Moisture Damage in Asphalt Mixtures--A State-of-the-Art Report

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