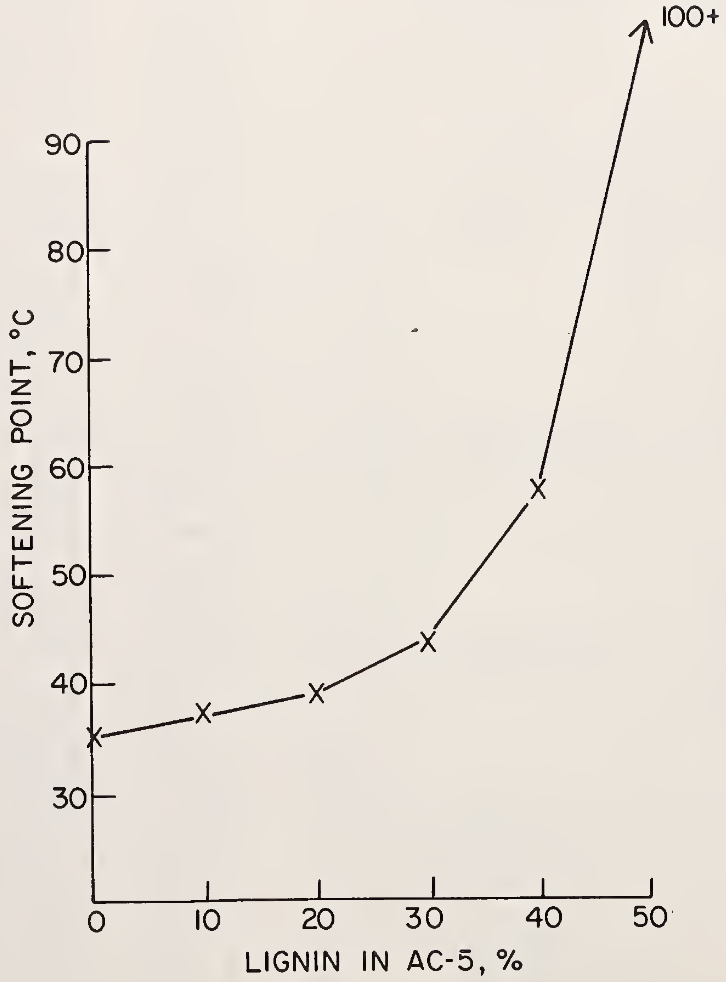


Figure 3.15. Relationship between softening point and percent lignin in asphalt.

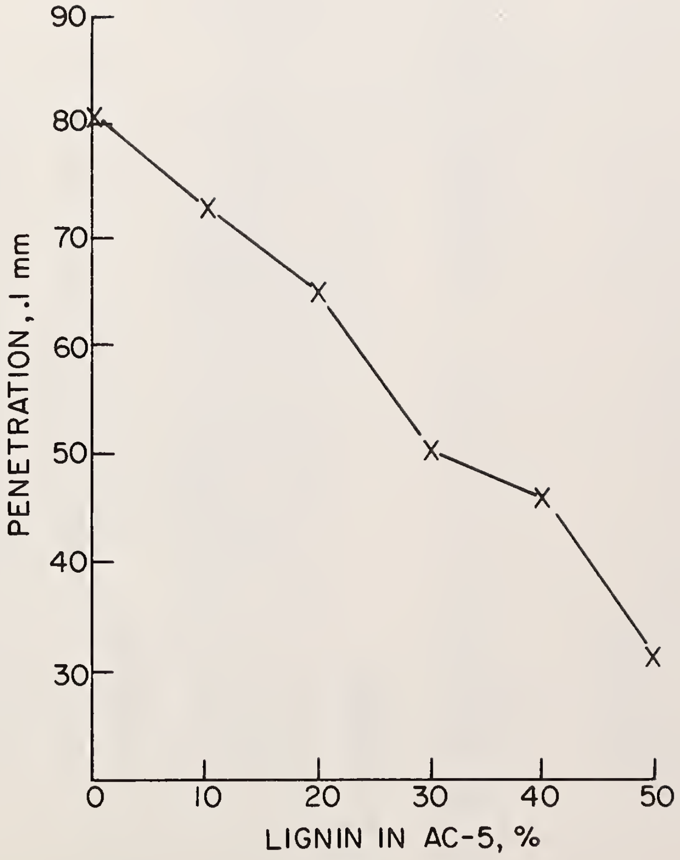


Figure 3.16. Relationship between penetration and percent lignin in asphalt.

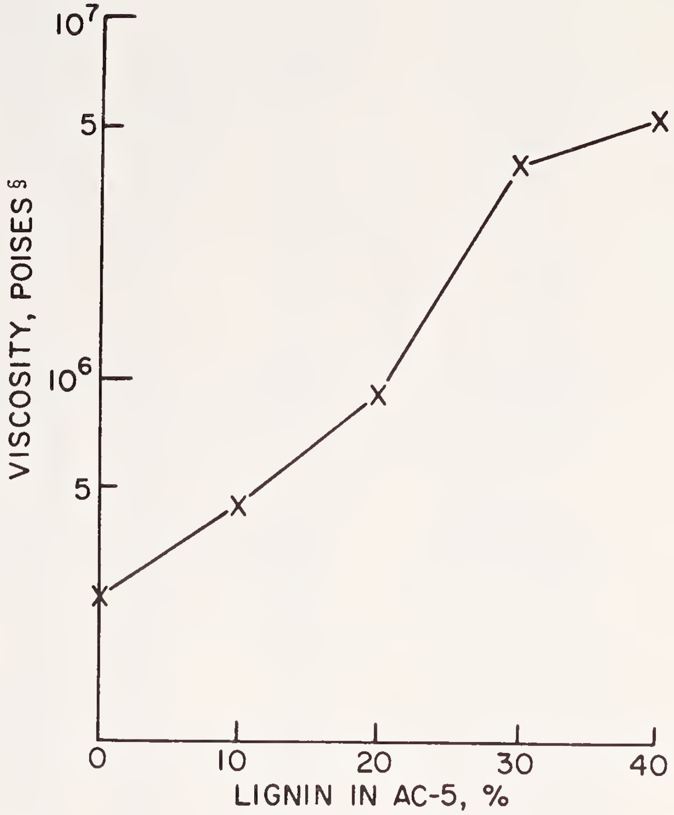


Figure 3.17. Relationships between viscosity and percent lignin in asphalt.

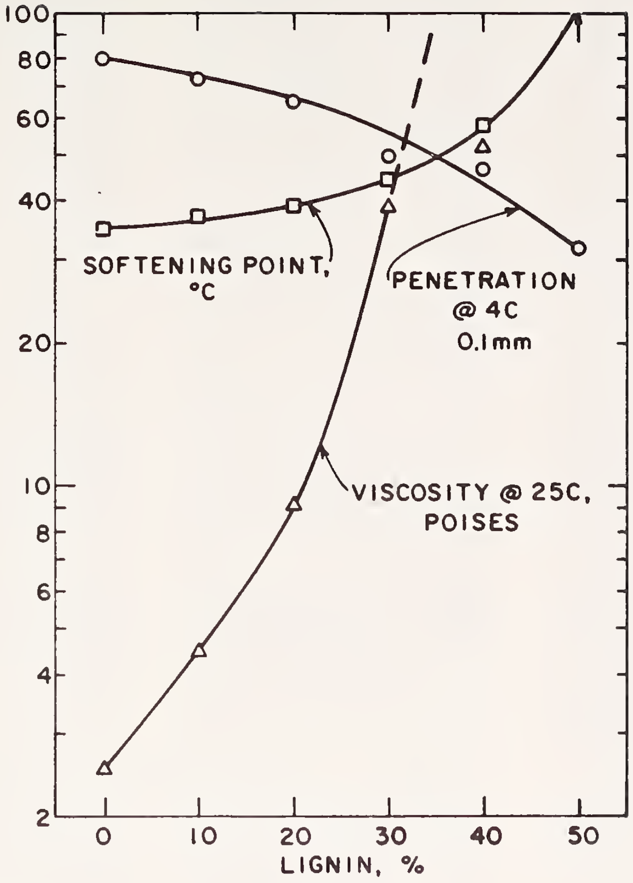


Figure 3.18. Effect of mixing AC-5 asphalt cement with varying amounts of powdered kraft lignin.

[§] To convert to Pa·s: Poises x 1.0 x 10^{-1}

Results from another study, using benzene to extract the asphalt from the lignin extended asphalt binder and then calculate the difference in asphalt contents originally blended with lignin and after extraction, indicated that there was only slight difference and therefore it appeared that lignin-asphalt binders were physical mixtures of insoluble lignin suspended in asphalt. In other words, there was no permanent chemical reaction between asphalt and lignin.

Based on the results of this study, it appears that the presence of the well dispersed lignin in asphalt simply increases the internal friction or resistance to deformation of the asphalt. That is, it increases the viscosity resulting from surface energy of attraction, or adsorption between the lignin particles and asphalt. Adsorption is promoted by lignin particles which are suspended in the asphalt and which are subdivided in such a manner that the maximum amount of asphalt is adsorbed. In the ideal condition the effects of adding lignin to asphalt are entirely beneficial if the proportion of lignin is enough to effect the maximum amount of asphalt but not enough to cause repulsion between coated lignin particles, and if the mixture retains acceptable workability.

Beneficial effects result from the addition of lignin to asphalt. In addition to binder stiffening, when used with aggregate, the paving mixture may have better resistance to water action, cracking, and excessive softening at high pavement temperature and in general result in a more durable pavement.

During the early part of this phase of the investigation, binder samples were tested by Matrecon, Inc. Several combinations of kraft lignin-asphalt binder were evaluated for viscosity and other parameters as shown in Table 3.9.

Mixture Test Results

Several laboratory experiments were performed to determine the characteristics and behavior of mixtures made with the three major binders. Each evaluation is presented as a subphase: Phases C-1, C-2 and C-3. In addition, Phase C-4 includes the follow-on evaluation of variations of the above.

E. Evaluation of Kraft Lignin - Asphalt Binder (Phase C-1)

A more detailed testing procedure was developed (6) to evaluate kraft lignin as an extender for asphalt. A flow chart representing the various activities involved in the mix design process and design criteria is shown in Figure 3.19.

In addition to the lignin-asphalt (L/A)* binder specimens, AC-5 and AR-4000 specimens were prepared and tested to provide a better comparison of the behavior of L/A mixes with conventional mixes.

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*L/A is used as a general term for lignin extended asphalt binder, however, AC-5/30 KL refers specifically to 30% kraft lignin in AC-5 asphalt cement.

Table 3.9 Viscosity and other properties of lignin binders.

Identification:	AC-5 Asphalt	AC-5/30 CaLS	AC-5/30KL/ 2 Sul PB	AC-5/30KL/ 4 Sul PB
Original properties of binder:				
Absolute viscosity[a] at 60°C,P	518	1860	1905	2600
Viscosity[b] at 25°C				
at 0.05 s^{-1}, MP	0.26	1.71	2.05	3.04
at 0.01 s^{-1}, MP	0.27	2.92	4.60	6.32
at 0.001 s^{-1}, MP	0.28	6.33	14.8	18.0
Shear susceptibility[c]	0.02	0.33	0.51	0.46
Equivalent penetration[d]	164	69	63	54
Specific gravity at 25°C	-	1.124	1.098	1.116
Rolling Thin Film Test[e] at 163°C:				
Change in weight, %	-0.77	-3.0	-2.0	-4.1[f]
Viscosity[a] at 60°C, P	1660	4640	12,600	22,200
Viscosity[b] at 25°C				
at 0.05 s^{-1}, MP	1.51	3.82	11.7	18.1
at 0.01 s^{-1}, MP	1.60	5.78	17.9	31.2
at 0.001 s^{-1}, MP	1.72	10.4	33.1	67.2
Shear susceptibility[c]	0.04	0.26	0.27	0.34
Equivalent penetration[d]	73	49	32	27
Benzene extract of original binder:				
Viscosity[b] at 25°C				
at 0.05 s^{-1}, MP	0.34	0.42	0.96	1.02
at 0.01 s^{-1}, MP	0.37	0.48	1.20	1.08
at 0.001 s^{-1}, MP	0.42	0.57	1.32	1.18
Shear susceptibility[c]	0.05	0.08	0.03	0.04
Equivalent penetration[d]	144	132	90	87
Insoluble residue, %	0.03	28.4	26.7	30.9
Benzene extract of RTFC residue:				
Viscosity[b] at 25°C				
at 0.05 s^{-1}, MP	1.44	1.40	6.46	11.0
at 0.01 s^{-1}, MP	1.55	1.52	7.96	12.4
at 0.001 s^{-1}, MP	1.72	1.73	10.6	15.0
Shear susceptibility[c]	0.05	0.05	0.13	0.08
Equivalent penetration[d]	74	75	40	33
Insoluble residue, %	0.04	29.2	26.8	28.5
Pellet abrasion loss, mg/rev:				
At 10°C, unaged	2.62	12.1	9.71	16.3
aged 7 d at 60°C	8.98	23.1	18.3	26.9
average (unaged and aged)	5.80	17.6	14.0	21.6
At 25°C, unaged	0.08	0.43	0.51	1.76
aged 7 d at 60°C	0.86	3.62	3.47	5.32
average (unaged and aged)	0.47	2.02	1.99	3.54

[a] Absolute viscosity at 60°C in poises (P) determined in a vacuum capillary viscometer (ASTM D2171)

[b] Viscosity at 25°C in megapoise (MP), determined in sliding plate microviscometer at various shear rates (California Div. of Highways Method 348-A).

[c] Shear susceptibility reported is the slope of the best-fit straight line drawn plotting log viscosity against log shear rate. Newtonian materials have zero shear susceptibility, i.e. viscosity not dependent on shear rate.

[d] Equivalent penetration is calculated from viscosity at 0.05 s^{-1} shear rate using formula of Saal, Baas, and Heukelom for soft asphalts (penetration >60, viscosity <2.2 x 10^6P)

$$(\text{pen})^{2.16} = \frac{1.58 \times 10^{10}}{n}$$

and formula of Carre and Laurent for harder asphalts (penetration <60, viscosity >2.2 x 10^6P)

$$(\text{pen})^{2.60} = \frac{9.5 \times 10^{10}}{n}$$

Reference Saal, Baas and Heukelom, J. Chim. Phys. 43:235, 1946; Carre and Laurent, Association Franciase des Techniciens Petrole, Bulletin No. 157, p. 1-54, Jan. 31, 1963.

[e] Aging in rolling thin film oven at 163°C (325°F) for 75 min. (Calif. Div. of Highways Method 346-F).

[f] Part of the sample ran onto the outside of the RTFC bottle during test; there is a possibility that some dripped off, which would cause the weight change value to be high.

Conversions used in this table:

$$°F = \frac{9}{5}°C + 32$$

$$\text{Pa}\cdot\text{s} = \text{P (poises)} \times 10^{-1}$$

Table 3.10. Viscosity and pellet abrasion measurements of lignin-asphalt[a] Binders, both unaged and aged under various conditions.

Lignin in binder, weight, %	0	10	20	30	40	50
Original properties of binder:						
Absolute viscosity[b] at 60°C, P	534	734	1445	4258	22430	(c)
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	0.24	0.64	0.62	1.80	3.4	-
at 0.01 s^{-1}, MP	0.28	1.92	2.43	5.0	9.0	-
at 0.001 s^{-1}, MP	0.34	9.3	10.1	21.3	36	-
Shear susceptiblity[e]	0.091	0.68	0.62	0.63	0.60	-
Equivalent penetration[f]	167	106	108	66	51	-
Rolling Thin Film Test at 163°C[g]:						
Change in weight, %	-0.68	-0.99	-2.00	-1.27	-1.09	(h)
Viscosity[b] at 60°C, P	1666	2517	4466	12810	78690	-
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	1.5	1.4	3.1	5.4	7.3	-
at 0.01 s^{-1}, MP	1.6	2.3	6.0	11	20	-
at 0.001 S^{-1}, MP	1.9	4.7	15	33	88	-
Shear susceptibility[e]	0.061	0.31	0.40	0.46	0.63	-
Equivalent penetration[f]	71	74	53	43	38	-
UV exposed[i] 24h:						
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	21	14	18	18	12	-
at 0.01 s^{-1}, MP	37	24	31	38	35	-
at 0.001 s^{-1}, MP	84	52	80	110	160	
Shear Susceptibility[e]	0.36	0.34	0.41	0.47	0.65	-
Equivalent penetration[f]	25	30	27	27	32	-

Table 3.10. Continued.

Lignin in binder, weight, %	0	10	20	30	40	50
UV exposed[i] 48h:						
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	120	24	20	22	8.0	-
at 0.01 s^{-1}, MP	130	56	44	52	24	-
at 0.001 s^{-1}, MP	150	190	130	170	120	-
Shear susceptibility[e]	0.054	0.52	0.48	0.51	0.71	-
Equivalent penetration[f]	13	24	26	25	37	-
Extraction of original binder, with benzene:						
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	.273	-	.305	-	.300	-
at 0.01 s^{-1}, MP	.303	-	.320	-	.360	-
at 0.001 s^{-1}, MP	.354	-	.346	-	.472	-
Shear susceptibility[e]	.068	-	.031	-	.117	-
Equivalent penetration[f]	160	-	152	-	153	-
Lignin in residue, %	0	-	19.26	-	38.59	-
RTFC residues extracted with benzene:						
Viscosity[d] at 25°C						
at 0.05 s^{-1}, MP	1.35	-	1.35	-	0.86	-
at 0.01 s^{-1}, MP	1.54	-	1.48	-	1.14	-
at 0.001 s^{-1}, MP	1.87	-	1.68	-	1.72	-
Shear susceptibility[e]	0.086	-	0.058	-	0.176	-
Equivalent penetration[f]	76	-	76	-	94	-
Lignin in residue, %	0	-	11.83	-	38.28	-

Table 3.10. Continued.

Lignin in binder, weight, %	0	10	20	30	40	50
Pellet abrasion loss, mg/rev.:						
At 10°C, unaged	3.43	4.86	6.92	7.70	16.7	26.5
Aged 7 days at 60°C	7.31	11.5	16.1	17.9	25.6	56.5
Average (unaged and aged)	5.37	8.2	11.5	12.8	21.2	41.5
At 25°C, unaged	0.002	0.03	0.05	0.16	1.96	5.12
Aged 7 days at 60°C	0.25	0.13	0.76	1.93	3.92	83.2
Average (unaged and aged)	0.13	0.08	0.40	1.04	2.94	44.2

---

[a] Chevron AC-5 Asphalt and Indulin AT.

[b] Absolute viscosity at 60°C in poises (P) determined in a vacuum capillary viscometer (ASTM D2171).

[c] Too stiff to measure in viscometer.

[d] Viscosity at 25°C in megapoise (MP), determined in sliding plate microviscometer at various shear rates (California Div. of Highways Method 38-A).

[e] Shear susceptiblity reported is the slope of the best-fit straight line drawn plotting log viscosity against log shear rate. Newtonian materials have zero shear susceptiblity, i.e. viscosity not dependent on shear rate.

[f] Equivalent penetration is calculated from viscosity at 0.05 s^{-1} shear rate using formula of Saal, Baas, and Heukelom for soft asphalts (penetration >60, viscosity <2.2×10^6P)

$$(\text{pen})^{2.16} = \frac{1.58 \times 10^{10}}{n}$$

and formula of Carre and Laurent for harder asphalts (penetration <60, viscosity >2.2×10^6P)

$$(\text{pen})^{2.60} = \frac{9.5 \times 10^{10}}{n}$$

Reference Saal, Baas, and Heukelom, J. Chim. Phys. 43:235, 1946; Carre and Laurent, Association Francaise des Techniciens Petrole, Bulletin No. 157, p. 1-54, Jan. 31., 1963.

[g] Aging in rolling thin film oven at 163°C (325°F) for 75 min. (Calif. Div. of Highways Method 346-F). RTF residues for 10, 20, and 30% lignin-asphalt binders appeared to leave part of the lignin deposited in the container. RTFC residue with 40% lignin could not be poured; it had to be scraped from container.

[h] Binder rolled up into a "log" in the RFTC test, and pieces of it fell into bottom of oven. The container was removed from the oven after 10 minutes.

[i] Exposed to ultraviolet and visible light under fluorescent sunlamps, ASTM D1501, Procedure A. Asphalt and 10% lignin preparations were exposed as 20μ films; 20, 30, and 40% lignin preparations as 27μ, 32μ, and 41μ films respectively. These were the thinnest films that could be obtained with the higher lignin contents.

[j] Benzene insoluble material.

Conversions used in this table: $°F = \frac{9}{5}°C + 32$; Pa·s = P(poises) x 10^{-1}

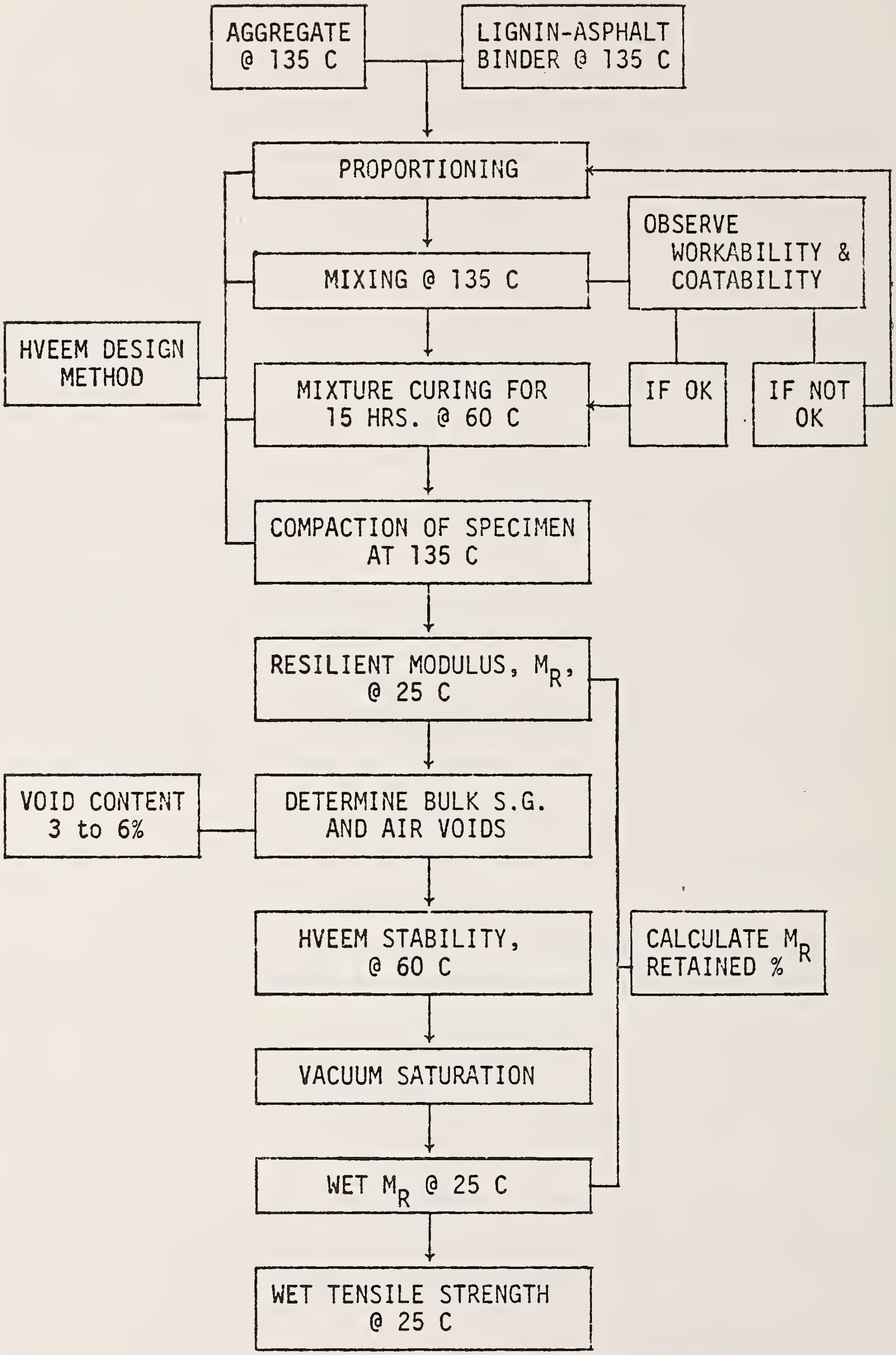

Figure 3.19. Mix design procedures.

Evaluation of Results

Results of mix designs for specimens made with L/A binders and asphalts are shown for comparison in Table 3.10. Relationships between binder contents and various test results are presented in Figures 3.20 through 3.26. The mechanical properties or behavior of L/A paving mixtures appeared to follow a conventional pattern similar to normal asphalt concretes. In addition, the properties can be compared even though the mixtures have different ranges of binder content.

The relatively higher binder contents expressed in weight percent of the L/A mixes were the consequence of the viscous nature of the L/A binder which requires more binder to coat all the aggregate as compared to asphalt alone.

The principal findings in this phase of research can be summarized as follows:

1. The midline gradation of aggregate of the class B range was found to be too dense for all mixes (AR-4000, L/A and AC-5). It had to be adjusted in order to meet the air void criteria of 3 to 6%.

2. Adding lignin to asphalt appeared to increase the volume of the paving mixtures. The amount of aggregates to make one specimen of about 2.5 in. (61.3 mm) in height had to be reduced.

3. During the experiment, the L/A binders was somewhat difficult to mix with aggregate. It took one or two minutes additional time during mixing for the L/A binder to coat all the aggregate particles. This is believed to be caused by the more viscous nature of the L/A binder compared to asphalt.

4. The bulk specific gravity of the L/A mixes were generally slightly lower than for aphalt mixes except at 7% binder (See Fig. 3.20).

5. The Hveem stability of all mixes appeared to be virtually the same, ranging from 41 to 49. They all meet the 35 criteria specified by the Washington State Highway Department Specifications for Roads.

6. The ability of the L/A mixes to resist water damage (based on percent resilient modulus retained) appeared to be as good as, or even better than conventional asphalt concretes. This is believed to be caused by the stronger bond or adhesion between L/A binder and aggregate particles.

7. The resilient modulus of L/A mix appeared to be higher than AC-5 mix but lower than AR-4000 mix. From this it seems that lignin increases the M_R of the AC-5 mix.

8. The tensile strength of L/A mix appeared to be between the AC-5 and AR-4000 mixes. Again the lignin seems to increase the strength of a mix.

Table 3.11. Summary of various mix design data.

Mix Type	Binder Content %	Workability	Bulk Specific Gravity	Hveem Stability	Dry M_R 1 x 10^3 psi§		M_R After Val. Sat. 1 x 10^3 psi§		M_R Retained %	Indirect Tensile Strength After Sat.	Maximum Specific Gravity	Air Void %
					Test Values	Average	Test Values	Average				
AC-5	3	Fair	2.324	46	184 172	178	110 81	96	54	73 psi§	2.500	7.0
	4	Good	2.362	45	180 186	183	107 114	111	61	84 psi		5.5
	5	Good	2.403	41	171 178	175	127 123	125	71	84 psi		3.9
AR-4000	3.5	Good	2.346	49	394 407	401	213 213	213	53	110 psi	2.513	6.6
	4.5	Good	2.400	47	337 353	345	241 243	242	70	132 psi		4.5
	5.5	Excellent	2.441	40	292 292	292	220 218	219	75	125 psi		2.9
L/A	6	Fair	2.328	43	176 166	171	110 105	108	63	72 psi	2.457	5.3
	7	Good	2.363	45	210 222	216	159 156	158	73	94 psi		3.8
	8	Excellent	2.374	41	227 249	238	144 157	151	63	87 psi		3.4

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§To convert to MPa: psi x 6.894 x 10^{-3}.

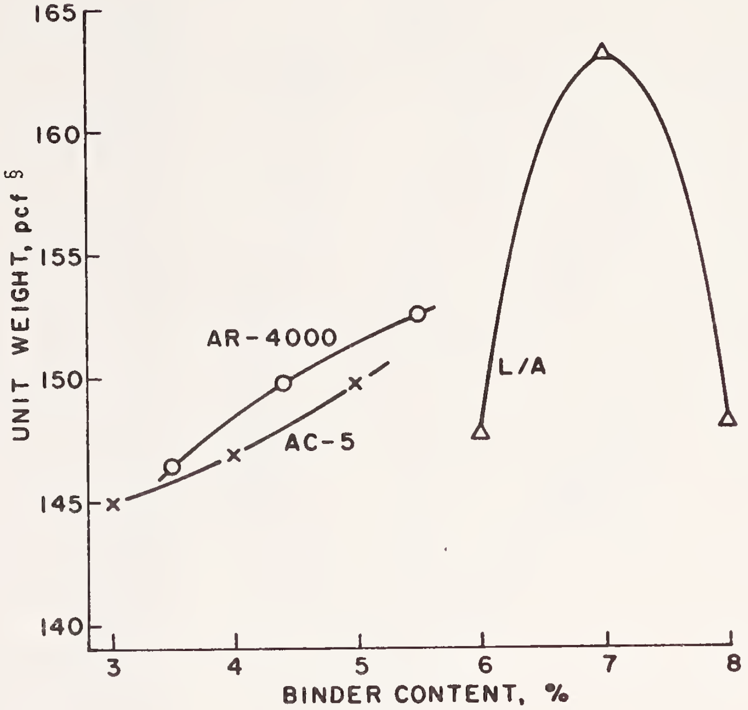

Figure 3.20. Unit weight vs. binder content.

§To convert to kg/m^3: pcf x 1.601846 x 10

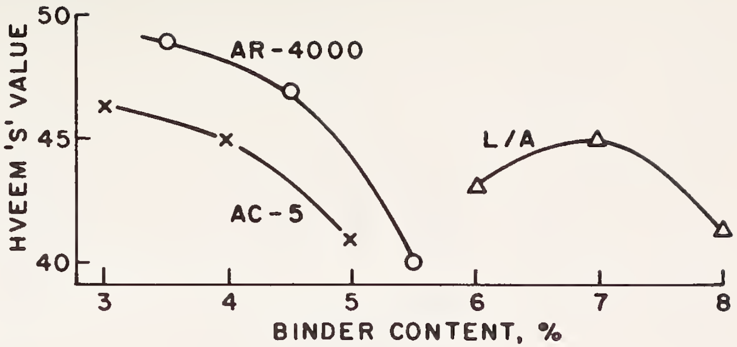

Figure 3.21. Hveem stability vs. binder content.

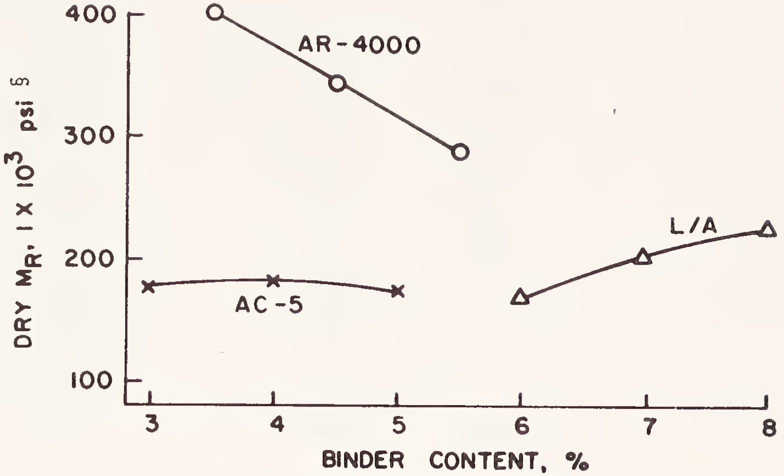

Figure 3.22. Resilient modulus vs. binder content.

§To convert to MPa: psi x 6.894 x 10^{-3}

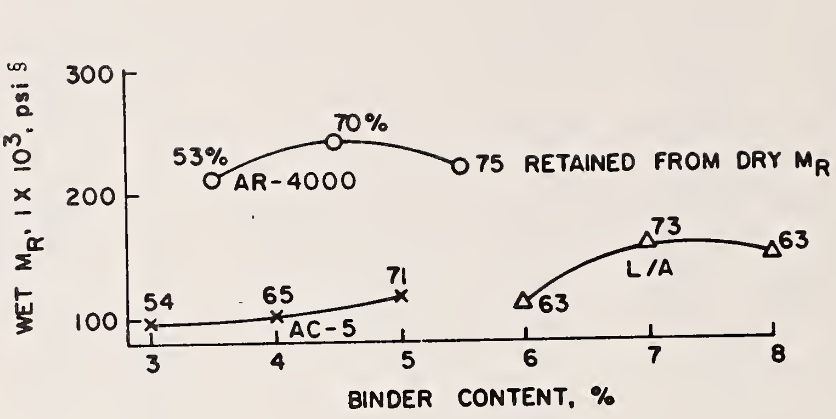

Figure 3.23. Resilient modulus vs. binder content after vacuum saturation.

§To convert to MPa: psi x 6.894 x 10^{-3}

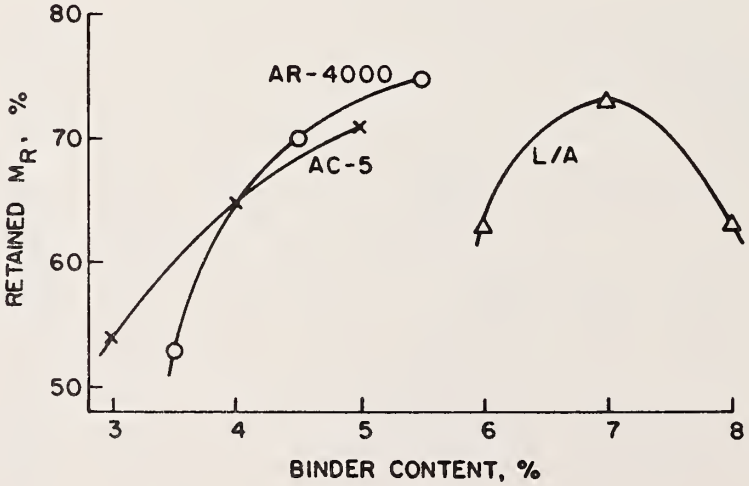

Figure 3.24. Relative resilient modulus retained after vacuum saturation.

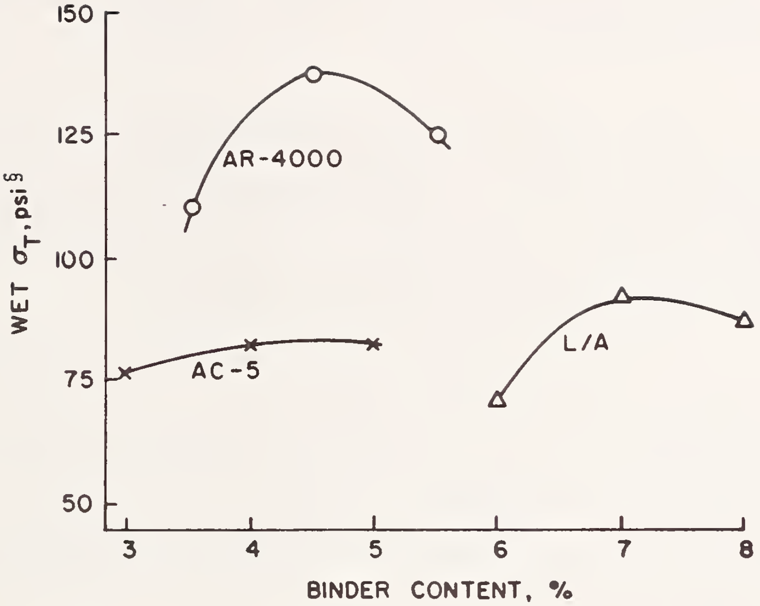

Figure 3.25. Tensile strength vs. binder content after vacuum saturation.

§To convert to MPa: psi x 6.894 x 10^{-3}

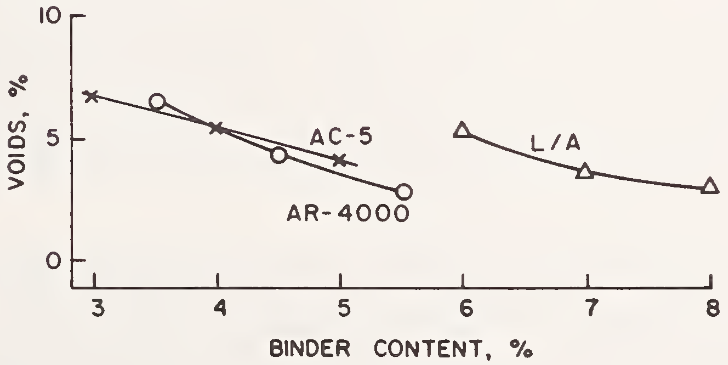

Figure 3.26. Voids in mixtures vs. binder content.

9. It appeared that test methods used to evaluate various mixes in this mix design phase were sufficiently sensitive to discern those factors relating to pavement performance.

In summary, during the laboratory experiments the L/A binders exhibited reasonable qualities with respect to workability, compaction, moisture damage resistance and elastic properties.

With regard to the effect of lignin on paving mixtures, it appeared that when the L/A binder was produced in the described manner, the lignin behavior was similar to a mineral filler in a paving mixture (7). It tends to make a paving mixture more dense by reducing the large size voids and total void contents. At the same time it also stiffens or increases the viscosity of the asphalt layer on the aggregate particles in a mix resulting from surface energy attraction or adsorption as discussed previously.

As discussed above, three separate mixture designs were prepared. The control mixture was made with AR-4000 asphalt cement. The other mixtures contained AC-5 asphalt cement only and lignin blended with AC-5 with L/A ratio of 30/70 percent by weight. Also, as discussed earlier, a softer asphalt such as AR-1000 or AC-5 was easier to blend with powdered lignin used as an extender. However, the ability of this blend to coat aggregate was lessened when mixing by hand. A powered mixer might have been used and this problem overcome, but since the hand method was used as a standard for binder evaluations, it was retained for these mixtures as well.

No criteria were available for L/A mixtures, but those shown in Table 3.9 appear to be reasonable. Because of the different range of binder content required for coating, the results are difficult to compare. If each binder is considered on its own, optimum binder contents as shown in Table 3.12 will result. However, without too much rationalization, one could arrive at somewhat different values.

For example, if either the AR-4000 or AC-5 binder as seen in Figure 3.20 were considered without the benefit of the L/A results, an optimum binder content of 5.5 and 5.0 would result. In fact, with the aggregate type and gradation selected, the optimum would likely be about 6.0 percent or more if mixtures had been prepared in this range. Similarly, if the desirable Hveem stability (Figure 3.21) were selected at 40, similar binder contents would be determined for AR-4000 and AC-4 as above; but the L/A mixtures is inconclusive, with the value selected about 5.5 or 8.0 percent depending upon how the designer viewed the test results.

Figures 3.22 and 3.23 show the results of resilient modulus tests and more complete data for M_R and Poisson's ratio are shown in Table 3.9. Mixtures utilizing AR-4000 and AC-5 resulted in M_R values on the range to be expected as noted in Figure 3.22; the M_R is very much dependent upon the nature of the binder since the stresses under test are essentially tensile. The L/A bound mixtures were between the others in actual values, but since the range of binder was somewhat higher, they were not directly comparable.

A key factor in evaluating the L/A binders was resistance to water. Following vacuum saturation at room temperature and 24 hour soaking, the resilient modulus was again measured with the results shown in Figure 3.23. The percent of M_R retained compared to the original dry M_R is noted in Figure 3.23 and these values are also plotted in Figure 3.24. The results of these tests indicate that the L/A binder has at least as good a water resistance as the pure asphalt binders and that the degree of water resistance is a function of the binder content. At the optimum binder content, all three binders show approximately 70% M_R retention. Since this is considered adequate for soaking only (i.e., without first being vacuum saturated), the results would appear to be satisfactory.

The ultimate strength in indirect tension, σ_t, for all mixtures is shown in Figure 3.25. The values shown are for wet specimens (following vacuum saturation) and follow a similar trend as for M_R. Figure 3.26 indicates the void range for the mixtures and is included to show that voids are controlled during compaction in the range of about 4-6 percent in order to reduce their effect on performance tests. Although it is recognized that different binders will affect the compactability, this variable was purposely avoided.

Table 3.12. Optimum binder content, percent by weight of dry aggregate.

	AR-4000	AC-5	L/A
Unit Weight (peak or maximum)	5.5	5.0	7.0
S Value (1/2% < 37)	4.7	4.7	7.6
Dry M_R (peak or maximum)	(3.5)*	(4.0)*	(8.0)*
Wet M_R (minimum 70% retained)	4.5	5.0	6.4
Wet σ_t (peak or maximum)	4.5	4.0	7.0
Voids (4%)	4.6	4.8	6.8
Average	4.5	4.5	7.2
Used in subsequent mixtures for characterization	4.5	4.0	7.0

* Not included in average

F. Evaluation of Kraft Lignin - Sulphur-Asphalt Binders (Phase C-2)

As a result of the findings in Phase B of the study, binder with 30% kraft lignin was blended with 68, 64 and 62% of AC-5 and 2, 4 and 6% of sulfur to further characterize a binder similar to No. 6 as noted in Table 3.2. The Parr reactor was used in most of the binder preparations. The open vessel method was also used for limited samples. Figure 3.27 shows the binder preparation process for this investigation.

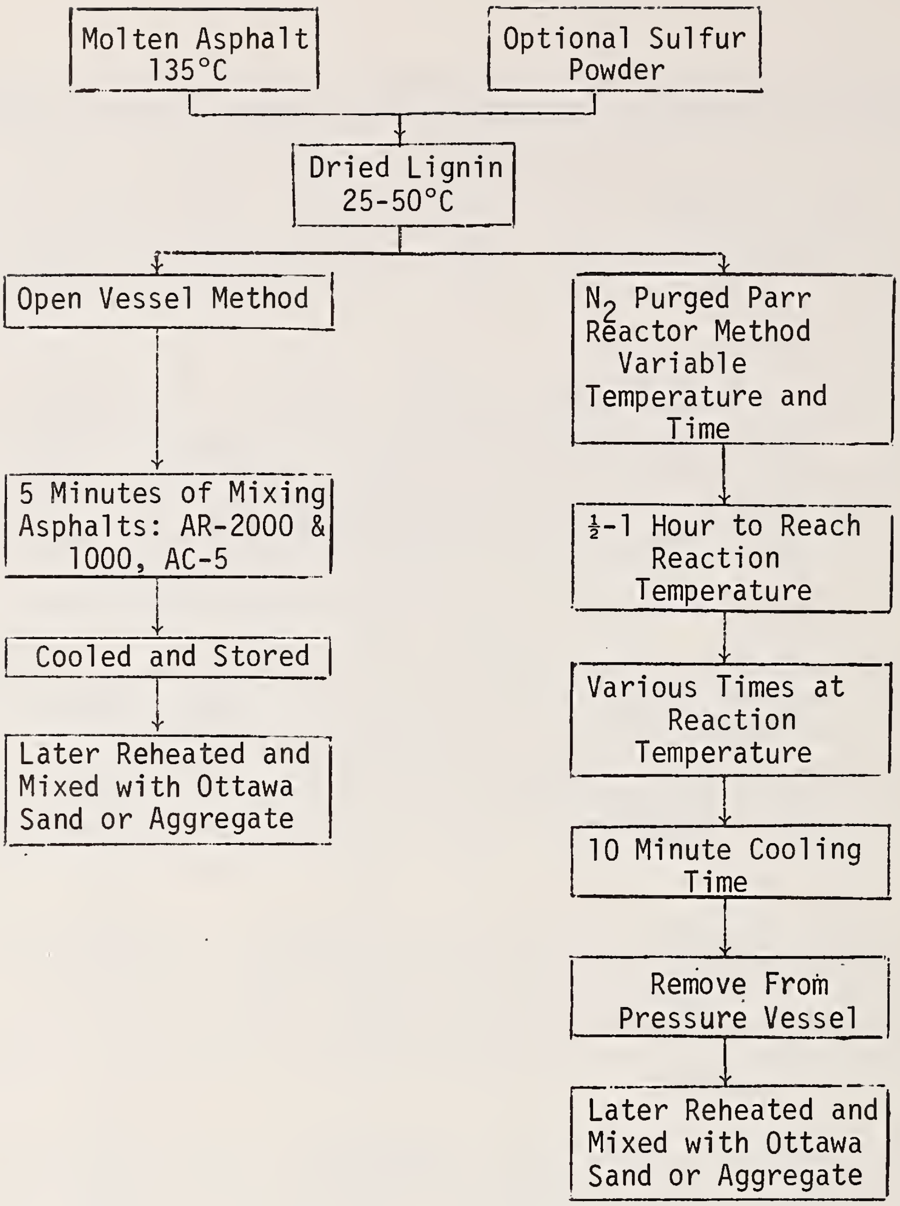

Figure 3.27. Binder preparation method.

Tests and Results

Early screening tests indicated that small amount of sulfur was beneficial in improving the resilient modulus of lignin-asphalt mixtures. Although 4% was used initially, a later test series showed that 2% was better (see Fig. 3.28)(10). The data from this figure would indicate that even less, say 1% might be as beneficial. Although no complete tests were conducted at these low sulfur contents, it was evident in the laboratory that 1% or less was difficult to disperse throughout the mixture, and was therefore not used. The properties of AC-5/30 KL/2 Sul, hereafter referred to as AKS, had properties as shown in Table 3.13. This table includes data developed by Matrecon, Inc. and shows the difference in binders with 2 and 4% sulfur.

Figures 3.29 (A, B, C, D, E, and F) are comparisons of test results of AKS with AR-4000, AC-5 and kraft lignin/asphalt as discussed in Phase C-1. These results indicate that:

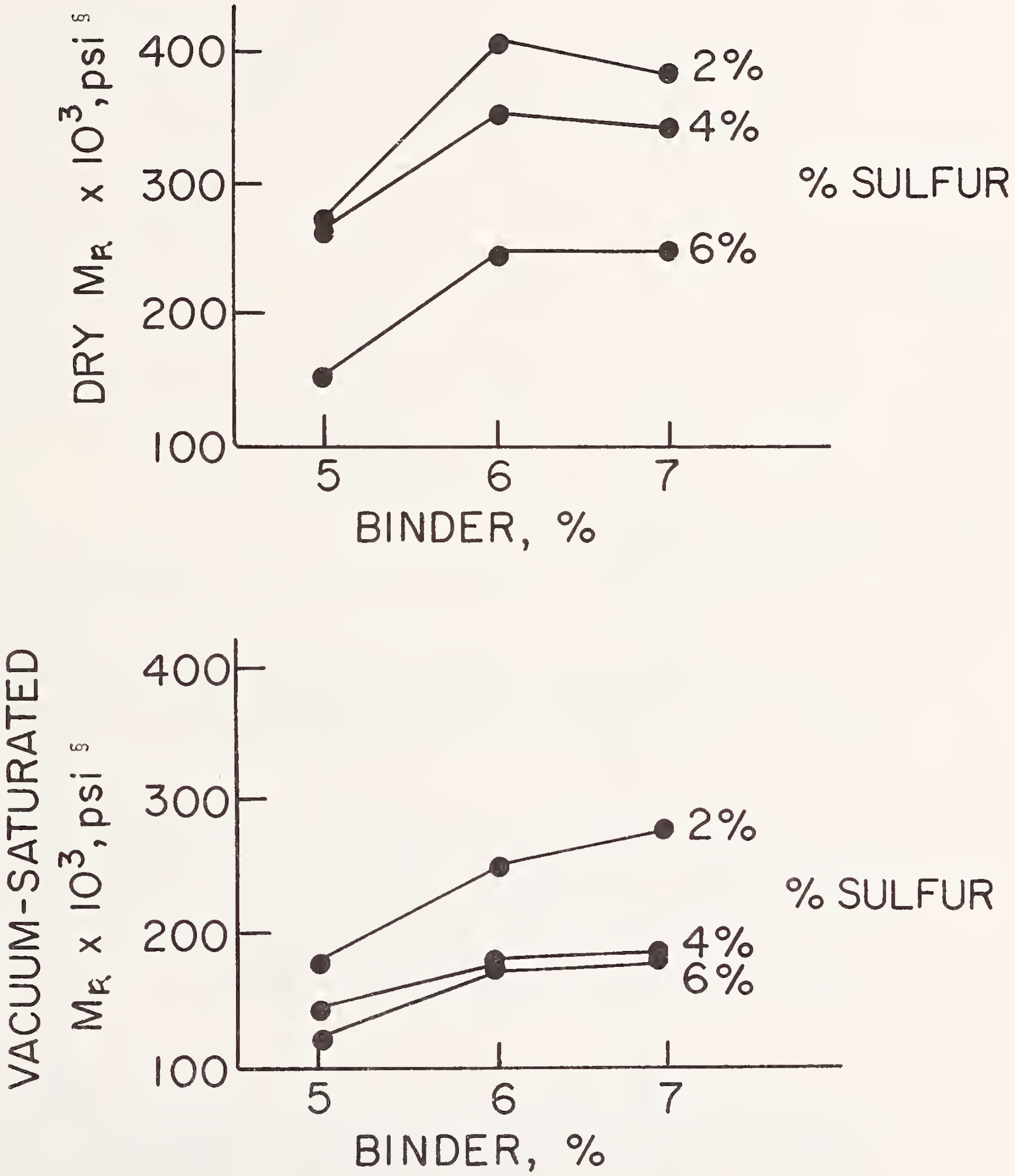

Figure 3.28. M_R vs. various sulfur contents binders.

§ To convert to MPa: psi x 6.894 x 10^{-3}

Table 3.13. Preliminary binder properties.

Phase C-2

	AC-5	AC-5/30 KL/4 SUL OV	AC-5/30 KL/2 SUL PB
Penetration 25°C, 100 gm.	139.5	117	76
Penetration 4°C, 200 gm.	69	52.5	41
Softening Point °C	35.7	45	43.5
Ductility, cm.	100+	21.5	34
Viscosity poises 25°C x 10^6	0.25	3.9	2.25

1. For the same mixture strength, a lower percentage of AKS binder is required as compared to using lignin-asphalt alone (Figures 3.29D and E). Thus using sulfur would promote cost savings since sulfur is lower cost material.

2. The decrease in M_R due to freeze-thaw is less than with low voids and higher binder content than with high voids and lower binder content. Whether the improvement is a consequence of the lignin is not clear, but in comparing AR-4000 with 4.5% asphalt and AKS with 6% binder (4.2% asphalt) with the same gradation and percent voids, the ASK specimens showed 20% better M_R retention (Fig. 3.30).

3. The moisture permeability is a function of asphalt viscosity and affects the rate of deterioration due to freeze-thaw action. Higher asphalt viscosities obtained by adding kraft lignin to the AC-5 asphalt increase the freeze-thaw resistance of the mixes.

4. The reduction in the M_R is at least partially reversible on drying. Those binders with the higher binder contents also showed the highest percentage of retained indirect tensile strength after freeze-thaw cycling and drying.

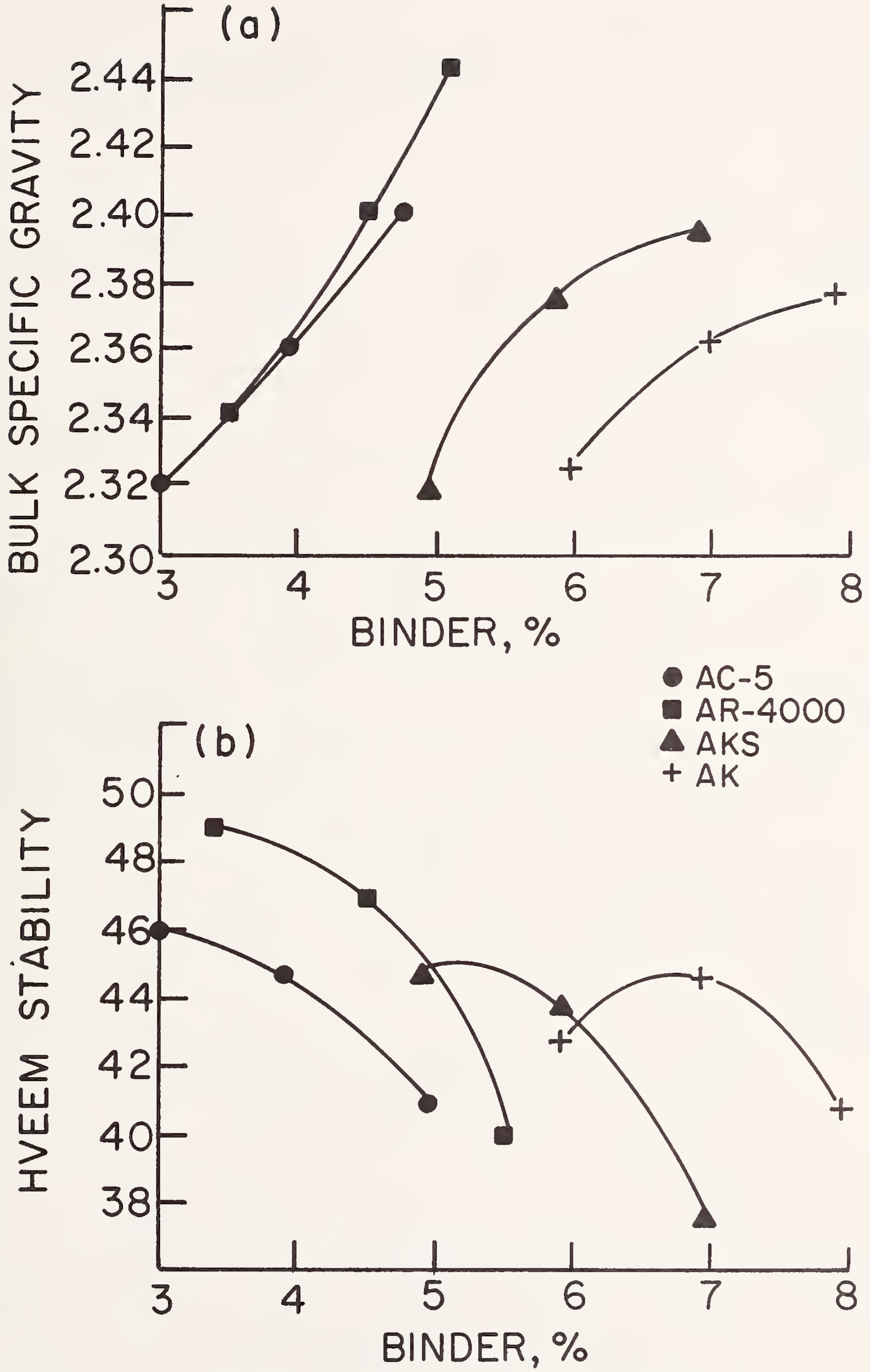

Figure 3.29. Comparison of AR-4000, AC-5, AKS and AK test data.

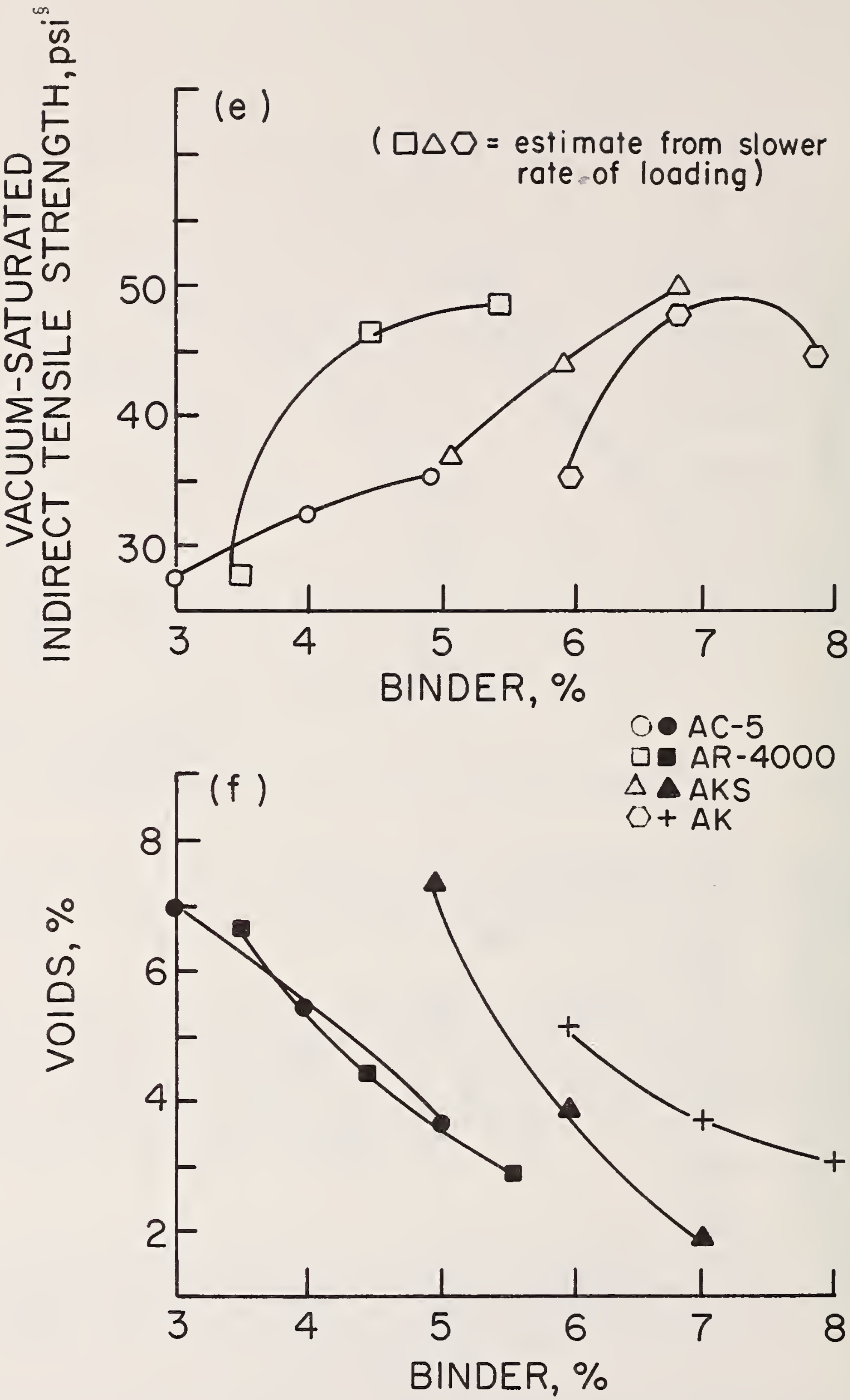

Figure 3.29. Continued.

[§] To convert to MPa: psi x 6.894 x 10^3

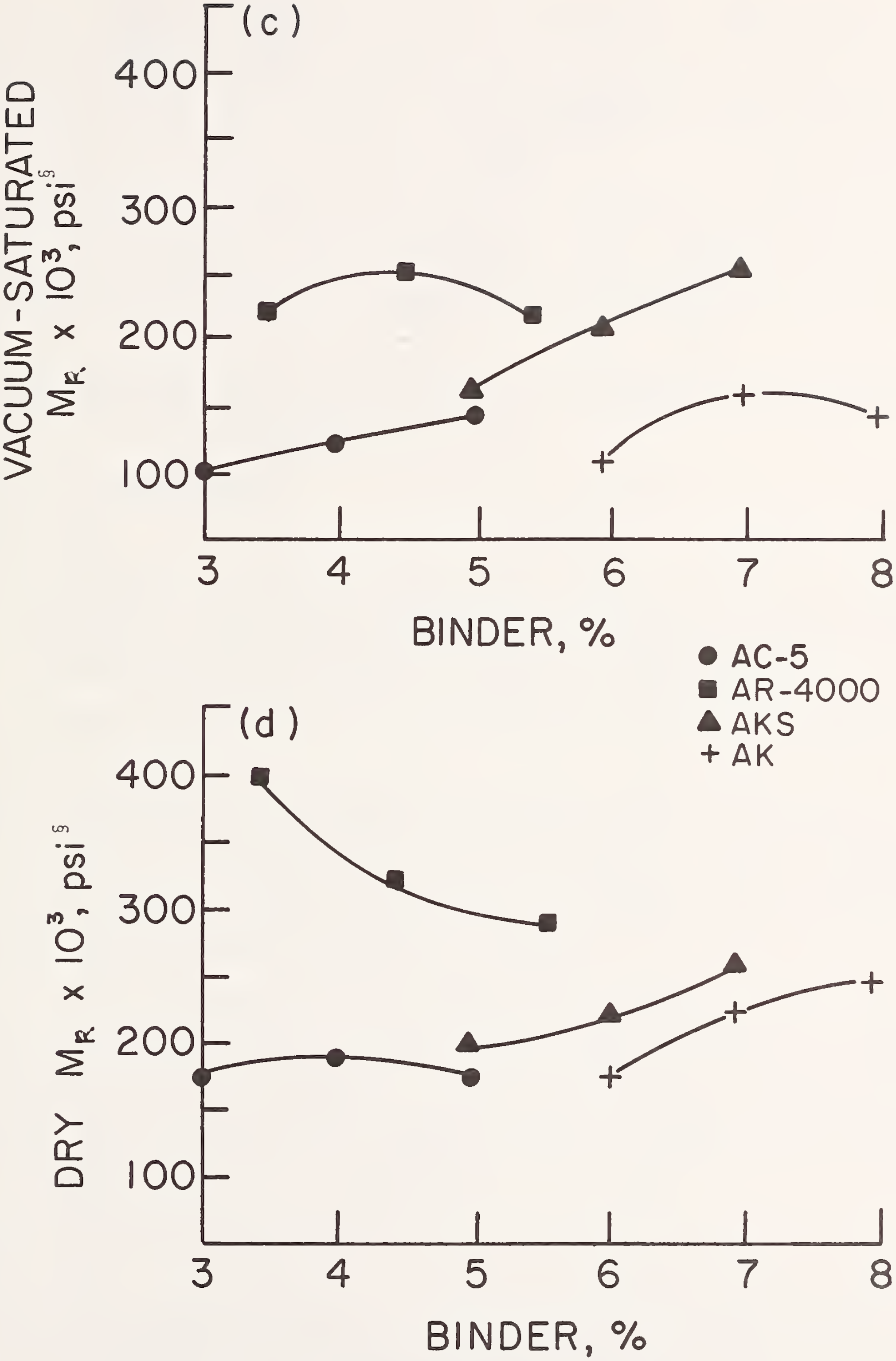

Figure 3.29. Continued.

§To convert to MPa: psi x 6.894 x 10^{-3}

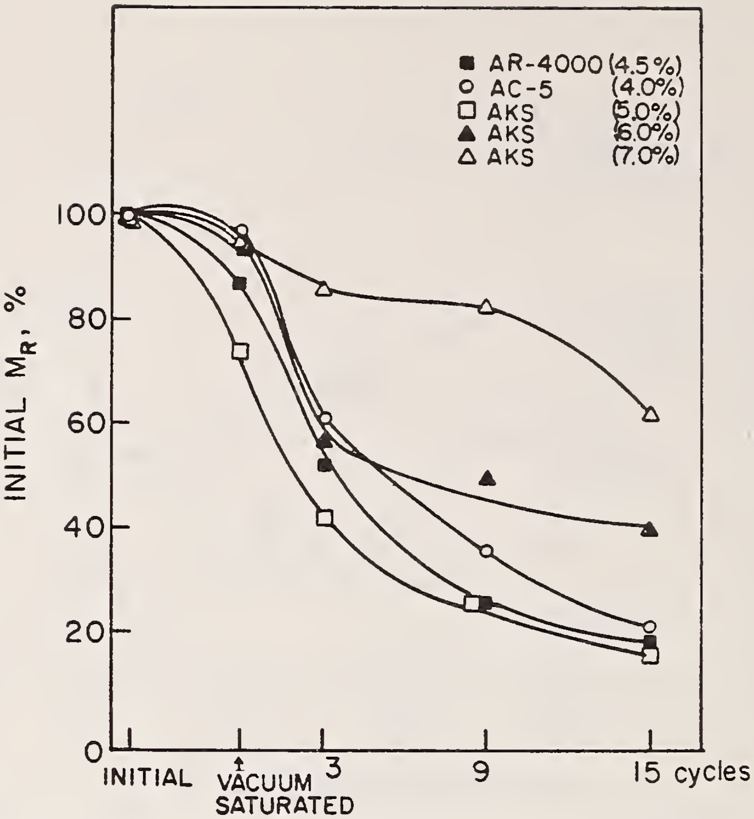

Figure 3.30. Percent of retained M_R after freeze-thaw conditioning.

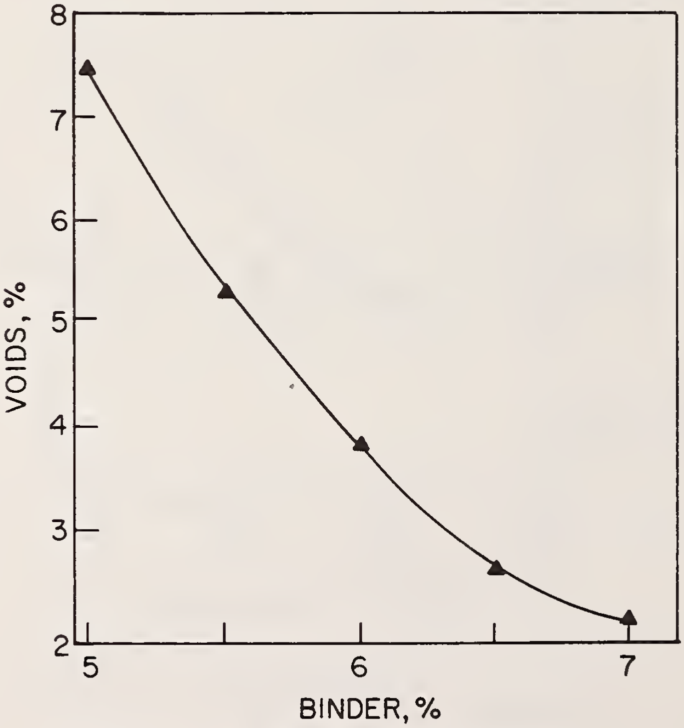

Figure 3.31. AKS percent voids.

G. Evaluation of Acid Pretreated Lignin Sulphonate - Asphalt Binder (Phase C-3)

The basic difficulty in approaching the utilization of lignin sulfonates in pavement technology is the fact that the lignin sulfonates in spent liquors are soluble in water and therefore, when a dried road surface becomes wet with rain, the lignin sulfonates dissolve and lose their utility as a road binder.

In this approach toward use of lignin sulfonates as extenders of asphalt, once again (as in the case of utilization of lignin sulfonates as substitutes to asphalt) attempts were made to bring about insolubility or limited solubility in the lignin sulfonates and thereby avoid the problems created by contact of water with road surfaces.

To achieve this goal, lignin sulfonates were converted into high molecular weight materials and placed under appropriate conditions for final reactions by application of heat, pressure and chemicals.

Pretreatment Procedure

Materials

1. Commercial concentrated spent sulfite liquor (50% solid) produced at Georgia Pacific under the commerical name of "Lignosite", with the main component of calcium lignin sulfonate (CaLS).

2. Concentrated technical grade hydrochloric acid with a normality of 10 to 11.

Six hundred grams of calcium lignin sulfonate were enclosed in a stainless steel reaction vessel which had a maximum volume of 1000 ml. Percentages of 1.9, 3.8, or 5.7 hydrochloric acid based on the total weight of the mixture (10 ml, 20 ml and 30 ml, respectively) was added to the mixture. The reaction vessel was air tight to create enough pressure for the reactions (pressure was estimated to be approximately 200 psi (1.38 MPa)).

The oven was preheated to three different temperatures, 374°F, 392°F and 437°F (175°C, 200°C, and 225°C). The reaction vessel was placed in the oven and heated for variable durations (2, 3, and 4 hours). At the end of each heating time the vessel was removed from the oven and cooled immediately by applying cold water on the outside of the vessel. After the reaction vessel was cooled, it was opened and the substances were removed from the vessel and examined for water solubility and stiffness.

Results and Observations

From Figures 3.32A through 3.32C it was observed that the characteristics of all materials prepared depended on the treatment conditions, such as heating temperature and duration, and amount of acid added. These materials can be divided into three groups based on their solubility in water:

1. Easily soluble lignin sulfonates. The characteristics of these materials were obviously not changed by the treatment and were not much different for our use from the untreated conditions.

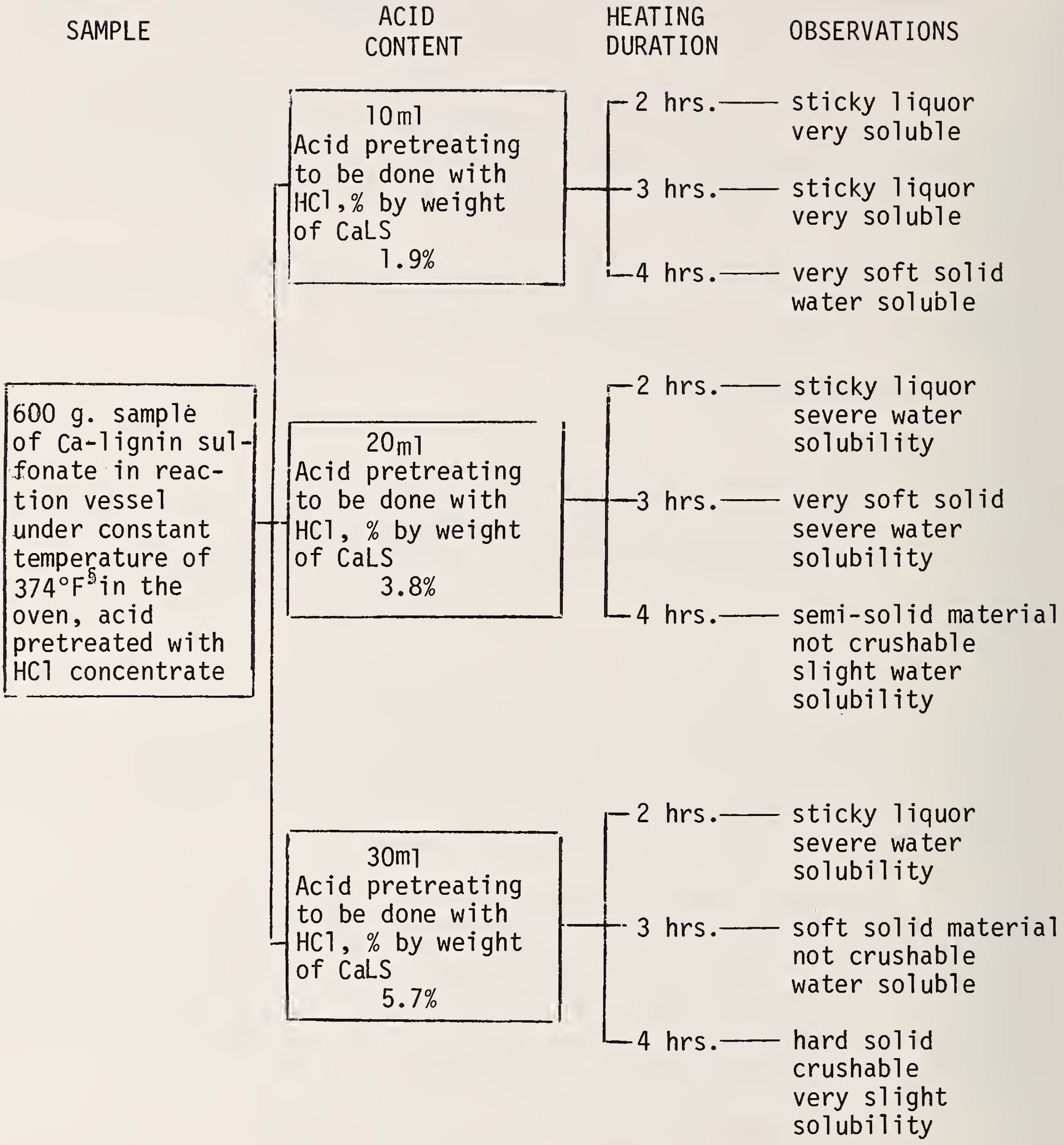

Figure 3.32A. Acid pretreatment test series.

§To convert to °C: 5/9(°F - 32)

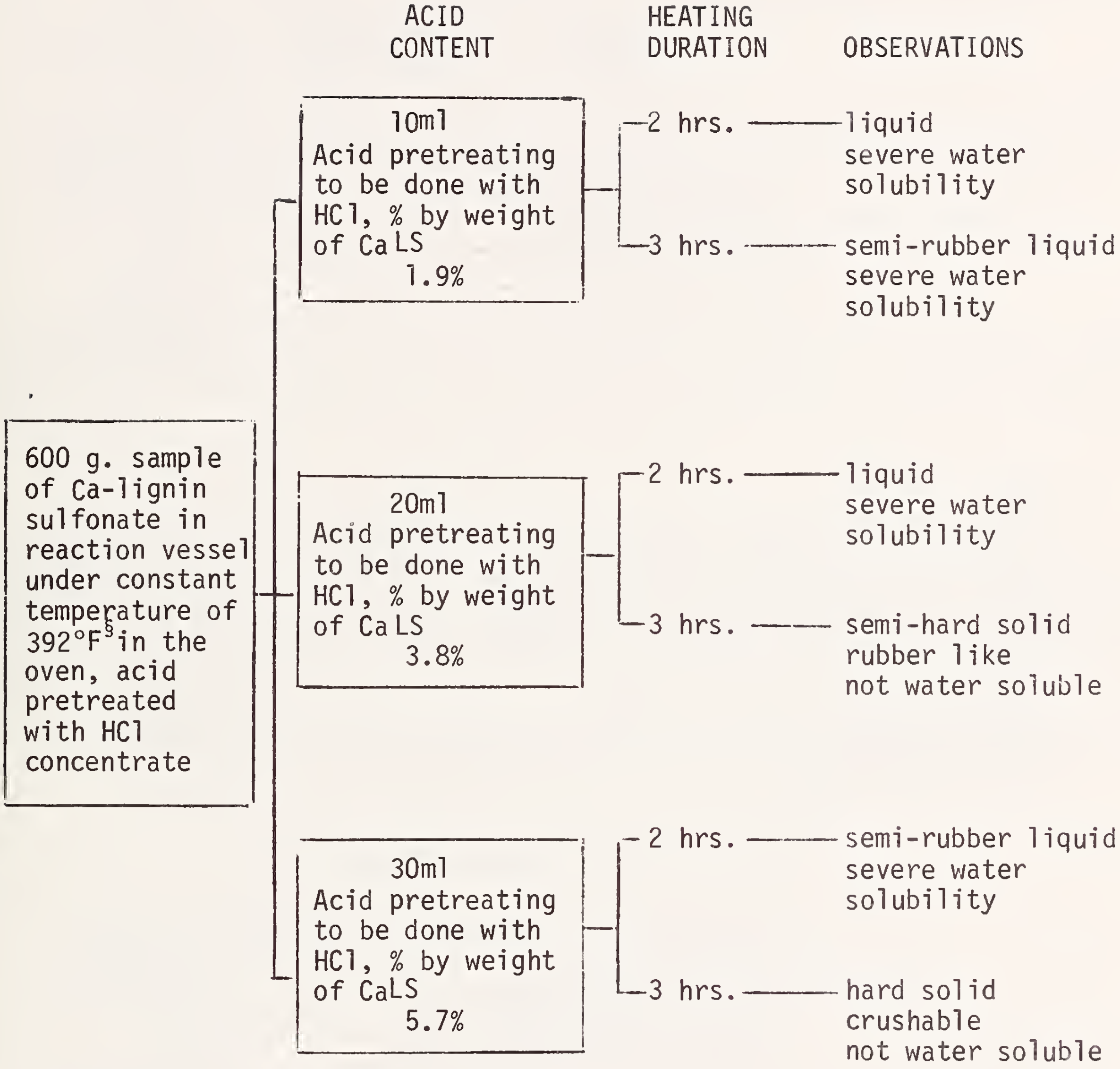

Figure 3.32B. Acid pretreatment test series.

§To convert to °C: 5/9(°F - 32).

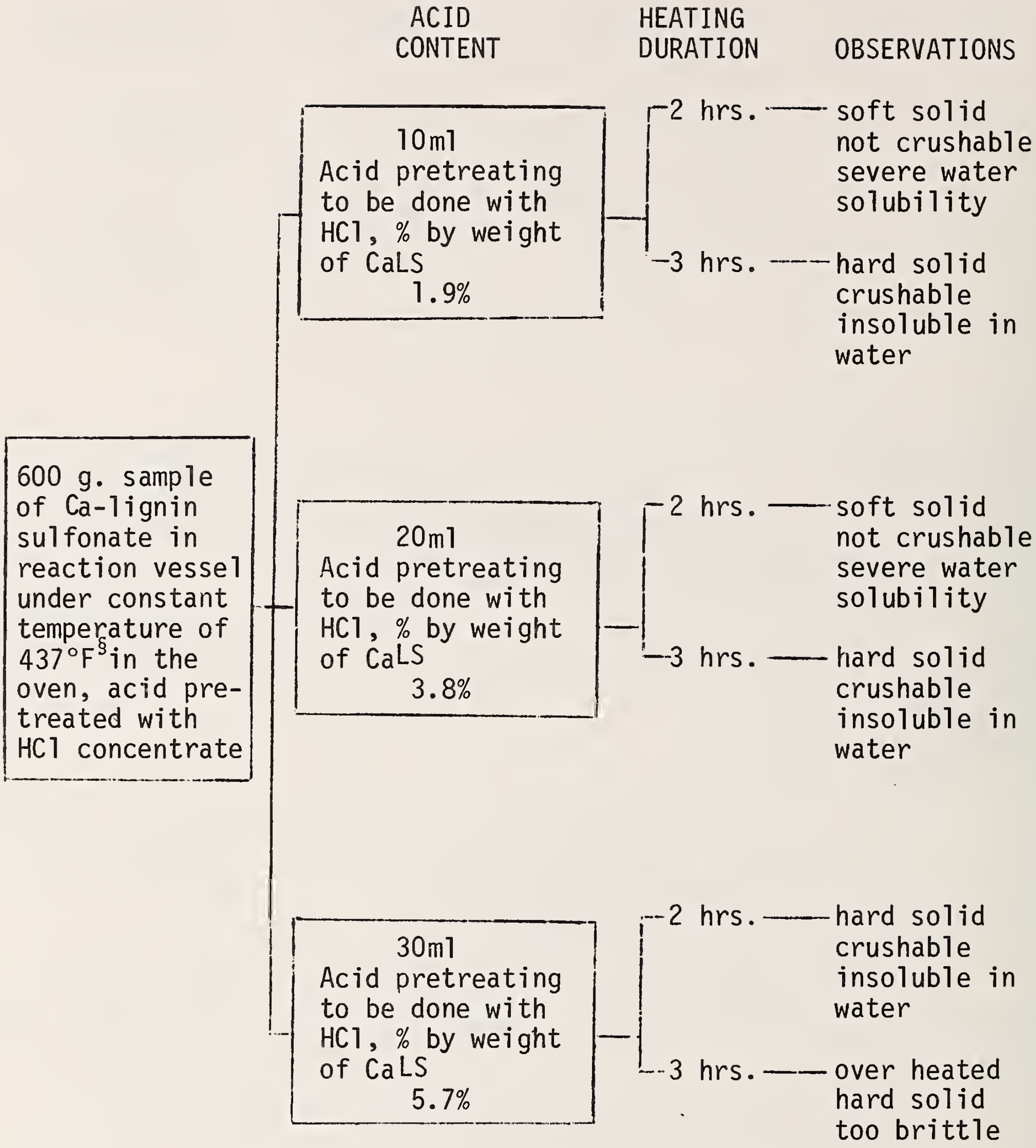

Figure 3.32C. Acid pretreatment test series.

§ To convert to °C: 5/9(°F - 32).

2. Incompletely soluble lignin sulfonates. These materials were soft solids in room temperature but after heating or mixing with hot asphalt, changed into very brittle materials. When mixed with sand, their solubility increased remarkably.

3. Insoluble lignin sulfonates. These are the materials produced under severe conditions of acid content, temperature and heating duration. These are hard solid materials with no water solubility at all. Because these are hard rubber-like materials, they are not readily mixed with asphalts. Therefore, the material if used as an extender to asphalt has to be ground into smaller size particles to facilitate mixing and hopefully reacting with asphalts.

From the discussion above it is concluded that the optimum method in pretreating calcium lignin sulfonate in the laboratory is by the addition of 5.7% HCl, based on total weight of the mixture and then heating at 437°F (225°C) for 2 hours.

Binder Formation

Pretreating calcium lignin sulfonate to the stage where it is water insoluble results in a rubber-like solid material. To blend this material with asphalt it had to be crushed, washed, dried, ground and sieved. A simple method was developed to blend calcium lignin sulfonate with asphalt. Figure 3.33 schematically illustrates the formation of the binder, which can be outlined as follows:

1. The pretreated calcium lignin sulfonate when removed from the reaction vessel is a solid material which needs to be crushed into small particles.

2. Wash with cold water to remove the extra acid, if any.

3. Washed material is dried at room temperature overnight.

4. Dried material is ground with the help of a pulverizer.

5. The material is passed through a No. 200 sieve.

6. Predetermined amount of the lignin sulfonate is transferred to a mixing bowl.

7. Calculated proportion of AC-5 asphalt, preheated at 275°F(135°C) for 1 hr., is added to the mixing bowl along with the calcium lignin sulfonate.

8. The mixing bowl with binders is placed on a hot plate and mixed vigorously with a semi-flexible spatula for five minutes.

9. Binder is checked for uniformity and homogeneity visually and by spreading a thin film on a piece of non-adsorbent paper.

10. If lumps can be seen, the mixing bowl is put back on the hot plate and mixing is continued until complete blending is achieved.

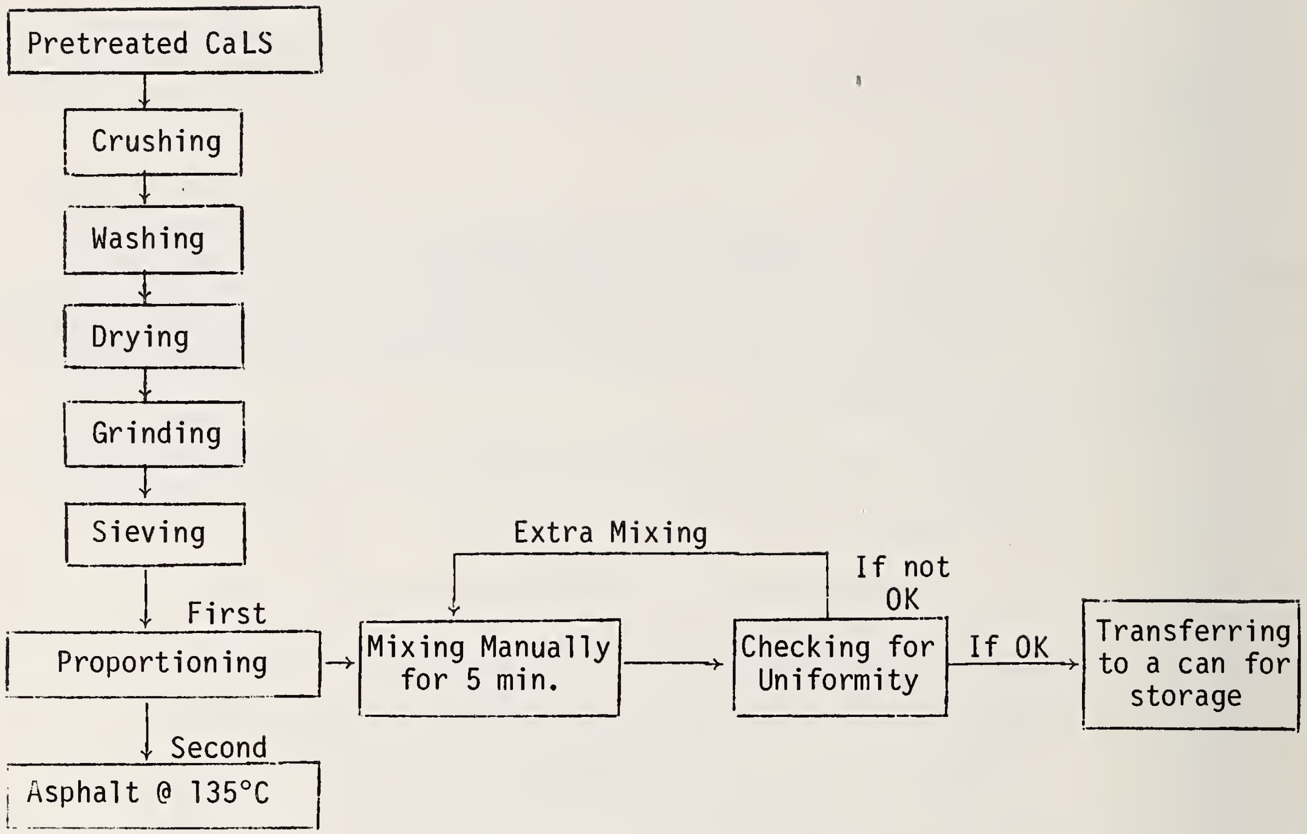

Figure 3.33. Modifying and blending calcium lignin sulfonate with asphalt.

Physical Properties of Binders

Results of the tests performed on the binders are summarized in Table 3.14. Based on these results and earlier work of Rimsritong (8), it was concluded that the presence of the well-dispersed lignin in asphalt increases the internal friction or resistance to deformation of the asphalt.

The specific gravity of the calcium lignin sulfonate extended asphalt binders were all about 1.0. The addition of different percents of calcium lignin sulfonate to AC-5 asphalt did not change the specific gravity of the asphalt. In addition, data for this binder that was developed by Matrecon, Inc. are shown in Table 3.14.

Because of experience with AR-4000 paving grade asphalt cement, it was selected as a control binder and for comparison with other mixtures. Since the new binder (CaLS) is the result of mixing CaLS with AC-5 asphalt, a series of test specimens were prepared with AC-5 asphalt alone to compare the changes in its properties and behavior due to the addition of CaLS. The other study was the effect of aggregate type on the behavior of CaLS binder. For this reason a series of test specimens were prepared by mixing CaLS binder with limestone aggregate having an identical gradation to that of the granite aggregate.

Results of tests performed to determine the optimum binder content for each of the four are summarized in Table 3.15 and 3.16, respectively.

From the relationships between the binder content and various test results, it can be observed that:

1. The mechanical behavior of CaLS paving mixtures are similar to those for conventional asphaltic concrete.
2. While the optimum binder content for AR-4000 is 4.5% and for AC-5 is 4.0%, the optimum binder content for CaLS when mixed with granite aggregate is 5.5% and when mixed with limestone aggregate is 6.0%.
3. The relatively higher binder contents expressed in weight percent of CaLS mixes are the result of higher viscosity as noted for other binders. Therefore, it requires more binder as compared to asphalt alone to coat all the aggregate particles.
4. All the physical properties of CaLS mixtures with optimum binder content satisfy the requirements for asphalt concrete specifications.

The optimum binder content for CaLS mixtures (5.5%) is relatively higher than that of conventional asphalt mixtures, but considering that of this 5.5%, 1.65% is CaLS and 3.85% is asphalt. Figures 3.34 through 3.39 illustrate the relative behavior of CaLS mixtures and AC-5 and AR-4000 mixtures. These figures show that the CaLS mixture follows the same behavior pattern as AC-5 and AR-4000, and that properties of CaLS mixtures with optimum binder content

Table 3.14. Summary of binder test results.

CaLS Binder, %	Penetration 0.1 mm	Softening Point, °C	Viscosity Poises x 10^6 [§]	Ductility cm	Specific Gravity	Viscosity Kinematic Centistokes
0.0	68	37	.6	100+	1.021	204
10.0	56	38	2.5	72	1.017	231
20.0	52	40	2.1	53	1.016	309
30.0	49	42	2.4	39	1.014	456
40.0	46	45	4.5	30	1.012	1000+
AR-4000	52	40	4.2	100+	1.032	387

[§] To convert to Pa·s: Poises x 10 x 10^{-1}

Table 3.15. Summary of test results for calcium lignin sulfonate mixtures using granite aggregates.

Binder Cont.	Samp. No.	Thickness In.	Hveem Stab.	Bulk Sp. Gr.	Unit Wt. pcf§	Wet Ind. Ten. St. psi§	Dry M_Rx10^3 psi§	Wet M_Rx10^3 psi§	Max. Sp. Gr.	Voids %
AC-5 4.0%	1	2.44	39	2.388	149	95	138	123	2.515	5.0
	2	2.47	42	2.366	148	84	163	154		5.9
	3	2.44	37	2.395	149	88	165	143		4.7
	Ave	2.45	39	2.383	149	89	155	140		5.2
AR-4000 4.5%	13	2.44	41	2.417	151	167	342	342	2.516	3.9
	14	2.44	47	2.407	150	165	342	342		4.3
	15	2.47	41	2.415	151	158	338	285		4.0
	Ave	2.45	43	2.413	151	163	341	323		4.0
CaLS 5.0%	25	2.56	52	2.311	144	65	193	149	2.505	7.7
	26	2.56	49	2.307	145	68	132	109		7.0
	27	2.56	48	2.320	145	62	193	182		7.3
	Ave	2.56	50	2.312	145	65	173	147		7.3
CaLS 5.5%	37	2.56	49	2.339	146	103	253	235	2.471	5.3
	38	2.56	45	2.331	145	107	414	325		5.6
	39	2.59	45	2.333	146	104	321	232		5.5
	Ave	2.57	46	2.334	146	105	329	264		5.5
CaLS 6.0%	49	2.56	43	2.357	147	102	235	219	2.494	5.4
	50	2.56	45	2.360	147	105	253	253		5.3
	51	2.53	40	2.366	148	103	366	256		5.1
	Ave	2.55	43	2.361	147	103	285	243		5.3
CaLS 6.5%	61	2.56	41	2.387	149	93	203	193	2.485	3.9
	62	2.56	38	2.369	148	99	203	193		4.6
	63	2.53	43	2.387	149	94	221	195		3.9
	Ave	2.55	41	2.381	149	95	209	194		4.1
CaLS 7.0%	73	2.50	35	2.426	151	83	187	187	2.500	2.9
	74	2.53	37	2.393	149	97	184	184		4.2
	75	2.50	31	2.403	150	92	208	187		3.8
	Ave	2.51	34	2.407	150	94	193	186		

§To convert to kg/m^3: pcf x 1.601846 x 10
To convert to MPa : psi x 6.894 x 10^{-3}

Table 3.16. Summary of test results for calcium lignin sulfonate mixture using limestone aggregate.

Binder Cont.	Thickness In.§	Hveem Stab.	Bulk Sp. Gr.	Unit Wt. pcf§	Wet Ind. Ten. St. psi §	Dry M_Rx10^3 psi§	Wet M_Rx10^3 psi§	Max Sp. Gr.	Voids %
AC-5 4.0%	2.50	44	2.395	149	54	153	129	2.525	5.1
AR-4000 4.5%	2.50	47	2.404	150	85	278	198	2.512	4.2
Ca LS 5.0%	2.50	46	2.325	145	61	167	150	2.525	7.9
Ca LS 5.5%	2.50	50	2.339	146	67	167	156	2.500	6.4
Ca LS 6.0%	2.50	49	2.360	147	67	208	168	2.481	4.8
Ca LS 6.5%	2.50	39	2.369	148	65	178	129	2.487	4.7

Note: All test results are the average of the three specimens tested under identical conditions.

§To convert to mm: in. x 25.4
" " " kg/m^3: pcf x 1.601846 x 10
" " " MPa: psi x 6.894 x10^{-3}

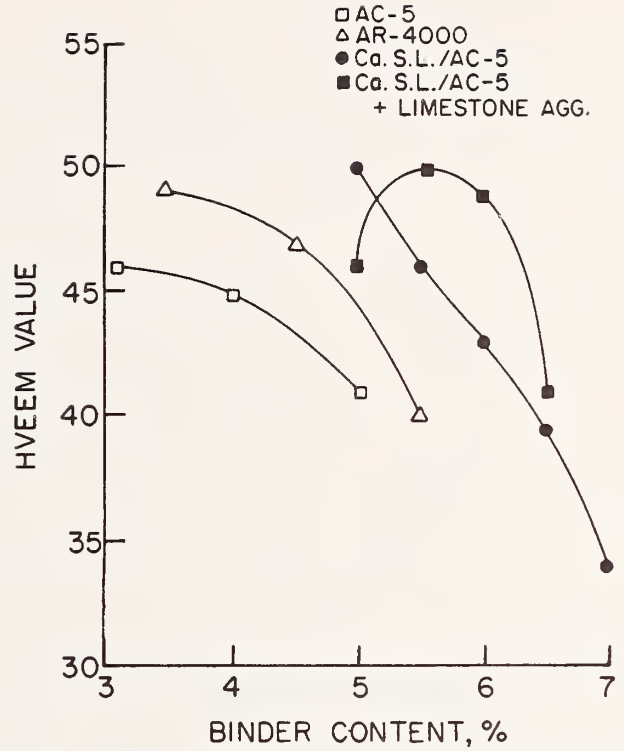

Figure 3.34. Hveem stabilometer value vs. percent binder.

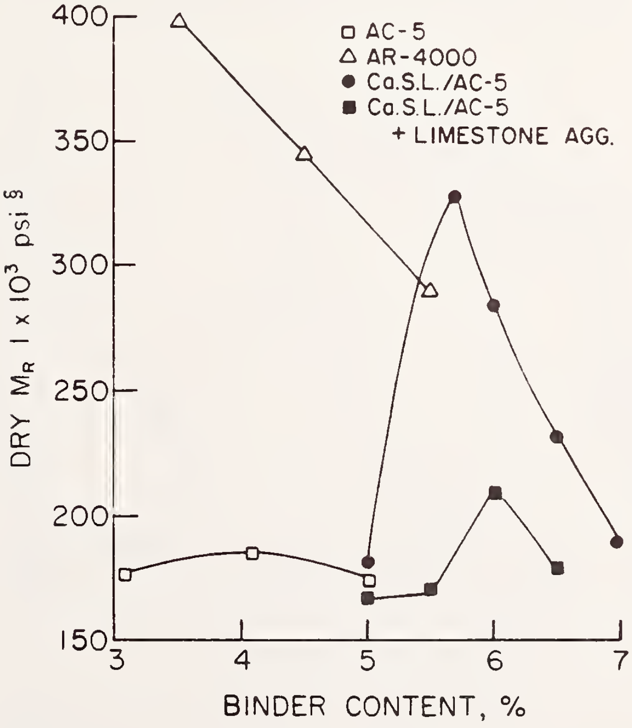

Figure 3.35. Initial dry resilient modulus (M_R) vs. percent binder.

§To convert to MPa: psi x 6.894 x 10-3

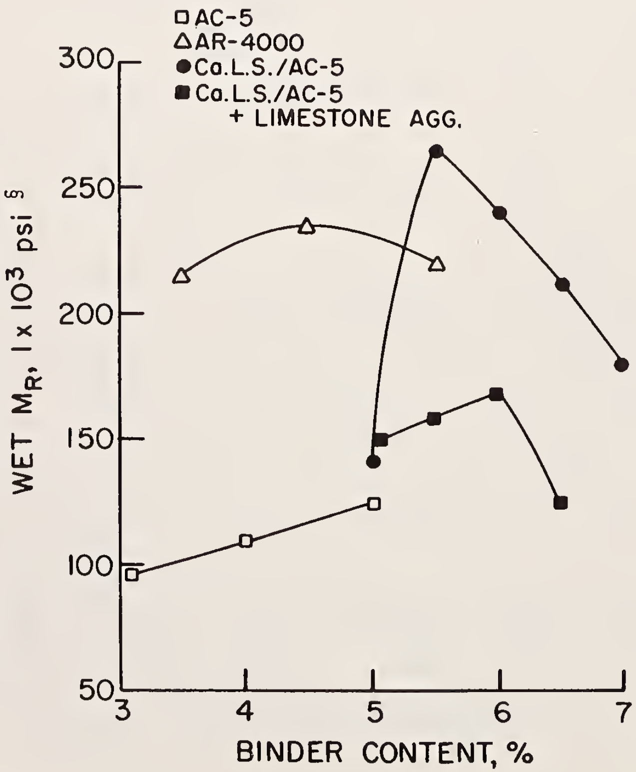

Figure 3.36. Vacuum saturated resilient modulus (M_R) (Wet M_R) vs. percent binder.

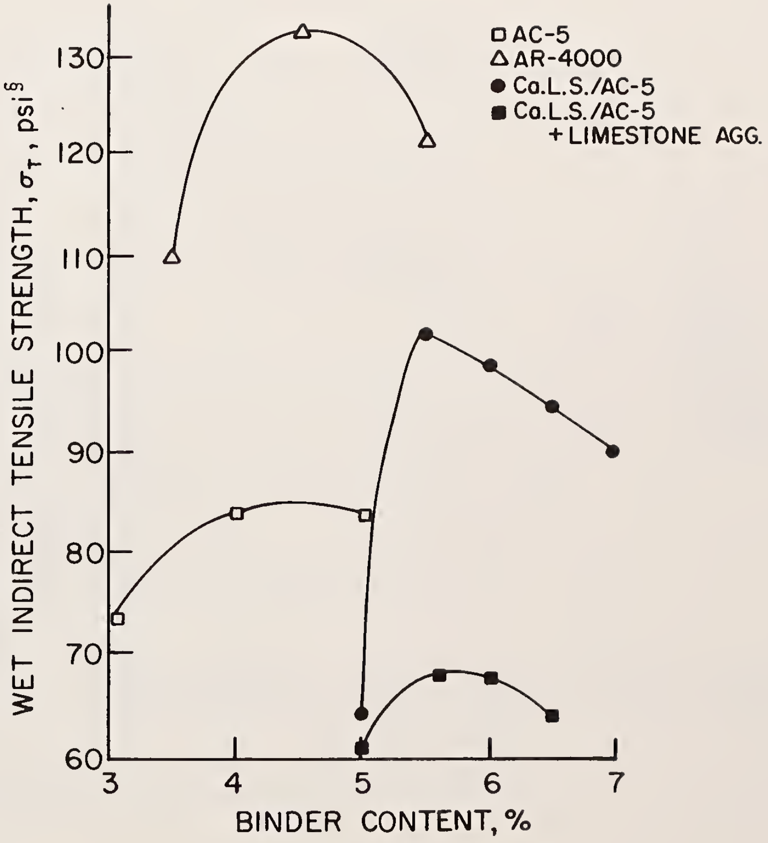

Figure 3.37. Vacuum saturated wet indirect strength vs. percent binder.

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§ To convert to MPa: psi x 6.894×10^{-3}

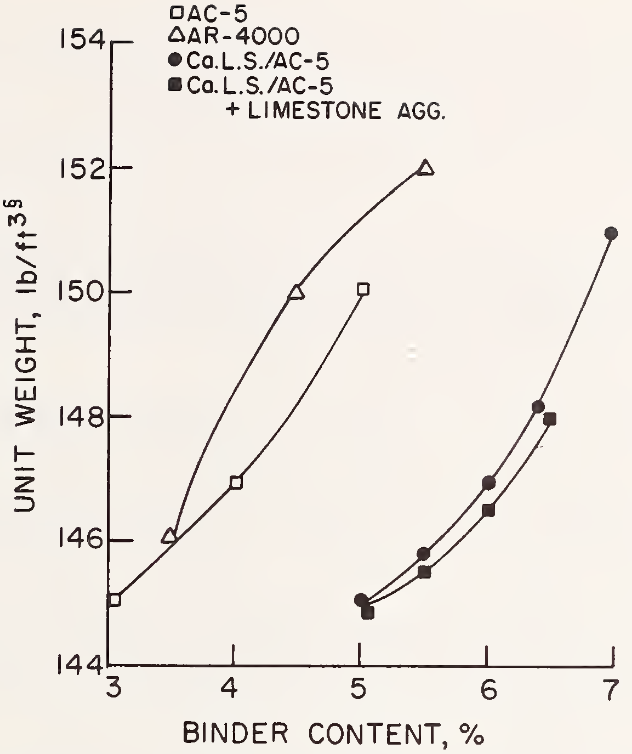

Figure 3. 38. Unit weight vs, percent binder.
§To convert to kg/m^3: lb/ft^3 x 1.60184 x 10

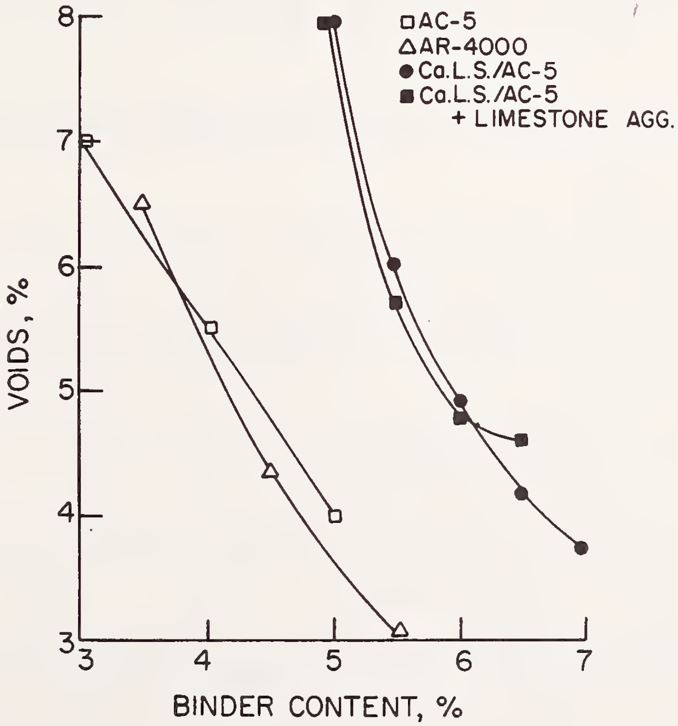

Figure 3.39. Percent voids vs. percent binder.

may be better than AC-5 and equal to or very close to AR-4000 mixture properties. The following observations support this statement:

1. The Hveem stability of all mixes appear to be virtually the same, ranging from 40 to 50. They all meet the 35 minimum requirement.

2. The ability of the CaLS mixtures to resist water damage (based on the wet M_R test) better than conventional asphalt concretes is believed to be caused by the stronger bond or adhesion between the CaLS binder and the aggregate particles.

3. The resilient modulus of the CaLS mix is higher than the AC-5 mix, and lower but very close to the AR-4000 mix.

4. The tensile strength of the CaLS mix is higher than the AC-5 mix and lower than the AR-4000 mix, which shows that CaLS increases the strength of a mix.

The above observations indicate that extending asphalt with CaLS not only increases the strength of the mix, it also increases its ability to resist moisture and other damage.

Characterization of CaLS Mixtures after Laboratory Conditioning

Following the mixture design evaluation, additional tests were conducted to approximate field behavior. Of these laboratory tests mentioned above, the most commonly used ones are fatigue, creep, freeze-thaw conditioning, and accelerated temperature conditioning. Because of the scope of this study, three of these tests were selected.

Table 3.17 through 3.20 and Figures 3.40 through 3.46 illustrate the results of the freeze-thaw conditioning 156°F (60°C) accelerated conditioning and weather exposure tests.

From the relationships between the binder content in the mixtures and various test results, it was observed that:

1. Freeze-thaw cycle conditioning damages the asphalt mixture samples (based on resilient modulus test after 3, 9, and 15 cycles).

2. Adding CaLS to AC-5 asphalt does not improve sample resistance to freeze-thaw cycle conditioning.

3. Although addition of CaLS to asphalt improves its initial resilient modulus, these samples lose much of their initial high strength after freeze-thaw conditioning.

4. Accelerated conditioning at 156°F (60°C) increases the strength of the mixtures (based on resilient modulus test).

5. Specimens exposed to the natural elements experienced minor increases and decreases of modulus in the first four week period

Table 3.17. Resilient modulus (M_R) after freeze-thaw conditioning for different binder contents.

Binder Cont.	Sample No.	Thickness In.§	Hveem Stability	Initial $M_R x10^3$ psi§	Wet $M_R x10^3$ psi§	+3 cycl $M_R x10^3$ psi§	+9 cycl $M_R x10^3$ psi§	+15 cycl $M_R x10^3$ psi§
AC-5 4.0%	10	2.44	43	191.47	181.32	137.55	111.32	93.12
	11	2.44	49	191.47	163.93	143.31	119.07	95.73
	12	2.44	44	181.32	163.93	149.58	108.30	90.66
	Ave	2.44	45	188	170	144	113	93
AR-4000 4.5%	22	2.47	51	262.57	238.70	210.99	161.86	130.56
	23	2.44	55	310.83	284.93	241.76	202.83	163.93
	24	2.44	47	379.91	284.93	284.93	230.13	181.32
	Ave	2.45	44	318	270	246	198	159
CaLS 5.0%	34	2.56	49	406.55	325.24	182.13	103.01	86.23
	35	2.59	56	459.04	401.66	200.83	124.27	95.30
	36	2.59	53	459.04	401.66	321.32	111.90	85.20
	Ave	2.58	53	423	276	235	113	89
CaLS 5.5%	46	2.56	46	406.55	361.37	271.03	172.47	136.32
	47	2.59	46	401.66	321.32	190.61	140.58	120.28
	48	2.56	46	406.55	361.37	218.91	182.13	136.32
	Ave	2.57	46	405	348	227	165	131
CaLS 6.0%	58	2.53	42	365.84	232.81	174.60	110.80	87.30
	59	2.56	43	370.41	277.80	197.76	134.11	98.88
	60	2.53	41	365.84	256.09	195.32	132.46	118.80
	Ave	2.52	42	367	256	189	126	102
CaLS 6.5%	70	2.53	36	221.16	157.86	138.01	118.80	97.66
	71	2.56	41	229.96	163.79	148.80	103.01	91.06
	72	2.50	40	259.28	208.35	167.88	120.28	101.90
	Ave	2.53	39	237	177	152	114	97
CaLS 7.0%	82	2.53	36	299.32	232.81	232.81	221.61	221.61
	83	2.49	36	306.90	210.99	238.70	210.99	227.22
	84	2.50	37	259.29	176.78	297.76	197.76	208.35
	Ave	2.51	36	288	207	223	210	219

§To convert to mm: in. x 25.4
" " " MPa: psi x 6.894 x 10^{-3}

Table 3.18. Percentage M_R retained after freeze and thaw conditioning.

Binder %	Sample No.	Initial % M_R Ret.	Wet % M_R Ret.	+3 cycl. % M_R Ret.	+9 cycl. %M_R Ret.	+15 cycl. % M_R Ret.
AC-5 4%	10-11-12	100	90	76	60	49
AR-4000 4.5%	22-23-24	100	85	77	62	50
CaLS 5.0%	34-35-36	100	88	55	27	21
CaLS 5.5%	46-47-48	100	86	56	41	32
CaLS 6.0%	58-59-60	100	70	51	34	28
CaLS 6.5%	70-71-72	100	75	64	48	41
CaLS 7.0%	82-83-84	100	79	77	73	71

Table 3.19. Resilient modulus (M_R) after 60°C temperature conditioning.

Binder Content	Sample No.	Thickness In.§	Hveem Stab.	Initial $M_R \times 10^3$ psi§	+1 day $M_R \times 10^3$ psi§	+2 days $M_R \times 10^3$ psi§	+3 days $M_R \times 10^3$ psi§	+4 days $M_R \times 10^3$ psi§	+5 days $M_R \times 10^3$ psi§	+10 days $M_R \times 10^3$ psi§
AC-5 4.0%	7	2.43	41	191	93	244	202	214	172	265
	8	2.46	45	154	59	227	162	179	126	200
	9	2.45	43	154	71	277	179	179	141	227
	Ave	2.45	43	166	74	233	181	191	144	231
AR-4000 4.5%	19	2.46	43	311	141	337	227	310	227	375
	20	2.46	40	241	118	311	200	241	141	311
	21	2.40	46	269	140	346	247	389	269	385
	Ave	2.44	43	274	133	331	225	280	212	357
CaLS 5.0%	31	2.56	50	299	142	406	361	406	325	464
	32	2.59	48	295	130	402	357	402	321	402
	33	2.59	46	357	190	535	459	452	301	643
	Ave	2.58	48	317	154	448	392	448	349	503
CaLS 5.5%	43	2.59	53	296	147	402	321	357	296	459
	44	2.56	51	542	203	542	542	542	465	650
	45	2.56	47	465	203	406	465	406	361	650
	Ave	2.57	50	434	184	450	443	435	374	586
CaLS 6.0%	55	2.56	45	271	113	361	325	325	271	465
	56	2.53	47	274	166	329	303	329	274	470
	57	2.53	46	274	138	329	303	329	303	470
	Ave	2.54	46	273	139	340	310	328	283	468
CaLS 6.5%	67	2.56	39	182	82	232	319	252	219	465
	68	2.56	44	149	78	182	164	193	164	325
	69	2.56	33	149	81	203	164	193	164	361
	Ave	2.56	39	160	80	206	182	213	182	384
CaLS 7.0%	79	2.56	35	203	91	253	164	203	164	299
	80	2.53	39	184	95	274	184	221	184	329
	81	2.46	38	214	89	227	170	200	170	337
	Ave	2.52	37							

§To convert to mm: in. x 25.4
" " " MPa: psi x 6.894×10^{-3}

Table 3.20. Resilient modulus (M_R) after weather exposure.

Binder Content	Sample No.	Thickness In.§	Hveem Stab.	Initial $M_R \times 10^3$ psi§	+7 days $M_R \times 10^3$ psi§	+14 days $M_R \times 10^3$ psi§	+28 days $M_R \times 10^3$ psi§	+56 days $M_R \times 10^3$ psi§	+112 days $M_R \times 10^3$ psi§
AC-5 4.0%	4	2.47	44	154.45	113.61	81.26	106.93	227.22	263
	5	2.47	45	170.01	121.81	79.30	117.57	227.22	239
	6	2.53	43	150.64	150.64	85.36	127.53	205.78	233
	Ave	2.49	44	158	129	82	117	220	
AR-4000 4.5%	16	2.53	44	299.32	274.38	150.64	274.38	411.57	470
	17	2.47	44	337.59	281.33	154.45	238.70	421.99	482
	18	253	48	274.38	329.26	184.38	274.38	411.57	470
	Ave	2.51	45	304	295	163	262	415	474
CaLS 5.0%	28	2.53	47	165.81	184.38	104.29	184.38	299.32	449
	29	2.53	52	232.81	256.09	127.33	204.78	470.37	449
	30	2.56	49	271.03	295.67	163.79	271.03	464.62	542
	Ave	2.54	49	223	245	132	220	411	480
CaLS 5.5%	40	2.59	41	292.11	316.11	179.94	292.11	459.04	535
	41	2.59	44	321.32	328.16	161.81	292.11	459.04	535
	42	2.62	41	317.49	317.49	198.43	302.77	453.56	529
	Ave	2.60	42	310	320	180	295	457	533
CaLS 6.0%	52	2.60	42	271.03	294.67	203.27	229.96	406.55	464
	53	2.53	41	299.32	299.32	205.78	274.38	411.57	470
	54	2.56	40	271.03	295.67	203.27	252.96	406.55	464
	Ave	2.56	41	280	297	204	252	409	466
CaLS 6.5%	64	2.53	38	157.86	205.78	144.05	157.86	232.81	274
	65	2.53	42	184.38	256.09	165.81	184.38	299.32	366
	66	2.56	35	148.80	218.91	142.29	163.79	271.03	361
	Ave	2.54	38	164	227	151	169	268	334
CaLS 7.0%	76	2.50	38	167.88	224.38	145.85	186.68	235.71	278
	77	2.47	38	170.01	210.99	141.50	161.86	238.70	262
	78	2.50	35	152.52	208.35	139.73	176.78	235.71	278
	Ave	2.49	37	164	214	143	175	237	273

§To convert to mm: in. x 25.4
" " " MPa: psi x 6.894×10^{-3}

but from then on increased their strength continuously. Addition of CaLS to AC-5 asphalt increases its resistance to weather exposure considerably. The M_R value of the CaLS mixture specimens is even higher than AR-4000 samples.

Summary and Comparison of Mixtures Evaluated in Phases C-1, C-2, and C-3

As discussed earlier, the three primary binders were prepared using the following three methods:

1. Kraft lignin mixed with asphalt in an open vessel;

2. Kraft lignin mixed with asphalt in Parr bomb with addition of sulfur; and

3. Calcium lignin sulfonate mixed with asphalt in an open vessel.

These were investigated and tested for their physical properties and mechanical behaviors and have been reported in the previous pages. By way of summary, the results of the several common principal tests performed in different phases of the study are compared.

Figures 3.47 through 3.52 compare the various test results for these three binder mixtures versus the percent binder content in the mixture.

H. Evaluation of Other Binder Modifications (Phase C-4)

Substantial testing and evaluation of the three primary binders resulted in encouraging information. The considerable time expended on researching these binders left less time to explore the remaining possibilities. Early in the research program numerous ideas were discussed. Several of these have been briefly investigated. These fall into two general categories: precoating of the aggregate and use of admixtures and other pretreatment.

A prime reason for such study was to overcome the relatively high binder content when lignin was used as an extender. The high (compared to AR-4000 asphalt cement alone) values resulted primarily because of the relatively higher viscosity exhibited by these binders. One goal was to reduce the required binder while other goals were aimed at general binder quality improvement.

Precoating

Aside from some factors with respect to the shape, surface texture, specific gravity, size and gradation of the aggregate, the ability of the aggregate to become properly distributed and coated is influenced by the method of introducing the asphalt binder. The arrangement of both the

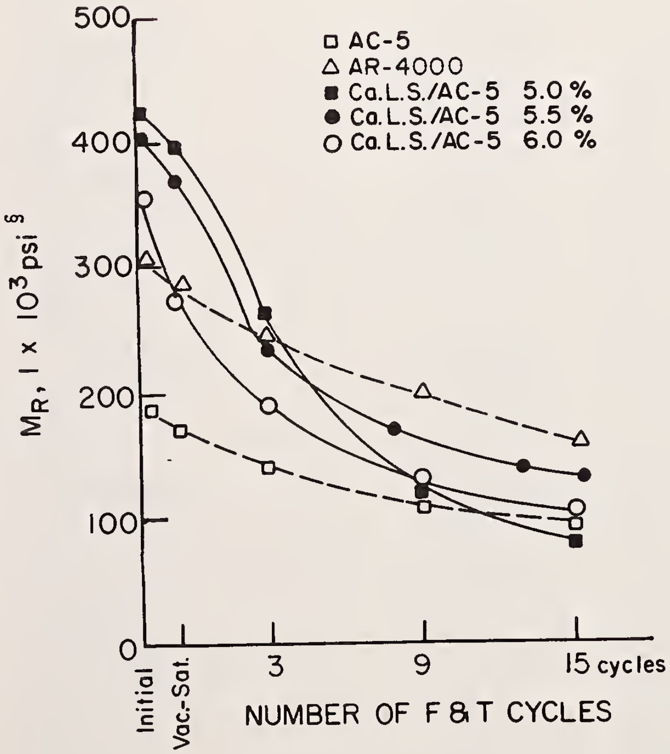

Figure 3.40. Resilient modulus (M_R) after freeze-thaw conditioning.

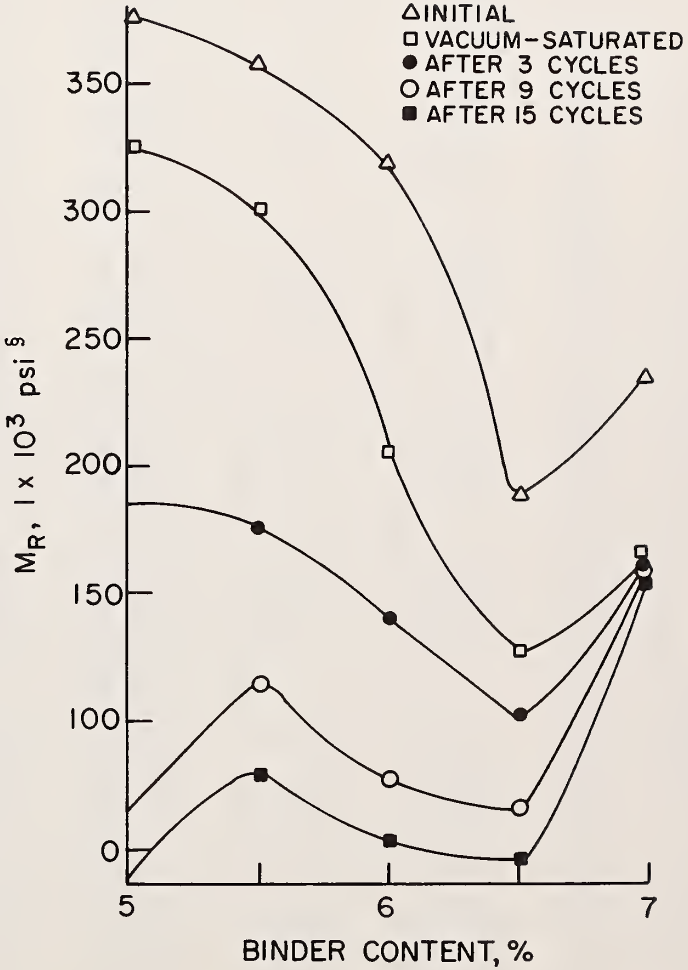

Figure 3.41. Resilient modulus (M_R) after freeze-thaw conditioning vs. percent binder content.

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§To convert to MPa: psi x 6.894 x 10^{-3}

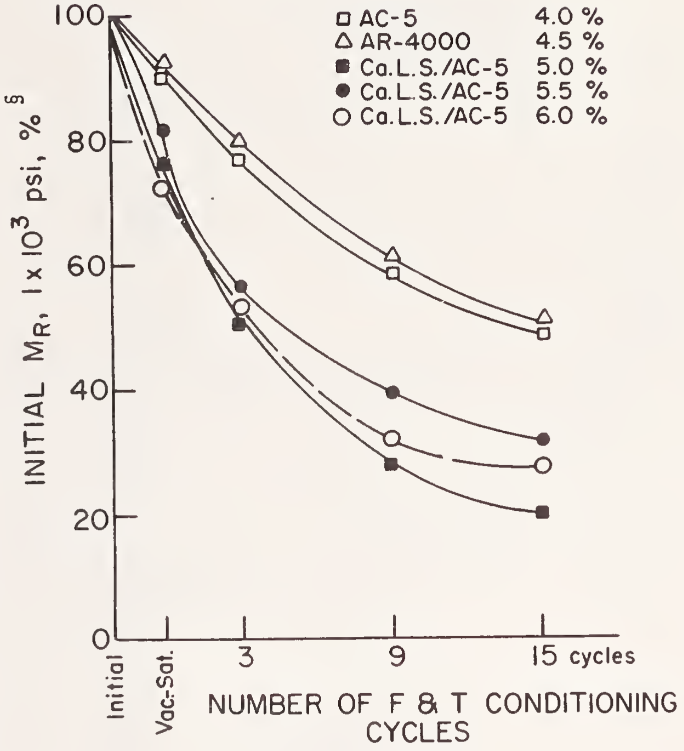

Figure 3.42. Percent of initial resilient modulus retained after freeze-thaw conditioning.

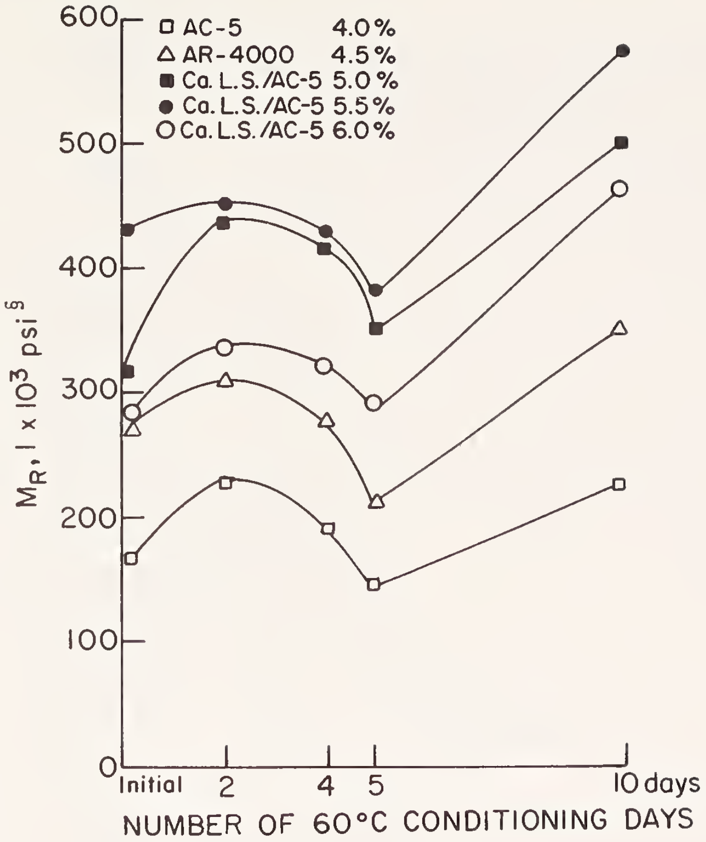

Figure 3.43.. Resilient modulus vs. duration of 60°C conditioning.

[§] To convert to MPa: psi x 6.894 x 10^{-3}

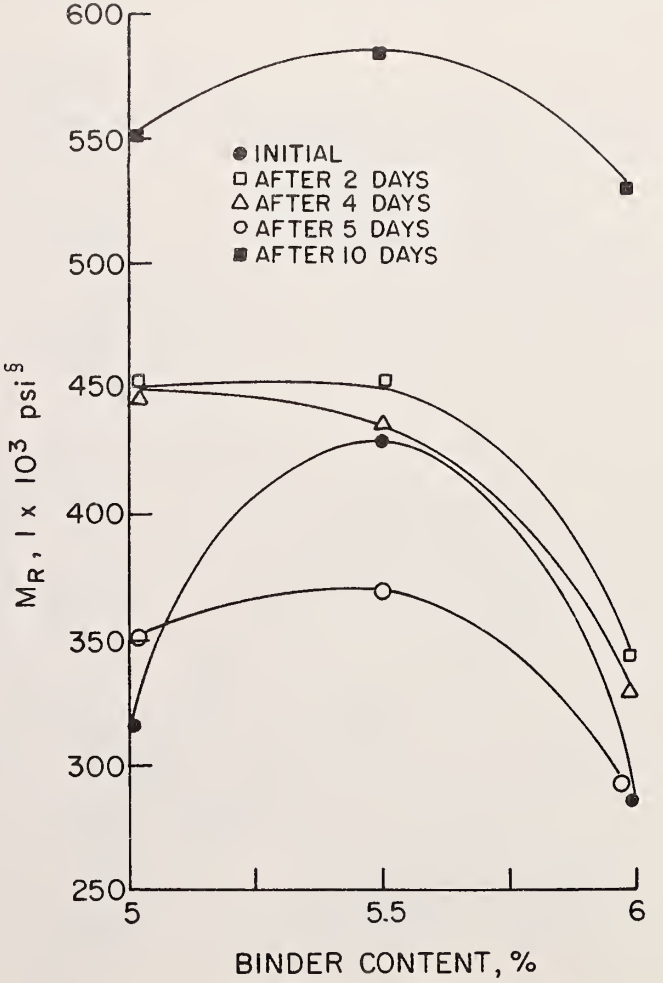

Figure 3.44. Resilient modulus after 60°C conditioning vs. binder contents.

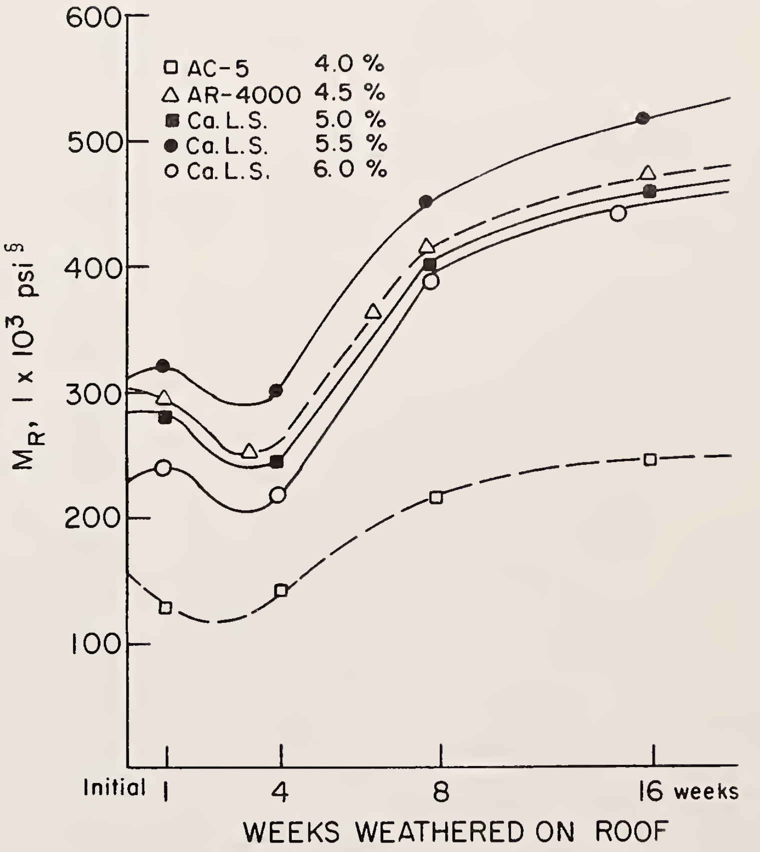

Figure 3.45. Resilient modulus after weather exposure.

§To convert to MPa: psi x 6.894 x 10^{-3}

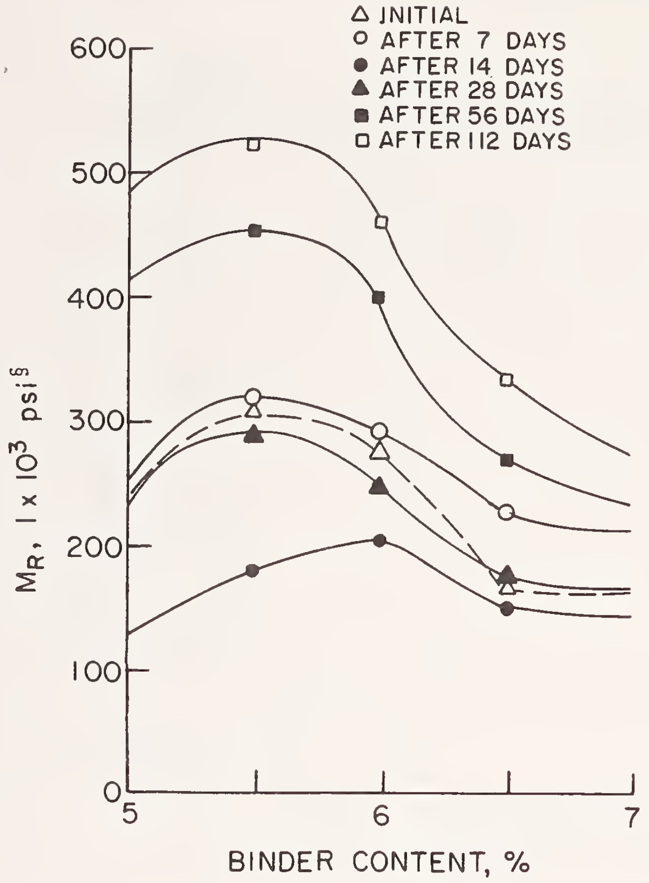

Figure 3.46. Resilient modulus after weather exposure.

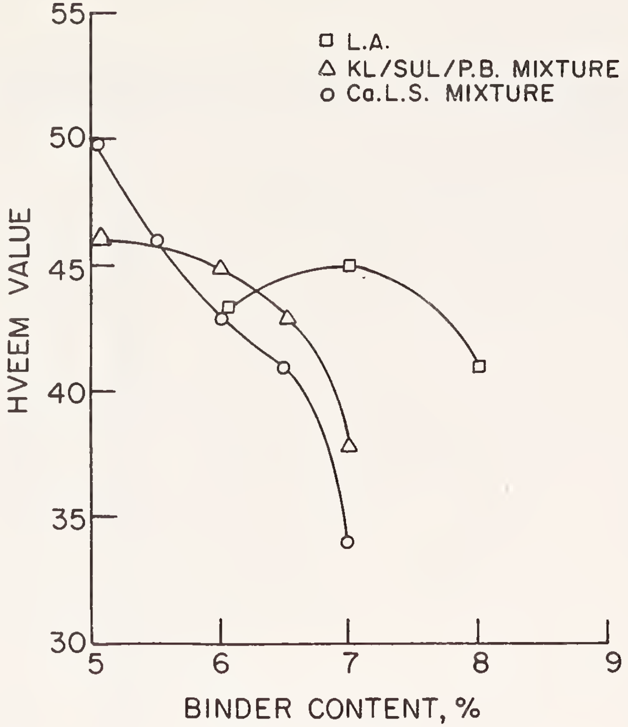

Figure 3.47. Comparative Hveem stability value vs. percent binder content.

[§] To convert to MPa: psi x 6.894 x 10^{-3}

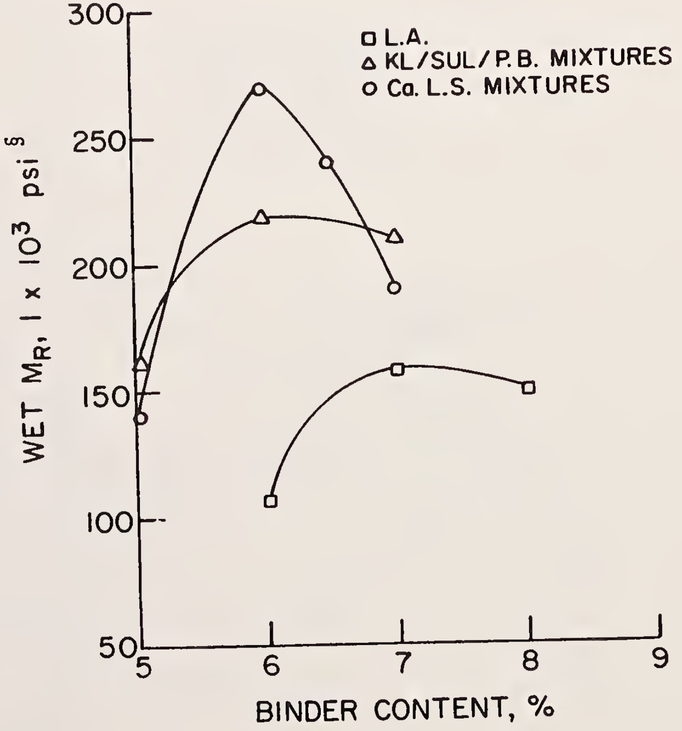

Figure 3.49. Comparative vacuum saturated resilient modulus (Wet M_R) vs. percent binder.

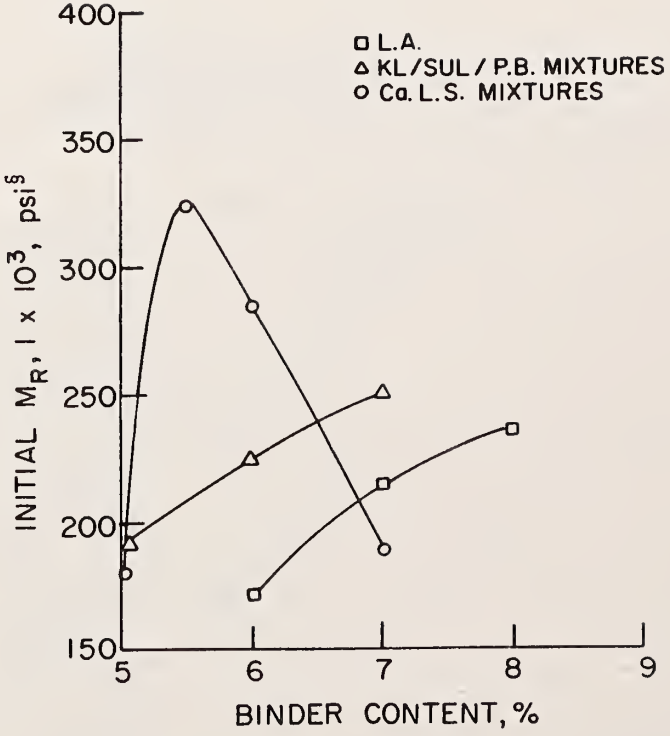

Figure 3. 48. Comparative resilient modulus vs. percent binder content.

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§ To convert to MPa: psi x 6.894 x 10^{-3}

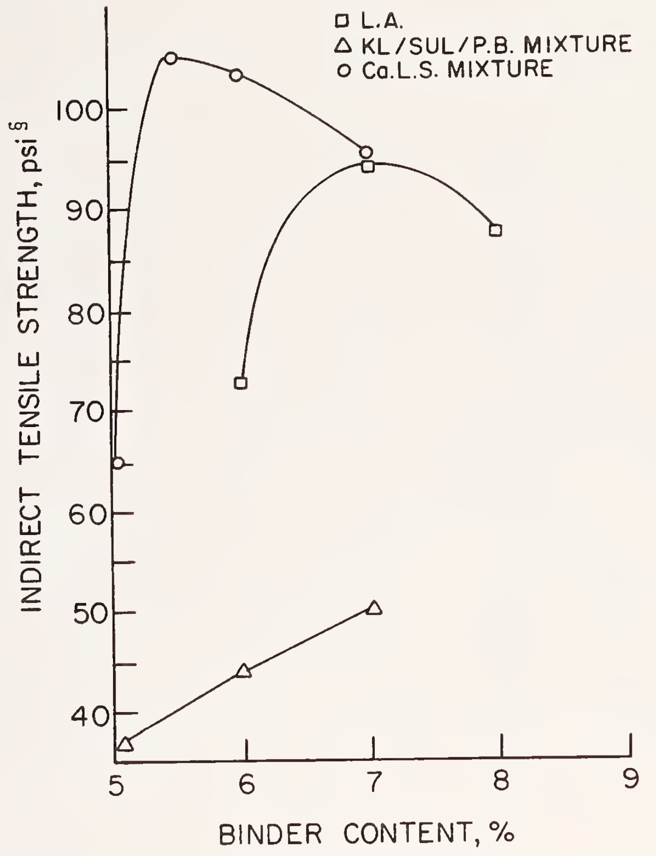

Figure 3.50. Comparative indirect tensile strength vs. percent binder content.

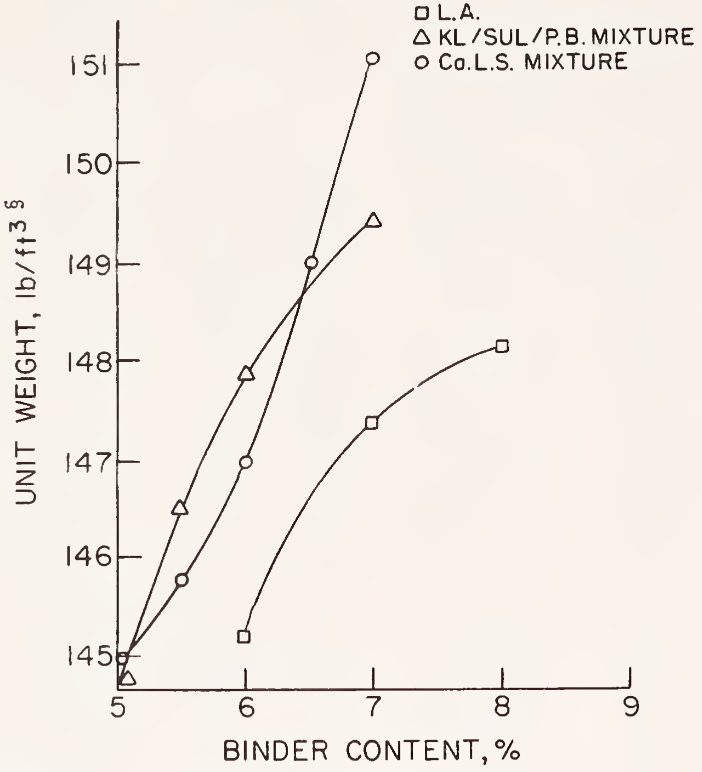

Figure 3.51. Comparative unit weight vs. percent binder.

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§To convert to MPa: psi x 6.894×10^{-3}
" " " kg/m^3: lb/ft^3 x 1.601846 x 10

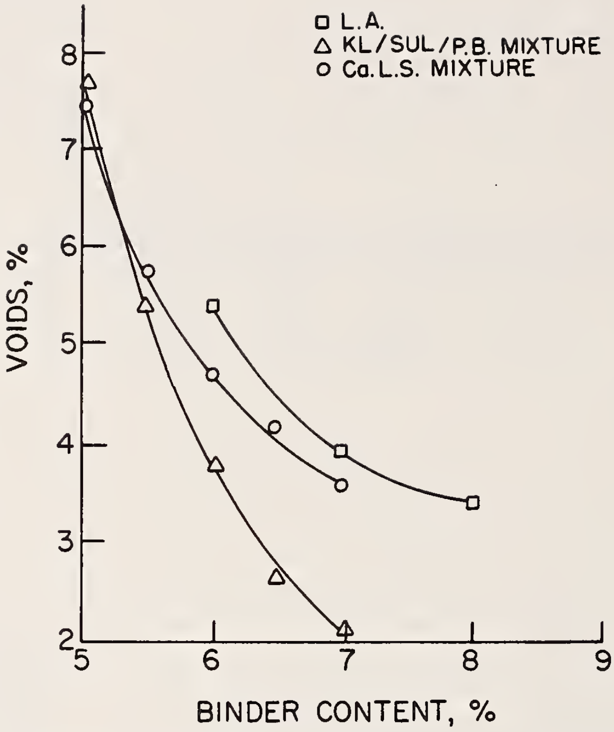

Figure 3.52. Comparative percent voids vs. percent binder.

aggregate and the binder may significantly affect the mixing efficiency. In general, mixing is facilitated as the initial distribution of the asphalt binders covers a wider range.

The research reported was intended to improve mixing efficiency, both in terms of workability and coatability, by altering the mixing procedures. The precoated coarse aggregate, the uncoated fine aggregate and the L/A binder were arranged in three different ways as briefly described below (a schematic diagram is shown in Figure 3.53):

Procedure A: After the coarse aggregate is precoated, the fines and binder are added and then mixed together.

Procedure B: After the coarse aggregate is precoated, binder is introduced and mixed with the precoated aggregate first. Then the fines are added and all is mixed together.

Procedure C: The fines are premixed with the binder, then the precoated coarse aggregate is added and the whole is mixed together.

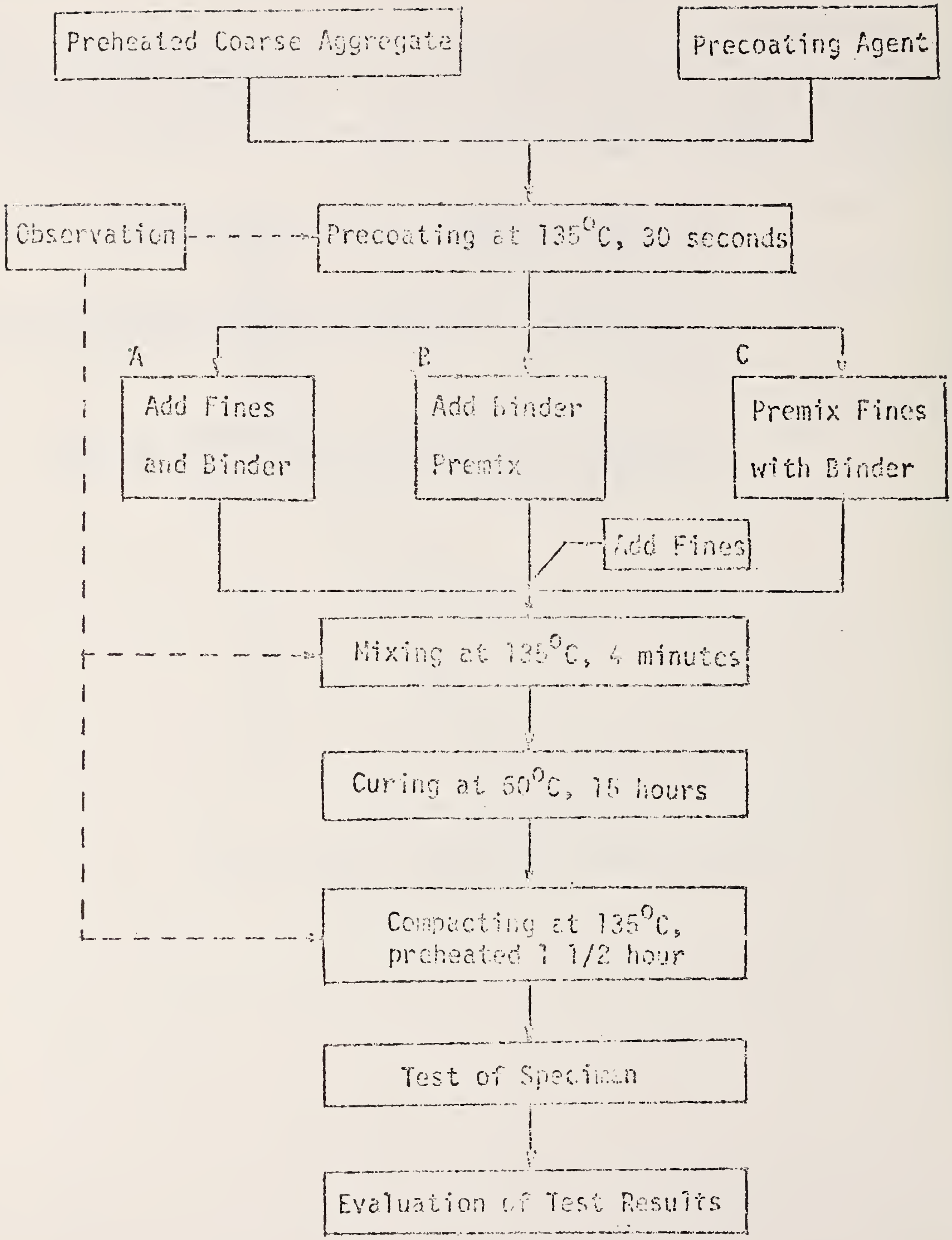

Figure 3.53. Flow diagram showing the hot precoating mix design procedures.

Precoating the coarse aggregate was conducted either at room temperature (cold precoating) or at 135°C (hot precoating). As an example, the steps followed in hot precoating are shown in Figure 3.63. The precoating procedures of each precoating agent are as follows:

Lime Precoating

Several methods have been tried to precoat the aggregates with hydrated lime. One of the most suitable means is to precoat the coarse aggregate with 1% lime (by weight of aggregate) in 50% slurry form.

Procedures:

1. Add lime slurry to the coarse aggregate and mix thoroughly.
2. After the coarse aggregate is coated, add the fine aggregate and mix. The mixture is then put in an oven until it dries out and reaches the mixing temperature.
3. Add proportioned binder and mix the while in an open vessel for five minutes.

Sulfur Precoating

In this study the sulfur used was 0.5%, 1%, 1.5% and 2% (by weight of aggregate) in molten form.

Procedures:

1. Precoat the coarse aggregate with molten sulfur by mixing for one minute.
2. Add the proportioned L/A binder and mix the precoated coarse aggregate for one minute.
3. Then introduce the fine aggregate in and mix the whole in an open vessel for three minutes.

Kraft Liquor Precoating

1. Proportion kraft liquor mix with preheated coarse aggregate to facilitate the evaporation of excess water content.
2. The fines are then added to the precoated coarse aggregate and mix.
3. Introduce the binder and mix the whole together in an open vessel for 5 minutes.

Portland Cement Precoating

Portland cement as well as hydrated lime was used to precoat the coarse aggregate. One percent of portland cement in 40% slurry form was considered to be adequate.

Precoating and mix procedures are the same as lime precoating stated above.

Asphalt Cement Precoating

AC-5 was tried in different percentages and to precoat various fractions of the coarse aggregates. In preliminary design mixing, 1% of the AC-5 for precoating the plus No. 4 sieve coarse aggregate was found to be adequate.

Procedures:

1. Precoat the coarse aggregate with 1% of AC-5 at 275°F (135°C) for about 30 seconds until well coated.

2. Add the preheated fines and binder in accordance to the procedures presented in Figure 3.53.

3. Then mix the whole in the open vessel at 275°F (135°C) for 4 minutes.

Asphalt Emulsions Precoating

CRS-2 was used for both hot precoating and cold precoating. CMS-2S was used only for cold precoating.

Hot Precoating Procedure:

1. Precoat the coarse aggregate with 1% of CRS-2 at 275°F (135°C) for about 30 seconds.

2. Add the fines and binder, and then mix in an open vessel at 275°F (135°C) for 4 minutes.

Cold Precoating Procedure:

1. Precoat the coarse aggregate with 1.5% of CRS-2 or CMS-2S at room temperature (about 1% of water was added to dilute the emulsions for better workability).

2. Add fines to the precoated coarse aggregates and mix. The mixture is cured in an oven at 221°F (105°C) overnight.

3. Add preheated binder to the mixture and then mix them at 275°F (135°C) for 3 to 5 minutes.

Evaluation of Test Results for Precoating

Figures 3.54 through 3.63 summarize the primary results of the precoating tests.

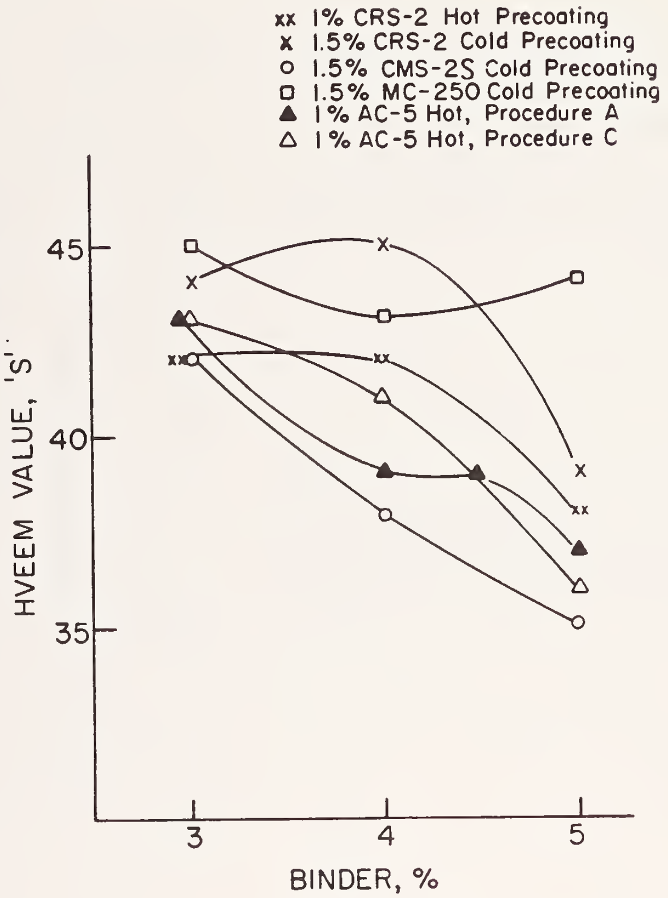

Figure 3.54. Hveem value for precoated mixtures.

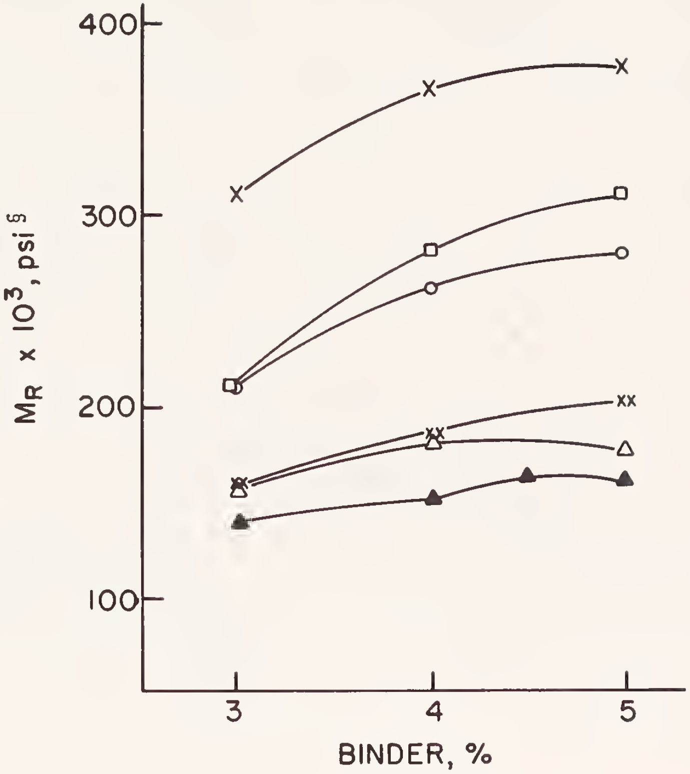

Figure 3.55. Dry M_R comparison.

§To convert to MPa: psi x 6.894 10^{-3}

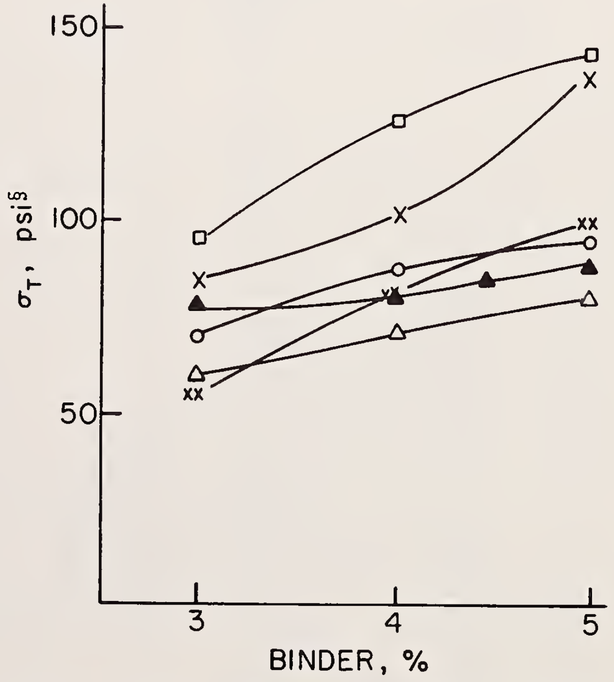

Figure 3.56. Indirect tensile strength.

§To convert to MPa: Psi x 6.894 x 10^{-3}

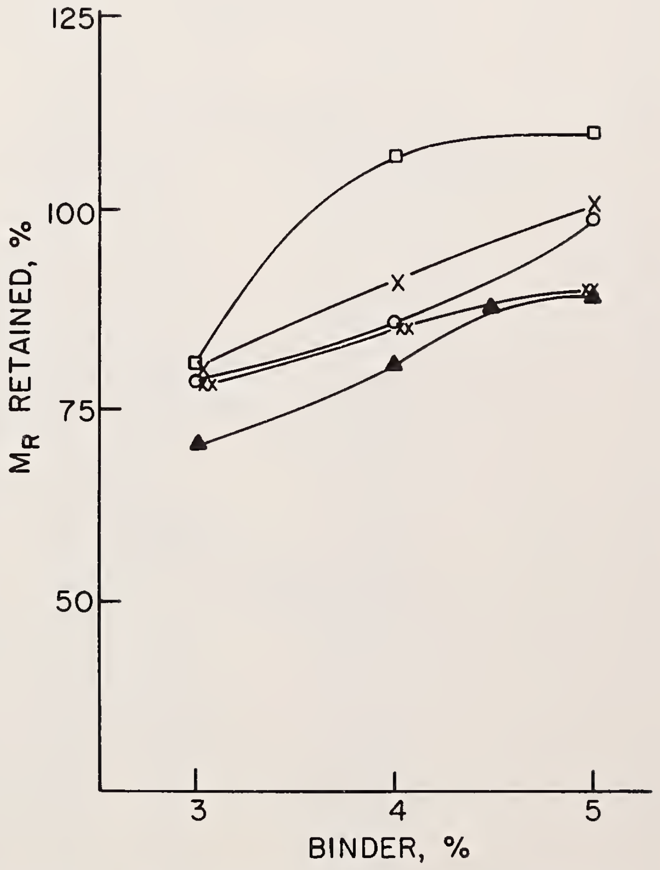

Figure 3.57. M_R retained after variable saturation.

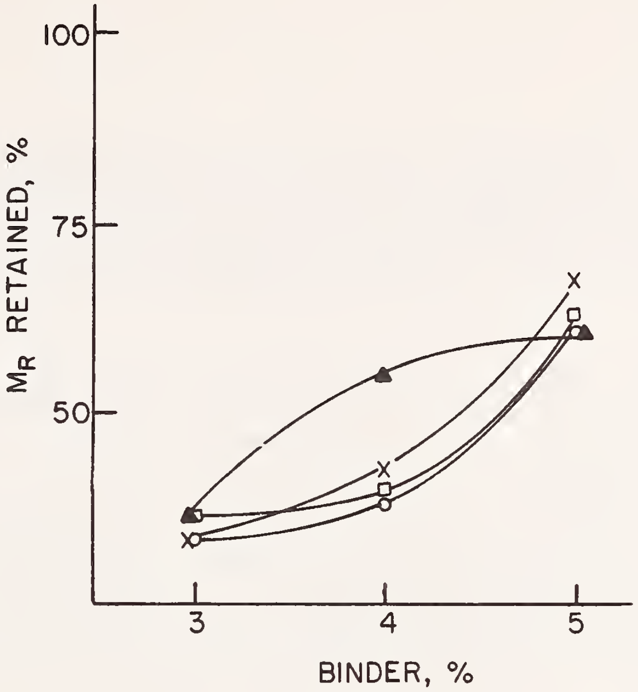

Figure 3.58. M_R retained after 15 cycles freeze-thaw.

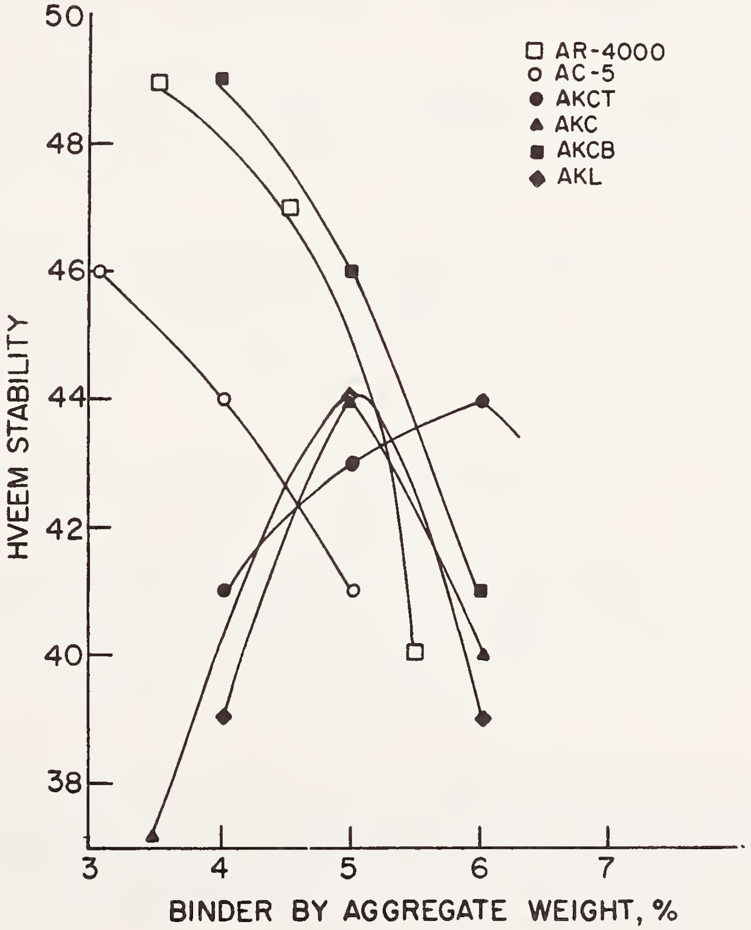

Figure 3.59. Comparison of the Hveem stability test results.

Early in the aggregate precoating portion of this study, it was observed that asphalt cement and asphalt emulsions were the most promising precoating materials, while the others were found to be less workable with the viscous L/A binder. The scope of this research then emphasized the precoating effect of the asphalt cement (AC-5) and the asphalt emulsion (CRS-2).

The principal findings in this phase of the research are summarized as follows:

AC-5 Precoating

1. The precoating agent, AC-5, acted as a lubricant for the viscous L/A binder during hot mixing. It helped to distribute the binder well and prevented the fines from clustering with the binder. Thus, it improved both the workability and coatability.

2. Separating the coarse and the fine fractions of the aggregate is reasonable because this prevents the surface of coarse aggregate from being contaminated by the fines, which will defer coating.

3. With 1% of AC-5 precoating, a mixture with 3% L/A binder seems lean and is easy to scarify. When the binder content exceeds 5%, the specimen bleeds after compaction. The optimum binder content is about 4.5%.

4. With 1% AC-5 precoating, the optimum binder content could be reduced from 7.25% (without precoating) to 4.5% (excluding the 1% precoating). The reduction of binder content is not only a result of reducing the surface area (12% being precoated in this particular mix) but also a consequence of improving workability and coatability.

5. Among the three different mixing procedures shown in Figure 3. Procedure A seemed to be the most practical, for the workability is best. When there is no good coating, Procedure B would be useful. Procedure C is not practical, because the fines clump with the binder and these clumps are difficult to break apart and do not mix well.

Asphalt Emulsion Precoating

1. When hot precoating aggregate with asphalt emulsions, the mass became sticky and less workable than hot precoating with AC-5. Therefore, the cold precoating process is recommended.

2. In cold precoating, CRS is too stiff to mix so that a small amount of water (e.g., 1% by total weight of aggregate) is required to dilute the emulsions and facilitate the mixing. A medium setting type of emulsion (CMS) is comparatively more workable than a rapid setting type of emulsion (CRS).

3. The curing temperature (221°F; 105°C) of the emulsion precoated mixture was probably too high. It was observed that the asphalt emulsions coalesced at that high temperature. The majority of the aqueous part of the emulsions evaporated rapidly after the precoating process; thus, a lower temperature might be enough to facilitate the required curing. From the viewpoint of energy conservation, the curing temperature could be less for field storage.

4. The percentage of M_R retained after vacuum saturation and freeze-thaw tests was very high. It shows that emulsion precoating provides good resistance to water damage and temperature variation.

5. With emulsion precoating, the mixture was found to be less workable than that with AC-5 precoating. However, gratifying results were obtained with greater stability and other properties. These results are believed to be the results of the harder base asphalt of the emulsion. Additionally, they could possibly be due to the effect of the surface energy of attraction while the curing effect of the emulsion precoated mixture was not significant.

6. Similar to precoating with AC-5, the optimum binder content of precoating with 1.5% asphalt emulsions was about 4%. Aside from savings of asphalt binder, better performance was also obtained by utilizing the precoating method.

Sulfur Precoating

1. It was observed that the optimum percentage of sulfur for precoating was about 1% while 0.5% showed no effect and 2% caused excessive stiffness.

2. Sulfur facilitated the coatability of the aggregate. It also seemed to increase the bond between the aggregate and asphalt with good results. In general, sulfur acted better than lime as a precoating agent; higher Hveem value and higher M_R were obtained with a relatively low binder content.

3. However, a deterimental problem was also observed in that the sulfur treated mixtures gave off a gas during the mixing process and this continued to occur upon heating even after a long period of curing. As safety is a concern, therefore, sulfur is not recommended to be used as a precoating agent.

Lime Precoating

1. Lime formed a crust over the coated aggregate; this crust absorbed asphalt readily. Both workability and coatability wre found to be very poor.

2. When a lime slurry was added to fine aggregate particles, they became clustered and it was difficult to mix them with the L/A binder.

3. In this study, lime was not found suitable because it required the addition of a very high binder content. However, lime could be used as an adhesion promoting agent to increase the affinity of the aggregate particles and prevent the binder from stripping. (Lime-treated mixtures showed a high percentage of M_R retained after freeze-thaw tests.)

Cement Precoating

The same results were obtained from the cement precoated mixture as that of the lime-treated mixture. The cement precoated mixture also required a very high binder content. Thus, from the standpoint of saving binder, further tests of the cement-treated mixtures were not performed.

Kraft Liquor Precoating

1. Attempts to use kraft liquor as an asphalt substitute failed because it was water soluble. With 7% kraft liquor alone as the binder, the mixture performed well in the absence of moisture, but it became spongy when saturated.

2. Using kraft liquor in precoating, the problem of leaching out still remained. During the mixing process, kraft liquor dried out quickly and became sticky; i.e., had poor workability. Kraft liquor can not be utilized in ordinary form until some beneficial modifications are achieved.

Cutback Asphalt Precoating

1. When mixed with hot aggregate, MC-250 cutback asphalt spread rapidly and easily coated the aggregate. Using 2.5% MC-250, nearly all the aggregate, including fines, were coated. Although precoating with MC-250 was discontinued in this study, the feasibility of precoating techniques used as discussed earlier was confirmed.

2. When mixed with cold aggregate, the MC-250 cutback asphalt did not coat well and is not recommended for further study.

Silicone Additive

1. Using silicone additives showed no significant change in consistancy of the L/A binder at low concentrations. But when the concentration was as much as 1×10^4 ppm, it showed some decrease in viscosity.

2. Slight leaching was observed when the specimens were vacuum saturated, but this is not considered a problem.

3. Due to limited tests, it was impossible to draw any representative conclusions. The effect of silicone as a dispersing aid was observed but was not significant. However, the results of mixtures with silicone additives were slightly lower than those without silicone additives.

Diethyl Butanoic Acid Pretreated Kraft Lignin

1. While blending asphalt cement with the liquor consisting of diethyl butanoic acid treated with 33% solid kraft lignin, it was observed that the asphalt cement was dissolved in the liquor. This mixture was determined to be non-homogeneous because lumps of the kraft lignin with asphalt formed after the mixture was dried and it was difficult to mix.

2. Specimens made with this binder became spongy following vacuum saturation with water. Also, following soaking, the percentage of M_R retained was very low. In addition, when the soaked specimens were dried, the cohesiveness of the mixture was lost.

3. Another approach was to use the binder immediately after the diethyl butanoic acid pretreated kraft lignin was blended with asphalt, without drying. Mixing aggregate with this liquid binder showed excellent workability and coatability because the aqueous part of the binder imparted good fluidity. Again, the problem of leaching remained.

4. The liquor of diethyl butanoic pretreated kraft lignin gave off a very bad odor. In addition, it caused considerable corrosion to metal. Therefore, it is not recommended for use as an asphalt extender. Nevertheless, the method of using a semi-liquid binder seems promising because it imparts greater workability and coatability. In addition, it is expected that a higher proportion of lignins could be added in this type of binder.

Acetylated Kraft Lignin

1. The behavior of acetylated kraft lignin is similar to that of

untreated kraft lignin although the particle size of acetylated kraft lignin is somewhat relatively coarser. Their binder consistencies are about the same.

2. Test results showed that specimens with acetylated kraft lignin were slightly lower than those with untreated kraft lignin. However, the percentage of M_R retained after vacuum saturation and freeze-thaw cycles is comparatively higher. The good water resistance property of a mixture with acetylated kraft lignin might be due to the effect of improved reactions between the treated lignin particles and asphalt.

Effect of Precoating

Ohlson (7) described a method in which mineral aggregate particles having sizes about .08 in. (2 mm) form the stabilizing or structural part of the mix while particles of .08 in. (2 mm) or less form a plastic mortar with the binder between the structural particles. In order to obtain good stability and other desirable properties of the mixture, it is important that the mortar be evenly distributed among the structural particles. In other words, these should be a homogeneous mixture so that no concentrations of relatively higher plasticity exist.

It was found that aggregate particles having sizes below .08 in. (2 mm) will agglomerate when mixed with free binder and, furthermore, those small particles below .02 in. (0.5 mm) are easily retained in the binder. However, there are problems in evenly distributing the mortar part of the particles between .02 in. (0.5 mm) and .08 in. (2 mm) as such particles are not so easily retained in the binder as the smaller ones.

These problems could be solved by the precoating method in which fine particles (which are important for the mortar part of the mix) are introduced into the mixture at a stage in which the structural particles (the coarse aggregate) have already been coated with a binder film in which the mortar particles are caught and enclosed. In this case, the fine particles will not form agglomerates with the excess binder content but will come into contact with the binder coatings of the coarse aggregates and thereby convert the coatings into an evenly distributed mortar.

The study presented herein confirmed that the precoating method was essential: precoating aggregate showed good performance with good results. Even without a precoating agent, coarse aggregate should be premixed with the binder first and then the fines should be added. This procedure gave better results than did mixing the binder with the whole aggregate portion.

Summary and Conclusions on Precoating

Attempts to use the paper manufacturing by-products, lignins, as an asphalt extender have been conducted. The current study indicated that the lignin-asphalt mixture possesses many of the desirable properties for good paving performance. However, the binder content was relatively high compared to normal asphalt cement. The objective of the research was to develop and verify a practical and reasonable way for applying the L/A binder economically.

Precoating aggregate was found to be a promising method to reduce the binder content of the L/A mixture. Early in the aggregate precoating study, it was determined that the asphalt cement and asphalt emulsions were the most promising precoating materials while the others were found to be less workable with the stiff L/A binder. With 1% of asphalt cement (AC-5) or 1.5% of asphalt emulsion (CRS-2 in 70% distillation) precoating, there was a common trend toward the optimum binder content falling between 4 and 4.5% of L/A binder. This was a large reduction compared to the unprecoated 7.25%, which means considerable saving of the binder.

With 1% AC-5 precoating, the total amount of asphalt required was equal to 4.15% in which 1% was for precoating and 3.15% was the pure asphalt content of the 4.5% L/A binder.

With 1.5% CRS-2 precoating, the total amount of asphalt required was 3.85% in which 1.05% was for precoating and 2.8% was the net asphalt content of the 4% L/A binder.

Without precoating, the total amount of asphalt required was equal to 5.08% with respect to 30% lignin extender.

Aside from saving binder, the following lists the advantages of using the precoating method:

1. The presence of a dusty or dirty coating on the coarse aggregate prevents wetting of the coarse aggregate surface by the asphalt and makes it difficult to achieve a good coating that will not strip from there. Precoating the aggregate could prevent the coarse aggregate from contamination by the fines and thus achieve better coating. Precoating prior to stockpiling for later construction also has the advantage of eliminating subsequent dusting by traffic and there will be less loss of aggregate by traffic throw-off.

2. As mentioned before, precoating could decrease the balling effect of the fines. Rather than simply bring fresh surfaces of aggregate and asphalt in contact with each other, the mastic balls not only require additional time for dispersion but also need additional power to break them up. When energy effects are concerned, precoating means saving in the operation cost.

3. During the curing process of the emulsion precoating, the excess water will evaporate from the premix and the emulsions will form a film which securely adheres to the aggregate particles. With

the binder film on the aggregate, no dust will be produced and the premix will not deteriorate during storage over a considerable period of time. The precoating must be such that it does not allow the gravel to agglomerate, which could have an adverse effect on even spreading, and it must permit the perfect adhesion of the aggregate by the surface of the binder. A proportion of 0.5 to 1% is considered to be suitable.

4. The hot precoating method may be applicable in central plant mixing. In the case of a batch plant, the aggregate could be split into coarse and fine fractions. The pug mill would be changed first with the coarse aggregate and premixed with all or part of the binder. Then the fine aggregate would be introduced along with the remaining binder, if any. Mixing would then continue until completed.

Use of Admixtures

Another study involved the use of external agents such as carbon black, coal, coal tar, kraft liquor blown with carbon dioxide, kraft lignin pretreated either in dioxide or benzene. These were used as catalysts between the lignin and asphalt so that a linkage can be formed.

Although numerous tests were performed on these binders (as indicated in Table 3.21), selected information is included here in Figures 3.59 to 3.62. Materials included the aggregates, asphalt, and lignin utilized in earlier studies. Other additives are as follows:

Carbon Black

The carbon black used in this investigation was Microfill 8 from Cabot Corporation. The size of the carbon black particles was between 1/10 to 2/10 μ.

The carbon black was in pellet form to facilitate handling. It was mixed with AC-5 asphalt at 275°F (135°C) in a high speed blender for five minutes, then poured into cans, sealed and left in the oven for 30 minutes more until the carbon black was completely dispersed in the asphalt.

Carbon black is a recognized reinforcing agent that has been used in the rubber industry to reinforce tires and give them their color.

Coal Tar

The coal tar used in this investigation was RT-8 road tar. It was provided by the American Tar Company. The RT-8 is produced by removing the benzene and toluene of the coal tar produced at the steel company. Then the chemical plant removes three percent of the water and xylenes and most of the naphthalene. The RT-8 was in a liquid state. Its color was black and was 99 percent pure coal tar. The coal tar alone does not mix with asphalt, although it was expected that in the presence of lignin this could work as a linkage agent.

Table 3.21.Physical Properties of lignin extended asphalt binders

	Binder Description	Penetration 0.1 mm, 4°C 200g, 1 min	Softening Point °C	Viscosity ctg	Density
1.	AC-5/Kraft lignin/Coal 70/26/4	44	48.5	-	1.096
2.	AC-5/Kraft lignin/ Coal Tar 66/30/4	46	59.0	-	1.115
3.	Coal tar/Kraft lignin 70/30	Too soft to do test		-	-
4.	Coal tar	-	-	-	1.193
5.	AC-5/Kraft liquor 50% solids 70/30	54	48	353	1.109
6.	AC-5/Kraft lignin 70/30	49	47	462	1.097
7.	AC-5/Carbon black 90/10	63	-	291	-
8.	AC-5/Carbon black 85/15	49	45.0	744	-
9.	AC-5/Carbon black 80/20	44	-	3660	-
10.	AC-5/Kraft lignin pretreated in dioxane 70/30	130	38	-	1.066
11.	AC-5/Kraft lignin pretreated in benzene	88	42.5	-	1.057
12.	AC-5	80	35	-	1.027

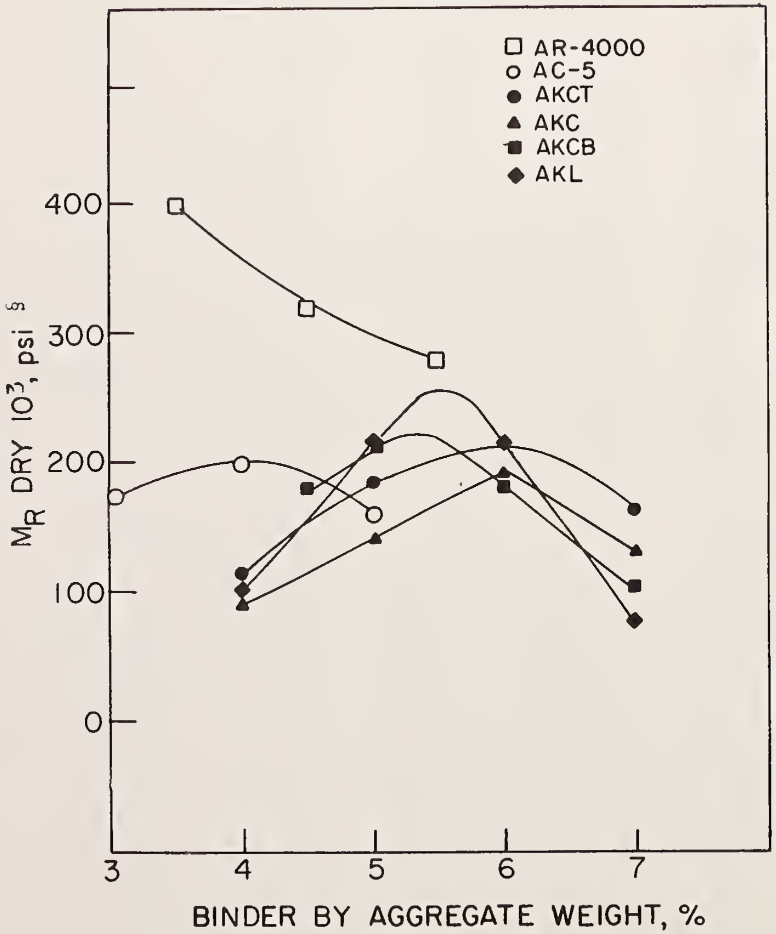

Figure 3.60. Comparison of M_R dry test results.

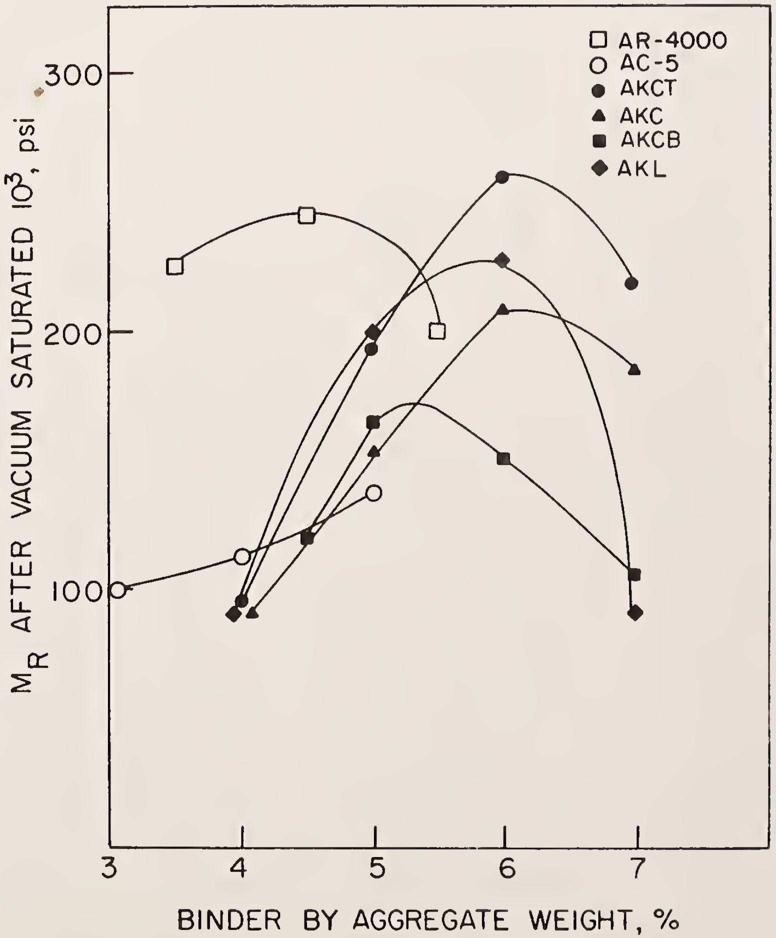

Figure 3.61. Comparison of M_R after vacuum saturation.

§To convert to MPa: psi x 6.984 x 10^{-3}

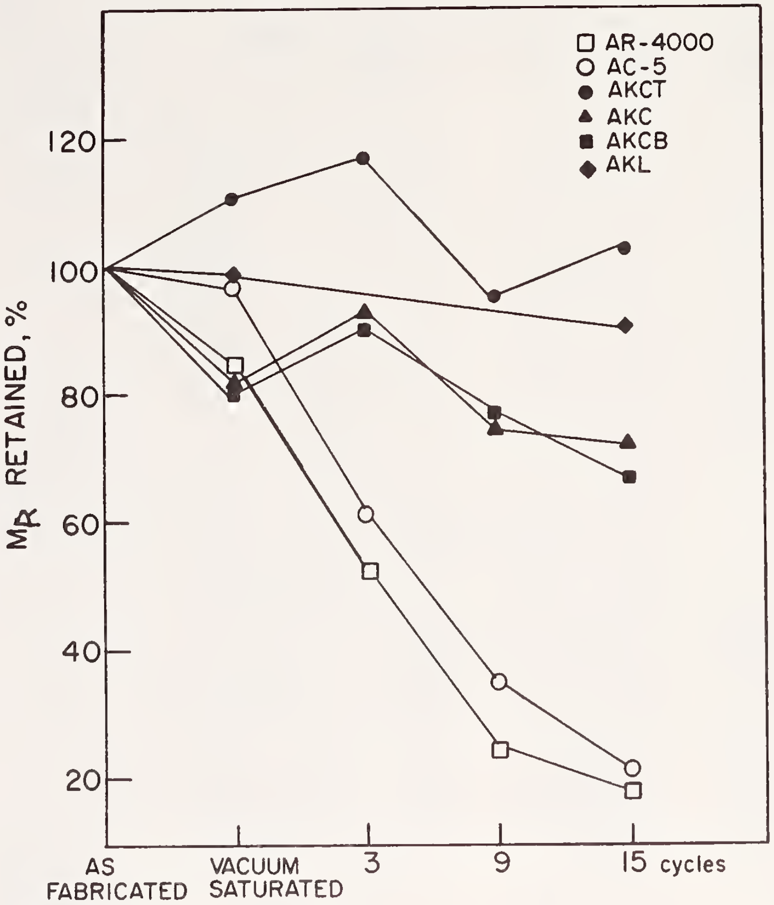

Figure 3.62. Comparison of the % M_R retained after the freeze and thaw test.

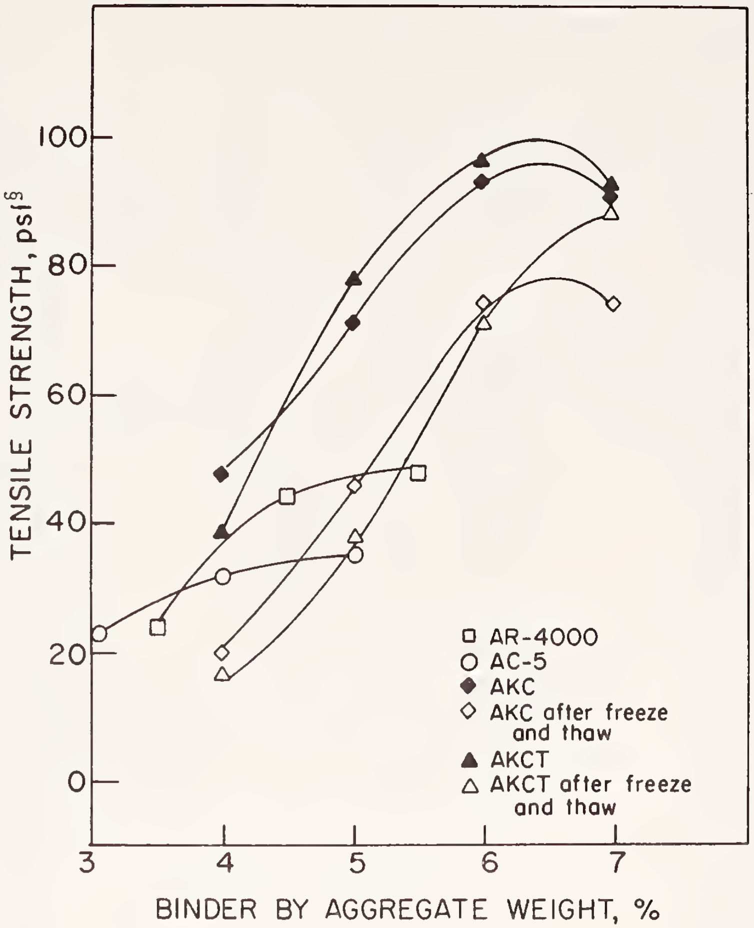

Figure 3.63. Comparison of the tensile strength before and after the freeze and thaw test.

§To convert to MPa: psi x 6.894×10^{-3}

Table 3.22. Proximate analysis of coal.

	As Received	Dry Basis
% Moisture	5.92	XXXXX
% Ash	9.69	10.30
% Volatile	41.66	44.28
% Fixed Carbon	42.73	45.42
	100.00	100.00
Btu	12086	12847
% Sulfur	0.54	0.57

FUSION TEMPERATURE OF ASH

	Reducing	Oxidizing
Initial Deformation	2160°F[§]	2210°F[§]
Softening (H=W)	2180°F	2230°F
Softening (H=1/2W)	2200°F	2250°F
Fluid	2220°F	2270°F

[§] To convert to °C: 5/9(°F - 32)

HARDGROVE GRINDABILITY INDEX = 44.2 at 5.11% Moisture

MINERAL ANALYSIS OF ASH	Percent Weight Ignited Base
Silica, SiO_2	60.95
Alumina, Al_2O_3	12.95
Titania, TiO_2	0.48
Ferric oxide, Fe_2O_3	4.17
Lime, CaO	9.20
Magnesia, MgO	2.58
Potassium oxide, K_2O	1.21
Sodium oxide, Na_2O	1.42
Sulfur trioxide, SO_3	5.33
Phos. pentoxide, P_2O_5	0.19
Undetermined	1.52
	100.00

Alkalies as Na_2O, Dry Coal Basis = 0.23
Silica Value = 79.26
Base: Acid Ratio = 0.25
ESTIMATED VISCOSITY at critical viscosity
Temperature of 2400°F = > 2000 Poises (200 Pa·s)
T_{250} Temperature = 2640 °F (1148°C)

Acidity (pH)

Eq. Pot.	1:5 Solution	1:20 Solution
7.85	8.55	8.90

Coal

The coal used in this investigation was taken from the stockpile of the Physical Plant at the University of Washington. The coal was crushed and then pulverized. All the coal that passed the sieve #200 was used for the preparation of the binders. See Table 3.22 for chemical analysis.

Pretreated Kraft Lignins

Two different types of pretreated kraft lignin were used. Pretreated kraft lignin in dioxide and pretreated kraft lignin in benzine. They were in a solid state and with a moisture content of 40 and 30 percent, respectively. This lignin was prepared by Mr. W. Wallaba from the College of Forest Resources at the University of Washington under supervision of Professor G. G. Allen from the same department. The method of preparation for these lignins is included in the Appendix. In general, the draft lignin was preapred with acid in the presence of heat and pressure and washed with water. By doing this, it was hoped it would create a physical ramification on the lignin so the lignin could link with the asphalt in a physical way.

Preparation of Binders

There are several factors to be considered when developing a new binder. These include at least the following: 1) increase the strength of the binder so that the overall thickness of pavement can be reduced, 2) improve the durability in order to increase fatigue life and resistance to aging (i.e., oxidation), 3) improve the temperature susceptibility and resistance to moisture, and 4) reduction of the quantity of binder required in the mixture for equal performance.

With these objectives in mind, several admixtures were evaluated. A primary goal was to identify admixtures which could act as a catalyst and provide a linkage between asphalt and lignin. Those materials tested in this phase of the research included coal, coal tar, kraft liquor treated with CO_2, kraft lignin pretreated in dioxane and kraft lignin pretreated with benzene.

Prior to mixing of the various binders, the asphalt cement was melted at a constant temperature (135°C) in a covered container for 45 to 60 minutes to minimize the amount of the aging in the oven. All proportioning was on the basis of the weight of total mixture. The weight of lignin was always on the basis of its oven dry state. For the kraft liquor and the pretreated kraft lignin (one each in dioxane and benzene), the water content was determined the day prior to mixing. Thus, knowing the water content of the powderded lignin, it was possible to determine the amount of dry lignin for each batch.

The binders were mixed in an open vessel with a spatula until they reached a homogeneous consistency; generally this was achieved in 3 to 5 minutes. The binder was then placed in the oven (135°C) for about two minutes, then poured into a metal can, sealed with a lid and stored for future use.

As an example of the above procedure, to prepare 1000 g. of binder in the ratio of 70% asphalt and 30% lignin, 700 g of asphalt and 300 g of dry lignin are needed. If the kraft lignin (kraft liquor or pretreated kraft lignin) has a water content of 20%, 300/.75 = 400 g of the lignin material will give 300 g of dry kraft lignin.

In the case of kraft liquor, the method of blending was somewhat different. The kraft liquor and the asphalt were blended and then poured into the Parr reactor. To simulate the open vessel mixing procedure, all of the valves in the reactor were left open and CO_2 was blown through the binder while mixing. The intent of this step was to lower the pH of the kraft liquor, making it insoluble, and thus removing the water in the binder. The CO_2 was blown at a constant pressure of 2 psi (1.4×10^{-3}MPa) and the mixing temperature was maintained between 221°F (105°C) and 275°F (135°C) for the two-hour mixing time. Following this, the binder was stored as described above. Unfortunately, the resulting binder was still soluble in water.

Mixture Tests

This portion of the study was an attempt to reduce the amount of binder required in asphalt paving mixtures. Earlier tests had shown that the optimum L/A binder content was about 7.25 % based on the dry weight of aggretate. This is somewhat higher than for asphalt alone; higher binder demand would negate some of the potential benefits of utilizing lignin.

All of the procedures and mixture variables were kept constant with respect to the earlier work in this project so that comparison would be easier. In general, the experiment was to add a range of admixtures to the 30:70 ratio of L/A, anticipating the possibility of cross linkage between the lignin and asphalt. So far as is know, this linkage did not occur.

In addition to those above, a microfiller material, carbon black, was used with L/A binders in an attempt to evaluate the filler-like aspect of lignin. Further limited tests were made using kraft liquor directly with asphalt, precoating the coarse aggregate with portland cement, and using pretreated kraft lignin (as compared to pretreated lignin sulphonate) with asphalt. However, due to limited time, these were not continued.

In general, binder preparation for these mixtures was conducted in the same manner as described in Phase C-1, with only slight variations caused by introducting the admixtures.

Preparation of Laboratory Specimens

Laboratory specimens were proportioned by blending 1150 g of aggregate with binder as shown in Table 3.2 for each specimen. Binder percentage was based on dry aggregate. The aggregate was preheated overnight in an oven set at 221 °F(105°C) and the temperature was raised to 275°F (135°C) two hours prior to mixing. Following mixing, the mixture was then cured for 15 hours at 140°F (60°C).

Prior to compaction, the mixture was heated to 275°F (135°C) for 2 hours. Compaction was accomplished using the Hveem procedure as outlined in ASTM Standard Method D1561. The compactor foot pressure was reduced, however, to 350 psi (2.41 MPa) to minimize crushing of the aggregate during compaction. This was followed by a leveling load of 12,650 lbs (56.3 KN) for 1 minute using a single plunger. Standard procedures were otherwise followed throughout. Figure 3.27 indicates the general mixture test procedures.

Summary on Use of Admixtures

In this study, out of ten different binders that were formulated, four were considered suitable for the binder reduction study. These were:

1) AC-5/Kraft Liquor (AKL) ratio 70/30;

2) AC-5/Carbon Black (AKCB) ratio 85/15:

3) AC-5/Kraft Lignin/Coal (AKC) ratio 70/26/4; and

4) AC-5/Kraft Lignin/Coal Tar (AKCT) ratio 66/30/4.

Figures 3.62 to 3.63 show comparative results of the tests performed with these binders and those of the control specimens (AR-4000 and AC-5). From these results, an optimum binder content of about 5.5% is recommended for AKL, AKCB, AKC, and AKCT mixtures. This value represents a net asphalt usage of about 3.85%. Thus, the addition of external agents such as coal or coal tar could result in a reduction of lignin-asphalt binder content in the mixture and yet produce a pavement mixture having comparable qualities as those of conventional asphalt binders.

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IV. KRAFT LIGNIN IN EMULSIFIED ASPHALT BINDERS

A. Introduction

Another approach to the use of lignin in road building and paving materials is as a partial replacement for emulsified asphalt. Asphalt emulsions are useful and effective binders for aggregates and have been used for such purposes since the early part of the century in road building and maintenance. Recent demands to reduce pollution and energy requirements have increased the interest in emulsified asphalt. It was, therefore, desirable to investigate the feasibility of using lignin in this type of binder system.

Kraft lignin possesses an interesting combination of properties which make it potentially useful with emulsified asphalt. Kraft lignin is insoluble in water and acids, but can be dissolved with bases to yield solutions that are compatible with many emulsions and latices. If the solution is acidified, or if a volatile base, such as ammonia, is used to dissolve the lignin, the lignin will precipitate from the solution as insoluble fine particles.

This process forms the basis for the kraft lignin reinforcement of rubbers that are prepared as latices. To accomplish filler reinforcement, a solution of the sodium salt of lignin is blended with a rubber latex and the mixture "shock" coagulated by mixing with an acid solution. If an ammoniacal solution of lignin is added to the rubber latex, a reinforced rubber can be obtained by spray drying this mixture.

In both procedures the lignin precipitates as very fine particles in the rubber hydrocarbon matrix. The fine particles of lignin that are formed reinforce the rubber much in the same manner as does fine carbon black. If the rubber has some polar groups, bonding between the rubber and the polar lignin particles can further enhance reinforcement.

This phase of the work was undertaken to explore the feasibility of applying this technology to asphalt-lignin mixtures as binders for paving mixtures.

B. Materials and Experimental Procedures

The materials investigated as binder components for concrete containing lignin were aqueous solutions of kraft lignins, emulsified asphalts, and rubber latices. Watsonville granite was used as the aggregate in the paving mixes. Chapter IV is essentially the work of Materecon, Inc., subcontractor to the University of Washington.

Lignins

All lignin materials used were based on kraft pine lignin (Tab. 4.1). They include Indulin AT (kraft lignin modified), Indulin C (a sodium salt of kraft lignin), and Indulin W-1 (a lignin amine). Aqueous solutions of these were prepared at various solids contents for assessing their compatibility with the other water-based components. Ammonium hydroxide was used to solublize the Indulin AT. Because of its volatility, both the ammonia and water evaporate from an ammoniacal solution leaving the lignin as a water insoluble material. The 25% ammoniacal solution of lignin used in most of the compositions tested was made by the following procedure:

> Add 25 parts (by weight) of kraft lignin (Indulin AT) to 50 parts water at ambient temperature with stirring to form a slurry. Continue stirring while adding 25 parts of a 1:1 dilution of strong ammonia, i.e., 14% NH_3 in the dilution. Cover and allow to stand overnight for completion of reaction before use. Remix thoroughly and remove sample for determination of actual solids content by drying at 221°F (105°C). Store in closed container to avoid loss of ammonia and oxidation of the lignin which increases its viscosity.

Solutions containing 25% lignin remained usable for a few weeks. More concentrated solutions, e.g., 3 %, were highly viscous and difficult to mix with asphalt emulsions and latices. The effect of concentration of an alkaline solution of lignin is shown in Figure 4.1 for the sodium salt of lignin (Indulin C). Ammoniacal solutions behave similarly; thus, relatively large amounts of water must be incorporated in the binder containing lignin to maintain a workable viscosity.

Asphalts and Asphalt Emulsions

In the initial work by Matrecon, Inc., the asphalt emulsions used in mixtures with lignin solutions and latices were a commercial cationic (type CSS-1) emulsion of 120 pen. San Joaquin Valley asphalt and an anionic (type SS-1h) emulsion of 60 pen. San Joaquin Valley. After an AC-5 asphalt from Arabian light crude was selected for use in other phases of the project, an anionic emulsion of that asphalt was prepared in the laboratory by the following procedure.

> Prepare a 6% solution of lignosulfonate emulsifier (Georgia-Pacific E3596) in water. Heat 40 parts of solution to 176°F (80°C) and circulate with pre-heated HomoMixer at low speed. Add 60 parts AC-5 asphalt at 266°F (130°C), increasing the speed to reach mximum at end of asphalt addition. Continue mixing at high speed for 60 seconds. Immediately transfer to a closed container to avoid evaporation of water. Cool to ambient temperature, remix thoroughly, examine for presence of coagulated or unemulsified asphalt, and remove a sample for determination of actual solids content by drying at 325°F (163°C).

Details of the various asphalt used in this work are presented in Table 4.2.

Table 4.1. Kraft pine lignins[a].

Material[a]	Description	Solids content, %	Consistency
Indulin AT[b]	kraft pine lignin	95.8	Free-flowing brown powder
Indulin AT, 25% Solution NH_3	-	24.3	Pourable
Indulin AT, 33% Solution NH_3	-	32.0	Nonpourable
Indulin C	Sodium salt of kraft pine lignin	90.4	Dry powder
Indulin C, 10% aqueous solution[a]	-	9	-
Indulin C, 45% aqueous solution	-	40	Pourable
Indulin SA-L	Solution of sodium salt of lignin[b]	41.4	-
Indulin W-1	Lignin amine	-	Dry powder
Indulin W-1, aqueous solution	-	20	Low viscosity
Indulin W-1, aqueous solution	-	30	Pourable
Indulin W-1, aqueous solution	-	26	Liquid

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[a] Indulin is a trade name of Westvaco, Chemicals Division, Polychemicals Department

[b] Specific gravity 1.34.

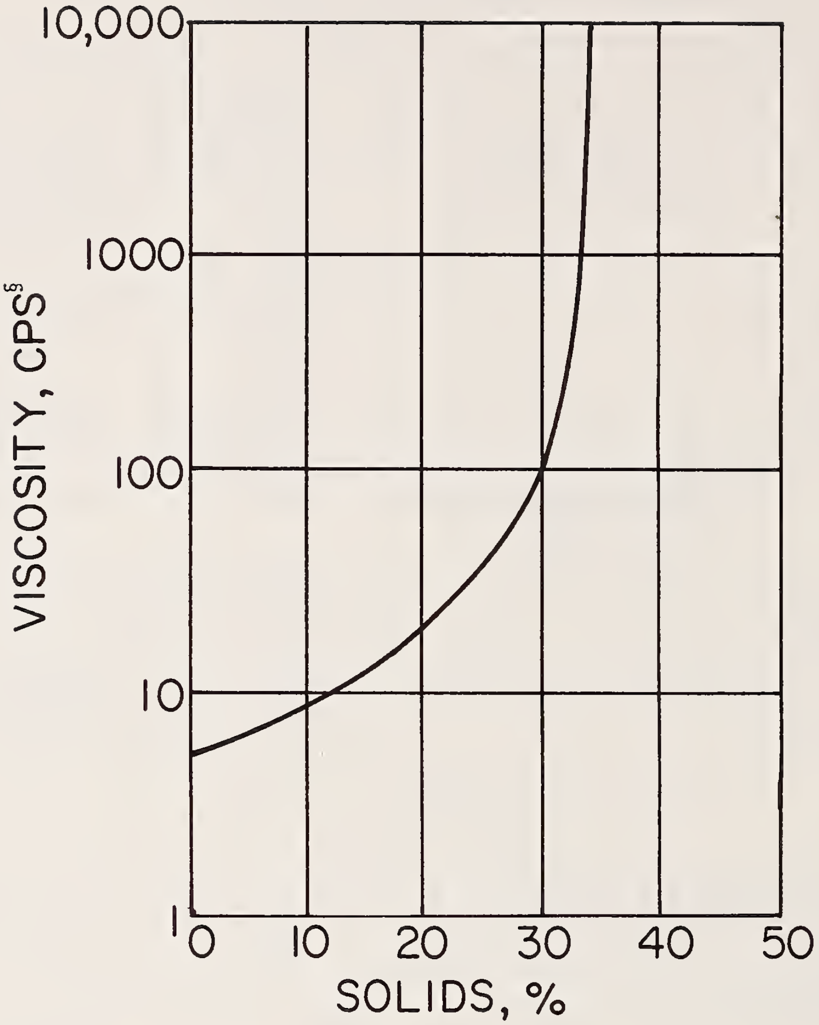

Figure 4.1. Viscosity at 25°C of aqueous solution of Indulin C, the sodium salt of kraft pine lignin (1).

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§To convert to Pa·s: cps x 10^{-3}

Table 4.2. Asphalt and emulsified asphalts.

Designation	Description	Solids, %	Properties
San Joaquin Valley	-	100	121 pen. at 25°C
AC-5[a]	-	100	500 cps[§] at 60°C
CRS-1	Cationic rapid-set emulsion of 120 pen. S.J. Valley asphalt	60	-
CSS-1	Cationic slow-set emulsion of 120 pen. S.J. Valley asphalt, made with lignin-amine surfactant	61.3	-
SS-1h[b]	Anionic slow-set emulsion of 60 pen. S.J. Valley asphalt	66	-
SS-1[c]	Anionic slow-set emulsion of AC-5 asphalt	64	-

[a] Furnished by University of Washington; specific gravity = 1.02. Composition: Asphaltenes, 19.9%; nitrogen bases, 24.0%; first acidaffins, 18.1%; second acidaffins, 26.9%; paraffins, 11.1%.

[b] Prepared in laboratory colloid mill using a lignosulfonate surfactant supplied by Georgia Pacific.

[c] Prepared in laboratory Homo-Mixer using lignosulfonate surfactant.

[§] To convert to Pa·s: cps x 10^{-3}

<u>Latices</u>

The elastomeric polymers which comprise the third group of binder constituents were introduced into the binder mixture as latices. They were principally copolymers of butadiene with styrene, acrylonitrile, or vinyl pyridine. Also included were a carboxylated styrene-butadiene copolymer and a latex of polyvinyl acetate. Data on the rubber latices are presented in Table 4.3.

Table 4.3. Rubber latices

Designation	Composition	Solids, %	Composition
SBR latex type 1500[a]	Butadiene/styrene, 76.5/23.5	20.7	Like water
SBR latex type 1707[b]	Butadiene/styrene, 76.5/23.5	20.0	Like water
SBR latex type 1808[c]	Butadiene/styrene, 76.5/23.5	17.3	Like water
Pliolite SBR type 4675	Butadiene/styrene	70.4	-
Chemigum nitrile type 61A	Butadiene/acrylonitrile	40.7	-
Chemigum nitrile type 550	Butadiene/acrylonitrile	38.2	-
Vinyl pyridine type LVP	Butadiene/vinyl pyridine	41.5	-
Polysar 774[d]	Carboxylated butadiene/ high styrene (60%)	49.0	150 cps
Polysar 775	Carboxylated butadiene/ styrene	52.3	-
UCAR 131	Polyvinyl acetate	60	-

[a] Base polymer, 50 Mooney viscosity (ML-4).
[b] Base polymer, 112 Mooney viscosity (ML-4).
[c] Base polymer, 150 Mooney viscosity (ML-4).
[d] pH = 9.5.

Aggregates

Granite aggregate from Watsonville, California, was used in the preparation of all mixtures. This aggregate has a specific gravity of 2.72. The three gradations that were used in this work are shown in Table 4.4. These gradations included two "dense" gradations for asphalt concrete, both .5 in. (12.7 mm) maximum, one "medium" and the second "coarse", and an aggregate having a .38 in. (9.53 mm) maximum for open-graded asphalt concrete. These aggregates are designated in this report as A, B, and C, respectively. The initial work was done with A and C. Later, the slightly more open "dense" Aggregate B was used to allow a greater wet binder content, i.e., more water at time of compaction.

Evaluation of Binders Containing Lignin

The study of binder formulations was conducted in three stages:

1. Examination of binder mixtures containing various types and proportions of lignin, asphalt, and rubber latex.
2. Assessing the behavior during mixing of paving mixtures of binder with granite aggregate.
3. Determination of properties of compacted concrete specimens of paving mixtures.

Our test protocol relied heavily on visual observation in all phases. Incompatibility of components or lack of strength was generally obvious on either a macroscopic or microscopic scale; this provided a means for evaluating interactions of many types of materials. The list of candidates for quantitative measurments was thus narrowed down to those presenting the greatest likelihood of success.

Testing of Lignin Binder Mixtures in Aqueous Forms and Films

Visual observation of the binders was initially made to determine compatibility of the components, consistency when mixing, viscosity of the prepared mixes, and appearance of films cast on glass plates.

Incompatible mixtures were eliminated; most of these exhibited coagulation or inadequate dispersion. Mixtures that proved compatible ranged in viscosity from those of readily-pourable consistency to very stiff pastes. Thin films were cast on glass plates for microscopic examination as well as observation of general appearance and behavior. Removing the dried films from the plates provided an opportunity to observe their cohesiveness and brittleness. Those exhibiting undesirable characteristics, i.e. flaking, cracking, were eliminated from further testing at this point.

In addition to observation of binders during mixing or as films on glass plates, the pellet abrasion test (2) was used to measure the impact resistance of binders passing the initial screening.

Table 4.4. Gradations of aggregates used in lignin concrete mixes.

Caltrans Specifications[a]

	Aggregate					
	A		B		C	
	Aggregate for Asphalt Concrete, 1/2" Maximum				Open-Graded Asphalt Concrete, 3/8" Maximum	
Sieve Size	Specification 39-2.02 Medium	Measured[b]	Specification 39-2.02 Coarse	Measured[c]	Specification 39-2.06A	Measured[d]
3/4 inch[§]	100	100	100	100	--	--
1/2 inch	89-100	99	89-100	100	100	--
3/8 inch	75-100	85	70-95	80	88-100	100
No. 4	50-77	66	45-72	55	23-42	37
No. 8	33-60	50	30-55	38	4-22	10
No. 16	--	35	--	--	0-12	7
No. 30	14-38	24	10-34	18	--	--
No. 200	1-10	5.0	1-10	3.5	0-4	1.4

[a] Caltrans Specification Section 39; data are given in percentage passing the sieve size shown.

[b] Sieved fractions of granite from Logan Quarry of Granite Rock Company, Watsonville, CA, weighed out for each specimen in the following proportions: 15% "1/2 x 3/8"; 20% "3/8 x No. 4"; 10% "No. 4 x 8"; 25% "Granite Sand"; 30% "Crusher Fines".

[c] Blend of 20% "1/2 x 3/8", 25% "3/8 x No. 4", 15% "No. 4 x No. 8", 20% "AC sand", 20% "Crusher Fines"; all Watsonville granite from Granite Rock Company, Logan Quarry.

[d] Fractions of granite as given in footnote (b) weighed out for each specimen in the following proportions: 65% "3/8 x No. 4", 25% "No. 4 x 8", 10% "Crusher Fines".

[§] To convert to mm: in. x 25.4.

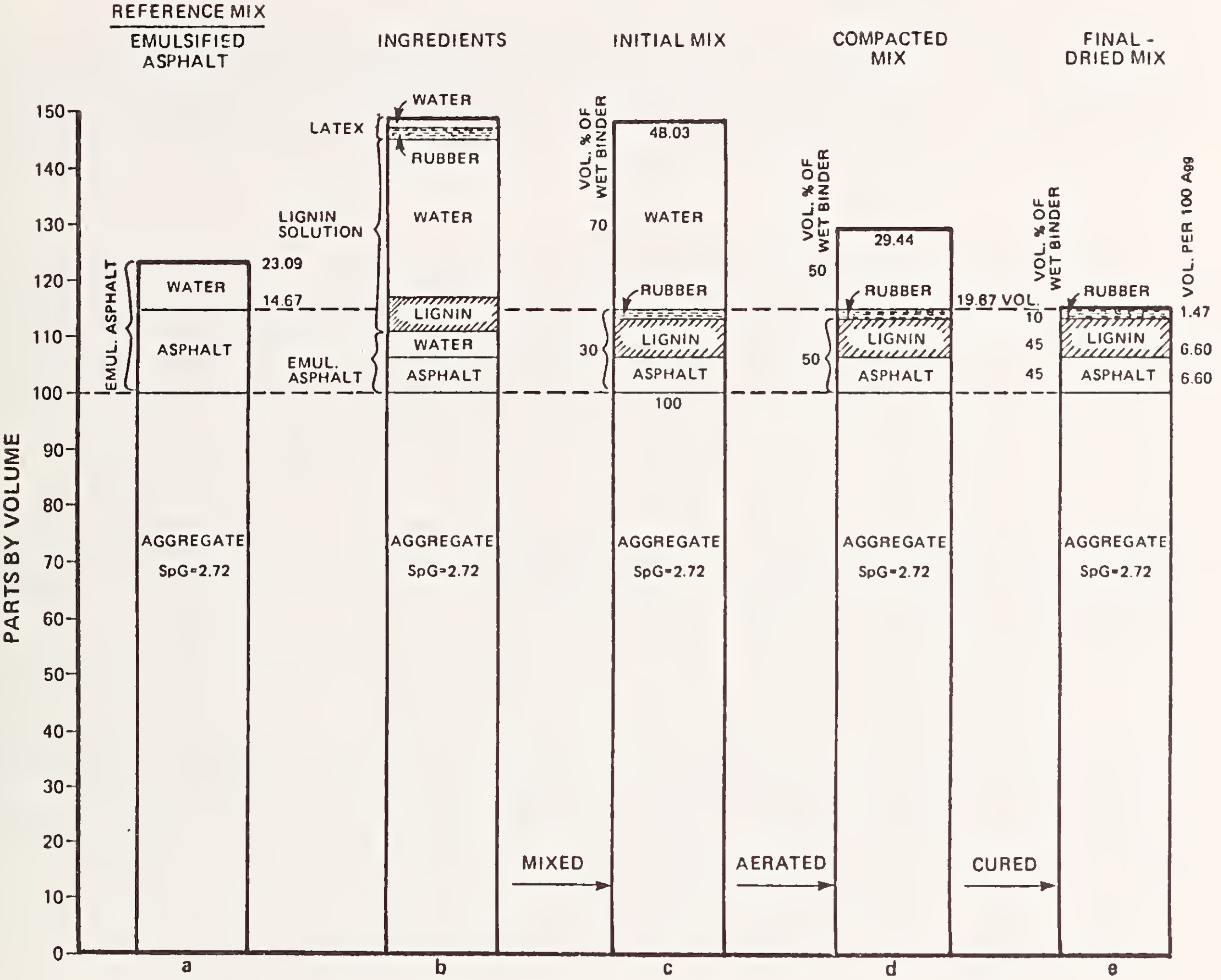

Figure 4.2. Design of the lignin-asphalt-rubber mixes used in this investigation.

Evaluation of Lignin-Asphalt Binders in Concrete

Binder compositions which showed promise were incorporated into paving mixes and compacted cylindrical briquets.

Attempts to prepare specimens of macadam-type construction by applying lignin-asphalt-rubber binders to loosely-compacted open-graded aggregate were abandoned because of the difficulty in obtaining uniform application of the binder at desired application rates and in curing the specimens within a reasonable time without deforming the specimens.

Design of the Lignin Concrete Mix

The major effort of the evaluation of the lignin binders was in concrete mixes. In view of the difference in specific gravity between the lignin (Specific Gravity 1.34) and the other components of the mix, i.e. asphalt (1.02) and rubber (0.95-1.00), all binder combinations were made and compared at a constant volume of dry binder in the aggregate. As our reference mix we used one which had been used previously with Aggregate A (Tab. 4.4). This mix consisted of 5.5 parts by weight (pbw) of asphalt with 100 pbw of granite aggregate (Aggregate A). On a volume basis, this mix equals 5.39 volumes of asphalt per 36.67 volumes of aggregate or 14.67 volumes of binder per 100 volumes of aggregate. The specific gravities of the asphalt and the aggregate are 1.02 and 2.72, respectively.

The proportions of binder components were calculated to yield specific volume ratios and the fixed total volume of dry binder. This mix design is illustrated in Figure 4.2. The volume of the dry binder was maintained constant regardless of the volume ratio of the lignin, asphalt, and rubber, and of the aggregate gradation. The volume of binder selected was 14.67 volumes per 100 volumes of aggregate, which is equal to 5.5 parts asphalt by weight on 100 parts by weight of dense-graded Aggregate A. The high water content of wet lignin binder compared with emulsion asphalt is illustrated in Bar C. Also shown is the water content of the mixes at various stages from initial mixing to the final dried concrete.

Preparation of Concrete Mixes

Specimens of asphalt concrete containing aqueous binders were prepared by mixing manually for small (2-inch diameter) briquets or mechanically for larger (4-inch diameter) briquets. The preferred procedure was:

> Blend lignin solution and asphalt emulsion. Add latex and blend thoroughly. Add required amount of blended binder to aggregate while mixing with spatula or in Hobart mixer. Continue stirring slowly while drying with stream of ambient-temperature air to bring to the desired water content.

As with the wet binders, the initial screening tests for concrete mixtures were qualitative in nature. Incompatibility between aggregate and binder showed up early, i.e. failure to coat the rock. Binder viscosity presented some problems, particularly in the macadam and mechanical mixing, but was not necessarily detrimental when other techniques were employed.

No physical tests were performed on uncompacted mixtures.

Compaction of Test Briquets

Concrete mixes were compacted into cylindrical briquets essentially following the procedures of ASTM D1074 (static compaction of 2-inch specimens) and D1561 (kneading compaction of 4-in.(101 mm) specimens). With few exceptions all mixing and compaction were performed at ambient temperature.

Curing of Briquets

Some briquets were tested for unconfined compressive strength (ASTM D1074) immediately after compacton, without curing. Following compaction most of the briquets were air dried to constant weight in a stream of ambient-temperature air in the laboratory; some were dried outdoors. The curing generally required several weeks. It was necessary to use an air oven at 100°F (38°C) to dry and cure some of the 4-in.(101 mm) briquets.

Testing of Briquets

Table 4.5 lists the test methods used for evaluation of asphalt composition, for compaction and post-treatment of test briquets, and for determining density, compressive strength, and cohesion. In many cases, half the air-dried briquets were immersed for seven days in ambient-temperature water, then tested for unconfined compressive strength, while replicate specimens were tested dry.

Density (bulk specific gravity) of dense graded briquets was determined by immersion (ASTM D2726); density of open-graded briquets was calculated from weight and measurement of the dimensions. Cohesion of selected dry and immersed briquets at 140°F (60°C) was determined in the Hveem Cohesiometer.

Table 4.5. Methods of preparation and testing of concretes containing kraft lignin.

Property	Test Method
Compaction, static	ASTM D1074 (2 in. diameter briquets)
Compaction, kneading	ASTM D1561 (4 in. diameter briquets)
Unconfined compressive strength	ASTM D1074
Cohesion	ASTM D1560
Density	ASTM D2726
Impact strength (Pellet abrasion)	Ref. 2

C. Test Results

Study of Binder Mixtures

Compatability of Binder Components

Two-component mixtures of asphalt and rubber in equal parts on a dry basis were prepared from CSS-1 asphalt emulsion and each of five latices two nitrile copolymers, one vinyl pyridine copolymer, and two carboxylated SBR. These were intended for use with various proportions of lignin to determine the levels of lignin content compatible with the asphalt-rubber blends. However, three of the mixtures (Chemigum 61-A , Pliocord LVP, Polysar 776) coagulated immediately due to incompatibility of the latex emulsifiers with the cationic asphalt emulsion. The mixture with the other nitrile latex, Chemigum 550, contained some short strings of coagulum. Only the CSS-1 mixture with Polysar 774 was homogeneous.

Films of Lignin-Asphalt-Rubber Binder

Preliminary experiments established that CSS-1 asphalt emulsion could be blended with ammoniacal Indulin AT solutions without coagulating. Consequently, a series of 1:1:1 mixtures of lignin:asphalt:rubber was prepared, mixing the asphalt emulsion and lignin solution before addition of the latex. The mixture with Chemigum 61-A was readily pourable, that with Pliocord LVP barely pourable, and those with Chemigum 550, Polysar 774, and Polysar 775 were stiff pastes. Films on glass plates were prepared from all five mixtures, diluting the three stiff pastes with sufficient water for forming the films. The clarity of the films is indicative of the compatibility of the components. Films 0.030" in. (.76 mm) thick (wet) were prepared using a film-former, and thinner films were prepared by smearing with a spatula to obtain transparent films. The films of the mixture with Chemigum 500 contained large particles of coagulated rubber.

Impact Resistance of Binders

To assess the strength of these binders with an aggregate, mixtures with 20 to 30 mesh Ottawa sand containing 2 parts binder solids per 100 sand were prepared with the above mixtures. Pellets 0.5 in.(12.7 mm) in diameter by 0.5 in. (12.7 mm) high were formed from the sand mixtures for testing pellet abrasion resistance. The results of the pellet abrasion test are shown in Table 4.6.The procedure for preparing the sand mixtures and pellets for the pellet abrasion test was similar to that described by Halstead, Rostler, and White (3); the sand mixtures were prepared without heating and the pellets were allowed to dry in air at room temperature before testing. The abrasion values are high compared with hot-mixed asphalts; however, they do indicate the low abrasion resistance of emulsion asphalt and the value of adding a rubber to the mix.

Compatibility Studies

Several additional binders were formulated incorporating ammoniacal solutions of Indulin AT at different concentrations, anionic asphalt emulsions, and UCAR 131 (polyvinyl acetate), as well as the four most successful latices described above. No incompatibility problems were encountered, although the UCAR 131 blends were not as resilient as the others.

Reducing the Viscosity of Alkaline Lignin Solutions

The high viscosity of alkaline solutions of kraft pine lignin above 30% solids concentration required that, to make workable binders, much higher water contents must be used than is required for emulsified asphalt. For the latter only 35-40% water and other volatile material was needed, whereas when lignin solutions were used, the moisture contents of the binder are 60-65%. The additional water interfered with compaction and must be evaporated from the mix in order to achieve good properties in the compacted concrete. Consequently, some efforts were made to reduce solution viscosity and thus water content.

For example, the addition of minor amounts of an alcohol can significantly reduce the viscosity of polymer solutions. This method was explored with butanol. The addition of butanol to an alkaline solution of lignin (Indulin C) was found to reduce viscosity, but not to reduce water content significantly. Furthermore, the binder containing butanol did not wet the granite aggregate. No attempt was made to prepare concrete mixes with lignin binders containing butanol.

The solutions of Indulin C, the sodium salt of lignin, were somewhat less viscous than the ammoniacal solution of Indulin AT, possibly indicating lower molecular weight for the lignin in Indulin C. Lignin was recovered from Indulin C solution by precipitation with formic acid, a volatile acid, and then redissolved with ammonia solution. The resulting solution of lignin was not significantly less viscous than the similar solution made from Indulin A. Work to reduce viscosity of the ammoniacal lignin solution was dropped, though it would appear that reduction in viscosity and water requirement could be effected.

Paving Mixtures

The initial attempts in the development of paving mixtures employing lignin-asphalt-rubber binders were primarily exploratory. Problems such as high solution viscosity, high water content, and aggregate incompatibility were encountered. These trials were followed by a more systematic series of experiments aimed at improving concrete mixing and compaction techniques and optimizing the proportions of the various components. The following items present a brief description of the successive experiments, highlighting the mix parameters, the variables introduced, and the results of the tests applied in each.

Lignin-Asphalt-Rubber Binder in Macadam-Type Specimens

The preparation of concrete specimens by the macadam technique (2) appeared to be a feasible method of using the high-water content binders containing lignin solutions. This technique was tried, therefore, but with only partial success.

The composition of the specimens made were basically:

Aggregate: Granite 3/8 x No. 6, "Medium Screenings" for macadam.

Binder:
33.4% lignin, as 33% ammoniacal solution
33.3% 120 pen. asphalt, as CSS-1 emulsion
33.3% vinyl pyridine rubber, as latex.

To prepare specimens the "screenings" were loosely tamped in a mold which was then filled with binder solution and drained. The specimens were dried with a stream of ambient-temperature air before removal from molds. Variations tried were dry or pre-wetted aggregate, aggregate pre-treated with formic acid to coagulate binder, various dilutions of binder to adjust viscosity for best penetration and deposition of binder. None of the specimens was satisfactory for testing.

The best specimens were produced by two applications of binder which had been diluted with 10% water. These specimens were dried between applications. Because of the length of time required for drying specimens in molds, the preparation of macadam-type concrete specimens was discontinued. It was necessary to dry in the molds as the specimens were not sufficiently cohesive to hold their shape when removed from the molds before drying.

Lignin-Asphalt-Rubber Binders in Open-Graded Concrete

The compositions in this series contain a variation in the type of rubber, all at 20% volume of the binder on a dry basis. The materials in this series had the following compositions:

Aggregate: "C" (open-graded; see Table 4)

Binder:
40% lignin, as 33% ammoniacal solution
40% 120 pen. asphalt, as CSS-1 emulsion
20% rubber (nitrile, vinyl pyridine, or carboxy), as latex.

The control binder was 100% asphalt, as CSS-1 emulsion.

These compositions were mixed manually and not aerated to reduce water content. Two-inch (50.8 mm) diameter briquets were molded by double-end static compaction. The briquets were then dried at ambient temperature. Densities of half of the briquets were determined; these briquets were then immersed 7 days at ambient temperature. Unconfined compressive strengths of both the immersed and dry specimens were measured.

Excess water exuded during compaction indicating that the water contents of the binders was too high in spite of the high voids of the open-graded aggregate. The density and compressive strength were low (Tab. 7.7, Col. 1) The density of the controlwas significantly higher than those of the experimental lignin briquets.

Lignin-Asphalt-Rubber (40:40:20) Binders in Dense-Graded Concrete

In contrast to the composition described above, this series of concretes

Table 4.6. Properties of Ottawa sand mixes[a] with lignin-based binders.

Composition of Binder			Weight Dry Basis	Pellet Abrasion[b] Test at Room Temperature mg/rev		
Lignin	Asphalt	Rubber		Series 1	Series 2	Series 3
None	CSS-1	None	0:100:0	-	2.08	2.98
Indulin AT[c]	CSS-1	Nitrile 61-A	33.3:33.3: 33.3	0.90	1.86	2.04
Indulin AT[c]	CSS-1	Pyridine LVP	33.3:33.3: 33.3	0.21	1.09	2.02
Indulin AT[c]	CSS-1	Carboxylated high styrene butadiene styrene rubber(774)	33.3:33.3: 33.3	1.09	1.56	1.88
Indulin AT[c]	CSS-1	Carboxylated high styrene butadiene styrene rubber(775)	33.3:33.3: 33.3	0.76	1.34	2.01
Indulin AT[c]	None	Styrene butadiene rubber 1707	50:0:50	Dry pellets showed some choesion, but broke apart easily.		
Indulin AT[c]	None	Styrene butadiene rubber 1707	90:0:10	Pellets cracked very easily; no cohesion.		
Indulin AT[c]	CSS-1	None	50:50:0	Pellets crushed easily.		
Indulin AT[c]	CSS-1	None	90:10:0	Pellets could not be made.		

[a] Two percent binder by weight on 20-30 Ottawa sand; pellets molded cold and dried before testing.
[b] Reference 3
[c] In ammoniacal solution of 32% lignin content.

Table 4.7. Density and unconfined compressive strength of lignin-asphalt-rubber concretes.

Nitrile, Pyridine, and Carboxylated Rubbers in
Open- and Dense-graded Concrete

Gradation of Aggregate	Open[a]	Dense[b]		
Lignin:asphalt:rubber[c]	40:40:20	40:40:20	45:45:10	30:60:10
	(1)	(2)	(3)	(4)
Nominal water content of binders[d],%	*ca.* 65	36	20	20
Density, pcf:§				
Nitrile rubber (61A)	138.2	145.7	136.9	131.0
Pyridine rubber (LVP)	140.2	144.3	138.5	131.6
Carboxylated rubber (774)	139.1	141.4	141.4	126.7
Emulsified asphalt (control)[e]	148.2	151.4	150.7	136.8
Dry strength, psi:§				
Nitrile rubber	207	898(37)[d]	494(17)[d]	716(15)[d]
Pyridine rubber	210	599(36)	718(22)	940(22)
Carboxylated rubber	248	928(37)	658(17)	1239(20)
Emulsified asphalt (control)[e]	254	239(5)	284(21)	284(21)
Strength after immersion in water for 7 d at room temperature, psi:				
Nitrile rubber	184	?(39)	118(20)	209(20)
Pyridine rubber	108	254(37)	156(21)	260(22)
Carboxylated rubber	138	289(36)	189(21)	203(19)
Emulsified asphalt (control)[e]	165	239(39)	280(26)	212(20)

[a] Aggregate C (see Table 4.4). None of the mixes was dried before compaction.

[b] Aggregate A (see Table 4.4).

[c] Volume ratio on a dry basis.

[d] Water content of lignin-containing binders at the time of compaction, in weight percent. Actual water contents for individual briquets given in parentheses.

[e] Binder 100% asphalt as CSS-1.

§To convert to kg/m^3: pcf (1.601846 x 10)
MPa: psi (6.894 x 10^{-3})

was made with a dense-graded aggregate (Aggregate A) using the same binder compositions (dry basis) as were used in preparing the open-graded mixes. Also included in this series was an additional control of hot-mixed asphalt.

These mixes were prepared manually and dried over low heat with stirring to reduce the water content of the binder to 33%. Two-inch(50.8 mm) diameter briquets were molded by double-end static compaction. They were air dried at ambient temperature; half of the briquets were then immersed for 7 days at room temperature. Unconfined compressive strengths were measured on both immersed and dry specimens.

The results are reported in Table 4.7(Column 2) and Table 4.8.Compared with the open-graded mixes, density and compressive strengths were significantly higher. Also, the strengths after a 7-day water soak were better. The hot mix asphalt concrete exhibited better compressive strength and better retention of strength after water soaking.

Lignin-Asphalt-Rubber (45:45:10) Binders with Dense-Graded Aggregate

Compared with the previous series this series of briquets featured a lower rubber content, i.e., 10% vs 20%, in the binder and a lower water content, i.e., 20% vs 33%, in the binder at the time of compaction.

The briquets had the following composition:

Aggregate A (Dense-graded)

Binder: 45% lignin, as 33% solution
45% 120 pen. asphalt, as CSS-1 emulsion
10% rubber (nitrile, vinyl pyridine, or carboxy), as latex.

Control: 100% asphalt, as CSS-1 emulsion.

Except for drying out the mix to a lower water content (20%) in the binder at the time of compaction, the briquets in this series were prepared and tested in the same manner as the previous set.

The compaction of the briquets was difficult; they were dry and crumbly, probably reflecting the low water content of the binder at the time of compaction. The density and compressive strength results are given in Table 4.7, Column 3. The densities and compressive strengths were lower as compared with the previous series which contained 20% rubber in the binder, and were dried to 30% water content before compacting.

Lignin-Asphalt-Rubber (30:60:10) Binders in Dense-Graded Concrete

This series was a continuation of the previous two series and includes the following compositions:

Aggregate A (Dense-graded, medium)

Binder: 30% lignin, as 25% solution
60% 120 pen. asphalt, as CSS-1 emulsion
10% rubber (nitrile, vinyl pyridine, or carboxy), as latex.

Control: 100% asphalt, as CSS-1 emulsion.

As with the previous series, these mixes were also dried to a binder water content of 20% before compaction.

Some difficulty again was encountered in the compaction of the mixes containing lignin. The densities of this series were significantly lower than the previous series (Tab. 4.7, Cols. 4 vs. 3); however, the compressive strengths of both the dry and water-soaked specimens were higher than the previous set, probably reflecting the higher asphalt content of the present set (60% vs. 40%).

<u>Lignin-Rubber Binders in Dense-Graded Concrete with Anionic Asphalt Emulsion, SS-1h</u>.

In this series of mixes, an anionic asphalt emulsion containing harder asphalt (60 pen.) was used. In addition, a second carboxylated butadiene-styrene rubber latex (Polysar 775) was used. This latex was unstable when mixed with the cationic asphalt emulsion (CSS-1). Also, two mixes were made of anionic emulsified asphalt and lignin solution without rubber.

The composition of these materials was:

Aggregate A (Dense-graded, medium)

Binder: 40% lignin, as 25% solution
40% 60 pen. asphalt, as SS-1h emulsion
20% rubber (nitrile, vinyl pyridien, or carboxy), as latex.

Control: 100% asphalt, as SS-1h emulsion.

The mixes were prepared in a manner similar to that described for the preceding series, except that the water content was varied. The specific contents for each of the mixes are shown in parentheses in Table 4.8, in which the test results for the densities and compressive strengths of the mixes are presented.

For purposes of comparison, results of the matching compositions containing cationic asphalt emulsion (from Tab. 4.7) are also included in the table. The mixtures made with the anionic asphalt emulsion yielded higher compressive strengths than the cationic emulsion. However, the densities of the latter were higher. The results on the nonrubber-containing binders also show that the 50:50 lignin:asphalt binders yielded good compressive strength on soaking. However, at a 75:25 content, the values were poor. Also, the data show the emulsified asphalts give lower densities and lower compressive strengths than the comparable hot-mix asphalt concrete.

Lignin-Rubber Binders in Dense-Graded Concrete with Anionic Asphalt Emulsion, SS-1h, Having Lower Rubber and Higher Asphalt Concrete

The objective of this series of mixes was to determine the effects of reducing the rubber content and simultaneously increasing the asphalt content of the binder. In addition, it was desired to assess higher water contents in the mixes. The composition of these mixes was:

Aggregate A (Dense-graded, medium)

Binder: 30% lignin, as 25% solution
60% 60 pen. asphalt, as SS-1h emulsion
10% rubber (nitrile, vinyl pyridine, or carboxy), as latex.

Control: 100% asphalt as SS-1h emulsion.

The procedure of preparation was similar to that used in the previous series except the water content of the binder was higher for some of the briquets. The specific water contents of the binders in individual briquets are shown in Table 4.8. The mixes with higher water content of the binder were easier to compact and yielded higher compressive strengths. Also, the concretes with the higher asphalt and lower rubber contents in the previous set had better properties. In addition, the concretes containing anionic asphalt emulsion were better than the comparable materials containing the cationic emulsifier; however, the latter were compacted at lower water contents in the binder.

Cohesion of Dense-Graded Concrete with Lignin-Asphalt and Lignin-Asphalt-Rubber Binders

The composition of the mixes in this series was:

Aggregate A (Dense-graded, medium)

Binder 1: 50% lignin
50% 120 pen. asphalt (as CSS-1 emulsion)

Binder 2: 45% lignin
45% 120 pen. asphalt
10% vinyl pyridine rubber

Control: 100% asphalt as CSS-1 emulsion.

The mixes were prepared manually and dried to water content of 40% binder. Four-inch (102 mm) diameter briquets were molded by kneading compaction and dried at ambient temperature. Cohesion (Hveem Cohesiometer) at 140°F (60°C) was measured both dry and after water immersion at 140°F (60°C).

Cohesiometer values (Tab. 4.9) were highest for the lignin-asphalt-rubber binder, but all values were lower than normally obtained with hot-mixed asphalt concrete.

Table 4.8. Density and unconfined compressive strength of dense-graded[a] mixes contining alkali lignin, asphalt, and rubber. Anionic vs cationic emulsified asphalts[b].

Composition of binder[c]				Binder with anionic asphalt Emulsion SS-1h			Binder with cationic asphalt Emulsion CSS-1		
Lignin:asphalt:rubber (volume basis)			Rubber type	Density[d]	Compressive strength, psi[§]		Density[d]	Compressive strength, psi[§]	
					Dry	Saturated[e]		Dry	Saturated
40	40	20	Nitrile	138.3	584(26)[f]	159(25)[f]	145.7	898(37)[f]	-(39)[f]
40	40	20	Pyridine	140.6	958(25)	247(26)	144.3	599(36)	254(37)
40	40	20	Carboxy-774	137.7	1257(23)	237(26)	141.4	928(37)	289(36)
40	40	20	Carboxy-775	139.8	1047(24)	223(24)	-	-	-
30	60	10	Nitrile	139.5	1437(40)	283(25)	131.0	716(15)	209(20)
30	60	10	Pyridine	143.4	1257(40)	668(25)	131.6	940(22)	260(22)
30	60	10	Carboxy-774	139.0	1497(50)	257(40)	126.7	1239(20)	203(19)
50	50	-	None	144.1	958	268(40)	-	-	-
75	25	-	None	-	159	159	-	-	-
Asphalt controls:									
Emulsions									
0	100	0	None	147.6	1127(25)	183(25)	-	260	244
Hot-mixed asphalt									
0	100	0	None	149.5	1137(0)	613(0)	-	299(0)	304(0)
Penetration of asphalt:					60	60	-	120	120

[a] Aggregate A.
[b] San Joaquin Valley asphalts.
[c] Ratio on a volume basis.
[d] Density measured on specimen to be soaked in water.
[e] Soaked for 7 days at room temperature.
[f] Water content on weight basis of the binder at time of compaction of the respective briquets.
[§] To convert to MPa: psi x 6.894 x 10^{-3}

Table 4.9. Cohesion of dense-graded concrete[a] with lignin-asphalt and lignin-asphalt-rubber binders

Binder composition[b], %			Hveem Cohesiometer Value at 60°C	
Lignin	Asphalt[c]	Rubber[d]	Dry	Immersed 24 h at 60°C
50	50	-	73	58
45	45	10	130	78
-	100	-	63	72

[a] Four-inch (102 mm) briquets compacted at 40% binder water content, in kneading compaction.
[b] On volume basis of dry binder.
[c] 120 Pen. asphalt, added as CSS-1 emulsion.
[d] Vinyl pyridine rubber, as latex.

Crumbled pieces of a tested briquet bound with lignin-asphalt (50:50) were softened with dilute ammonia solution and remolded into a briquet of similar appearance to a freshly-molded briquet, indicating that recycling of lignin-bound compositions might be feasible by temporarily resolubilizing the lignin.

Polyvinyl Acetate in Lignin-Asphalt Binders

In this series of mixes a polyvinyl acetate latex was used as the rubber. This polymer is a relatively tough material when dry and should impart impact resistance. The compositions of the three concretes are:

Aggregate A (Dense-graded, medium)

Binder 1: 40% lignin, as 25% solution
40% 120 pens. asphalt, as CSS-1 emulsion
20% polyvinyl acetate, as latex

Binder 2: 45% lignin, as 25% solution
45% 120 pen. asphalt, as CSS-1 emulsion
10% polyvinyl acetate, as latex

Binder 3: 30% lignin, as 25% solution
60% 120 pen. asphalt, as CSS-1 emulsion
10% polyvinyl acetate, as latex.

The concretes were mixed manually and dried with a stream of ambient-temperature air before being molded into 2-in. (50.8 mm) diameter briquets by double end static compaction. The water contents of the respective briquets at compaction are shown in Table 4.10. After compaction, the briquets were divided into two sets, one of which was dried in the laboratory and the other on the roof.

Measurements of density and unconfined compressive strengths of the briquets were made (1) after drying in the laboratory, (2) after drying and weathering on the roof for 18 months, and (3) after drying as in (1) and (2) and water-soaking for 7 days at room temperature. The results of the testing are presented in Table 4.10.

The densities of the roof-dried and aged specimens were lower than the unaged laboratory-dried specimens. The dry specimens tended to be brittle and the compressive strengths were comparatively low. The briquets which had been dried and exposed on the roof for 18 months generally had better properties than the laboratory-dried briquets, both when tested dry and after soaking in water.

Effect of Water Content at Time of Compaction

This series was undertaken to determine the water content of the binder that should be used when compacting concrete made of Aggregate A. The composition of the mix was:

Table 4.10. Density and unconfined compressive strength of unaged and roof-aged Lignin concrete briquets[a] containing polyvinyl acetate.

Composition				Roof	Compressive strength, psi[§]				Retained strength after water soak[b], %	
					Dry		Wet			
Lignin:asphalt:polyvinyl acetate			Unaged[c]	aged[d]	Unaged[c]	Aged[d]	Unaged[c]	Aged[d]	Unaged	Aged
45	45	10	142.9	136.6	570(38)	360(36)	200(40)	330(40)	35	92
30	60	10	143.1	142.0	720(37)	620(37)	180(39)	410(39)	25	66
40	40	20	141.1	136.7	420(32)	570(35)	190(34)	310(34)	45	54
0	100	0	150.0	146.0	-(36)	800(33)	270(23)	580(20)	-	73
		Average:	144.3	140.3	570	588	210	408		

[a] Two inch (50.8 mm) briquets, static compacted at room temperature with a binder of CSS-1 asphalt emulsion, 25% ammoniacal solution of Indulin AT, and polyvinyl acetate latex. Water contents of the respective mixes at time of compaction are s shown in parentheses.

[b] Dried briquets immersed in water for 7 days at room temperature.

[c] Briquets were air dried in the laboratory at room temperature to constant weight.

[d] Briquets were dried and aged on the roof of laboratory in Oakland, CA, for 18 months, beginning July 1977.

[§] To convert to MPa: psi x 6.894 x 10^{-3}.

Aggregate A (Dense-graded, medium)

Binder: 45% lignin
45% AC-5
10% vinyl pyridine rubber

Control: 100% AC-5, as emulsion.

The lignin containing mixes were dried to binder water contents of 30, 35, 40, and 45% on a weight basis before compaction. Two-inch (50.8 mm) diameter briquets were molded by double-end static compaction.

Binder or water exuded from briquets which were compacted at water content above 40% in the binder. The density of these AC-5 briquets were determined with the following results:

Water Content of Binder, %	Density-lb/ft^3 (gm/cm^3)
30	140.6, 143.9 (2.25, 2.31)
35	145.1(2.33)
40	144.6(2.32)
45 (exuded)	144.6(2.32)

These results would indicate that water content of the binder of 40% is probably preferable for use with this aggregate

Variation in Rubber Type in Lignin-Asphalt-Rubber Bound Concrete

This series of concretes compares various polar rubbers in dense-graded concrete at 10% volume level in the binder. The water content of the wet binder at the time of compaction was 40% for all the briquets.

The compositions of the concretes in this series were:

Aggregate A (Dense-graded, medium)

Binder 1: 45% lignin
45% AC-5 asphalt
10% nitrile rubber

Binder 2: 45% lignin
45% AC-5 asphalt
10% vinyl pyridine rubber

Binder 3: 45% lignin
45% AC-5 asphalt
10% carboxy rubber

Control: 100% AC-5, as emulsion

These concretes were mixed manually and dried to a binder water content of 40%. Two-inch (50.8 mm) diameter briquets were molded by double-end static compaction and air dried to constant weight. Densities and unconfined compressive strengths were determined on both air-dried specimens and dried specimens that had been saturated with water by soaking for 7 days at room temperature. Similar tests were also run on specimens that were dried and weathered on the roof for nine months.

The results presented in Table 4.11 indicate that the differences among the three rubbers were not significant. All of the concretes containing rubbers were less dense than the asphalt control. Roof aging reduced the density of the briquets. However, the aged briquets retained more strength on water soaking than did the briquets which had been dried only. The retention of strength on water soaking of the aged briquets containing lignin and rubber was greater than that of the 100% asphalt control.

Optimum Water Content for Compaction by Double-End Static Method

The basic composition of these lignin concretes are:

Aggregate B (Dense-graded, coarse)

Binder: 45% lignin
45% AC-5 asphalt
10% vinyl pyridine rubber

Control: 100% AC-5, as SS-1 emulsion.

These concretes were mixed manually and dried to various water contents between 40% and 62% of the binder. Two-inch (50.8 mm) diameter briquets were prepared by double-end static compaction. Density and compressive strength were determined before drying, after drying, and after subsequent immersion.

Maximum density and strength values were obtained at 50-55% water content in the binder as shown in Table 4.12 and Figures 4.3. and 4.4. This was in contrast to the somewhat less open Aggregate A which yielded a mix that exuded on compaction at 45% binder water content.

Effect of Water Content on Kneading Compaction

The basic composition of the lignin concretes are:

Aggregate B (Dense-graded, coarse)

Binder: 45% lignin
45% AC-5 asphalt
10% vinyl pyridine rubber

Two batches were mixed in a Hobart planetary-action mixer, dried to a water content of 55% and 50%, respectively. Four-inch (102 mm) diameter briquets were compacted at ambient temperature in the kneading compactor.

At 55% water in the binder, the mix was unstable and could not be compacted at full compaction pressure, though no binder exuded. Compaction was normal at 50% water in the binder. This water content was used for the next test series.

Table 4.11. Effect of variation in type of rubber on density and compressive strengths of lignin-asphalt-rubber bound concrete.

Unaged *vs*. Aged and Dry *vs*. Wet

	Density, pcf[§]		Unconfined compressive strength, psi[§]				Retained strength after water soak[d], %	
			Dry		Wet[d]			
Rubber[b]	Unaged	Aged[c]	Unaged	Aged[c]	Unaged	Aged[c]	Unaged	Aged[c]
Pyridine	144.8	141.0	720	330	310	390	43	118
Nitrile	144.6	142.9	510	-	290	370	57	-
Carboxylated	144.4	142.0	520	410	-	400	-	98
Asphalt only	150.5	149.0	370	510	90	450	24	88

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[a] Two-inch (50.8 mm) briquets, statically compacted from mixes having 40% binder water content, and air dried in the laboratory.

[b] Binder composition: 25% Indulin AT solution, SS-1 asphalt emulsion, rubber latex; lignin: asphalt: rubber = 45:45:10 (dry volume basis).

[c] Briquets similar to those in (a) aged for 9 months on the roof of laboratory in Oakland, CA.

[d] Immersed in water for 7 days at room temperature.

[§] To convert to MPa: psi x 6.894 x 10^{-3}
kg/m^3: pcf x 1.601846 x 10

Table 4.12. Effects of water content of binder at time of compaction of briquets[a]

Composition of binder (dry,%) Lignin-asphalt-rubber			Water[b] in binder, %	Briquet no.	Exudate[c], g	Density[d] lb/ft^3[§]	Compressive strength, psi[§]		
							Immediately	Dry	Dry + 7d water soak
45	45	10	62	159	1.8	144.8	33	-	-
45	45	10	62	156	0.9	135.0	-	-	204
45	45	10	58	155	1.0	138.8	-	-	272
45	45	10	55	157	1.3	151.1	109	-	-
45	45	10	55	172	2.3	-	-	1170	-
45	45	10	54	158	1.2	142.2	-	-	483
45	45	10	52	154	0.9	144.1	-	-	556
45	45	10	50	161	0.5	148.0	196	-	-
45	45	10	50	165	0	142.6	-	-	436
45	45	10	50	171	0.4	-	-	1260	-
45	45	10	46	173	0	-	-	1130	-
45	45	10	45	160	0	148.6	201	-	-
45	45	10	45	168	0	-	-	1160	-
45	45	10	45	169	0	143.7	-	-	429
45	45	10	40	162	0	149.6	200	-	-
45	45	10	40	166	0	-	-	1160	-
45	45	10	40	167	0	143.8	-	-	393
0	100	0	30	163	0	153.2	95	-	-
0	100	0	30	164	0	151.7	-	-	425
0	100	0	30	170	0	-	-	707	-

[a] Total dry binder content - 6.4% by weight (14.7% by volume); briquets are 2 x 2 in. (50.8 x 50.8 mm) cylinders, prepared by double-end static compaction.

[b] Initial water content of mixes containing lignin and rubber, immediately after mixing; the lower values are achieved by drying and mixing.

[c] Exudate collected during compaction of briquets.

[d] Density was not determined on briquets tested for dry strength.

[§] To convert to MPa:$_3$ psi x 6.894 x 10^{-3}
kg/m^3: lb/ft^3 x 1.601846 x 10

Table 4.13. Compressive strength of lignin-asphalt-rubber concrete four-inch briquets compacted in kneading compactor at binder water content of 50%

Lignin:asphalt:rubber			Density	Voids, %	Dry[a] strength, psi[§]	Wet[b] strength, psi[§]	% retained after immersion	% of control[c]	
								Dry	Wet
0	100 (control)	0	150.9	8.0	278	265	95	100	100
47.5	47.5	5	138.8	16.1	220	191	87	79	72
45	45	10	137.8	17.2	252	156	62	91	59
42.5	42.5	15	136.4	18.0	271	126	46	97	47

[a] Dried to constant weight.

[b] After 7 days soaking in water at room temperature.

[c] Control mix with emulsified asphalt, SS-1, only.

[§] To convert to MPa: psi x 6.894 x 10^{-3}

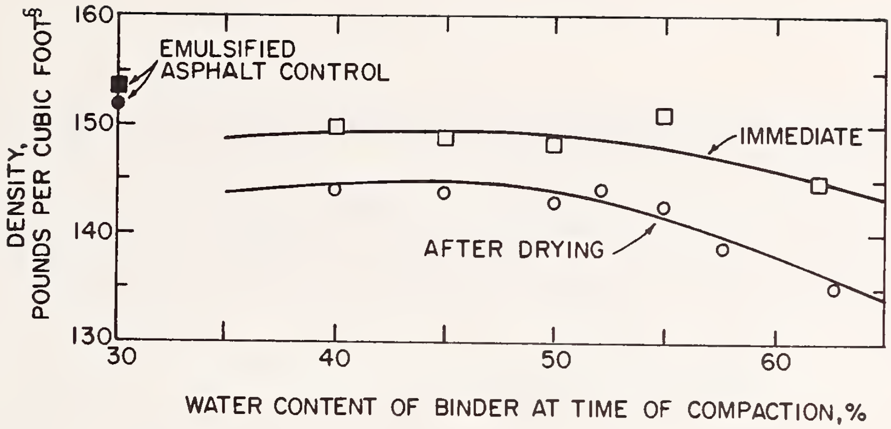


Figure 4.3. Density of compacted briquets of lignin-asphalt-rubber mix as a function of the water content of the binder at the time of compaction. Data are shown for briquets immediately after compaction by double-end static compaction and after air drying to constant weight.

§To convert to kg/m^3: lb/ft^3 x 1.601846 x 10

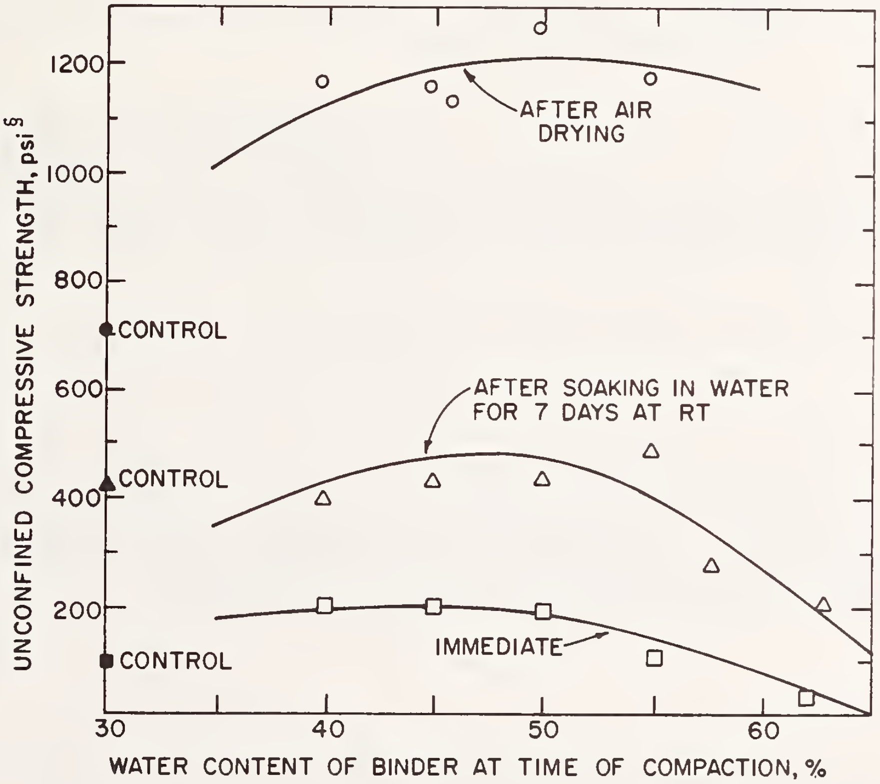


Figure 4.4. Unconfined compressive strength of lignin-asphalt-rubber mixes as a function of the water content of the binder at the time to compaction. Data are shown for (1) the strength of the briquets immediately after compaction, (2) the strength after drying to constant weight, and (3) strength of water saturated briquets which were dried and subsequently immersed in water for 7 days at room temperature.

§To convert to MPa: psi x 6.894 x 10^{-3}

Varied Content of Rubber in Four-Inch (102 mm) Diameter Briquets Compacted by Kneading Compactor

The compositions of the lignin concretes were:

Aggregate B (Dense-graded, coarse)

Binder 1: 47.5% lignin
47.5% AC-5 asphalt
5% vinyl pyridine rubber

Binder 2: 45% lignin
45% AC-5 asphalt
10% vinyl pyridine rubber

Binder 3: 42.5% lignin
42.5% AC-5 asphalt
15% vinyl pyridine rubber

Binder 4: 0% lignin
100% AC-5 asphalt
0% vinyl pyridine rubber

These mixes were prepared in a Hobart planetary-action mixer, dried to a water content of 50% in the binder, and compacted at ambient temperature with a kneading compactor. They were dried at100°F (38°C). Half of the specimens were immersed in ambient-temperature water on the 28th day. Compressive strength was measured on the 28th day and the 35th day.

Both density and compressive strength were lower than for the 2 x 2 inch (50.8 x 50.8 mm) briquets previously prepared by static compaction, possibly because a longer drying time may be required for 4 inch (102 mm) diameter briquets. Density and compressive strength for the briquets bound with the lignin-asphalt-rubber binders were lower than for the control briquets bound with the asphalt emulsion only. Of the briquets bound with lignin-asphalt-rubber, dry strength increased with increasing rubber content, but wet strength and percentage of dry strength retained after immersion decreased with increasing rubber content (Tab. 4.13).

D. Discussion

This exploratory investigation was carried out in a sequential manner. The major objectives were to determine:

1. The general feasibility of using kraft lignin with emulsified asphalt as the binder in road-paving mixes.

2. The principal properties of the binder and compacted paving concrete mixes.

3. The principal variables that control the properties of the mixes.

The experiments which are described in this report indicate that a continuous spectrum of binder is possible, depending on the composition. The mix properties, in turn, depend on the binder and the preparation of the mix. The principal variables which are apparent from this study are discussed briefly.

Water Content

The water content of the binder at the time of compaction affects both compaction behavior and the strength of the mix. There appears to be an optimum content for a given aggregate. At low levels, the mix was dry and the aggregate was not lubricated sufficiently to allow full compaction. At high levels, the mix exudes binder or was not stable in the kneading compactor.

Lignin Content

Increasing the lignin content in the binder increased stiffness and brittleness. At 75% lignin-asphalt without rubber, the mix was dry and crumbly.

Openness of the Aggregate

The openness of the aggregate had a decided effect on the optimum water and binder contents. In our study we did not vary the volume of the binder in the mix. A fixed volume was selected based on a hot mixed asphalt concrete with a crushed granite aggregate (14.67 volumes of binder per 100 volumes of aggregate). This was an important variable that should be studied.

Asphalt Type

Several asphalts of different consistencies (60 pen. to 157 pen.) were included in these experiments. The harder asphalts yielded higher compressive strengths. Also included were asphalt variations in nitrogen base content (24-38%). There was no indication that the higher nitrogen content increased the compatibility of the asphalt and lignin. The latter exists in the asphalt binder as fine solid particles.

Rubber Type and Amount

A variety of rubbers was added as latices to the wet binder. The amount was varied from 0-20% volume of the binder on a dry basis. Most of the binders contained 10%. The addition of rubber resulted in improved impact strength and compressive strength, but, at the same time, lower density and higher voids in the final compacted mix. The relative effectiveness of the different types of rubber needs to be investigated further as does their cost effectiveness in paving mixtures.

E. Summary

In this phase of the project, the effectiveness of kraft pine lignin in combination with asphalt and rubber as a binder for paving concrete was investigated. Our efforts were directed toward the replacement of a portion of the asphalt in an emulsified asphalt concrete mix with lignin as an extender and reinforcer. The lignin was incorporated with emulsified asphalt as an annoniacal solution. Small amounts of rubber were added to the lignin-asphalt binder as a minor component to counteract the stiffness and possible brittleness imparted by the lignin. Since these binders are formulated with aqueous solutions and emulsions, their development depends on the technology and methodology of emulsified asphalt in paving mixtures.

The work was carried out in two stages:

1. Study of the binder cement to determine the compatibility of the ingredients and their properties independent of the aggregate. This included studies of aqueous solutions of the binder and dried films of the binder.

2. Study of mixtures of the binder with various aggregates in macadam construction and in concrete mixes containing Ottawa sand and crushed granite aggregate.

The principal variables that were investigated include:

- Asphalt variation, type (viscosity and nitrogen bases), and amount.
- Emulsifier variation, cationic and anionic, and amount.
- Various rubbers, including polar and nonpolar, and amount.
- Aggregate gradations (voids variation).
- Water content of the binder.
- Method of compaction of test briquets.
- Methods of drying of test briquets.

Results from this phase of the work include at least the following:

1. Kraft lignin appears to be a feasible partial replacement and extender of asphalt in emulsified asphalt paving mixes. The lignin should be incorporated with emulsion as an ammoniacal solution so that it will become water insoluble through volatile loss of the ammonia.

2. The lignin, after drying of the concrete and the volatilization of the ammonia, is in the form of fine particles, which stiffen the dry asphalt binder and increase compressive strength and brittleness. These effects may require special design of the paving mix and limit the amount of lignin that can be added.

3. The addition of minor amounts of a rubber to the binder in the form of a latex appears to improve impact strength and general properties of the binder and the final compacted mix. A polar rubber is preferred.

4. Asphalt with a high content of nitrogen bases did not show unusual compatibility or solubility with lignin. The latter appears to be insoluble in all asphalts.

5. Recycling of concrete bound with lignin-asphalt-rubber appears to be feasible. The softening of old lignin-bound concrete can be accomplished by the addition of ammonium hydroxide solution.

6. Additional work is required to develop and optimize this binder system. This system may have immediate application to emulsified asphalt as a means of modifying modulus and other properties, particularly for base courses.

Suggested Further Work

Considering the status of the results, work in the following areas needs to be done to optimize the mix and to demonstrate the capability and costs of this type of binder system on a firmer basis:

1. Determine the optimum binder content for aggregates of different voids content. Binder water content at the time of compaction must be optimized for a given aggregate to provide the necessary lubrication of the aggregate without excessive exudation of binder.
2. Simultaneously with (1), determine the optimum water content of the binder at the time of compaction.
3. Investigate a broader range of lignin content, particularly levels down to 25%.
4. Research ways to reduce the water content of the binder to avoid the need of aerating the mix prior to compaction.
5. Investigate methods of reducing the viscosity of lignin solutions, so as to increase solids content at workable viscosities.
6. Search for other sulfate and alkali lignins having lower solution viscosities and water contents.
7. Assess warming the mix as a means of improving compaction and curing.
8. Investigate types of aggregate other than the granite that was used in this study.
9. Determine the modulus and aging characteristics of compacted mixes.
10. Investigate whether the use of lignin requires modification in paving techniques used with emulsified asphalt alone as the binder.
11. Investigate acid flocculation of binder *in situ* as a means of reducing the time of curing of lignin-asphalt-rubber bound mixes.

F. References

1. Westvaco Product Data Bulletin, "Indulin C".

2. Standard Specification, Section 30, Bituminous Macadam Surface, State of California, Division of Highways, July, 1940.

3. Halstead, W.J., F.S. Rostler, and R.M. White, Proc. AAPT 35:91, 1966.

V. ENVIRONMENTAL EFFECTS ON LIGNIN BINDER

A. Introduction

One of the basic difficulties in utilizing wood lignins as paving materials is their possible solubility in the presence of water, when a dried road surface becomes wet in rain. Thus, the environmental effects on the lignin binder is an important consideration in the study to utilize lignins as substitutes for asphalt. It is quite necessary that any newly developed binder be similar in water solubility to conventional asphaltic materials.

This chapter is devoted to a series of experiments that were performed on various binder formulations to evaluate the characteristics of such binders upon exposure to simulated environmental weathering conditions.

Generally, two types of samples were tested:

1. Briquettes with aggregate

2. Asphalt binder alone.

Leaching tests were made to assess physical changes and the release of binder constituents for both types of samples. Briquette samples (height = 3 cm and radius = 5.0 cm) were quarter section cuts from larger cylinders, while pure binder samples (5 cm x 1.8 cm) were preheated, poured into a glass petri dish and weighed.

Duplicates of either briquette or poured binder were placed into 500 ml of either .001 NaOH, .001 N HCl or distilled water. The system was contained in a one liter glass jar with plastic screw top cover.

Leaching was carried out for two weeks or longer, during which the following tests were run:

1. Daily visual observation of the change in color of the leachate solution (i.e., the aforementioned 500 ml of acid, base, or neutral solutions).

2. Daily pH readings of the 500 ml leachate solution.

3. Chemical oxygen demand tests were conducted once every 24 hours for the first 5 to 7 days of leaching and finally two more times (on the 10th and 14th days).

4. Alkalinity and acidity tests were conducted once a week in some test series.

5. Spectrophotometric readings were taken of the leachate. This involved scanning in the visible and ultraviolet regions. Water and isooctane were used as solvents for the leachate. The purpose

was to determine the color of the samples and to find whether or not lignin, with a characteristic absorption at 280 nm, was leached into solution from the sample.

6. Ultraviolet radiation exposures of the samples were made using: (a) high intensity UV exposure chamber designed originally for oxidation in total nitrogen analysis; and (b) a General Electric IF8 ultraviolet lamp. Exposure of the sample surface normal to the radiation lasted for sixty minutes, when using the UV nitrogen oxidizing device (#a). The samples were enclosed within the chamber and were 6 cm (2.36 in.) from the light source. Samples were weighed prior to exposure, immediately after exposure and 24 hrs. after exposure (at 77°F [25°C]). After weighing, the samples were placed in acid/base/water solution and leached for two weeks.

UV exposure tests accomplished while using a G.E. IF8 sun lamp, operated under the following parameters (see Fig. 5.1):

Peak Wavelength = 3600 Angstrom

Voltage = 115 VAC

Operating Power = 15 Watts

Temperature under the lamp was 75.2°F(24°C) at 6 cm (2.36 in.) distance to the binder samples. Total exposure time was 70 hours. The sample surfaces were placed normal to the incident radiation.

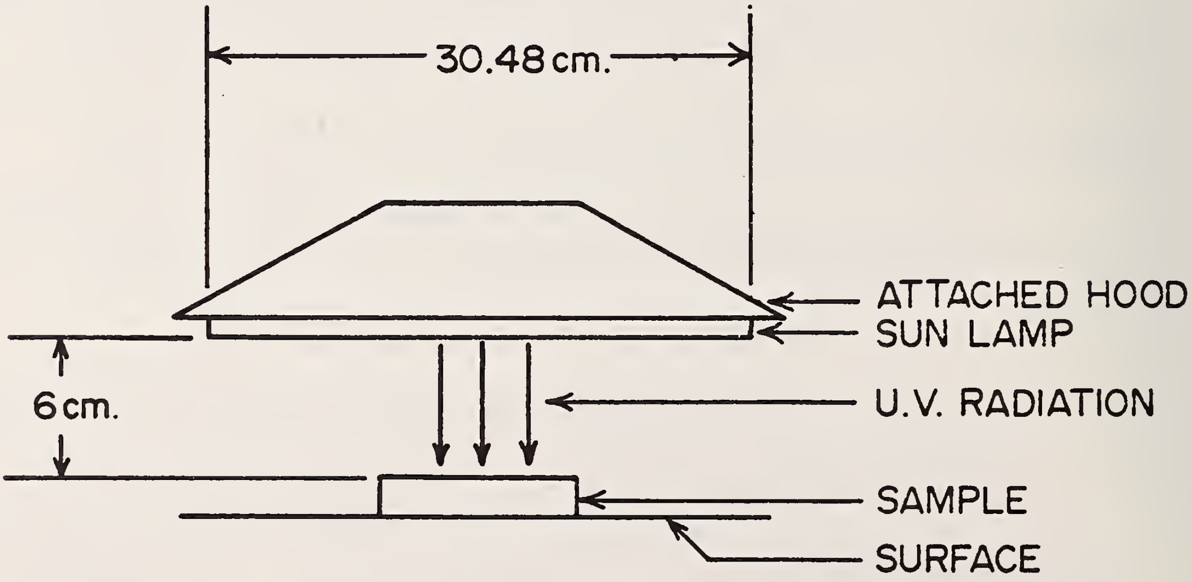


Figure 5.1. General Electric IF8 U.V. lamp test set-up.

B. Analytical Methods

The analytical methods employed were pH measurements, chemical oxygen demand (COD) tests, acidity and alkalinity tests, ultraviolet radiation, and spectrophotometric readings. pH readings were conducted on a "Metrobon/ Brinkman pH-104" pH meter. Calibration of the pH meter with pH 7 and pH 4 buffers was done before each set of readings.

The COD and acidity and alkalinity tests were run under the conditions specified in Standard Methods for the Examination of Waste Water, 14th ed., 1975. The sample size selected for the COD was 10 ml. The reagent quantities used were in accordance with the specifications for a 10 ml sample size as indicated in the above mentioned reference.

Chemical oxygen demand tests were run on 1.0 grams of kraft lignin dissolved in 500 ml of .001 N NaOH. The theoretical COD result of the above solution is 2000 mg/l. The COD experimental result was ≅ 1200 mg/l. Therefore, as a measurement of total lignin in solution, COD values measure 60% of the total dissolved concentration of lignin.

Table 5.1. The radiated energy in watts of Hanovia Vapor Lamp.

	Hg-Lines Angstrom	Energy Watts
I.R.	13673	10.15
	11287	6.93
	10140	31.60
Visible	5780	69.35
	5461	40.52
	4358	53.00
	4045	24.20
U.V.	3660	ΣE =
	↓	337.19
	2224	
U.V. Peaks	3660	97.10
	3130	50.60
	3025	32.90
	2652	27.80
	2537	24.10

Ultraviolet radiation exposure, using the nitrogen oxidizing apparatus was found to be invalid because a glass cover was placed between the UV source and the sample surface. Details of the procedure are presented for future reference. A Hanovia high pressure quartz mercury vapor lamp was used. The following is a specification list of operating parameters of the lamp:

Lamp watts = 1200 watts

Lamp volts = 285 volts

Current amps = 4.7 amps

Arc-length (in.) = 12 ins. (304.8 mm)

The temperature within the UV chamber after 60 minutes of operation was 131°F (55°C). Binder samples in petri dishes were suspended by a copper wire within the chamber 6 cm (2.36 in.) from the incident radiation.

Upon completion of the exposure, the samples were weighed on a Mettle Analytical Balance, stored for 24 hours at 77°F (25°C). They were reweighed and then placed in an acid or base leachate. The glass cover between the UV lamp and the surface of the binder sample cut off all radiation below 3800A (upper limit of UV). The net effect of this method was a heating of the sample to 131°F (55°C), followed by cooling at 77°F (25°C).

Some spectrophotometric tests were run on a Beckman SK-2A scanning spectrophotometer. Due to mechanical malfunctions of the machine, scans below 360 nm could not be made. A Perkin Elmer (Coleman 139 Model) Spectrophotometer was used for measurements below 360 nm. Quartz cuvettes, 5 cm and 1 cm, were used for the Beckman and Perkin Elmer, respectively. Visible and some UV spectra were determined by pipetting a sample of leachate from the binder leaching test. It was placed in a cuvette; distilled water was used as a blank in the double beam instruments.

Due to the reduced solubility of lignin and asphalt constituents in polar solvents, iso-octane was used with some samples to extract from the aqueous leachate sample. A 10 ml sample of leachate was placed in a test tube with 10 ml of iso-octane. The liquids were then shaken for 1-2 minutes and left over night (covered with aluminum foil). Following this was a 15 minute immersion in a boiling water bath. After cooling, the samples were placed in a separatory funnel and the iso-octane fraction was separated, to be used for sepctrophotometer analysis.

C. Test Series

Four test series were completed on briquet and binder samples. The first two test series were run on briquet samples. The third and fourth sets were composed of binder samples. It should be noted that:

a) The third test series, although irradiated in the UV chamber, represents only the leaching behavior of an unirradiated sample. The radiation exposure was short in any case and the UV radiation was blocked by the glass cover.

b) The fourth test series is primarily concerned with qualitative results, i.e., appearance of the exposed surface area of the binder and discoloration of the leachate.

Following is a chronological listing of the completed test series. Each series contains a sample description, tests conducted and a flow chart of the operation.

Test Series 1

Four briquette samples were exposed to both acid and base leaching. The samples containing kraft lignin had a binder with 50% AC-5 asphalt cement and 50% Indulin AT (Tab. 5.2). The fraction of lignin was very high and the briquettes were noticeably less compacted than the AC-5 controls. The leaching test subsequently demonstrated that the lignin containing briquets were unstable.

The tests conducted are presented in Figure 5.2.

Table 5.2. Composition of 4 briquets samples used in Series 1.

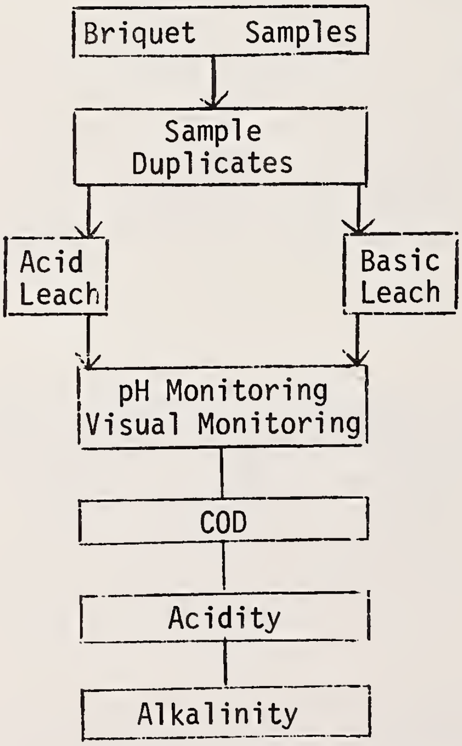
Sample No.	Sample Composition	Sample Weight (grams)	Exposed Sample Surface Area (cm^2)
1	94% aggregate 6% binder [50% AC-5 50% Indulin AT]	150.0	91.0
2	Duplicate of No. 1	160.0	100.0
3	94% aggregate 6% binder (100% AC-5)	143.0	89.0
4	Duplicate of No. 3	155.0	96.0

Test Series 2

In this test series, the amount of lignin in the binder phase was reduced from that of the previous samples (50%) to 30%. Another parameter change was the type of lignin. In addition to testing Indulin-AT or kraft lignin, calcium lignin sulfonate and ammonium lignin sulfonate were also used. Binder portions varied from 8% to 5% of total asphalt mixture.

Table 5.3. Composition of 10 briquet samples used in Series 2.

Sample No.	Sample Composition	Volume (cm^3)	Surface Area (cm^2)	Weight (grams)
1	NH_4-Lignin sulfonate % binder = 8%	110	145	256
2	Duplicate of 1	105	145	277
3	CA-Lignin sulfonate % binder = 8%	105	140	232
4	Duplicate of 3	110	140	234
5	Kraft lignin % binder = 5%	90	130	160
6	Duplicate of 5	85	130	160
7	AR-4000, no lignin	105	145	244
8	Duplicate of 7	110	150	250
9	AC-5, no lignin	125	160	250
10	Duplicate of 9	125	160	258



Testing from:

Series 1: 8/8/77-8/26/77
Series 2: 8/29/77-9/8/77

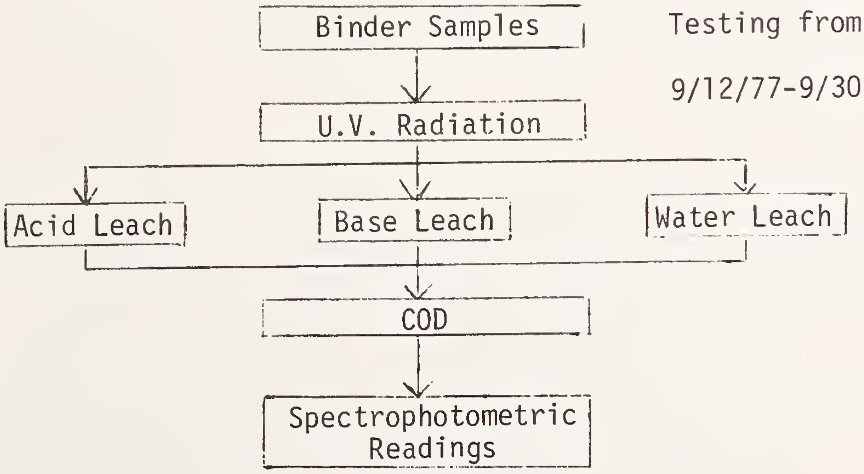
Figure 5.2. Flow chart showing testing and measurement for Series 1 and 2.

Test Series 3

This set of samples consisted of 100% binder poured into Petri dishes. The binder samples all contained 30% lignin by weight. Included were kraft lignin, ammonium lignin sulfonate, and calcium lignin sulfonate.

Table 5.4. Composition of 10 briquet samples used in Series 3.

Sample No.	Sample Composition	Leaching Solution	Sample Weight (grams)	Exposed Surface Area (cm^2)
1	kraft lignin	acid	4.6	19.7
2	duplicate	base	6.2	19.7
3	duplicate	distilled H_2O	3.5	19.7
4	ammonium lignin sulfonate	acid	4.8	19.7
5	duplicate	base	5.5	19.7
6	calcium lignin sulfonate	acid	6.3	19.7
7	duplicate	base	6.3	19.7
8	AC-5 asphalt cement	acid	6.2	19.7
9	duplicate	base	5.0	19.7
10	duplicate	water distilled	6.0	19.7



Testing from:

9/12/77-9/30/77

Figure 5.3. Testing flow chart for binder pour plate samples in Test Series 3.

Test Series 4

Half of the poured binder samples were exposed to the low intensity sunlamp for 60 hours then leached in base or H_2O. The other half were leached without exposure to UV. Samples are described in Table 5.5 with exposure and observations described in Figure 5.4.

Table 5.5. Composition of 19 binder samples used in Series 4.
Date: 10/1/77-10/13/77

Sample No.	Binder Sample Composition	Sample Weight (Grams)	Exposed Sample Surface Area (cm^2)	Leachate Solution	Duration of UV exposure Westinghouse lamp (hours)
1	4% sulfur 26% NH_4-lignin 70% AC-5 (Parr Bomb mixing)	8.0	19.4	H_2O	60
2		6.5	19.4	.001 N NaOH	60
3		7.9	19.4	H_2O	0
4		7.3	19.4	.001 N NaOH	0
5	4% sulfur 26% NH_4-lignin 70% AC-5 (Parr Bomb mixing)	9.4	19.4	H_2O	60
6		8.4	19.4	.001 N NaOH	60
7		6.2	19.4	H_2O	0
8		5.6	19.4	.001 N NaOH	0
9	(HCl) acid Pretreated NH_4-lignin sulfonate (open vessel mixing)	4.0	19.4	H_2O	60
10		4.0	19.4	.001 N NaOH	60
11		-	19.4	H_2O	0
12		-	19.4	.001 N NaOH	0
13	30% kraft lignin 70% AC-5 (open vessel mixing)	2.5	19.4	H_2O	60
14		4.3	19.4	.001 N NaOH	60
15		-	19.4	H_2O	0
16		-	19.4	.001 N NaOH	0
17	100% AC-5 (control)	3.3	19.4	H_2O	60
18		4.1	19.4	H_2O	0

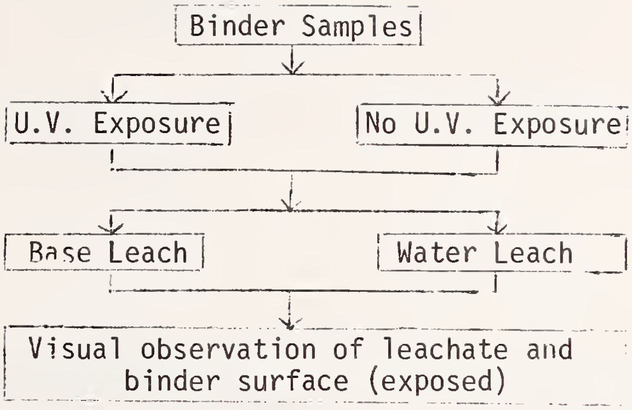


Figure 5.4. Flow chart of tests and measurements for Series 4. Date: 10/1/77-10/13/77

D. Test Results and Conclusions

First Test Series

Compared to the two briquet samples without lignin, the briquet samples containing 50% indulin AT exhibit a high rate of leaching as indicated by a severe discoloration of the water, high COD values and physical disintegration of the samples. The briquets were more prone to basic solution attack; severe disintegration occurs after 5-6 days leaching in 0.001 N NaOH, while disintegration in 0.001 N HCl occurs after 12 days. It should be noted here that prior to physical disintegration, the amount of leaching was rather similar for the four samples. The briquet containing lignin was poorly consolidated and subject to absorption of water and swelling. When disintegration took place, much more surface area was exposed resulting in higher leachate concentrations. Amounts of organic material absorbed ranged from 0.1 mg COD/cm^2 for the AC-5 samples to 0.2-0.4 mg COD/cg^2 (based on superficial briquette area) for the lignin containing binder.

Second Test Series

This test series compared briquet samples wherein the type of lignin in the binder was varied. However, the amount of lignin remained the same. From the COD tests and visual observations, kraft lignin (30% of binder) exhibited properties very similar to that of the control. These briquets had better compaction and consolidation than the 50% lignin samples of the first test series. There was insignificant swelling or physical disintegration of the kraft lignin binder briquets. Both in terms of COD leaching, pH change and physical appearance, the kraft lignin briquets were essentially the same as the AC-5 and AR-4000 control samples (Table 5.7).

For all samples, most of the leaching took place in the first 48 hours as can be seen in Figures 5.5 and 5.6.

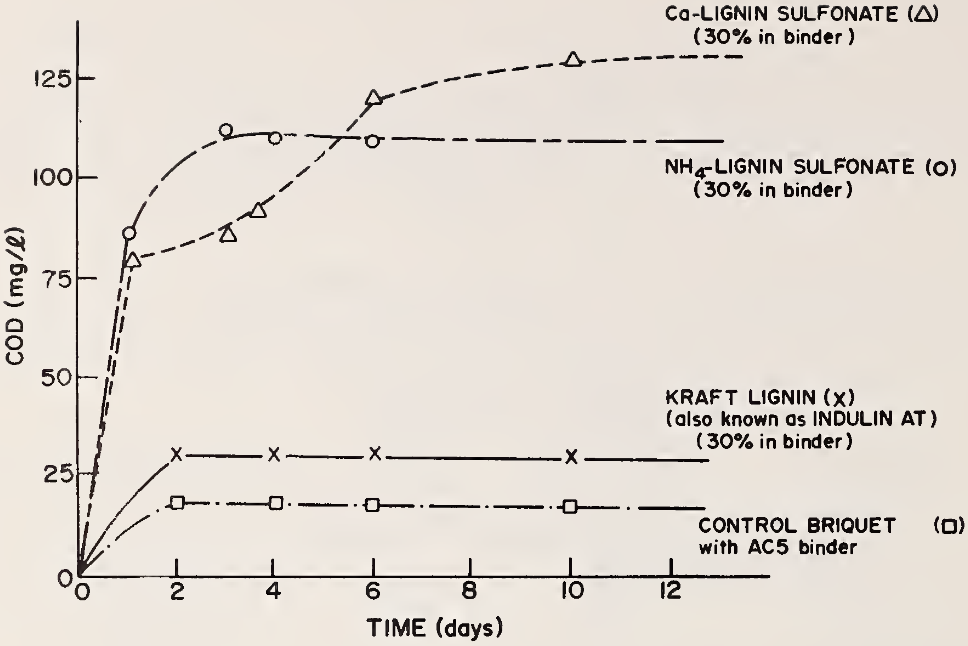


Figure 5.5. COD concentration vs. time for test series two in basic solution.

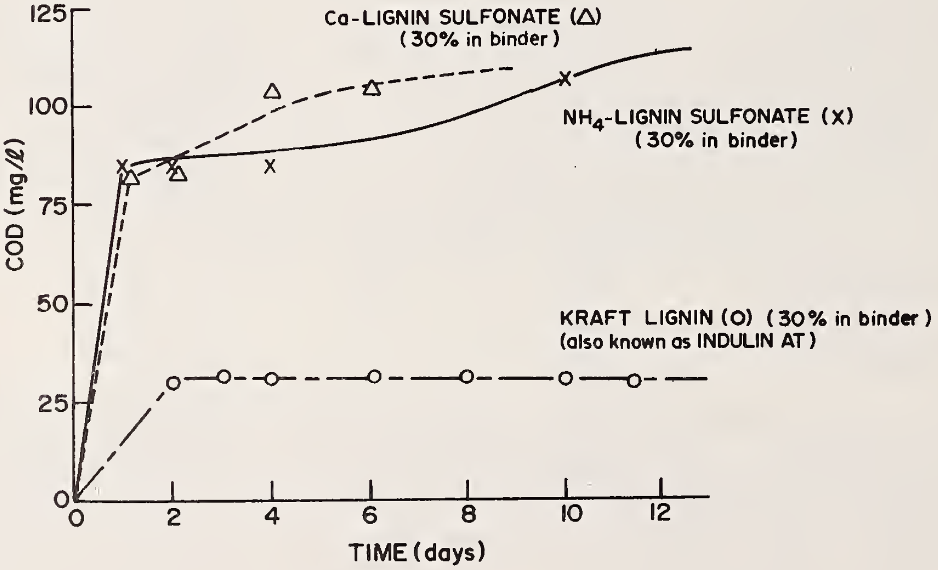


Figure 5.6. COD concentration vs. time for test series two in acid solution.

Table 5.6. Test results for Series One

Days Leaching	Sample No. 1 50% kraft in binder basic SOL			Sample No. 2 duplicate of No. 1 Acid SOL			Sample No. 3 Control AC-5 binder basic SOL			Sample No. 4 duplicate of Acid SOL		
	pH	COD*	mg/cm^2	pH	COD	mg/cm^2	pH	COD	C/S**	pH	COD	C/S
1	11.0	28	.15	3.3	24	.12	11.0	18.6	0.1	3.3	19	0.1
5	10.0	56	.30	3.3	41	.22	10.0	-	-	4.1	19	0.1
6	9.0	65	.35	3.5	37	.2	9.4	-	-	4.1	19	0.1
10	7.1	64	.35	3.8	37	.2	8.8	27.9	0.15	4.2	-	-
14	7.1	74	.40	3.8	37	.2	8.1	-	-	4.8	19	0.1

* COD = Concentration of organic material in leachate (mg/l).

** C/S - Amount of organic material in leachate per area exposed surface (mg/cm^2).

Table 5.7. Test results for Series Two.

Days Leaching	Ammonium Lignin-Sulfonate (30% of binder)						CA-Lignin Sulfonate (30% of binder)						Indulin-AT (30% of binder)						AC-5 Binder						AR-4000 Binder	
	Acid			Base			Acid			Base			Acid			Base			Acid			Base			Acid	Base
	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	COD	C/S	pH	pH
1	3.3	84	.5	11.2	84	.45	3.3	84	.45	11	80	.45	3.3	-	-	11.2	-	-	3.3	-	-	11.2	-	-	3.3	11.2
3	3.5	84	.5	10.0	111	.6	3.6	84	.45	10	85	.45	3.7	31	.15	10.4	28	.14	3.5	-	-	10.5	19	.15	3.5	10.2
4	3.7	84	.5	9.5	110	.6	3.6	110	.6	9.5	93	.5	3.8	32	.15	10.2	28	.14	3.7	-	-	10.3	19	.15	3.7	10.0
6	3.9	-	-	9.0	110	.6	4.0	110	.6	7.1	121	.65	3.9	31	.15	9.5	28	.14	3.8	-	-	9.5	19	.15	3.8	9.5
10	4.0	110	.6	8.0	-	-	3.9	110	.6	7.1	130	.7	3.9	31	.15	8.0	28	.14	4.0	-	-	8.5	19	.15	4.0	8.0

COD = Concentration of organic material in leachate (mg/l).
C/S = Amount of organic material in leachate per area exposed surface (mg/cm^2).

Briquettes with NH_4-lignin and Ca-lignin sulfonate exhibited a high degree of leaching followed by gradual physical deterioration of the sample after one week in basic solution.

Third Test Series

This test series was performed with the intention of evaluating the characteristics of pure binder samples of kraft lignin, ammonium lignin sulfonate and calcium lignin sulfonate. The samples were exposed in the UV chamber for one hour. However, the test was invalid due to the blockage of short wavelength UV by the glass coverslip. There was a temporary weight loss (≅ .01%) immediately after exposure. This weight loss was regained after 24 hours, indicating the loss was H_2O vapor, due to heat of T° ≅ 131°F (55°C) in the UV chamber.

Careful visual observations were made on all samples. The leaching appears to be strictly a surface phenomenon.

All pour plate samples were initially black, glossy and smooth. The appearance was unchanged by the UV chamber exposure. Leaching exposure to acid and base little effect on the AC-5 control sample which remained black and shiny. All the lignin samples showed some change, ranging from slight brownish color and loss of glossiness for the kraft lignin, to reddish brown, mossy or rumpled appearance for the Ca-lignin sulfonate. Changes were confined to a superficial film in the kraft lignin sample to perhaps a 0.5 mm layer in the Ca and NH_4-lignin sulfonate.

Test results are tabulated in Tables 5.8 through 5.10. Samples leached in acid maintained a pH ≅ 3.3 for the two-week exposure indicating little reaction with the acid. The pH of samples in the base dropped from pH = 11 to pH ≅ 7.5.

Invasion of CO_2 in the base samples could have caused some of the pH change, but only to a pH of about 8.3. The final pH values below 8 and the rapidity of the change in the unstirred bottles indicated that reaction between the base and the binder was a major cause of the pH decrease.

The pH changes with binder samples were quite different from those with briquette samples (Tables 5.6 and 5.7). The aggregate evidently was more reactive with the acid and base than the binder.

All samples in distilled water exhibited erratic pH changes for the first 48 hours, but after the fourth day, the pH values for all samples were constant at 6.5.

COD results indicated that kraft lignin binder behaves like AC-5, while NH_4-lignin and Ca-lignin exhibit much more COD leaching. Spectrophotometry was used as a confirmatory test to determine if the relative COD values were correct. There was a good correlation between COD and absorption at 280 nm in aqueous samples. Iso-octane extraction showed less absorbence in the UV. The partial solubility of lignin in iso-octane, and the apparent absence of asphalt in the samples rendered the extraction procedure uninformative at best.

In conclusion, kraft lignin binder behaves similarly to AC-5 binder for the tests performed. Ammonium and calcium lignin sulfonate binder in the present percent weight, binder form and manner of preparation, appear to be subject to high loss from the exposed surface area in leaching, followed by a wrinkled deformation of the exposed surface area.

The maximum amount of leaching (up to 3 mg/cm^2) corresponds roughly to 0.005 cm^3/cm^2 of binder. Based on visual observation, perhaps one third of the material in the affected surface layer is actually leached, leaving behind a wrinkled, brown residue. It is estimated that the affected layer is about $0.005\ cm/1/3 \cong 0.15$ mm in thickness. The reaction did not proceed very far during the two week experiment.

Fourth Test Series

The qualitative results of this series may be summarized as follows:

1. All samples unexposed to 60 hours of UV treatment and leached in water demonstrate no evidence of a discolored (brown) leachate. The exposed surfaces show no signs of any physical disturbance (cracking, lumping) or physical discolorations (Table 5.12).

2. All unexposed (to 60 hours UV) samples leached in .001 N NaOH solution (with the exception of the AC-5 asphalt cement control) show signs of "aging" after 5 days, as demonstrated by a browning and wrinkling of the exposed surface. The wrinkling is probably due to swelling of the lignin and subsequent leaching of lignin from the surface layer. The brown color in the leachate is due to the release of lignin from the exposed surface area into the surrounding aqueous solution. The discoloration of the leachate coincides (in time) with the aged sample surface appearance (Tab. 5.11).

3. All samples exposed to UV (GE 1F8 lamp) after 60 hours developed an "aged skin" over the exposed surface area. This was = 0.5 mm in depth. Samples exposed to base exhibited a browning of the leachate after 2 days and a pronounced aged appearance at the exposed surface after one day. Those samples leached in distilled water exhibit a slight browning of their exposed surface area, but no browning of the leachate occured even after 2 weeks.

For the limited tests performed, one could conclude that leaching or UV exposure causes a "skin" to develop over the exposed surface area. For the times of exposure used, the underlying material did not appear to change. The skin may not be an ultimate condition, but continued exposure might eventually "age" the full depth of material. However, for the tests conducted, surface changes occurred rapidly during the first 24-72 hours and then more slowly for the remainder of the two-week period.

This test series was qualitative in nature and was thus very limited in laying a factual and numerical basis for prediction. Its value was two-fold:

Table 5.8. Results of kraft lignin binder samples in Test Series No. 3

Days Leaching	Acid Leachate				In Basic Leachate				In Water Leachate			
	pH	COD	C/S	ABS	pH	COD	C/S	ABS	pH	COD	C/S	ABS
1	3.0	25	.7	-	11.2	25	.65	-	6.0	17	.45	-
7	3.0	24	.7	-	9.5	27	.7	-	7.0	19	.5	-
9	3.0	25	.7	-	8.7	29	.75	-	7.0	21	.55	-
13	3.0	26	.7	-	7.5	29	.75	-	6.9	21	.55	-
14	3.0	26	.7	.002	7.5	31	.8	.007	6.8	21	.55	.002

Notes:
Binder Sample = 30% kraft lignin with 70% AC-5.
COD = Concentration of organic matter/l solution (mg/l).
ABS = Absorbance at 280 nm.
C/S = Organic matter (mg) in leachate per area of exposed surface (mg/cm^2).
COD, C/S, ABS also refer to Tables 5.9 and 5.10.

Table 5.9. Results of 100% AC-5 control binder samples in Test Series No. 3.

Days Leaching	In .001 N HCl (Acid)				In .001 N NaOH (Base)				In Distilled H_2O			
	pH	COD	C/S	ABS	pH	COD	C/S	ABS	pH	COD	C/S	ABS
1	2.8	23	.6	-	11.2	0.0	0.0	-	6.0	16	.4	-
7	2.9	23	.6	-	9.0	23	.6	-	6.2	17	.45	-
9	2.9	23	.6	-	8.3	25	.65	-	6.0	17	.45	-
13	2.9	23	.6	-	7.9	25	.65	-	6.0	17	.45	-
14	2.9	23	.6	.002	7.9	29	.75	.002	6.0	17	.45	.002

See Notes for Table 5.8.

Table 5.10. Results of Test Series No. 3 for binder samples with 30 percent lignin.

Days Leaching	30% Ammonium Lignin Sulfonate in AC-5								30% Calcium Lignin Sulfonate in AC-5							
	In Acid				In Base				In Acid				In Base			
	pH	COD	C/S	ABS	pH	COD	C/S	ABS	pH	COD	C/S	ABS	pH	COD	C/S	ABS
1	2.9	0	0	-	11.2	-	-	-	2.8	-	-	-	11.2	85	2.2	-
7	3.0	27	.7	-	9.7	-	-	-	3.0	-	-	-	9.0	116	3.0	-
9	3.0	27	.7	-	9.1	39	1.0	-	2.9	39	1.0	-	8.0	116	3.0	-
13	3.0	27	.7	-	7.8	39	1.0	-	2.9	39	1.0	-	7.2	116	3.0	-
14	3.0	27	.7	0.15	7.8	41	1.05	0.2	2.9	39	1.0	0.2	7.2	120	3.1	1.2

See Notes for Table 5.8.

Table 5.11. Results of fourth test series binder samples exposed to U.V. radiation.

	4% Sulfur 26% NH_4-Lignin 70% AC-5		4% Sulfur 26% Ca-Lignin 70% AC-5		Acid Pretreated NH_4-Lignin Sulfonate		30% kraft lignin with 70% AC-5		100% AC-5
	H_2O	Base	H_2O	Base	H_2O	Base	H_2O	Base	H_2O
Δ Time days before browning of leachate	no browning after 2 weeks	2 slight	no browning after 2 weeks	2 slight	no browning after 2 weeks	2 slight	no browning after 2 weeks	2 slight	-
Δ Time days before aged appearance	2 slight aging	1	2 slight aging	1	2 slight aging	1	2 slight aging	1	no wrinkling

Table 5.12. Results of fourth test series binder samples not exposed to U.V. radiation.

	4% Sulfur 26% NH_4-Lignin 70% AC-5		4% Sulfur 26% Ca-Lignin 70% AC-5		Acid Pretreated NH_4-Lignin Sulfonate		30% Kraft Lignin with 70% AC-5		100% AC-5
	H_2O	Base	H_2O	Base	H_2O	Base	H_2O	Base	H_2O
Δ Time days before browning of leachate	no browning after 2 weeks	5	no browning after 2 weeks	6	no browning after 2 weeks	5	no browning after 2 weeks	5	no browning after 4 weeks
Δ Time days before appearance of surface	no evidence after 2 weeks	5	no evidence after 2 weeks	5	no evidence after 2 weeks	5	no evidence after 2 weeks	5	no evidence after 4 weeks

1. it does say something about the lignin binder structure upon simulated environmental exposure; i.e., the most sensitive part of the binder-lignin sample is the top .5 mm below the exposed surface, and

2. in terms of relative behavior in response to environmental exposure, the different samples in this series exhibited very similar changes in appearance in time.

In previous tests, 30% kraft lignin in AC-5 binder showed chemical characteristics similar to the AC-5 control. Thirty percent kraft lignin in AC-5 sample binder was one of the samples in this series. Relatively similar gross physical changes in time may point to similar chemical characteristics in terms of the experiments performed in the previous series.

Field Exposure Tests

A limited exposure experiment was conducted by Matrecon, Inc. with laboratory prepared samples. Briquets with a range of lignin-asphalt ratios as binders were exposed to the intense temperature and sunlight of Indio, California. As shown in Table 5.13, after 7.5 months, there was no significant change in air flow rates. The viscosity of the binder, however, did increase during the time of exposure and appears to be directly related to the intensity of exposure. However, it appears that any difference between mixtures containing only asphalt and those with lignin was insignificant.

Table 5.13. Lignin/AC-5 briquets exposure[a] tests at Indio, California.

Briquet Serial No.	130	131	132
Indulin AT:AC-5 (By Wt.)	0:100	20:80	40:60
Air-flow rate @ 0.25 in H_2O, ml/min			
Briquets, before exposure	21	41	43
Briquets, after exposure	22	38	46
Core[b]	<1	<1	-[c]
Viscosity of extracted binder @ 0.001 sec^{-1}, MP			
Before exposure[d]	1.4	1.3	1.4
After exposure, top	11.0	10.0	10.0
After exposure, middle	5.4	6.8	6.6
After exposure, bottom	4.5	5.4	6.3

[a] Four-inch (102 mm) diameter briquets exposed for 7.5 months (Sept. 77-April 78).
[b] One-inch (25.4 mm) diameter core taken from exposed briquet.
[c] Broken during coring.
[d] Extracted from slice taken at bottom of briquet.

CHAPTER VI. PAVEMENT DESIGN AND PERFORMANCE PREDICTIONS

A. Mixture Characterization for Pavement Analysis

In order to evaluate lignin asphalt mixtures as compared to conventional asphalt concrete, a series of diametral tension tests were conducted. Previous work has shown this test to be suitable for evaluation of new materials and is particularly sensitive to the binder. Both repeated load and static tests have been used effectively, although repeated load modulus and fatigue tests are more common. In this study, all specimens were 4 in. (102 mm) diameter by 2.5 in. (63.5 mm) high cylinders prepared by Hveem kneading compaction.

Figure 6.1 illustrates the general testing scheme and shows the key variables used. Temperatures and moisture conditioning were controlled by storing specimens in an environmental chamber and conducting the test outside the chamber within a limited (2 min.) time. Response to the various applied loads was measured by dual transducers coupled to a strip chart recorder.

The tests discussed in the following pages were aimed at comparing L/A mixtures to those with AR-4000 (control) and AC-5 asphalt binders. These results were then used to characterize the mixtures for pavement analysis and to illustrate relative behavior for a range of conditions.

Figures 6.2 through 6.5 show the resilient modulus, M_R, for the three mixtures being discussed. Variables included temperature, load, load duration, and load frequency. In each case, the AR-4000 mixtures were typically highest in M_R and the AR-5 mixtures were lowest, with the L/A in between. All of these results were for specimens that were freshly fabricated (at least 24 hours following compaction).

Because of the general sensitivity to water for most asphalt mixtures, as well as the concern for L/A mixtures, specimens were also subjected to vacuum saturation and freeze-thaw tests. The procedures were essentially those developed by others and have been shown to effectively predict potential water damage to in-service pavements. Figure 6.6 shows that L/A mixtures behave much like asphalt concrete when subjected to these conditions.

As discussed earlier, indirect tensile strength, σ_t, was used as an ultimate strength test rather than Hveem cohesion. In this test, the loading is similar to that for M_R, except that a constant load rate is applied (2 in/min) (50.8 mm/min) until failure occurs. Figure 6.7 shows the strength of dry mixtures over a range of temperatures, while Figure 6.8 indicates the relative effect of vacuum saturation and repeated freeze-thaw. As with the M_R tests, σ_t for L/A mixtures was consistent with results for pure asphalt mixtures.

Fatigue tests were also conducted using the diametral tension approach. A summary of results shown in Figure 6.9 indicates that L/A mixtures should perform approximately the same as AR-4000 mixtures over a reasonable range of repeated loads.

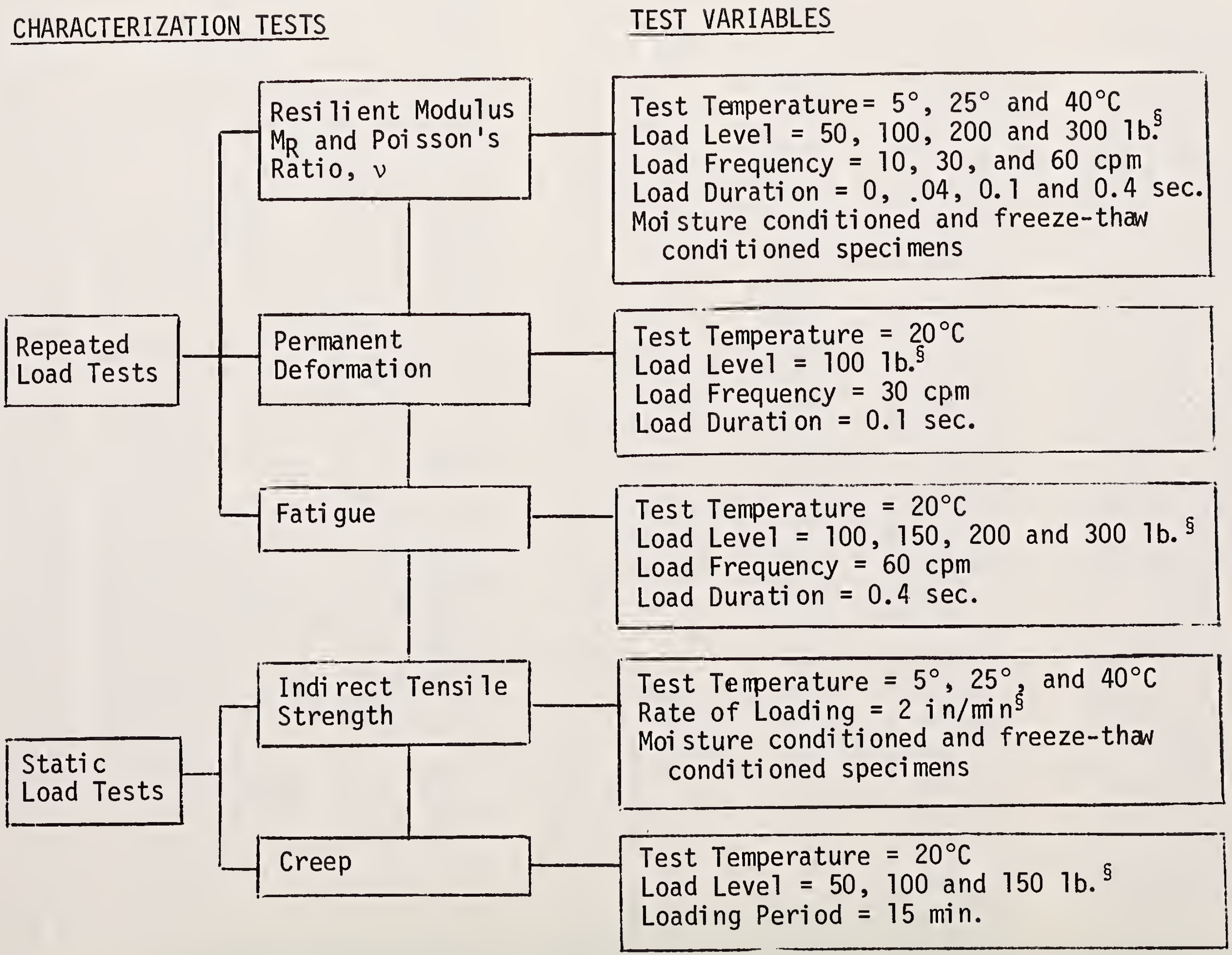


Figure 6.1. Mixture characterization testing scheme for pavement analysis.

§To convert to: kg: lbs x .45
mm: in. x 25.4

Again using repeated loading, the susceptibility of the several mixtures to permanent deformation is shown in Figure 6.10. As with previous results, it appears that L/A mixtures fall somewhere between those with asphalt binders.

B. Pavement Design Analysis

In recent years, the changes as a result of heavier wheel loads, higher traffic levels and the recognition of various distress modes contributing to pavement failure have led to the search for more rational pavement design methods. One such method is to represent the pavement as a multi-layered system with the pavement material characterized as ideally elastic, plastic, elastic-plastic or visco-elastic.

The multi-layered elastic model, the CHEV5L (1) computer program, developed by the California Research Corporation was used to determine various component stresses and strains in a theoretical three dimensional elastic layered system. Each hypothetical pavement layer was assigned a modulus value as required by the stress state and a Poisson's ratio.

In the analysis, 27 hypothetical cases of pavements of different combinations of surface and base thicknesses, and load were evaluated.

Using the criteria that the location of maximum horizontal tensile strain (ε_t) is at the bottom of the surface layer and maximum vertical compressive strain (ε_v) on top of the subgrade, and that these could be at the midpoint between dual wheels or at the center of one of the dual wheels depending on pavement structure and load levels, maximum strains related to fatigue (ε_v) or rutting (ε_t) at those two locations were checked when all the moduli were compatible with those required by the stress states.

The pavement analysis was limited to the case of lignin extended asphalt binder (L/A) and characterization of these materials included both static and dynamic loading. Table 6.1 is a summary of final moduli used for base and subgrade layers for a range of cases used in this analysis. Table 6.2 includes a summary of maximum ε_t and ε_v values.

These results show that the maximum horizontal tensile strain appeared to occur at the center of one of the dual wheels in all cases, while maximum vertical compressive strain was critical at the midpoint of dual wheels. To facilitate converting the horizontal tensile or radial strains to radial stresses or vice versa, from the computer outputs, various tensile strains were plotted against tensile stresses for various mixes (Fig. 6.11). The relationships appeared to be linear in all cases.

C. Development of Design Curves

From the results of this study, two types of thickness design curves were developed. One is based on tensile strain at the bottom of the surface layer (Fig. 6.12) and the other is based on vertical strain at the bottom of the subgrade (Fig. 6.13). Using limiting strain values or limiting number of load applications as a criterion, thickness designs can be developed from these charts.

Table 6.1. Summary of final moduli for base and subgrade layers determined at two critical locations.

INPUT VARIABLES§				MR. USED TO EVALUATE POINTS BELOW CENTER OF ONE WHEEL (psi)§			MR USED TO EVALUATE POINTS ALONG MIDPOINT BETWEEN TWO WHEELS (psi)§		
Material	Load.Lb.	Stress,psi	Surface,t	E_1 (psi)	E_2 (psi)	E_3 (psi)	E_1 (psi)	E_2 (psi)	E_3 (psi)
AC 5	4500	57.30	3 in.	12,000	6,500	3,400	12,000	6,500	3,400
			6	7,000	5,500	3,500	7,500	5,500	3,500
			9.5	5,500	4,500	3,500	5,500	4,500	3,500
	6000	76.39	3	13,000	6,500	3,300	12,500	7,000	3,300
			6	8,000	6,000	3,400	8,500	6,000	3,400
			9.5	6,000	5,000	3,400	6,000	5,000	3,400
	7500	95.49	3	14,000	6,000	3,300	13,000	7,000	3,300
			6	9,000	6,000	3,300	9,000	6,000	3,300
			9.5	6,000	5,000	3,200	6,000	5,000	3,200
L/A	4500	57.30	3	11,000	7,000	3,500	11,000	7,000	3,500
			6	5,500	5,000	3,500	7,000	5,500	3,500
			9.5	4,500	4,000	3,500	4,500	4,000	3,500
	6000	76.39	3	11,000	7,000	3,500	12,000	7,000	3,500
			6	7,500	6,000	3,500	7,500	6,000	3,500
			9.5	5,500	4,500	3,500	5,500	4,500	3,500
	7500	95.49	3	13,000	7,000	3,500	13,000	7,000	3,500
			6	8,000	6,000	3,500	8,000	6,000	3,500
			9.5	6,000	5,000	3,500	6,000	5,000	3,000
AR-4000	4500	57.30	3	11,500	6,500	3,500	11,500	6,500	3,500
			6	7,000	5,000	3,500	7,000	5,000	3,500
			9.5	5,000	4,000	3,500	5,000	4,000	3,700
	6000	76.39	3	12,000	7,000	3,500	12,000	7,000	3,500
			6	8,000	6,000	3,500	8,000	6,000	3,500
			9.5	5,500	4,500	3,500	5,500	4,500	3,500
	7500	95.49	3	13,000	7,500	3,500	13,000	7,500	3,500
			6	8,500	6,000	3,500	8,500	6,000	3,500
			9.5	6,000	5,000	3,500	6,000	5,000	3,500

§To convert to: MPa: psi x 6.894×10^{-3}, mm: in. x 25.4, kg: lbs x .45.

Table 6.2. Summary of maximum strains at bottom of surface layer and on top of subgrade at two critical locations.

WHEEL LOAD, LB.[§]	PAVEMENT NO.	RADIAL STRAIN 1×10^{-6} in/in[§]		VERTICAL STRAIN 1×10^{-6} in/in.[§]	
		POINT AT CENTER OF ONE WHEEL	MIDPOINT BETWEEN TWO WHEELS	POINT AT CENTER OF ONE WHEEL	MIDPOINT BETWEEN TWO WHEELS
4500	AC 1	424.0	-40.9	-1921.8	-2068.8
6000	AC 2	270.8	161.8	- 928.5	-1010.0
7500	AC 3	159.9	141.7	- 470.2	- 513.2
4500	AC 4	555.0	-58.8	-2591.4	-2786.0
6000	AC 5	355.4	210.7	-1266.5	-1376.6
7500	AC 6	212.1	187.8	- 645.6	- 704.4
4500	AC 7	684.6	-75.7	-3221.4	-3467.8
6000	AC 8	440.6	263.6	-1614.4	-1752.2
7500	AC 9	268.1	238.2	- 834.1	- 909.4
4500	L/A 10	322.2	46.2	-1619.6	-1760.0
6000	L/A 11	189.2	130.5	- 696.0	- 763.0
7500	L/A 12	105.9	97.4	- 323.7	- 348.6
4500	L/A 13	422.4	57.3	-2150.8	-2335.0
6000	L/A 14	247.0	171.3	- 942.1	-1024.2
7500	L/A 15	139.6	128.2	- 444.1	- 478.8
4500	L/A 16	519.4	66.8	-2676.4	-2903.0
6000	L/A 17	307.2	212.5	-1181.5	-1284.4
7500	L/A 18	173.3	158.8	- 563.5	- 597.4
4500	AR 19	292.8	63.4	-1531.6	-1666.2
6000	AR 20	166.4	120.3	- 635.0	- 690.8
7500	AR 21	91.8	84.0	- 292.6	- 303.6
4500	AR 22	384.7	79.1	-2035.6	-2212.6
6000	AR 23	217.8	156.1	- 859.9	-935.8
7500	AR 24	121.7	112.4	- 397.4	- 425.0
4500	AR 25	470.5	90.3	-2529.7	-2746.8
6000	AR 26	271.0	194.0	-1078.1	-1173.2
7500	AR 27	151.20	139.4	- 504.4	- 539.4

[§] To convert: kg: lbs x .45
mm: ins. x 25.4

D. Determination of Material Equivalencies

For determining material equivalencies between L/A mix and conventional asphalt mixes, all the 18 kips (80.7 x 10^3 N) axle load curves in Figures 6.12 and 6.13 can be utilized. Using the equal number of load repetitions concept, maximum allowable stresses and strains for 10^4, 10^5, 10^6 and/or 10^7 load applications were determined from data developed in Figure 6.14 and those from the AASHO Road Test (2) in Table 6.3. The required or minimum surface layer thicknesses to prevent fatigue or rutting failures were then determined from Figures 6.12 and 6.13.

Table 6.3. Limiting vertical strain on top of subgrade.

Load Applications	Compressive Strain ε_v on Top of Subgrade 1×10^{-6} in/in(x 25.4 mm/mm)
10^5	1,050
10^6	650
10^7	420
10^8	260

Tensile stresses obtained from Figure 6.14 were converted to tensile strains by using the following formula based on theory of elasticity of biaxial stress states (1):

$$\varepsilon_x = \frac{1.93\sigma_x}{M_R}$$

where ε_x = tensile or radial strain
σ_x = tensile stress
M_R = resilient modulus

Material equivalency charts based on fatigue criteria are presented in Figures 6.15. Similar results were obtained based on rutting criteria. From these figures, it appeared that material equivalencies between L/A mix and conventional asphalt mixes were as follows:

1 inch of L/A mix = 1.3 ins. (33 mm) of AC-5 mix
1 inch of L/A mix = 0.9 ins. (23 mm) of AR-4000 mix

These results were based on both the fatigue and rutting criteria.

E. Pavement Performance Predictions

Even though the mixture characteristics of the lignin-asphalt or modified lignins are quite satisfactory, there is some uncertainty as to the performance of these new pavement materials. Several approaches or computer programs can be used to predict the performance of such materials.

The Vesys IIM as developed under FHWA contract is one program that is capable of being able to predict the performance of pavements which might be built in the future using new materials such as lignin-asphalt, for which no construction experience is available.(3).

The outputs of the Vesys IIM include viscoelastic characterization of materials, prediction of fatigue cracking, rut depth, slope variance, present serviceability index (PSI) with time and service life. The most important departure of Vesys IIM from more conventional analytical methods is in the material characterization.

The material characterization includes creep compliance curves for viscoelastic responses, permanent deformation potential for each layer, and fatigue coefficient and exponent commonly used for asphalt concrete characterization with respect to temperature.

In this study, the Vesys IIM was used to predict the performance of the lignin-asphalt (L/A) mixture which was then compared to conventional asphalt concretes in identical conditions. Inputs to the program included:

1. Surface Geometry - thicknesses of surface and base courses.

2. Traffic Loading - radius of loaded area, intensity and duration of loads, number of 18 kip (80 x 10^3 N) equivalent axle loads per day.

3. Environmental Variables - mean temperature of the surface layer and moisture content in the subgrade.

4. Mechanical Properties of Materials

    a. creep, fatigue and permanent deformation of surface layer materials

    b. stress, strain and permanent deformation of untreated aggregate base

    c. creep and permanent deformation of the subgrade.

F. Results of Performance Prediction

From the described inputs, the Vesys IIM program was used to give as outputs three distress parameters; namely, rutting, cracking and roughness, and present serviceability index which represents the level of performance of a given pavement.

Rut Depth

In the rut depth model, rutting is primarily a function of the laboratory determined permanent deformation characteristics of the pavement materials. The predicted rut depths, based on the permanent deformation accumulative damage of the three layer system of various surface course thicknesses made of AR-4000, L/A and AC-5 mixes, are summarized for comparison in Table 6.4

Table 6.4. Summary of rut depth prediction results of various mixes with various thicknesses.

Material	Run No.	Surface Layer Thickness, in.§	Rut Depth, In.§ 1 yr.	5 yr.	10 yr.
AC-5 Mix	1	3	0.23	0.45	0.62
	2	6	0.50	0.10	1.57
	3	9.5	0.66	1.47	2.12
L/A Mix	4	3	0.18	0.35	0.47
	5	6	0.39	0.82	1.15
	6	9.5	0.50	1.08	1.52
AR-4000 Mix	7	3	0.13	0.23	0.30
	8	6	0.24	0.48	0.66
	9	9.5	0.31	0.62	0.86

Table 6.5. Summary of roughness prediction results of various mixeswith various thicknesses.

Material	Run No.	Surface Layer Thickness, in.§	Slope Variance, SV, Radian x 10^{-6} 1 yr.	5 yr.	10 yr.
AC-5 Mix	1	3	1.05	4.18	7.83
	2	6	4.52	21.71	44.17
	3	9.5	8.32	41.85	86.96
L/A Mix	4	3	0.69	2.56	4.65
	5	6	2.75	12.25	24.06
	6	9.5	4.91	22.84	45.81
AR-4000 Mix	7	3	0.33	1.09	1.88
	8	6	1.15	4.50	8.37
	9	9.5	1.90	7.88	14.98

[§] To convert to mm: in. x 25.4.

Table 6.6. Summary of fatigue cracking prediction results of various mixes with various thicknesses.

Material	Run No.	Surface Layer Thickness, in.§	Damage Index, 1 x 10^3 1 yr.	5 yr.	10 yr.
AC-5 Mix	1	3	0.89	5.31	11.95
	2	6	0.76	4.56	10.25
	3	9.5	0.17	1.01	2.26
L/A Mix	4	3	0.63	3.79	8.52
	5	6	0.51	3.07	6.90
	6	9.5	0.11	0.64	1.44
AR-4000 Mix	7	3	1.59	9.55	21.49
	8	6	0.96	5.78	13.01
	9	9.5	0.16	0.94	2.12

Table 6.7. Summary of pavement performance prediction results of various mixes with various thicknesses.

Material	Run No.	Surface Layer Thickness, in.§	Serviceability Index 1 yr.	5 yr.	10 yr.
AC-5 Mix	1	3	3.86	2.91	2.21
	2	6	2.78	0.15	-2.37
	3	9.5	2.10	-1.84	-6.06
L/A Mix	4	3	4.03	3.32	2.81
	5	6	3.24	1.44	-0.08
	6	9.5	2.74	0.20	-2.17
AR-4000 Mix	7	3	4.23	3.84	3.54
	8	6	3.81	2.82	2.09
	9	9.5	3.53	2.20	1.19

§ To convert to mm: in. x 25.4.

and Figures 6.15 through 6.17. It appeared that rut depths in the surface layer of all mixes increased with increasing thickness. This is because in a thin surface layer such as 3 in. (76 mm), the base and subgrade layer materials selected in this study, which had a relatively high resistance to deformation, tended to assist the surface layer to resist the load and therefore decrease rutting. In contrast to the 3 in. (76 mm) layer, the 6 and 9.5 in (152 and 241 mm) surface layers being thicker, the underlying materials tended to have less influence and initially had to deform to a certain value under load before the base and subgrade could have any effect. In this study, if a softer base and subgrade compared to the surface layer were selected, the results would have been different and very likely rutting would decrease with increasing thickness.

Rut depths of all the pavements appeared to increase with time. The rut depths at various ages for pavements made of L/A mix seemed to be between the AC-5 and AR-4000 mixes of equal thickness.

Roughness

In the roughness model, roughness is defined as the variation of deformation along the longitudinal profile of the roadway. In this model accumulated rut depth at any time along the wheel path is assumed to vary as a result of material variability and varying construction practices, and roughness is expressed by the AASHTO definition of slope variance. The results of roughness predictions of various pavements aare summarized in Table 6.5. As in the case of rutting, the base and subgrade appeared to have a major influence on the roughness of the pavements with time. Roughness of all pavements increased with increasing thickness of the surface layer and time. The slope variances at various years of pavement service made of L/A mix appeared to be between the AC-5 and AR-4000 mixes of equal thickness.

Damage Index

The Vesys IIM model was used in this study to predict the fatigue damage at the bottom of the surface layer. This fatigue model predicts the number of load applications for crack initiation based on Miner's law. Basically the law states that the load repetitions that a pavement can withstand, is a function of the tensile strain and the fatigue properties of the asphalt material, K_1 and K_2. The percent fatigue consumption, or the number of applied loads divided by the computed number of allowable loads is one fatigue parameter (the damage index) that is output by the Vesys computer program. The other is the cumulative area that has cracked. In the computation of the damage Index, the magnitude of tensile strain at the bottom of the surface layer represents an important parameter because as the strains increase, the number of loads for crack initiation decreases.

Results of predicted cracking of various pavements are summarized for comparison in Table 6.6. These results indicate that pavements with surface course made of AR-4000 mix had undergone the most damage based on theory. The least damaged pavements were those with L/A mix as surface material. When fatigue curves based on stress of various mixes were converted to curves based on strain using theory of elasticity, the L/A mix appeared to have the best fatigue properties and AR-4000 had the lowest fatigue resistance between 10^3 and 10^5 load repetitions. From this, it appeared that less stiff mix performed better with respect to fatigue life based on strain. Being soft or less stiff, a mix such as AC-5 or L/A is more flexible and therefore has more tolerance to strain without fracture than AR-4000. With the above reasoning, the AC-5 being the softest or least viscous should have the best fatigue properties, however, this is not the case and may be due to the fact that the AC-5 used here with regard to composition is waxy and high in asphaltenes, consequently more brittle.

The cracking index appeared to decrease with increasing pavement thickness and increase with time in all cases. Being thicker, more strain can be tolerated in a pavement and therefore longer fatigue life.

Present Serviceability Index (PSI)

The PSI gives an indication of the rideability of the pavement, relating the user to the pavement condition. A reasonably accurate prediction of the PSI over the design is necessary to limit the loss of serviceability to a minimum value, this preventing excessive user costs and unsafe condtions.

The prediction of a pavement's serviceability index in Vesys is related to slope variance. Slope variance or roughness depends on the correlation of rut depths along the wheel path. The Vesys roughness model computes this correlation based on two pavement roughness properties.

Predicted loss in PSI for various pavement sections are summarized in Table 6.7 and Figures 6.18 through 6.20. These figures show the decline of serviceability index with time for all cases. The L/A mix appeared to have serviceability index values between those of AR-4000 and AC-5 mixes.

Summary

The rutting, roughness, fatigue cracking potential of lignin-asphalt pavement material were compared with that of conventional asphaltic concretes under a variety of surface layer thicknesses using the Vesys IIM computer program. The results indicated that lignin-asphalt mixtures appear to be superior to AC-5 asphalt concrete in reducing rutting, roughness and fatigue cracking and preserving a high serviceability index.

In this study, the base and subgrade were assumed to be elastic to simplify the comparison between surface course materials and thus the predictions were not entirely accurate representations of pavements. The results do provide some basis for comparison, however.

The use of the indirect tensile test was a modification in the present Vesys IIM procedure, and although it shows promise, the method should be thoroughly studied to investigate the input parameters related to fatigue cracking. Furthermore, computations of strain are questionable in the analysis of visco-elastic materials.

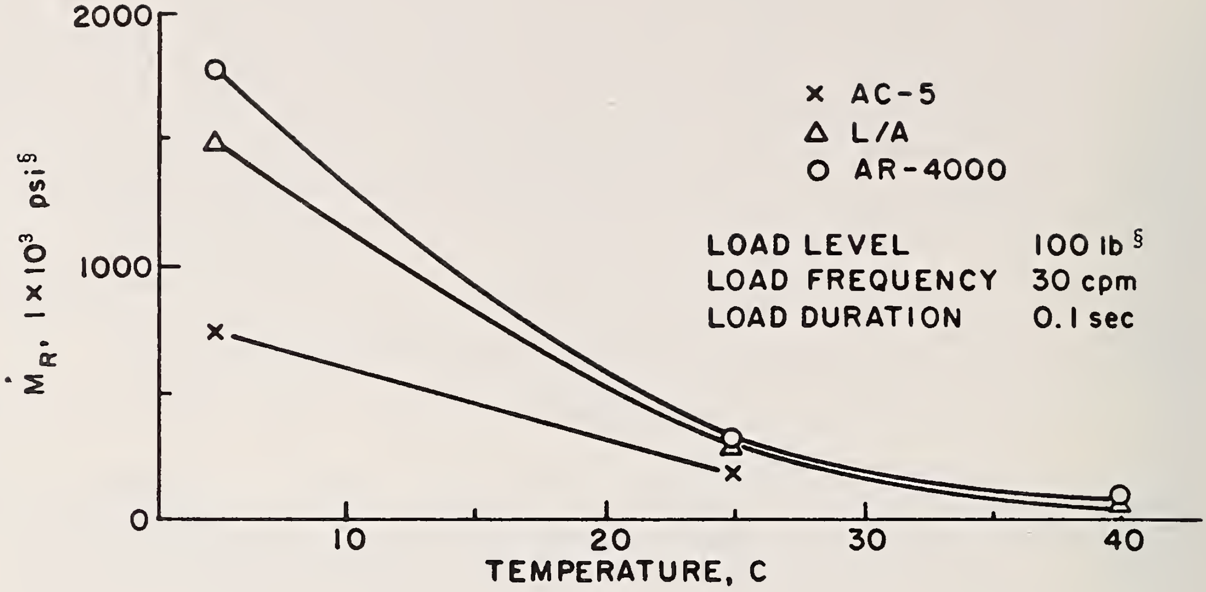


Figure 6.2. Effect of temperature on resilient modulus.

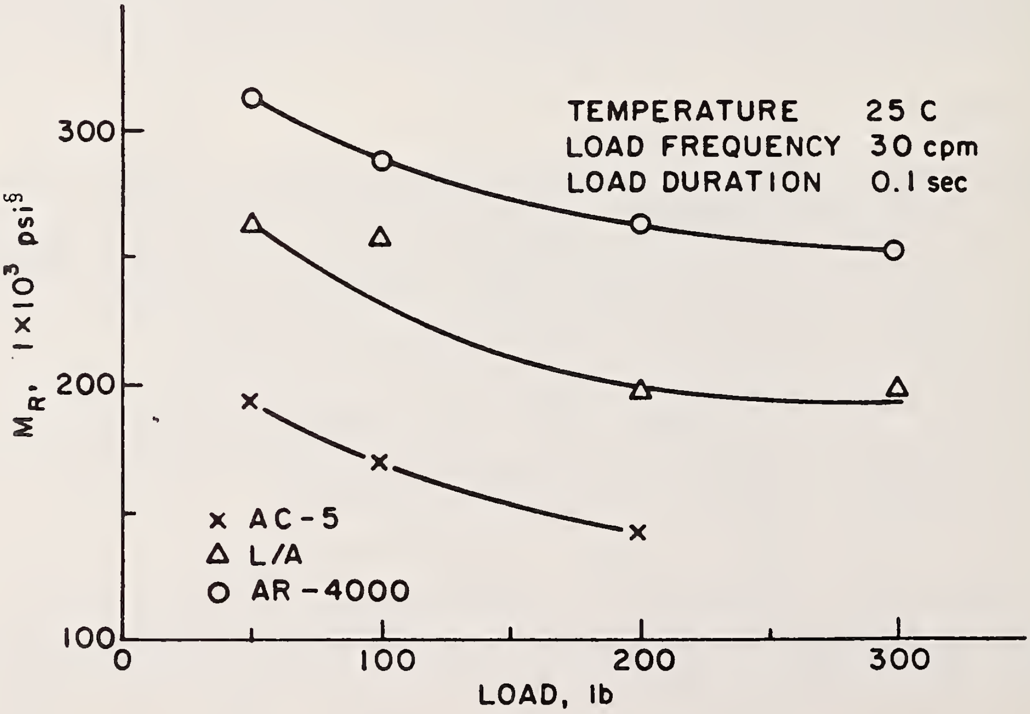


Figure 6.3 Effect of applied load on resilient modulus.

§To convert: to MPa: psi x 6.894×10^{-3}, to kg: lbs x .45.

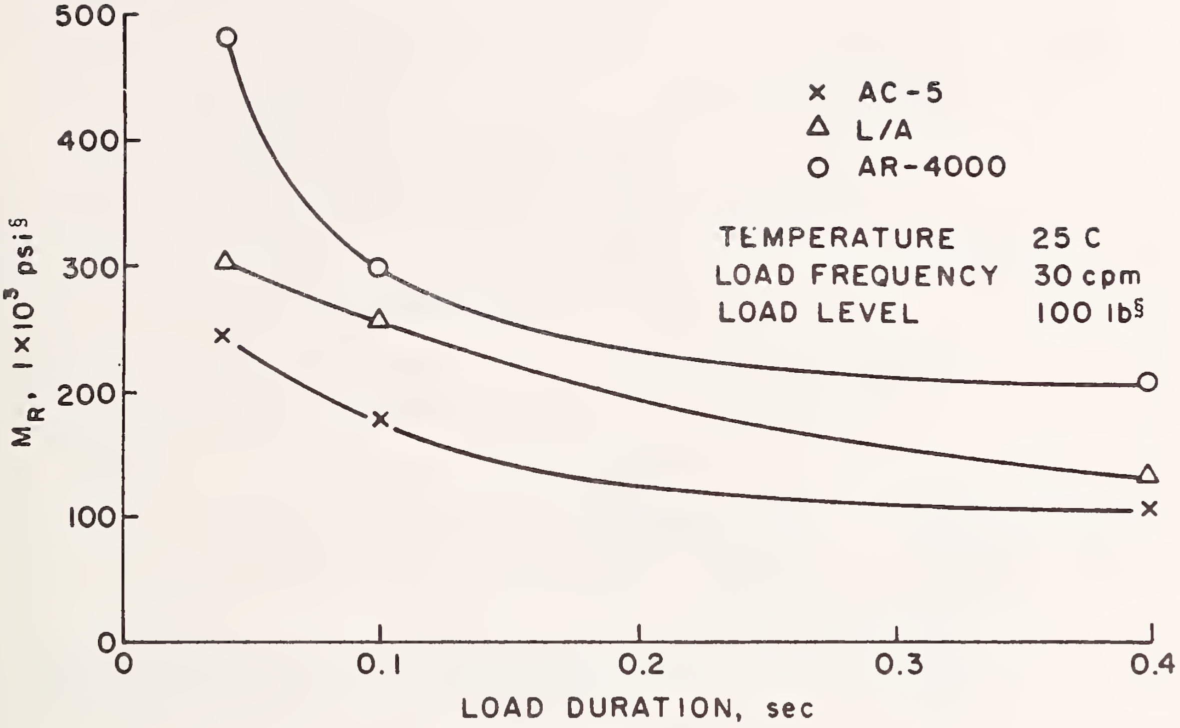


Figure 6.4. Effect of load duration on resilient modulus.

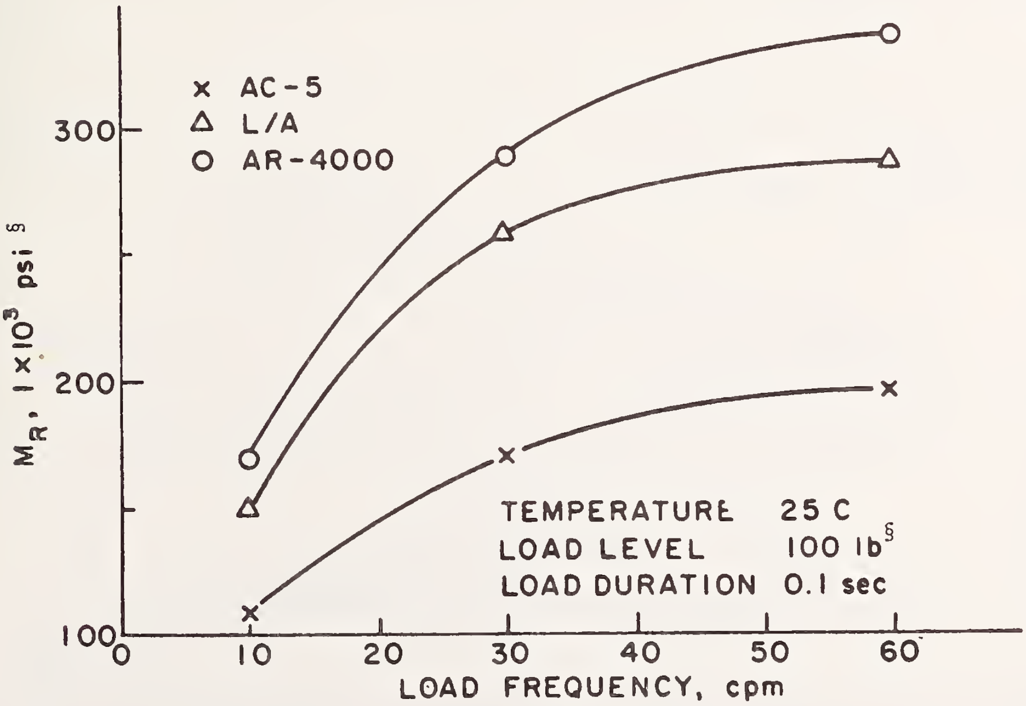


Figure 6.5. Effect of load frequency on resilient modulus.

§To convert: to MPa: psi x 6.894 x 10^{-3}, to kg: lb. x .45.

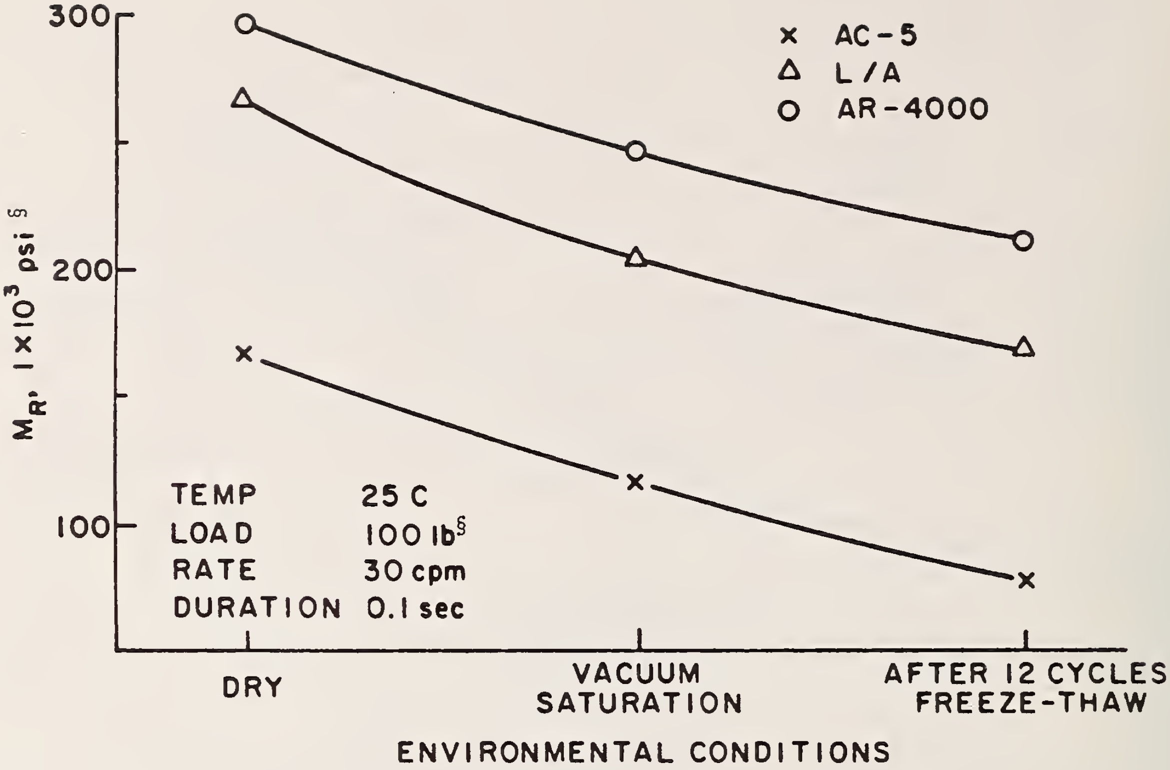


Figure 6.6. Effect of saturation and freeze-thaw cycles on resilient modulus.

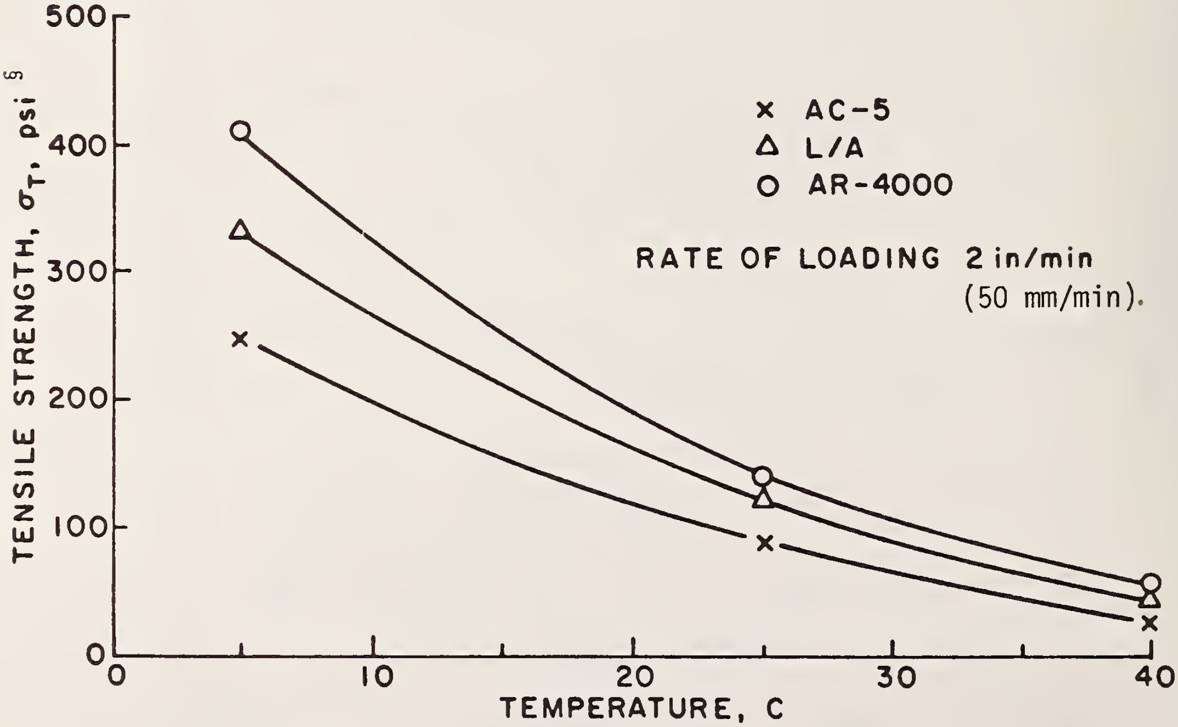


Figure 6.7. Effect of temperature on indirect tensile strength.

To convert: to MPa: psi x 6.894 x 10^{-3}, to kg: lbs x .45.

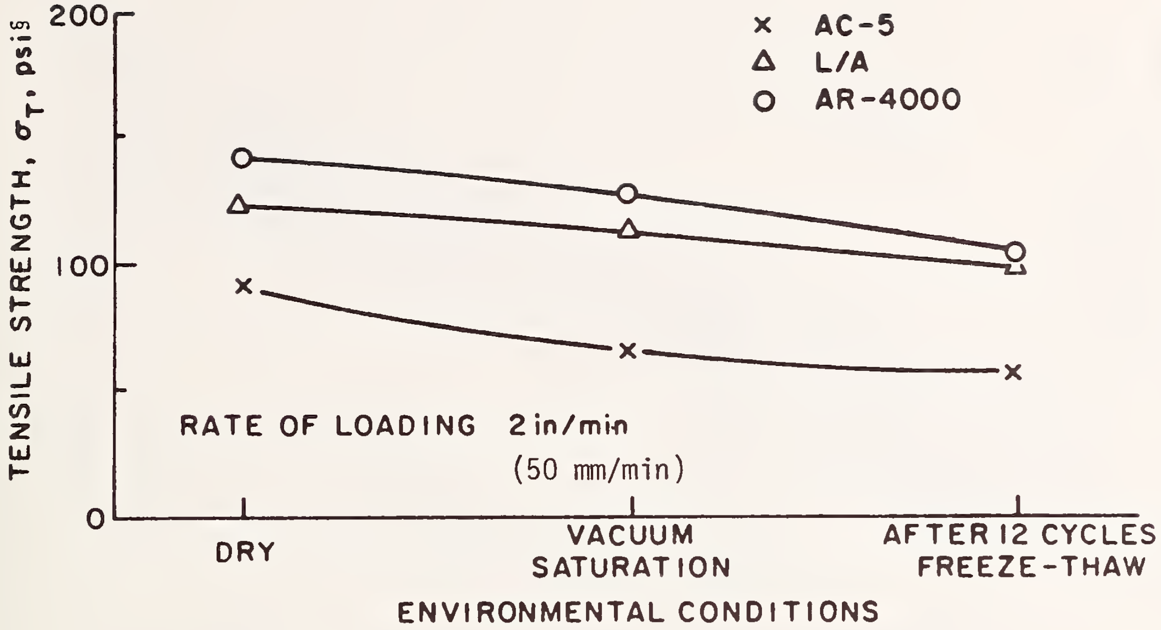


Figure 6.8. Effect of saturation and freeze-thaw cycles on indirect tensile strength.

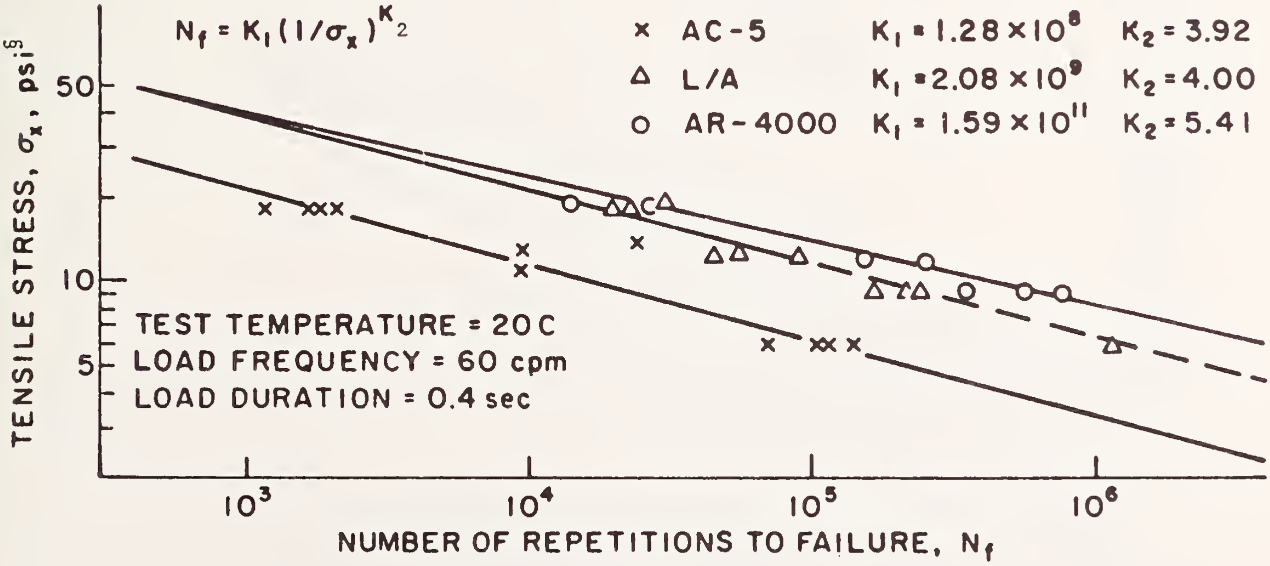


Figure 6.9. Fatigue response for various mixtures.

§To convert to MPa: psi x 6.894 x 10^{-3}.

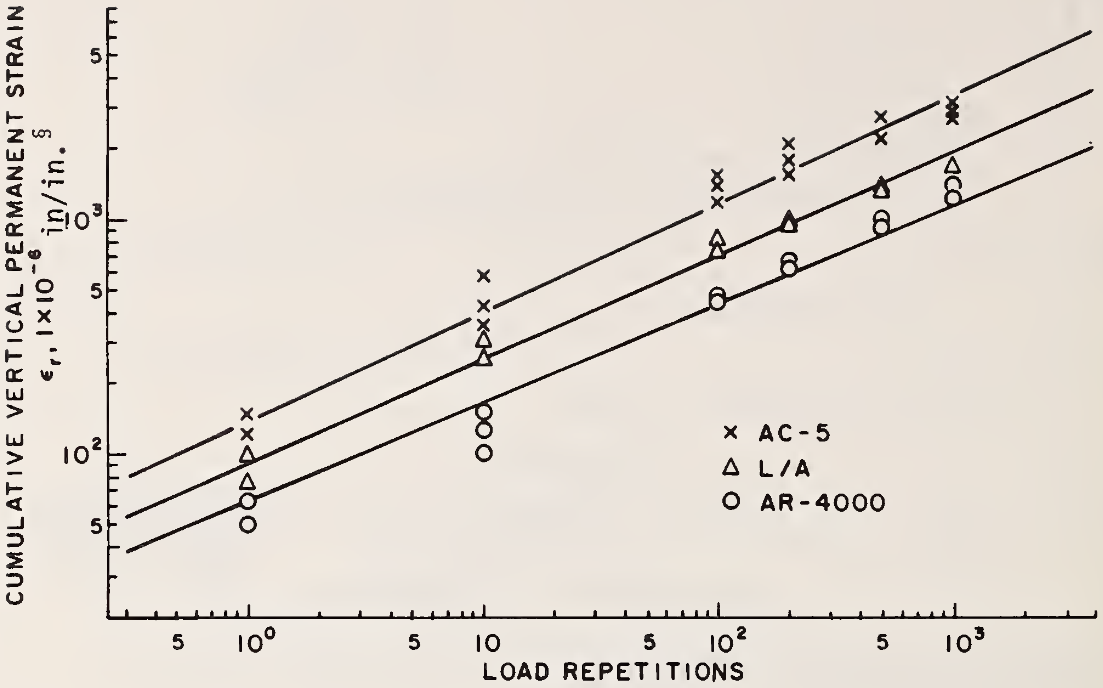


Figure 6.10. Effect of repeated loading on permanent strain.

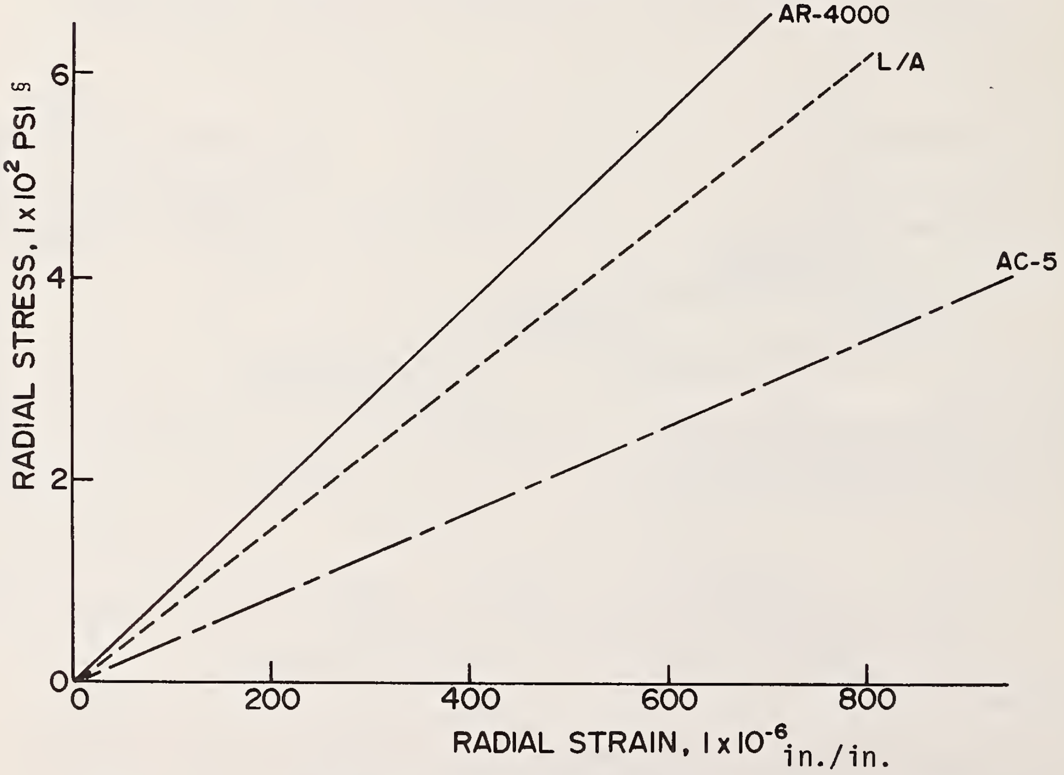


Figure 6.11. Relationship between radial strain and stress at the bottom of surface layer.

§To convert: to MPa: psi x 6.894 x 10^{-3}, to mm: in. x 25.4.

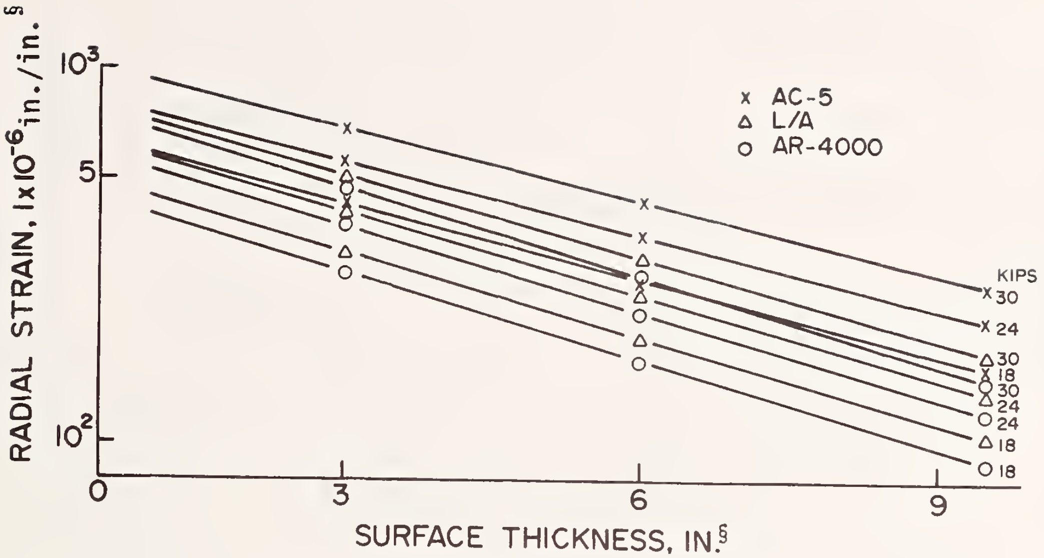


Figure 6.12. Relationships between radial strain at bottom of surface layer and required surface thickness to prevent fatigue failure of various mixes at various axle loads.

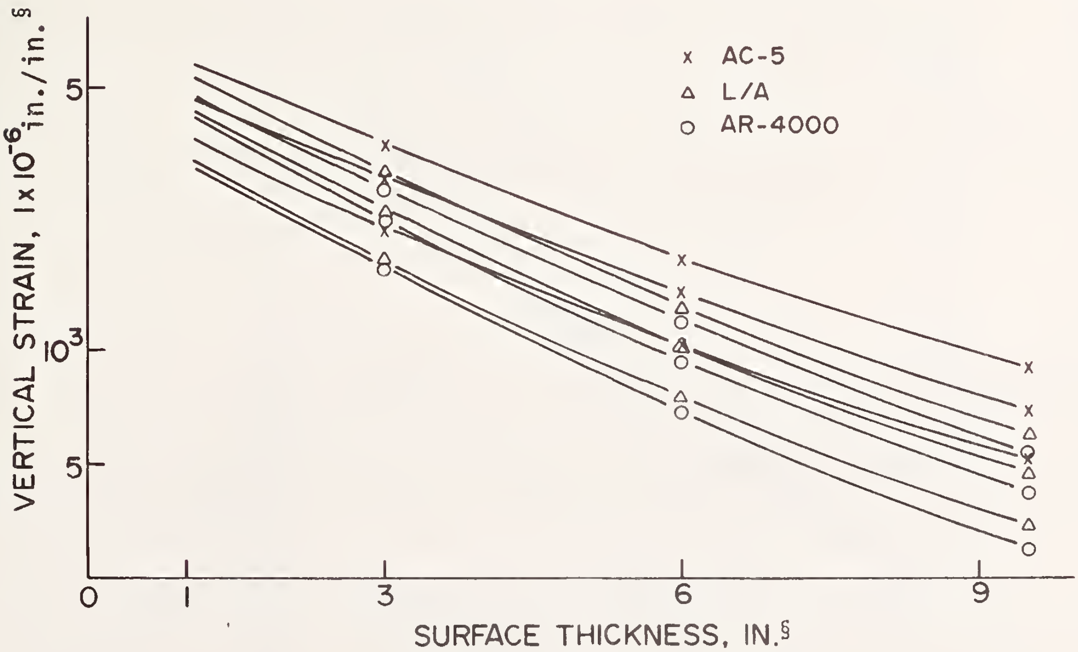


Figure 6.13. Relationships between vertical compressive strain on top of subgrade and required surface thickness to prevent rutting of various mixes at various axle loads.

§To convert to mm: in. x 25.4.

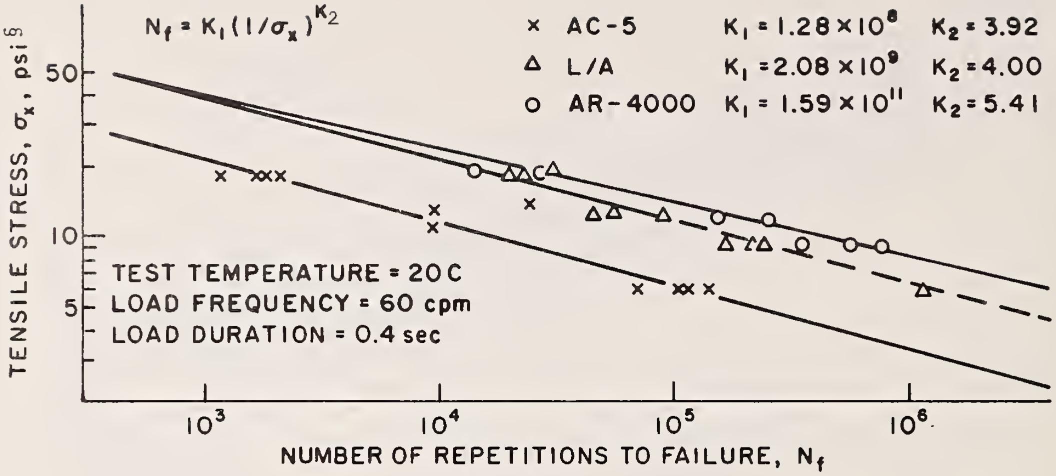


Figure 6.14. Fatigue responses for various mixtures.

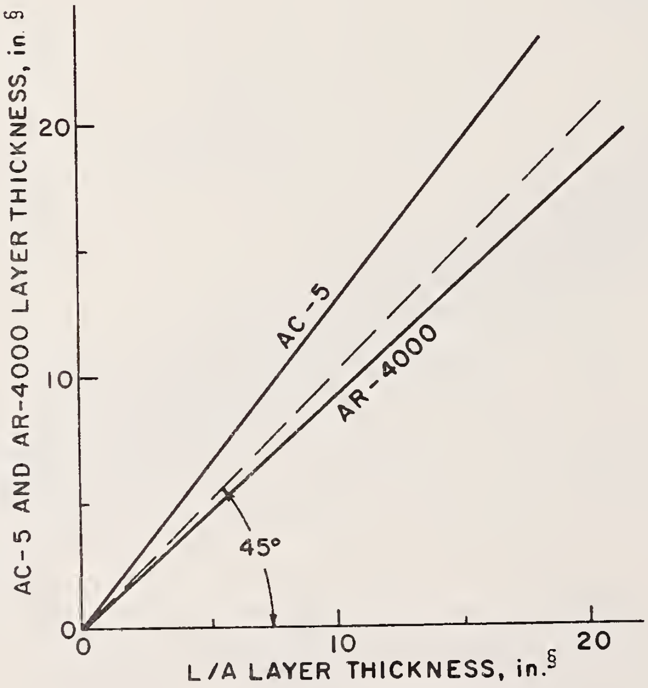


Figure 6.15. Layer equivalency.

Convert: to MPa: psi x 6.894 x 10^{-3}, to mm: in. x 25.4.

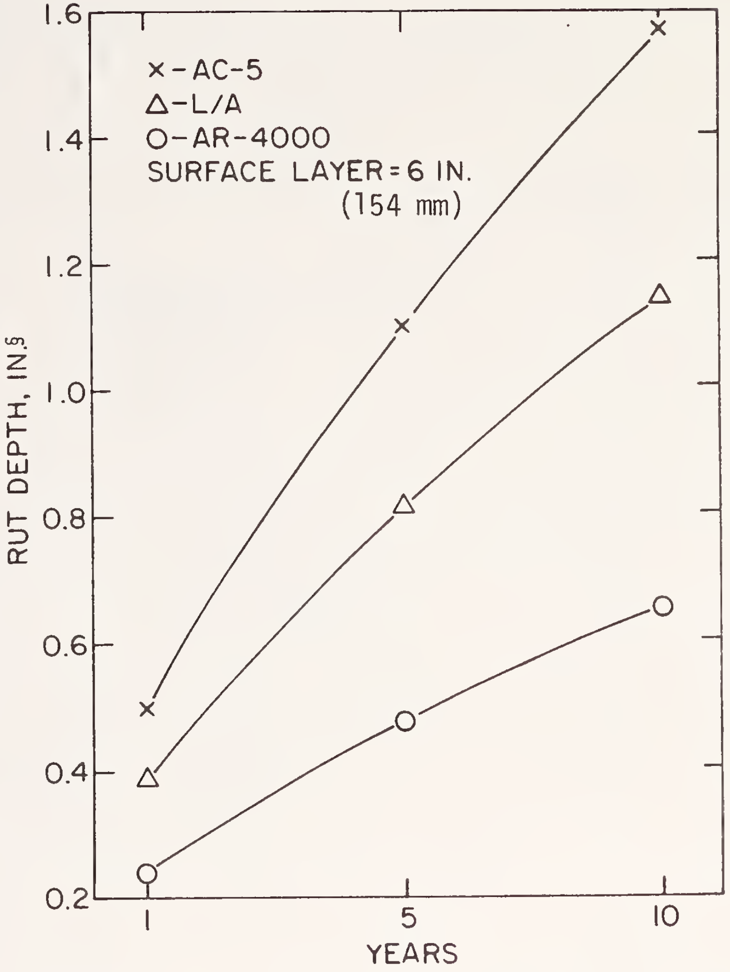


Figure 6.16. Relationships between predicted rut depth of surface layer of 6 in. (154 mm) made with various mixes and number of years.

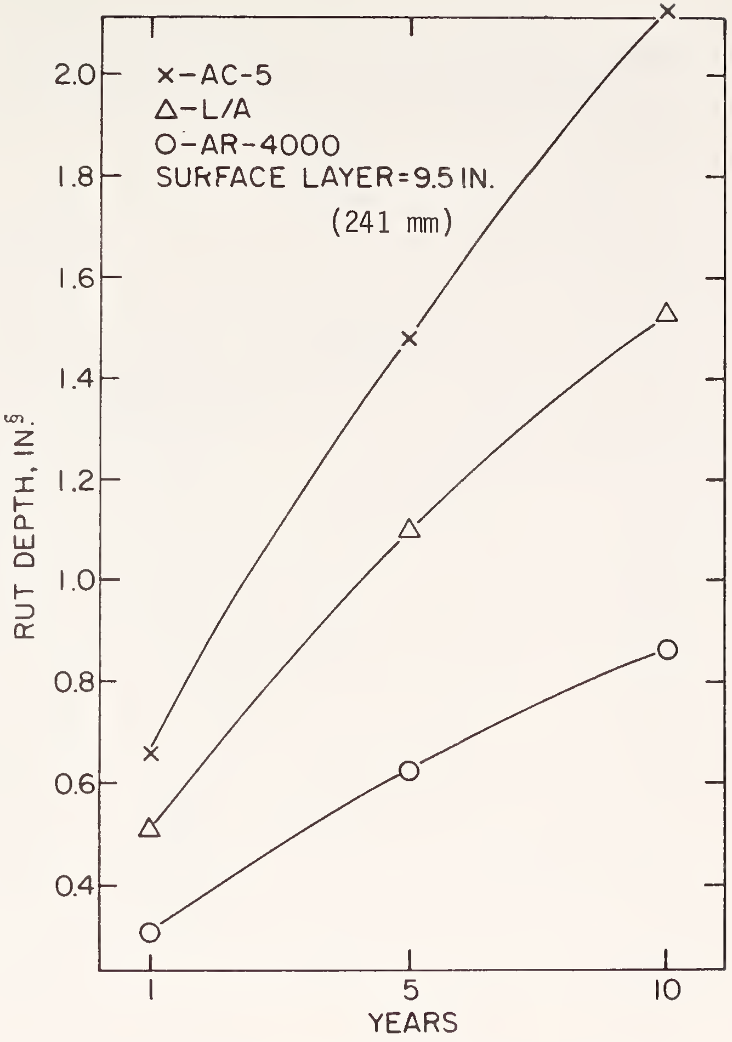


Figure 6.17. Relationships between predicted rut depth of surface layer of 9.5 in. (241 mm) made with various mixes and number of years.

[§] To convert to mm: in. x 25.4.

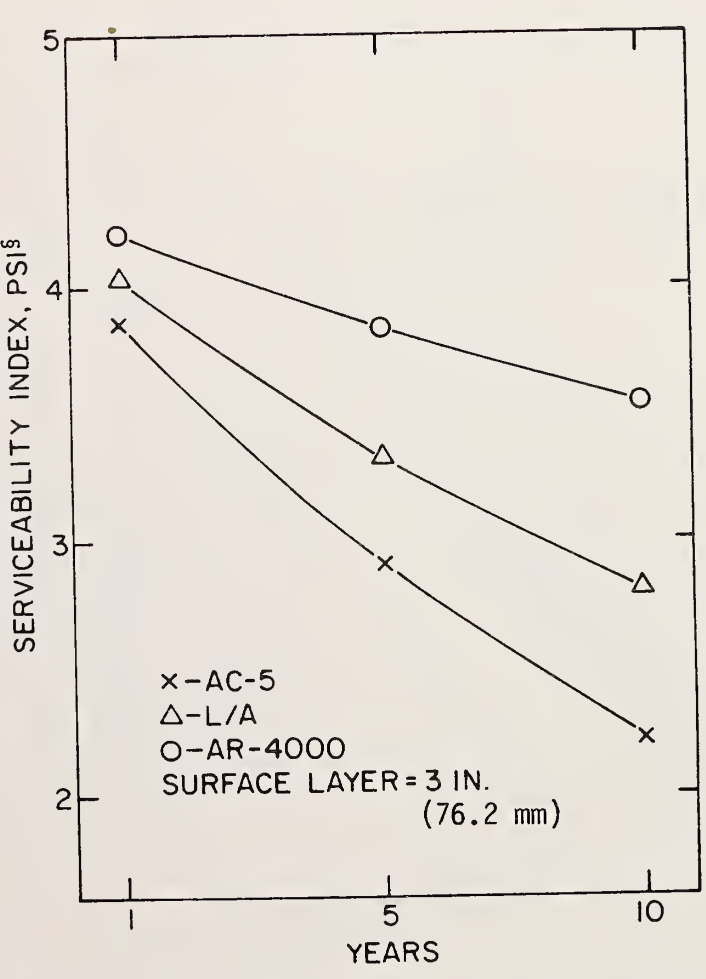


Figure 6.18. Relationships between predicted serviceability index of surface layer of 3 in. (76.2 mm) made with various mixes and number of years.

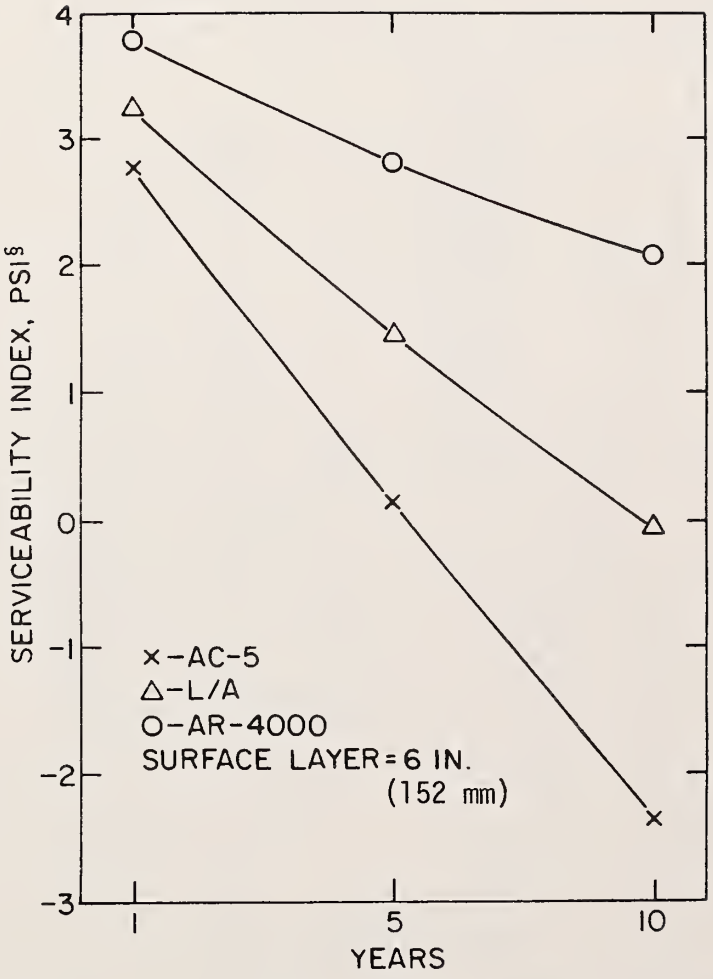


Figure 6.19. Relationships between predicted serviceability index of surface layer of 6 in. (152 mm) made of various mixes and number of years.

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§To convert to: MPa: psi x 6.894 x 10^{-3}.

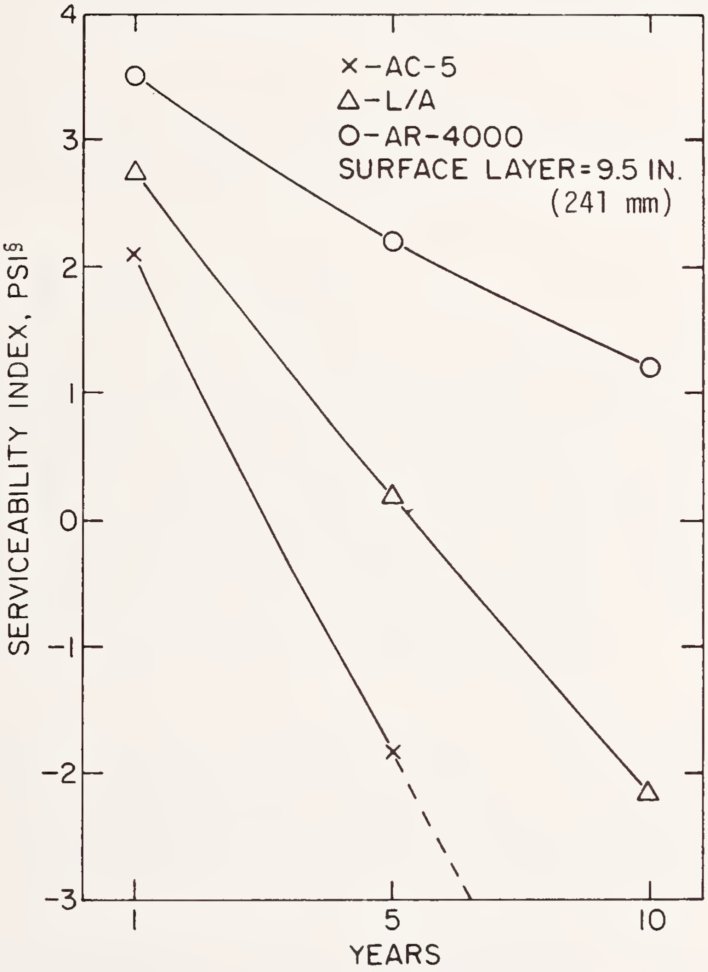

Figure 6.20. Relationships between predicted serviceability index of surface layer of 9.5 in. (241 mm) made of various mixes and number of years.

§To convert to MPa: psi x 6.894 x 10^{-3}.

F. References

1. Terrel, R.L., "Mechanistic Behavior of Pavement Systems", Seminar Handout Notes, Department of Civil Engineering, University of Washington, Seattle, 1976.

2. Monismith, Carl L. (University of California, Berkeley), "Design Considerations for Asphalt Pavements", Seminar, Department of Civil Engineering, University of Washington, 1970.

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VII. ECONOMIC FEASIBILITY

Although the feasibility of developing a binder material from wood lignins is technically possible, prospective users are doubtful as to the economics of using wood lignins in pavements. Much of this doubt can be attributed to the lack of cost information on wood lignin binders as compared to conventional asphalt binder material. The current cost of wood lignins might now be high, but due to the more inflationary trends of other construction materials, it may be possible to use wood lignins in the future.

Before wood lignins can be accepted as possible substitutes for asphalt, users would also like to have enough information as to their availability now and in the future so as to avoid attempting to utilize a product that is either scarce or being depleted.

This chapter considers the cost and production trends of both asphalt and wood lignins, and discusses the possibility of a part replacement of asphalt by wood lignin in pavement.

A. Cost and Production Trends of Asphalt

The cost of asphalt has been rising in proportion to crude petroleum, and since the 1973 energy crisis, has almost tripled in price. Table 7.1 is a cost summary of paving (85-100 penetration) asphalt for some cities in the U.S. from 1968 to 1978 as reported in the Engineering New Record. In 1968, the four city average price of asphalt was about \$24 per ton or \$0.012 per pound (\$0.027 per kg). In 1974, this average price rose dramatically to about \$72 per ton or \$0.036 per pound (\$0.079 per kg), three times the 1968 price. Since 1974, asphalt cement prices have been rising gradually with an average annual increase of about 6.5 to 9%, and in 1978 the average U.S. price of asphalt cement should be about \$84 per ton (\$0.092 per kg).

With this trend in the cost of asphalt, it is expected that with an annual price increase of 6.5%, the price of asphalt cement will be about \$180 per ton (\$0.198 per kg) in 1990. This projection is subject to both the domestic and international market of crude petroleum. Lower domestic production or excessive price increases by oil companies or cartels like the OPEC can raise the price of asphalt cement to as high as \$250 per ton (\$0.28 per kg) in the near future.

Asphalt production in the U.S. had been increasing annually until the 1973 energy crisis which brought about energy consciousness to all asphlat users. AFter 1973, there had been a gradual decrease in production as shown in Table 7.2. In 1973, approximately 36 million tons (3.3×10^{10}kg) of asphalt was produced while only 27.5 million tons (2.5×10^{10}kg) were produced in 1976. However, with the completion of the Alaska pipeline, the total asphalt production in the U.S. is expected to increase as from 1978.

In 1975, about 18 million of the nearly 30 million tons (1.6×10^{10}kg of 2.7×10^{10} kg) of asphalt were used for paving, or approximately 60% of the total asphalt produced in the U.S. Hot mix paving makes up the bulk of asphalt paving and again in 1975, 315 million tons (2.9×10^{11}kg) of mixture were produced.

Table 7.1. Cost of asphalt, paving 85-100 penetration, FOB city tank cars ($ per ton)[§]

Year	Seattle	Dallas	Boston	Pittsburgh	Des Moines	Houston	Omaha	Washington, D.C.	4-City Average
1968*	23	26	20	28	-	-	-	-	24.25
1969*	23	26.9	22	30	-	-	-	-	25.48
1970*	27	26.9	25	31.5	-	-	-	-	27.6
1971	-	-	-	-	28	23.5	28	33.8	28.33
1972	-	-	-	-	28.75	23.5	33	29	28.79
1973	-	-	-	-	-	37.6	37.3	33.8	36.23
1974	-	-	-	-	85	58.25	80	64.5	71.93
1975	-	-	-	-	81.25	64	81.5	76.63	76.35
1976	-	-	-	-	74	64	75	78.63	72.91
1977	-	-	-	-	74	66.5	85	83.63	77.28
1978**	-	-	-	-	74	85.55	85	93	84.38

*November prices only

**March prices only

Source: Engineering News Record, Material Prices Roundup compiled by McGraw Hill World News.

[§] To convert to $ per kg: ($ per ton) x 2.2

(with a national average of about 5.7% asphalt cement content). Figure 1 shows graphically the distribution of asphalts, i.e., asphalt cement, emulsion, and cutbacks. Also shown is the percentage of each use with respect to time. Cutbacks are on the decline because of their association with lower quality roads and in more recent years because of restraints by environmental control agencies. Emulsions, on the other hand, are being used increasingly, but have been limited somewhat by reluctance among engineers and apparent higher cost.

There are two opposing views as to the future utilization of asphalt for paving purposes as compared to other uses such as fuel. The first, based on past experience indicates that the more vehicles there are on the road, the more asphalt pavements will be required. The current ration of .25 ton (225 kg) of asphalt per vehicle would project to about 25% increase of asphalt needed in 1990. The second viewpoint has to do with economic ability and willingness to pay, if the cost is rising. If the dollars remain the same and at 6.5% inflation per year, available dollars will buy only about one-half the asphalt in 1990 as they will today.

B. Cost and Production Trends of Wood Lignins

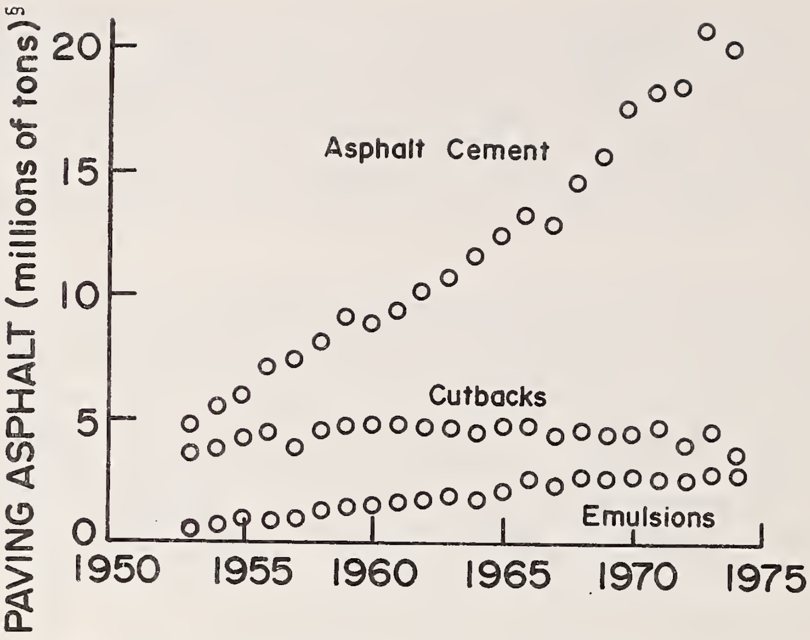
The two broad classes of modified wood lignins that are commercially available are lignin sulfonates and kraft lignin.

Pulp is generally produced from wood tissue by the sulfite process whereby aqueous solutions of calcium bisulfite and sulfurous acid are used at elevated temperature to dissolve lignin and some carbohydrates and leave behind cellulose sulfite pulp fibers. After the pulp fibers are separated by infiltration, the liquid remaining is called spent sulfite liquor and contains lignin sulfonates, certain sugars from the wood and also the process chemicals. The lignin sulfonates generally contain anionic sulfonate groups and a cation corresponding to the base (calcium, sodium, ammonium)

Table 7.2. Total Asphalt Production in the United States.

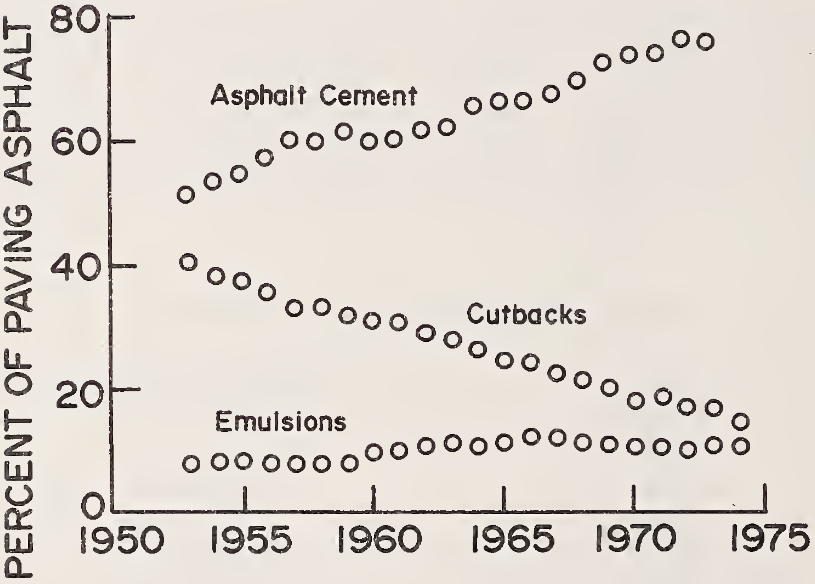
Year	Production (tons) (kg: x 9.1 x 10^2)
1967	28,836,000
1968	-
1969	28,948,000
1970	32,210,000
1971	32,270,000
1972	32,491,000
1973	35,834,000
1974	33,099,000
1975	28,582,000
1976	27,495,000

Source: Asphalt Institute, Olympia, Washington



§To convert to kg: tons x 9.1 x 10^2)

(a)



(b)

Figure 7.1. Utilization of various paving asphalt materials in the U.S.

of the pulping liquor. The presence of the sulfonate group makes lignin sulfonate water soluble. The cost of lignin sulfonates for pavement purposes therefore also involves a process that makes it insoluble in water.

The average price of wet, unrefined lignin sulfonate, 50% solid at the producing plant is about $20 to $24 per ton ($.010 to $.012 per pound [$.022 to $.026 per kg]). With acid treatment, the price of lignin sulfonate can be about $30 to $40 per ton ($.033 - $.044 per kg). One can anticipate increases in this price which, in today's market and considering the limited availability of lignin sulfonates, is certainly low. For pavement purposes, a a higher cost is expected if the acid treatment is performed separately rather than being incorporated in the processing. The process of making the lignin sulfonate insoluble can raise the price to as high as $60 per ton (($0.03 per pound [$0.066 per kg]).

The kraft lignins are not extensively recovered and are more expensive. These liginins are obtained by acid precipitations and washing of the produce to free them of inorganics and odiferous compounds. For a final product, the precipitate would be dried to powder.

The estimated cost of free acid kraft lignin in wet sludge form at the producing plant is about $40 per ton ($0.02 per pound [$0.044 per kg]). Drying the wet sludge generally costs about one cent per pound. Thus, when production cost and company profits are considered, liquid kraft lignin can be obtained at a cost of about $80 per ton ($0.04 per pound [$0.088 per kg]), while dry kraft lignin can be estimated to cost about $100 per ton ($0.05 per pound [$0.11 per kg]). However, these estimates seem conservative compared to prices quoted by some producers. One producer is now quoting between $400 and $500 per ton ($0.20 and $0.25 per pound [$0.44-$0.55 per kg]) of solids in dry form. This price reflects the fact that the kraft lignin produced by the manufacturer (packed in 50 lbs.[22.5 kg] bags) is sold to small businesses. The manufacturer indicated that for pavement construction where substantial quanitites are required, this price can be lowered to about $0.08 to $0.10 per pound ($0.178 to $0.22 per kg) depending on the quantity.

Unlike asphalt, the prices of wood lignins have remained fairly stable over the years and are not likely to escalate as fast as asphalt cement. The current price of lignin sulfonate for one produces is only 12% higher than his quotation 8 years ago. Assuming that an annual price increase of 2% is expected, then the projected prices of wood lignins in 1990 would be as follows:

Lignin Sulfonate	$50 per ton ($0.055 per kg)
Insoluble Lignin Sulfonate	$76 per ton ($0.084 per kg)
Wet Kraft Lignin	$101 per ton ($0.111 per kg)
Dry Kraft Lignin	$127 per ton ($0.140 per kg)

These prices would depend on the demand for and availability of wood lignin products in the future.

The production and availability of lignins may be analyzed by assuming that for each ton (900 kg) of pulp a mill produces, approximately 1000 lbs (450 kg) of lignin results. Using statistical data provided by the Lockwood

Directory of the Paper and Allied Trades and Wood Pulp Statistics-American Paper Institute, Inc., the total sulfite lignin production in the U.S. from 1968 to 1976 is as shown in Table 7.3. In general, the figures show that about 1.5 million tons (13.7×10^8kg) of sulfite spent liquor are produced in the United States annually. From the Lockwood's Directory, Table 7.4 shows kraft lignin production from 1971 to 1976. Kraft lignins are produced in much higher quantities and in 1976 about 16.5 million tons (150.2×10^8 kg) of kraft lignin were produced in the U.S.

Table 7.3. Sulfite lignin production in the United States.

Year	Total Sulfite Pulp Production (tons)§	Lignin Production (tons)§
1968	3,479,281	1,739,641
1969	3,398,425	1,699,213
1970	3,287,035	1,643,518
1971	2,972,108	1,486,054
1972	3,079,986	1,539,993
1973	3,233,131	1,616,566
1974	3,267,250	1,633,625
1975	3,140,200	1,570,100
1976	2,807,000	1,403,500

*Based on assumption that 2 lbs. (.9 kg) pulp = 1 lb. (.45 kg) lignin

Sources: Wood Pulp Statistics, Pulp and Raw Materials Group, American Paper Institute Inc., New York.

Lockwood's Directory of the Paper and Allied Trades, New York.

Table 7.4. Kraft lignin production in the United States

Year	Total Kraft Pulp Production (tons)§	Lignin Production (tons)§
1971/72	26,593,200	13,296,600
1973	28,290,000	14,145,000
1974	29,144,400	14,572,200
1975	30,356,400	15,178,200
1976	33,561,000	16,780,500

*Based on Assumption that 2 lbs. (.9 kg) pulp = 1 lb. (.45 kg) lignin

Source: Lockwood's Directory of the Paper and Allied Trades, New York.

§To convert to: kg: tons x 9.1×10^2, Much of the statistical data also show that lignin production and potential availability are somewhat regional. The largest quantities are in the Pacific Northwest, Upper Midwest and Southeast United States. This would imply that because of transportation costs, potential utilization of wood lignins for paving purposes might be on a local or regional basis. Nevertheless, there are sufficient quantities of wood lignin that can be utilized for pavment and other purposes now and in the future.

C. Lignin-Asphalt Binder

In order to achieve the goal of saving or using less asphalt in flexible pavements, the idea is to develop lingin-asphalt binders that can perform as well as paving asphalt alone at the same binder contents in the paving mixtures. This reduces the dependence on asphalt in the construction and maintenance of flexible pavements.

Based on this study at the University of Washington, it was concluded that lignin-extended asphalt binders containing 30% lignin performed adequately in hot mixes with dense-graded aggregate for the range of binder contents normally associated with paving grade asphalt. Lignin-extended binders containing more than 30% lignin were extremely viscous, difficult to mix with aggregate and did not perform well. The choice of 30% lignin-70% asphalt binder therefore would save 30% of asphalt by following appropriate procedures.

The cost of hot mix in-place asphalt pavement meeting state highway requirements during 1978 is about \$21 per ton (\$.032 per kg). This results in cost for asphalt pavement for new construction of \$1.05 per square yard per inch (\$0.35/m^2/cm) of depth. With 30% lignin sulfonate-70% asphalt binder, the cost difference from using asphalt alone won't be much at the present time. However, with 6.5% and 2% annual price increases for asphalt and lignin sulfonate respectively, it is expected that the lignin-asphalt binder would be cheaper in the near future. The problem with lignin sulfonate-asphalt pavement is the water solubility of the lignin sulfonate resulting in the lignin easily leaching out and the binders tending to swell or change in volume. Condensation of the lignin sulfonate with polyacrylamide might reduce the swelling property of the binder. Also, the acid preheated binder discussed in Chapter 3 could be utilized.

The most promising lignin extender asphalt binder is the 30% kraft lignin-70% asphalt binder. With 6.5% and 2.5% annual price increases for asphalt and lignin respectively, the projected construction costs of a flexible pavement using asphalt alone as binder and kraft lignin-extended asphalt binder are as shown in Table 5. The 1978 cost of kraft lignin-asphalt pavement is about \$1.25 per square yard per inch (\$0.41/m^2/cm) as compared to \$1.05 per square yard per inch (\$0.35/m^2/cm) for asphalt pavement. However, because of the more stable price of lignin and the higher price increase for asphalt, the cost of pavements using lignin-asphalt binders would be nearly the same as those using asphalt binders only in 1990. In 1990, the projected costs are \$2.23 and \$2.21 per square year per in (\$0.75/m^2/cm) for asphalt and lignin-asphalt binder pavements respectively. Thereafter, lignin-asphalt pavements will be cheaper.

Apart from the lower cost of lignin-asphalt pavements in the future, material properties of lignin-asphalt binders have indicated potentially thinner pavement section requirements and/or superior properties. Based on theoretical pavement designs using the elastic layered theory , the material layer equivalencies of lignin-asphalt mixture and conventional asphalt concrete are as follows (see Ch. 6):

1 in. (2.54 cm) of lignin-asphalt mix = 1.3 in. (3.30 cm) of AC-5 mix
1 in. (2.54 cm) of lignin asphalt mix = 0.9 in. (2.29 cm) of AR-4000 mix

This implies that though the current inch-to-inch cost of lignin-asphalt binder is more than that of the asphalt binder, a lignin asphalt pavement might be considered to have lower cost because of the thinner thickness requirements.

D. Conclusions

This analysis has shown that although the current cost of lignin-asphalt pavements are higher than conventional pavements of the same pavement section, because of the more stable prices of wood lignins, availability of wood lignins now and in the future, and possible thinner section requirements of lignin-asphalt pavements, utilizing wood lignins as part substitute for asphalt now and in the future is economically feasible. This would help reduce the total dependency on high cost asphalt for pavement construction purposes.

Table 7.5. Projected pavement cost using asphalt binder or lignin-asphalt binder.

Year	Pavement Cost ($ per square yard-inch)($ per m^2/cm)	
	Asphalt Binder	Lignin-Asphalt Binder
1978	1.05 (0.35)	70% Asphalt = .735 (.24) 30% Kraft Lignin = .515 (.17) Total = 1.250 (.41)
1980	1.19 (0.39)	70% Asphalt = .833 (.27) 30% Kraft Lignin = .515 (.17) Total = 1.250 (.44)
1985	1.63 (0.54)	70% Asphalt = 1.141 (.38) 30% Kraft Lignin = .596 (.20) Total = 1.737 (.58)
1990	2.23 (0.74)	70% Asphalt = 1.561 (.51) 30% Kraft Lignin = .653 (.21) Total = 2.214 (.72)

VIII. SUMMARY AND CONCLUSIONS

A. Summary

During the past few years the construction industry has seen a rapid rise in the price of asphalt, and questions as to the material's availability in the future have caused new concerns. Consequently, various government agencies who depend on asphalt have begun to look at alternatives. Wood lignins and other paper pulp industry by-products are being investigated by various researchers under sponsorship of the Federal Highway Administration.

Aside from being one of the nation's valuable renewable resources, wood lignin is one of the few materials which is expected to be in relatively abundant supply in the future (1). Appropriate uses for this material are being sought throughout the paper-pulp industry (1,2).

Lignin is a cementitious material that binds wood fibers together and is a major by-product of the paper making industry. Lignin is extracted from wood by treatment with chemicals. After the pulp fibers have been separated by filtration, the liquid remaining is called spent liquor and contains process chemicals, lignin, and other extractables. Approximately one ton (9.1×10^2 kg) of lignin is produced from two tons ofpulp. Annual production of lignin in the U.S. ranges up to 15 million tons (136.5×10^8 kg)(1).

Two principal chemical pulping processes are used in the U.S.: sulfite and kraft. The difference between the two is in the chemicals used to separate the lignin from the fiber. The kraft process is currently dominating the pulp industry and will probably continue to do so in the future. As compared to the sulfite process, the kraft methodology is relatively more simple and rapid, is less sensitive to different species of raw wood materials, and has the advantage of recovering the cooking chemicals and utilization of waste products. Because of its dominant position, the kraft process produces about two-thirds of all lignin in the U.S. paper industry (3).

The pulp industry has been seeking new uses for lignin, having traditionally disposed of the material. Recently, because of energy concerns, inroads have been made to produce in-plant process heating by drying the spent liquor and burning the residual lignin. Although most of the kraft lignin is presently used as fuel, higher uses are being sought. Most sulphite lignin, called lignin sulphonate, is not burned and has often been used in subgrade construction and base stabilization of roads. A serious drawback of this material is its solubility in water. Many other minor uses of lignin have been developed in the industry and are reported throughout the technical literature.

The overall objective of this research was to develop methods to use lignin as an extender for asphalt for the purpose of reducing the dependence on this material in highway paving mixtures. Beyond these activities, the specific objectives were:

1. To develop and verify a systematic procedure for evaluating and demonstrating the influence of lignin as an extender for asphalt in paving mixtures and the resultant effect on the pavement performance, and

2. Using the procedure developed above, determine mix design alternatives which will result in a saving of asphalt material.

The research at the University of Washington has been aimed at utilizing commercial lignin, either in solution or dried powder form, by itself or in combination with asphalt and other admixtures. The overall investigation has followed several different approaches:

1. Lignin sulfonate alone as an asphalt substitute;

2. Lignin sulfonate or kraft lignin used as an extender of asphalt in hot mixed asphalt concrete;

3. Kraft lignin-asphalt-rubber combinations for cold mixed binders; and

4. Miscellaneous combinations.

Early in the study, well over 100 different binders were developed and tested. These were eventually reduced to a handful for detailed evaluation. The more promising binders were tested for properties and behavior alone as well as in combination with Ottawa sand and later with graded aggregate. Specifically, several detailed studies were undertaken as follows:

1. Lignins used alone as substitutes for asphalt. The objectives of this study were to develop asphalt-like binders from lignin sulfonates that would have less water solubility. The general approach used was to convert lignin sulfonates to higher molecular weights and then convert them to an insoluble form using appropriate combinations of heat, pressure, and chemical treatment. Various binders formulated wre screened by mixing them with Ottawa sand, compacting specimens, curing, and testing them for compressive strength, solubility, and swelling potential. The major categories of lignin treatment included:

   a. heat treatment with and without acid
   b. oxidative coupling with hydrogen peroxide-potassium ferricyanide catalyst
   c. co-polymerization with urea-formaldehyde resin
   d. co-polymerization with phenol-formaldehyde resin
   e. condensation with polyacryamide.

2. Lignins used as an extender of asphalt. The objectives of this study were to determine the compatibility of lignin and asphalt materials, attempt to use them in various combinations and compare mixtures made from these binders with conventional asphalt

concrete mixtures. Binders in various combinations were generally prepared either by mixing in an open vessel or in a Parr reactor over a range of temperatures, pressures, and time. In this study, detailed physical tests of the binders were conducted to compare with asphalt cement. Those binders with promising properties were screened and further evaluated using conventional asphalt concrete mixture design procedures as well as characterization tests such as resilient modulus and fatigue resistance. Some materials were further tested for performance by freeze-thaw and heat conditioning. A detailed procedure was developed for systematically evaluating each binder and was utilized for each new material. Initially, sixteen potential binders were screened from the others for further testing, and these were eventually narrowed to three. Specifically, the major testing was accomplished on the following materials:

a. 70% AC-5 asphalt cement blended with 30% kraft lignin, in an open vessel;

b. 70% AC-5 asphalt cement blended with 26% kraft lignin and 4 percent sulfur, in a Parr reactor;

c. 70% AC-5 asphalt cement blended with 30% acid pretreated calcium lignin sulfonate, in an open vessel;

d. AC-5 and AR-4000 asphalt cement used as control materials.

The above binders resulted in relatively higher binder contents at optimum physical properties than did the asphalt cement alone. Consequently, further modification of the binders and procedures were attempted. These included the following:

a. Precoating the coarse aggregate with lime, sulphur, kraft liquor, portland cement, asphalt cement, asphalt emulsion and cutback asphalt;

b. Additives to the asphalt-lignin binders in an attempt to improve or otherwise change them, included silicone, diethyl butanoic acid pretreated kraft lignin, acetylated kraft lignin, carbon black, coal tar, coal, other pretreated kraft lignins.

3. Kraft lignin and rubber modifiers in emulsified asphalt binders. In addition to the hot type mixtures discussed earlier, a cold process was also studied. Previous research had shown that lignin was an effective reinforcement for rubber in tires. The approach used for this project was to replace a portion of the asphalt in conventional asphalt emulsion mixtures with lignin as an extender and reinforcer. Small amounts of rubber were added to the binder to offset the stiffening effect of lignin on the asphalt. Several ratios of lignin: asphalt:rubber were evaluated for strength, durability in water, compactibility, and curing.

4. Effects of the environment on lignin binders. Because of the potential problem due to solubility of some lignins in water, several special tests were conducted on binders and mixtures. Leaching tests were made to assess physical changes and the release of binder constituents. Ultraviolet light and some outdoor exposure was included. Analytical methods utilized included pH measurements, chemical oxygen demand, acidity and alkalinity, ultraviolet radiation, and spectrophotomic readings. Field exposure of briquets in a desert climate followed by evaluation of extracted binders were also made. Some field exposure on the roof of the Civil Engineering building at the University of Washington were monitored by following the change in resilient modulus with time.

5. Pavement design and performance. Although this study was restricted to the laboratory, the properties of mixtures prepared with lignin type binders can be utilized to design the thickness of pavements. As an illustration of how these properties might be used, the material properties were used in conjunction with elastic layer theory (computer program) to design a series of pavements. Applying appropriate criteria, these were compared to pavements with conventional asphalt concrete. It is shown that this procedure can be used to develop equivalencies for various binders based on performance factors such as fatigue and rutting. General performance predictions were also made for one mixture combination using the Vesys IIM program.

6. Economic feasibility. Based on reasonable assumptions and data for current and future material costs, a brief discussion of the economic practicality of using lignin type binders is presented. A combination of cost and expected availability of asphalt and lignin is also presented. Further, the cost of producing special binders from these "raw" materials must be considered.

B. Conclusions

Although the report contains detailed discussion and conclusions in each chapter, there appears to be several that can be summarized and warrant special consideration. These are as follows:

1. The utilization of wood lignin alone as a substitute paving binder was generally not as successful as hoped. After attempting many binder formulations, five (see Tab. 2.4) were examined in some detail. Of the five methods, only the condensation of lignin sulfonate with polyacrylamide may be feasible, but will require further work beyond the scope of this project.

2. The general concept of using lignin to extend asphalt appears to be feasible for development into a suitable replacement for asphalt alone. Using various techniques for preparation, lignin asphalt binders can be formulated that have physical properties similar to

those for paving grade asphalt. Up to 30% replacement of asphalt is readily attained with higher replacement values possible. Mixtures with physical properties such as resilient modulus that are equivalent to those for conventional asphalt concrete may be readily prepared, but at a slightly higher total binder content. Precoating of the coarse aggregate facilitates mixing and should lower the total binder content necessary without precoating.

3. Comparing the three principal lignin asphalt binders (i.e., Fig. 3.46-3.51), mixture design factors would point to the acid pretreated calcium lignin sulfonate as most desirable, although the two made with kraft lignin also have acceptable properties. In general, it would appear that the binders made with non-water soluble kraft lignin act as reinforcing agents with very little chemical reaction with asphalt. On the other hand, acid pretreated calcium lignin sulphonate and asphalt attains superior qualities, even after water saturation (even though raw calcium lignin sulphonate is extremely water soluble by itself).

4. Mixing aggregate with the somewhat stiffer lignin asphalt binders was often more difficult than for conventional asphalt mixtures because the coarse particles were slow to coat with binder. Precoating the coarse fraction with asphalt proved to be useful to aid mixing, but also permitted a significant reduction in total binder content, to values comparable to conventional asphalt mixtures.

5. Admixtures such as coal tar, coal, kraft liquor, or carbon black may be useful to enhance the reaction between lignin and asphalt. In general, the use of such admixtures permit relatively lower binder contents, thus reducing the asphalt requirement.

6. Kraft lignin appears to be suitable as a partial replacement of asphalt in emulsified asphalt paving mixtures. Lignin added in an ammoniacal solution becomes water insoluble upon volatile loss of the ammonia. As in hot mixtures with lignin and asphalt, upon curing (evaporation of the water emulsion and volatilization of ammonia) the finely divided stiffens the mixture, as well as increases strength. This brittleness can be reduced by the addition of small amounts of latex rubber.

7. Kraft lignin appears to be insoluble in asphalt, including those with a high content of nitrogen bases.

8. Environmental exposure tests revealed that mixtures made with kraft lignin are much less affected by leaching and ultraviolet exposure

than ammonium or calcium lignin sulphonates. The kraft lignin mixtures perform similar to those made from asphalt cement. While lignin sulphonate mixtures appear to exhibit more "weathering" due to leaching and ultraviolet exposure, it is a surface phenomenon and did not penetrate more than 0.5 mm below the surface. A protective "skin" develops that appears to retard further damage. Overall, the potential for detrimental damage to the environment from lignin asphalt mixtures appears to be minimal.

10. Pavement structures utilizing lignin asphalt materials appear to have behavior similar to those constructed from conventional asphalt concrete. Based on laboratory mixture characterization, comparison of expected behavior using elastic layer theory and the predictive computer program, Vesys IIM, it appears that pavements made with lignin asphalt mixtures can be designed to essentially match those of conventional materials. Although this phase of the research was limited to one type of mixture, several combinations seem feasible. Further, it should be noted that somewhat stiffer mixtures can be designed that may have their best utilization as base courses. Surface characteristics such as wear and skid resistance have not been evaluated.

11. Currently, the cost of lignin and uncertainties of production costs for binders made from lignin would indicate that pavements constructed from lignin-asphalt would be more expensive than conventional asphalt concrete. However, making reasonable assumptions based on current information and future trends, the economic feasibility may be closer than 10 years. Reasonably conservative estimates show that the cost will be equivalent by 1990. It should be noted that lignin utilization will probably be regional, at least initially, because of the cost of transportation.

In conclusion, both the technical and economic feasibilities of utilizing wood lignin as a partial replacement for asphalt are positive. Laboratory studies have shown that mixtures with similar and possibly improved properties can be fabricated. During the immediate future, while the economics are improving, it would appear that further evaluation is warranted. For example, the full scale production (at least pilot plant) of lignin asphalt binders needs to be evaluated as well as construction with conventional equipment. Further, the construction of several test pavements utilizing a range of mixtures and lignins would provide an opportunity to evaluate field performance, both in terms of aging and structural behavior.

APPENDIX A

PULP AND LIGNIN PRODUCTION IN THE U.S.

Part 1. Sulfite Mills

Part 2. Kraft Mills

The following abbreviations are used in Tables A-1 and A-2:

bl	bleached
Ca	calcium
hwd	hardwood
Mg	magnesium
N.A.	not available
NH4	ammonium
swd	softwood
T/D	tons per day
unbl	unbleached

Table A-1. Sulfite mills and production for 1975.

State	City	Company/Address	Base	Pulp Output (T/D)	Lignin* (T/D)
Alaska	Ketchikan	Ketchikan Pulp Co./P.O. Box 1619 99901	Mg base	Blswd 640	320
	Sitka	Alaska Lumber & Pulp Co. Inc./P.O. Box 1050 99835	Mg base	Blswd 600	300
Florida	Fernandina Beach	ITT Rayonier Inc./P.O. Box 2002 32034	NH_4 base	Blswd 450	225
Maine	Millinocket	Great Northern Paper Co./ 04462	Mg base	Unblswd 650	325
	Winslow	Scott Paper Co./ 04901	Ca base	Blswd/Hwd 485	242.5
Minnesota	Cloquet	Potlach Corp./ 55720	Ca base	Bl Hwd 120	60
New York	Glens Falls	Finch, Pruyn & Co./ 1 Glen St. 12801	NH_4 base	Blswd 250	125
Oregon	Lebanon	Crown Zellerbach Corp./P.O. Box 486 97335	NH_4 base	Unblswd 105	52.5
	Newberg	Publishers Paper Co./P.O. Box 70 97132	Mg base	Unblswd 200	100
	Oregon City	Publishers Paper Co./P.O. Box 551 97045	Mg base	Unblwsd 200	100
	Salem	Boise Cascade Corp./ 315 S. Commercial St. 97301	NH_4 base	Swd 275	137.5
Pennsylvania	Mehoopany	Charmin Paper Products Co./P.O. Box 32 18692	Ca base	N.A.	-----
Washington	Bellingham	Georgia Pacific Corp./ P.O. Box 1236 98225	Ca base	Blswd 500	250
	Anacortes	Scott Paper Co./ 1709 R. Ave. 98221	NH_4 base	Blswd 135	117.5
	Camas	Crown Zellerbach Corp./ 98607	Mg base	Unblswd 440	220
	Cosmopolis	Weyerhaeuser Co./ 98537	Mg base	Blswd 400	200
	Everett	Scott Paper Co./P.O. Box 925 98206	NH_4	Blswd 835	417.5
	Hoquiam	ITT Rayonier Inc./P.O. Box 299 98550	Na base	Blswd 475	237.5
	Longview	Weyerhaeuser Co./ 98632	Mg base	Blswd 350	175
	Port Angeles	ITT Rayonier Inc./ 98362	Ca base	Blswd 475	237.5
Wisconsin	Appleton	Consolidated Papers Inc./ 1130 E. John St. 54911	Ca base	Blswd 175	87.5
	Brokaw	Wausau Paper Mills Co./ 54417	Mg base	BlHwd 186	93
	Green Bay	American Can Co./P.O. Box 790 54305	Ca base	BlHwd 150	75

* based on the assumption that 2 lbs. ⇒ 1 lb. of lignin production

Table A-1. (cont.)

State	City	Company/Address	Base	Pulp Output (T/D)	Lignin* (T/D)
Wisconsin	Green Bay	Charmin Paper Products Co./ 54302	Ca base	N.A.	-----
	Oconto Falls	Scott Paper Co./ 106 E. Central Ave. 54154	NH_4 base	Blswd 110	105
	Park Falls	Flambeau Paper Co./200 N. 1st 54552	Ca base	Blswd 50 BlHwd 65	57.5
	Peshtigo	Badger Paper Mills Inc./P.O. Box 149 54157	Ca base	Blswd 110	55
	Port Edwards	Nekoosa Edwards Paper Co. Inc./ 54469	Mg base	Blswd 215	107.5
	Rhinelander	St. Regis Paper Co./515 W. Davenport Ave. 54501	Ca base	75	37.5
	Rothschild	Weyerhaeuser Co./ 54474	Ca base	Blswd 200	100

Source: Lockwoods' Directory of the Paper & Allied Trades
100th Edition 1976, Vance Pub. Corp., N.Y. 10022 (1976).

Table A-2. Kraft mills and production for 1975.

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
Alabama	Brewton	Container Corp. of America/P.O. Box 709 36426	Unblswd	550	275
			Blswd	350	175
	Butler	American Can Co./P.O. Box 315 36904	Blswd	930	465
	Coosa Pines	Kimberly-Clark Corp./Coosa River Newsprint Div. 35044	Blswd	350	175
			Blhwd	235	117.5
	Courtland	Champion Papers/Box 189 35618	Blswd	500	250
	Demopolis	Gulf States Paper Corp./Board Products Div. 36732	Blswd & Hwd	500	250
	Jackson	Allied Paper Inc./Southern Mill Div. 36545	Bl	500	250
	Mahrt	Alabama Kraft Co./P.O. Box 940, Phoenix City 36867	Unblswd	1000	500
	Mobile	International Paper Co./P.O. Box 2448 36601	Unbl	845	422.5
			Bl	455	227.5
		Scott Paper Co./P.O. Box 2447 36601	Bl & Unbl	1400	700
	Montgomery	Union Camp Corp./Box 326 36101	Unblswd	870	435
	Pine Hill	MacMillan Bloedel Inc./ 36769	Unblswd	1000	500
	Selma	Hammermill Papers Group/P.O. Box 1409 36701	Blswd	265	132.5
			Blhwd	265	132.5
	Tuscaloosa	Gulf States Paper Corp./P.O. Box 3199 35401	Unblswd	420	210
			Unblhwd	80	40
Arizona	Snowflake	Southwest Forest Ind. Inc./P.O. Box 128 85937	Unblswd	550	275
			Blswd	90	45
Arkansas	Ashdown	Nekoosa Edwards Paper Co., Inc./71822	Blswd	260	130
			Blhwd	140	70
	Camden	International Paper Co./Southern Kraft Div. 71701		750	325
	Crossett	Georgia-Pacific Corp./P.O. Box 520 71635	Unblswd	200	100
			Unblhwd	300	150
			Blswd	700	350
			Blhwd	200	100
	Morrilton	Arkansas Kraft Corp./P.O. Box 711 72110	Unblswd	800	400

Table A-2. Continued.

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
Arkansas	Pine Bluff	International Paper Co./ 71602	Bl	1220	610
		Weyerhaeuser Co./P.O. Box 7853 71601	Unblswd	250	125
California	Anderson	Simpson Lee Paper Co./P.O. Box 637 96007		150	75
	Antioch	Fiberboard Corp./San Joaquin Pulp & Board Mill Wilber Ave. 94509	Unbl Bl	450 200	225 100
	Fairhaven	Crown Simpson Pulp Co./P.O. Box 4718, Eureka 95501	Blswd	550	275
	Samoa	Louisiana-Pacific Corp./P.O. Box 158 95564	Blswd	600	300
Florida	Cantonment	St. Regis Paper Co./P.O. Box 87 32533	Unblswd Blswd	600 300	300 150
	Fernandia Beach	Container Corp. of America/N. 8th St. 32034	Unblswd	1500	750
	Foley	Buckeye Cellulose Corp./ 32347	Blswd	1000	500
	Jacksonville	Alton Box Board Co./P.O. Box 150 32201	Unblswd	675	337.5
		St. Regis Paper Co./P.O. Box 18020 32229	Unblswd	1470	735
	Palatka	Hudson Pulp & Paper Co./P.O. Box 919 32077	Unbl Bl	600 350	300 175
	Panama City	International Paper Co./32401	Unbl Bl	750 650	375 325
	Port St. Joe	St. Joe Paper Co./P.O. Box 190 32456	Blswd	1300	650
Georgia	Augusta	Continental Can Co. Inc./P.O. Box 1425 30903	Blswd Blhwd	400 400	200 200
	Brunswick	Brunswick Pulp & Paper Co./P.O. Box 1438 31520	Blswd	1600	800
	Cedar Springs	Great Southern Paper Co./P.O. Box 44 31732	Unblswd	1780	890
	Jesup	ITT Rayonier Inc./P.O. Box 207 31545	Blswd	1250	625
	Krannert	Georgia Kraft Co./P.O. Box 1551, Rome 30161	Unblswd	1550	775
	Macon	Georgia Kraft Co./P.O. Box 3215 31205	Unblswd	900	450
	Fort Wentworth	Continental Can Co./P.O. Box 4068 31407	Unblswd	675	337.5

Table A-2. Continued

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
Georgia	Riceboro	Interstate Paper Corp./ 31323	Unblswd	525	267.5
	Savannah	Union Camp Corp./P.O. Box 570 31402	Unblswd	2600	1300
	St. Mary's	Gilman Paper Co./ 31558	Unblswd	730	365
			Blswd	420	210
	Valdosta	Owen-Illinois Inc./P.O. Box 1048 31601	Unblswd	950	475
Idaho	Lewiston	Potlatch Corp./P.O. Box 1016 83501		950	475
Kentucky	Hawesville	Western Kraft/P.O. Box J 43248	Blhwd	300	150
	Wickliffe	Westvaco Corp./P.O. Box 278 42087	Blswd	300	150
			Blhwd	300	150
Louisiana	Bastrop	International Paper Co./Louisiana Mill 71220		1100	550
	Bogalusa	Crown Zellerbach Corp./P.O. Box 1060 70427	Unblswd	1200	600
			Blswd	140	70
	Campti	Western Kraft/ 71411		400	200
	Deridder	Boise Southern Co./P.O. Box 1000 70634	Unblswd	900	450
			Blswd	130	65
	Elizabeth	Calcasieu Paper Co./P.O. Box 520 70638	Unblswd	300	150
	Hodge	Continental Can Co., Inc./ 71247	Unblswd	1400	700
	Pineville	Pineville Kraft Corp./ P.O. Box 870 71360	Unblswd	880	440
	Port Hudson	Georgia-Pacific Corp./P.O. Box 430, Zachery 70791	Blswd	75	37.5
			Blhwd	455	227.5
	Springhill	International Paper Co./ 71075		1000	500
	St. Francisville	Crown Zellerbach Corp./P.O. Box 218 70775		530	265
	West Monroe	Olinkraft, Inc./P.O. Box 488		1150	575
Maine	Jay	International Paper Co./ 04239	Unbl	100	50
			Bl	500	250
	Lincoln	Lincoln Pulp & Paper Co. Inc./ 04457	Blhwd	340	170

Table A-2. Continued

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
Maine	Old Town	Penobscot Co./ 04468	Blhwd	425	212.5
	Rumford	Oxford Paper Co./ 04276	Blswd	190	95
			Blhwd	360	180
	Westbrook	S.D. Warren Co./89 Cumberland St. 04092	Blswd	70	35
			Blhwd	180	90
	Woodland	Georgia-Pacific Corp./ 04694		800	400
Maryland	Luke	Westvaco Corp./ 21540	Bl	755	377.5
Michigan	Escanaba	Escanaba Paper Co./ 49829	Blswd	200	100
			Blhwd	400	200
	Muskegon	S. D. Warren Co./2400 Lakeshore Dr. 49443	Blswd	100	50
			Blhwd	130	65
Minnesota	Cloquet	Potlatch Corp./ 55720	Blswd	220	110
			Blhwd	180	90
	International Falls	Boise Cascade Corp./ 56649		320	160
Mississippi	Monticello	St. Regis Paper Co./P.O. Box 608 39654	Unblswd	1700	850
	Moss Point	International Paper Co./ 39563		715	357.5
	Natchez	International Paper Co./ 39120	Bl	1000	500
	Vicksberg	International Paper Co./ 39180	Unbl	1200	600
Montana	Missoula	Hoerner Waldorf Corp./P.O. Drawer "D" 59801	Unblswd	1000	500
			Blswd	150	75
New Hampshire	Berlin	Brown Co./650 Main St. 03570	Unbl	100	50
			Bl	700	350
New York	Ticonderoga	International Paper Co./ 12883	Bl	590	295
North Carolina	Cantor	Champion Papers/ 28716	Blswd	850	425
			Blhwd	510	255
	New Bern	Weyerhaeuser Co./P.O. Box 1391 28560	Bl	700	350

Table A-2. Continued

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
	Plymouth	Weyerhaeuser Co./P.O. Box 787 27962	Unblswd Blswd Blhwd	850 300 200	425 150 100
	Riegelwood	Federal Paper Board Co., Inc./ 28456		1150	575
	Roanoke Rapids	Hoerner Waldorf Corp./P.O. Box 580 27870	Unblswd Unblhwd	480 120	240 60
Ohio	Chillicothe	Mead Corp./ 45601	Blhwd	600	300
Oklahoma	Valliant	Weyerhaeuser Co./ 74764	Unbl	1300	650
Oregon	Albany	Western Kraft/P.O. Box 339 97321	Unblswd	500	250
	Clatskanine	Crown Zellerbach Corp./ 97016	Unblhwd & Swd	840	420
	Gardiner	International Paper Co./P.O. Box 854 97441	Unbl	600	300
	Halsey	American Can Co./P.O. Box 215 97348	Blswd	300	150
	Springfield	Weyerhaeuser Co./P.O. Box 275 97477	Unblswd	1150	575
	St. Helens	Boise Cascade Corp./ 97051	Unblswd Blswd	125 800	62.5 400
	Toledo	Georgia-Pacific Corp./P.O. Box 580 97391	Unblswd	1075	537.5
Pennsylvania	Johnsonburg	Penntech Papers Inc./100 W. Center St. 15845	Blhwd	190	95
	Roaring Spring	Appleton Papers/ 16673	Blswd	180	90
	Spring Grove	P.H. Glatfelter Co./ 17362	Blhwd & Swd	500	250
South Carolina	Catawba	Bowater Carolina Corp./P.O. Box 7 29704	Blswd	1000	500
	Florence	South Caroline Industries, Inc./P.O. Box 4000 29501	Unblswd Unblhwd	1100 100	550 50
	Georgetown	International Paper Co./ 29440	Unbl Bl	1350 480	675 240
	North Charleston	Westvaco Corp./P.O. Box 5207 29406	Unblswd Unblhwd	1550 450	775 225

Table A-2. Continued

State	City	Company/Address	Pulp Production (T/D)		Lignin Output* (T/D)
Tennessee	Calhoun	Bowaters Southern Paper Corp./ 37309	Unblswd	540	270
	Counce	Tennessee River Pulp & Paper Co./P.O. Box 33 38326		N.A.	----
Texas	Evadale	Temple-Eastex Inc./P.O. Box 816, Silsbee 77656		1300	650
	Houston	Southland Paper Mills, Inc./P.O. Box 23011 77028	Unblswd Blswd	650 275	325 137.5
	Lufkin	Southland Paper Mills, Inc./P.O. Box 149 75901		400	200
	Orange	Owens-Illinois Inc./P.O. Box 2500 77630	Unblswd	1000	500
	Pasadena	Champion Papers/P.O. Box 872 77501	Unblswd	850	425
	Texarkana	International Paper Co./P.O. Box 870 75501	Bl	610	305
Virginia	Covington	Westvaco Corp./ 24426	Unbl Bl	138 910	69 455
	Franklin	Union Camp Corp./ 23851	Unblswd Unblhwd Blswd Blhwd	80 150 500 700	40 75 250 350
	Hopewell	Continental Can Co., Inc./P.O. Box 201 23860	Unblswd	896	448
	West Point	Chesapeake Corp. of Virginia, The/ 23181	Unblswd Unblhwd	900 250	450 125
Washington	Camas	Crown Zellerbach Corp./ 98607	Unblswd	730	365
	Everett	Weyerhaeuser Co., Pulp Div./P.O. Box 1228 98206	Blswd	360	180
	Longview	Longview Fibre Co./P.O. Box 639 98632	Unblswd Blswd	1400 400	700 200
		Weyerhaeuser Co./ 98632	Blswd	650	325
	Port Townsend	Crown Zellerbach Corp./P.O. Box 575 98638		420	210
	Tacoma	St. Regis Paper Co./P.O. Box 2133 98401	Unblswd Blswd	950 140	475 70
	Wallula	Boise Cascade Corp./ 99363	Unblswd	410	205

Table A-2. Continued

State	City	Company/Address	Pulp Production(T/D)		Lignin Ouput* (T/D)
Wisconsin	Kaukauna	Thilmany Pulp & Paper Co./P.O. Box 190 54130		400	200
	Mosinee	Mosinee Paper Corp./ 54455	Unblswd	174	87
	Nekoosa	Nekossa Edwards Paper Co., Inc./ 54457		310	155
	Wisconsin Rapids	Consolidated Papers, Inc./Kraft Div. 54494	Blswd & Hwd	400	200

* Lignin ouput based on the assumption that one ton of lignin is produced for each two tons of pulp production.

APPENDIX B

BINDER TEST RESULTS

Note: * Binder Content is the % of solid content in the mix based on the weight of sand.

** A - 105°C in the oven overnight.

B - Ambient temperature (≅ 73°F , 23.3°C).

C - 50°C overnight followed by two hours at 105°C.

*** 1 - One day at ambient temperature during curing.

2 - Two days at ambient temperature after curing.

3 - Three days at ambient temperature and one day soaked in water.

Table B-1. Lignin binders test results.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	*** Unconf. Comp. Strength, psi§			Solution Color	Degradation
					1	2	3		
CE 001	7/13/76	Liquid CaLS , 50% solid	6	A	178	116	0	7	Severe
CE 002	7/13/76	Dry CaLS	6	A	191	223	0	7	Severe
CE 003	7/25/76	Asphalt-Lignin Emulsion, 60% solid (75% LS, 25% AR 4000)	6	A	-	420	0	6	Moderate
CE 004	8/23/76	Liquid NH_4-L-S, 50.2% solid; sugar: 26.7% of solid	6	B	Disintegrated During Extruding Process because samples were still wet.				
CE 005	7/22/76	Liquid NH_4-L-S, 33.6% solid; sugar: 11.3% of solid	6	B	Disintegrated During Extruding Process because samples were still wet.				
CE 006	7/29/76	Liquid NH_4-L-S, 34% solid; sugar: 3.7% of solid	6	B	Disintegrated During Extruding Process because samples were still wet.				
CE 007	8/11/76	Dry Indulin ATRC (Kraft Pine), 99% lignin	6	A	-	0	0	1	Slight
CE 008	8/11/76	Dry Polyfon O (Kraft Pine), 99% lignin	6	A	-	81	0	7	Severe
CE 011	8/12/76	Liquid CaLS (50% solid) (CE 001) NaCl addition (15%)	6	B	2	10	0	7	Severe
CE 012	8/12/76	Liquid CaLS (50% solid) (CE 001) Acid treated with HCL (3.6%) Heated at 86°C for 2 hrs.	6	Mix was too stiff to mix.				-	-

Table B-1. Continued.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	*** Unconf. Comp. Strength, psi§			Solution Color	Degradation
					1	2	3		
CE 013	8/3/76	Dry NH_4-L-S	6	B	Disintegrated During Extruding Process because samples were still wet.			7	Severe
CE 017	8/18/76	Liquid CaLS (50% solid) (CE 001) treated with 2.2% HCl, heated at 85°C for 2 hrs.	6	B	Disintegrated During Extruding Process because samples were still wet.			7	Severe
CE 018	8/18/76	Liquid CaLS (50% solid) (CE 001) treated with 1% H_2O	6	B	Disintegrated During Extruding Process because samples were still wet.			7	Severe
CE 019	8/23/76	HT-115 Sample No. CP-1169			Not Tested.				
CE 020	8/23/76	HT-193 Sample No. CP-1170			Not Tested.				
CE 023	8/27/76	Liquid CaLS (CE 001) treated with 3.1% HCl, heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.				-
CE 027	8/31/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.8% HCl Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			6	Severe
CE 028	8/31/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.4% HCl Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			6	Severe

Table B-1. Continued.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	*** Unconf. Comp. Strength, psi§			Solution Color	Degradation
					1	2	3		
CE 029	8/31/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			7	Severe
CE 030	9/2/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl and 0.6% CH_2O Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			7	Severe
CE 031	9/2/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl and 1.2% CH_2O Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			7	Severe
CE 032	9/2/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl and 0.37% CH_2O Heated at 175°C for 2 hrs.	6	-	Mix was too stiff to mix.			7	Severe
CE 033	9/2/76	Liquid CaLS (50% solid) (CE 001) Treated with .35% HCl and 1.23% CH_2O Heated at 175°C for 2 hrs.	6	A	89	107	0	7	Severe
CE 035	9/7/76	Liquid CaLS (50% solid) (CE 001) Treated with 0.35% HCl and 1.85% CH_2O Heated at 175°C for 2 hrs.	6	A	65	88	0	7	Severe
CE 036	9/8/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl Heated at 150°C for 2 hrs.	6	A	100	121	0	7	Severe
CE 037	9/8/76	Liquid CaLS (50% solid) (CE 001) Treated with 1.05% HCl and .6% CH_2O Heated at 150°C for 2 hrs.	6	A	154	159	0	7	Severe

Table B-1. Continued.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	Unconf. Comp. Strength,psi*** §			Solution Color	Degra-dation
					1	2	3		
CE 038	9/8/76	Liquid CaLS (CE 001) Treated with 1.4% HCl Heated at 150°C for 2 hrs.	6	A	110	124	0	7	Severe
CE 039	9/8/76	Liquid CaLS (CE 001) Treated with 1.4% HCl and 0.6% CH_2O Heated at 150°C for 2 hrs.	6	A	16	18	0	5	Severe.
CE 042	9/13/76	Liquid CaLS (CE 001) Treated with 3.5% HCl Heated at 175°C for 2 hrs.	6	A	57	66	0	7	Severe
CE 043	9/13/76	Liquid CaLS (CE 001) Treated with 3.5% HCl and 0.6% H_2O Heated at 150°C for 2 hrs.	6	A	40	38	0	6	Severe
CE 044	9/15/76	Liquid CaLS (CE 001) Treated with 3.5% HCl No heat involved	6	A	Disintegrated During Extrusing Process because samples were still wet.			7	Severe
CE 045	9/15/76	Liquid CaLS (CE 001) Treated with 3.6% HCl, 1.23% CH_2O and 1.44% Phenol, no heat involved	6	-	Samples Expanded and Broke Apart During Curing			-	-
CE 046	9/15/76	Liquid CaLS (CE 001) Treated with 3.6% HCl Heated at 150°C for 2 hrs.	6	A	72	67	0	6	Severe
CE 047	9/15/76	Liquid CaLS (CE 001) Treated with 3.6% HCl and 0.9% CH_2O Heated at 150°C for 2 hrs.	6	A	53	32	0	6	Severe

Table B-1. Continued.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	***Unconf. Comp.§ Strength,psi			Solution Color	Degra-dation
					1	2	3		
CE 050	9/16/76	Liquid CaLS (CE 001) Treated with 1.05% HCl, 1.23% CH$_2$O, Heated at 150°C for 2 hrs. then added 4.3% asphalt	7	B	5	8	0	4	Severe
CE 051	9/16/76	Liquid CaLS (CE 001) Treated with 1.05% HCl, 1.44% Phenol and 1.23% CH$_2$O Heated at 150°C for 2 hrs. and then 4.1% asphalt added	7	B	18	12	0	5	Severe.
CE 054	9/20/76	Liquid CaLS (CE 001) Treated at 1.05% HCl Heated at 150°C for 1 hr. 4.4% asphalt added	11	A	Samples Expanded and Broke Apart During Curing				
CE 055	9/20/76	Liquid CaLS (CE 001) Treated with 1.05% HCl, 0.6% CH$_2$O Heated at 150°C for 2 hrs. 4.4% asphalt added	11	B	8	10	0	6	Severe
CE 058	9/22/76	Liquid CaLS (CE 001) Treated with 1.05% HCl Temp. 150°C for 2 hrs. Then 2.5% HCL added	10	B	8	9	0	6	Severe
CE 059	9/22/76	Liquid CaLS (CE 001) Treated with 3.2% HCl, 0.9% CH$_2$O Temp. 150°C for 2 hrs.	10	B	39	24	0	6	Severe.
CE 070	10/6/76	Liquid NH$_4$LSA-50% solid (CE 004) Heated at 150°C for 2 hrs.	6	Mix was too stiff to mix.					
CE 071	10/6/76	Liquid NH$_4$ LSA-50% solid (CE 004) Heated at 150°C for 2 hrs. 4.8% asphalt added, heated at 135°C for 1 hr.	6	Mix was too stiff to mix.					

Table B-1. Continued.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	*** Unconf. Comp. Strength, psi§			Solution Color	Degradation
					1	2	3		
CE 072	10/6/76	Liquid NH_4LSA-50% solid (CE 004) Heated at 150°C for 2 hrs. $AL_2 (SO_4)_3 \cdot 16 H_2O$ 4.8% added	6	Mix was too stiff to mix.					
CE 073	10/11/76	Liquid NH_4 LSA-50% solid (CE 004) $Ca(OH)_2$ of 1, 2 and 3% were added	6	Samples Expanded and Broke Apart During Curing.					
CE 074	10/18/76	Sand + NH_4 LSA (CE 004) (10%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 075	10/18/76	Sand + NH_4 LSA (CE 004) (10%)+Bark Phenol (11%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 076	10/18/76	Sand + NH_4 LSA (10%)+Bark Phenol (10%) + CH_2O (10%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 077	10/18/76	Sand + NH_4 LSA (10%)+Emul. Asphalt (6.4%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 078	10/18/76	Sand + NH_4 LSA (10%)+Emul. Asphalt (12.4%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 079	10/18/76	Sand + NH_4 LSA (10%)+Emul. Asphalt (5.7%)+Bark Phenol (10.2%) Heated at 105°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 080	10/18/76	Sand + NH_4 LSA (7.5%)+Emul. Asphalt (8.2%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 081	10/18/76	Sand + NH_4 LSA (7.5%)+Emul. Asphalt (8.2%) Heated at 150°C for 3 hrs.	-	A	-	-	0	7	Severe

Table B-1. Continued.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	*** Unconf. Comp. Strength,psi§			Solution Color	Degra-dation
					1	2	3		
CE 082	10/18/76	Sand + NH$_4$ LSA (6.2%)+Emul. Asphalt (9.7%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 083	10/18/76	Sand + NH$_4$ LSA (6.2%)+Emul. Asphalt (8.2%)+Bark Phenol (14.7%) Heated at 150°C for 2 hrs.	-	A	-	-	0	7	Severe
CE 084	10/21/76	Sand + NH$_4$ LSA (10%) Heated at 150°C for 2 hrs.,2.5% of Urea-Formaldehyde (¼) Resin added.	-	A C	- -	 -	96 73	2 4	Slight Slight
CE 085	10/22/76	Sand + NH$_4$ LSA (10%) Heated at 150°C for 1.5 hrs., 2.5% of Urea-Formaldehyde (¼) Resin added.	-	A	Samples Expanded and Broke Apart During Curing			4	Moderate
CE 086	11/4/76	Sand + NH$_4$ LSA (10%) Heated at 160°C for 2 hrs., 2.5% of Urea-Formaldehyde (¼) Resin added.	-	C	Disintegrated During Extruding Process because samples were still wet.			6	Severe
CE 089	11/12/76	Sand+10% NH$_4$LSA, heated at 150°C for 2 hrs., 2.5% of Urea-Formaldehyde (½) Resin added.	-	C		-	0	6	Severe
CE 090	11/12/76	Sand+10% NH$_4$LSA, heated at 150°C for 2 hrs., 2.5% of Urea-Formaldehyde (1/1) Resin added.	-	C		40	0	7	Severe
CE 091	11/12/76	Sand+10% NH$_4$LSA, no heat involved,2.5% of Urea-Formaldehyde (¼) Resin added.	-		Samples Expanded and Broke Apart During Curing.				

Table B-1. Continued.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	Unconf. Comp. Strength, psi*** §			Solution Color	Degradation
					1	2	3		
CE 084 CE 092	11/12/76	Sand+10% NH_4LSA, Heated at 150°C for 2 hrs., 2.5% of Urea-Formaldehyde (¼) Resin added, 20 ml of water was added.	-	50°C & 150°C	Samples Expanded and Broke Apart During Curing.				
CE 098	12/8/76	NH_4LSA (50% solid)+5% H_2O_s (30% consistency), heated at 50°C for 1 hr., then NaOH was added to bring PH=7.5-8.0, then sand was mixed, heated at 150°C for 2 hrs. then 2.5% of Urea-Formaldehyde (¼) was added.	-	60°C 2 days	-	-	86	6	Severe.
CE 099	12/8/76	Sand+Chitosan+NH_4LSA, heated at 150°C for 2 hrs., then 2.5% of Urea-Formaldehyde (¼) Resin was added with some water.	-	60°C 2 days	-	-	25	5	Severe

[§] To convert to MPa: psi x 6.894 x 10^{-3}.

Table B-2. Lignin-asphalt binders test results.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	***Unconf. Comp$_s$ Strength,psi			Solution Color	Degra-dation
					1	2	3		
CE 009	9/75	AR 4000 (Left over from Galena study)	6	B	13	13	22	0	None
					-	30	40	0	None
CE 010	7/31/76	Asphalt (AR 2000)-68%+NH_4-L-S (CE 013)-32%, Pressure (250 psig) reacted under N_2 at 194°C for 1 hr.	6	B	21	16	30	2	Slight
CE 014	8/14/76	Asphalt (AR 4000)-50% Dry NH_4-L-S (CE 013)-50%	6	B	14	19	12	6	Moderate
CE 015	8/14/76	Asphalt (AR 4000)-75% Dry NH_4-L-S (CE 013)-25%	6	B	14	13	17	6	Moderate
CE 016	8/14/76	Asphalt (AR 4000)-25% Dry NH_4-L-S (CE 013)-75%	6	Mix was too stiff to mix.				-	-
CE 021	8/24/76	60% asphalt (AR 2000) + 40% Indulin (CE 007) Heated to 80°C for 1.5 hr.	6	B	-	-	25	0	None
CE 022	8/24/76	60% asphalt (AR 2000) + 40% indulin (CE 007) Pressure (150 psig) reacted under N_2 at 198°C for 1 hr.	6	B	14	18	24	0	None
CE 024	8/31/76	Asphalt emulsion (CSS-1)-75% Liquid CaLS (CE 001)-25%	29	-	Mix was too wet to compact				-
			6	A	-	166	0	7	Severe
CE 025	8/31/76	Asphalt emulsion (CSS-1)-50% Liquid CaLS (CE 001)-50%	12	A	Disintegrated During Extruding Process because samples were still wet.			6	Severe

Table B-2. Continued.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	*** Unconf. Comp. Strength, psi§			Solution Color	Degradation
					1	2	3		
CE 026	8/31/76	Asphalt emulsion (CSS-1)-25% Liquid CaLS (CE 001)-75%	8	Dessicator at 26°C	Disintegrated During Extruding Process because samples were still wet.			5	Severe
CE 034	9/7/76	48.2% Dry NH_4-L-S (CE 013) 48.2% Asphalt (AR 2000) 3.5% sulfur Pressure reacted under air at 225°C for 1 hr.	12	A	153	225	5.4	4	Slight
CE 040	9/13/76	50% Dry NH_4-L-S (CE 002) 50% Asphalt emulsion (CSS-1)	16	Dessicator at 10 psi	25	35	0	7	Severe
CE 041	9/13/76	50% Dry CaLS (CE 013) 50% Asphalt Emulsion (CSS-1)	18	Dessicator at 10 psi	-	66	51	3	Severe
			6	A	-	470	0	7	Severe
CE 048	9/15/76	49% Asphalt (AR 2000) 49% Dry NH_4-L-S (CE 013) 1% Sulfur Heated at 90°C for 1½ hrs.	12	B	19	18	7	4	None
CE 049	9/15/76	49% Asphalt (AR 2000) 49% Dry NH_4-L-S (CE 013) 1% Sulfur Pressure reacted under N_2 at 220°C for 1 hr.	12	B	89	130	120	2	None
CE 052	9/17/76	45% Asphalt Cement (AR 2000) 25% Dry NH_4-L-S (CE 013) 25% Silvacon 490 Bark 5% Sulfur Heated at 90°C for 1½ hrs.	12	B	10	11	8	3	Slight
CE 053	9/17/76	Same materials as (CE 052) Pressure reacted under N_2 at 220°C for 1 hr.	12	B	88	86	80	1	None

Table B-2. Continued.

Number	Date Received	Description		Binder* Content,%	Curing** Condition	*** Unconf. Comp.§ Strength,psi			Solution Color	Degra-dation
						1	2	3		
CE 056	9/21/76	50% Asphalt Cement (AR 2000) 25% Silvacon 490 Bark 25% Dry NH_4-L-S (CE 013)	Heated at 90°C for 1½ hrs.	12	B	16	14	8	3	None
CE 057	9/21/76	Same materials as (CE 056)	Pressure reacted under He at 185°C for 1 hr.	12	B	25	13	16	1	None
CE 060	9/22/76	67% Dry NH_4-L-S (CE 013) 33% Asphalt Cement (AR 2000) Heated at 90°C for 1½ hrs.		9	B	15	17	13	6	Slight
CE 061	9/22/76	Same materials as (CE 060)	Pressure reacted under N_2 at 180°C for 1 hr.	9	B	25	25	30	2	None
CE 062	9/24/76	64% Dry NH_4-L-S (CE 013) 32% Asphalt Cement (AR 2000) 4.7% Sulfur	Oven heated at 90°C for 1½ hrs.	9	B	18	18	8	4	None
CE 063	9/24/76	Same materials as (CE 062)	Pressure reacted under N_2 at 198°C for 1 hr.	9	B	79	115	101	4	Slight
CE 064	9/28/76	27% Silvacon 490 Bark 73% Asphalt Cement (AR 2000) Oven heated at 90°C for 1½ hrs.		13	B	51	53	141	1	None
CE 065	9/28/76	Same materials as (CE 064)	Pressure reacted under N_2 at 180°C for 1 hr.	22	B	50	59	169	0	None

Table B-2. Continued.

Number	Date Received	Description	Binder* Content,%	Curing** Condition	Unconf. Comp. Strength, psi*** §			Solution Color	Degradation
					1	2	3		
CE 066	9/29/76	70% Asphalt Cement (AR 2000) 25% Silvacon 490 Bark 5% Sulfur Oven heated at 90°C for 1½ hrs.	23	B	35	45	88	1	None
CE 067	9/29/76	Same materials as (CE 066) Pressure reacted with He at 186°C for 1 hr.	23	23°C	251	253	506	0	None
CE 068	10/1/76	48% Asphalt Cement (AR 2000) 48% Kraft Lignin (Indulin) 4% Sulfur Oven heated at 90°C for 14 hrs.	12	23°C	48	52	53	1	None
CE 069	10/1/76	Same materials as (CE 068) In Parrbomb purged twice with N_2, heated at 186°C 300 psig for 14 hrs.	12	23°C	358	302	385	0	None
CE 069 CE 087	11/14/76	48% Kraft Lignin (Indulin AT)+48% AR 2000 + 4% Sulfur, sealed into a Parr reactor, placed under an inert atmosphere (He), heated at 240°C for 1 hr. pressure was 450 psig.	12	B	146	148	172	0-1	None
CE 088	11/10/76	50% NH_4LS+50% AR 2000, sealed into a Parr reactor, heated to 220°C for 12 hrs, pressure was 550 psig, then cooled to room temp., pressure was 225 psig.	12	B	91	81	78	1	None
CE 093	11/17/76	50% CaLS+50% AR 2000 sealed into a Parr reactor, purged with He, heated to 210°C for 1 hr., pressure was 400 psig, then cooled to 180°C.	12	B	56	88	72	2	None

Table B-2. Continued.

Number	Date Received	Description	Binder* Content, %	Curing** Condition	Unconf. Comp. Strength, psi*** §			Solution Color	Degradation
					1	2	3		
CE 094	11/19/76	48% CaLS+48% AR 2000+4% sulfur, sealed into a Parr reactor, purged with He, heated to 220°C for 1 hr. pressure was 500 psig, then cooled to 120°C for 24 hrs.	12	B	-	253	64	1	Slight
CE 034 CE 095	11/19/76	48% NH_4LS+48% AR 2000+4% sulfur, sealed into a Parr reactor, heated to 206°C for 1 hr. then cooled to 100°C for 12 hrs.	12	B	-	355	166	2-3	Slight
CE 096	11/31/76	50% Indulin AT+50% AR 2000, sealed into a Parr reactor, heated to 140°C for 10 hrs.	12	B	-	108	210	0	None
CE 097	12/1/76	50% NH_4LS+50% AR 2000, sealed into a Parr reactor, heated to 140°C for 10 hrs.	12	B	-	86	89	4	Severe

[§] To convert to MPa: psi x 6.894 x 10^{-3}.

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FEDERALLY COORDINATED PROGRAM (FCP) OF HIGHWAY RESEARCH AND DEVELOPMENT

The Offices of Research and Development (R&D) of the Federal Highway Administration (FHWA) are responsible for a broad program of staff and contract research and development and a Federal-aid program, conducted by or through the State highway transportation agencies, that includes the Highway Planning and Research (HP&R) program and the National Cooperative Highway Research Program (NCHRP) managed by the Transportation Research Board. The FCP is a carefully selected group of projects that uses research and development resources to obtain timely solutions to urgent national highway engineering problems.*

The diagonal double stripe on the cover of this report represents a highway and is color-coded to identify the FCP category that the report falls under. A red stripe is used for category 1, dark blue for category 2, light blue for category 3, brown for category 4, gray for category 5, green for categories 6 and 7, and an orange stripe identifies category 0.

FCP Category Descriptions

1. Improved Highway Design and Operation for Safety

Safety R&D addresses problems associated with the responsibilities of the FHWA under the Highway Safety Act and includes investigation of appropriate design standards, roadside hardware, signing, and physical and scientific data for the formulation of improved safety regulations.

2. Reduction of Traffic Congestion, and Improved Operational Efficiency

Traffic R&D is concerned with increasing the operational efficiency of existing highways by advancing technology, by improving designs for existing as well as new facilities, and by balancing the demand-capacity relationship through traffic management techniques such as bus and carpool preferential treatment, motorist information, and rerouting of traffic.

3. Environmental Considerations in Highway Design, Location, Construction, and Operation

Environmental R&D is directed toward identifying and evaluating highway elements that affect the quality of the human environment. The goals are reduction of adverse highway and traffic impacts, and protection and enhancement of the environment.

4. Improved Materials Utilization and Durability

Materials R&D is concerned with expanding the knowledge and technology of materials properties, using available natural materials, improving structural foundation materials, recycling highway materials, converting industrial wastes into useful highway products, developing extender or substitute materials for those in short supply, and developing more rapid and reliable testing procedures. The goals are lower highway construction costs and extended maintenance-free operation.

5. Improved Design to Reduce Costs, Extend Life Expectancy, and Insure Structural Safety

Structural R&D is concerned with furthering the latest technological advances in structural and hydraulic designs, fabrication processes, and construction techniques to provide safe, efficient highways at reasonable costs.

6. Improved Technology for Highway Construction

This category is concerned with the research, development, and implementation of highway construction technology to increase productivity, reduce energy consumption, conserve dwindling resources, and reduce costs while improving the quality and methods of construction.

7. Improved Technology for Highway Maintenance

This category addresses problems in preserving the Nation's highways and includes activities in physical maintenance, traffic services, management, and equipment. The goal is to maximize operational efficiency and safety to the traveling public while conserving resources.

0. Other New Studies

This category, not included in the seven-volume official statement of the FCP, is concerned with HP&R and NCHRP studies not specifically related to FCP projects. These studies involve R&D support of other FHWA program office research.

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* The complete seven-volume official statement of the FCP is available from the National Technical Information Service, Springfield, Va. 22161. Single copies of the introductory volume are available without charge from Program Analysis (HRD-3), Offices of Research and Development, Federal Highway Administration, Washington, D.C. 20590.

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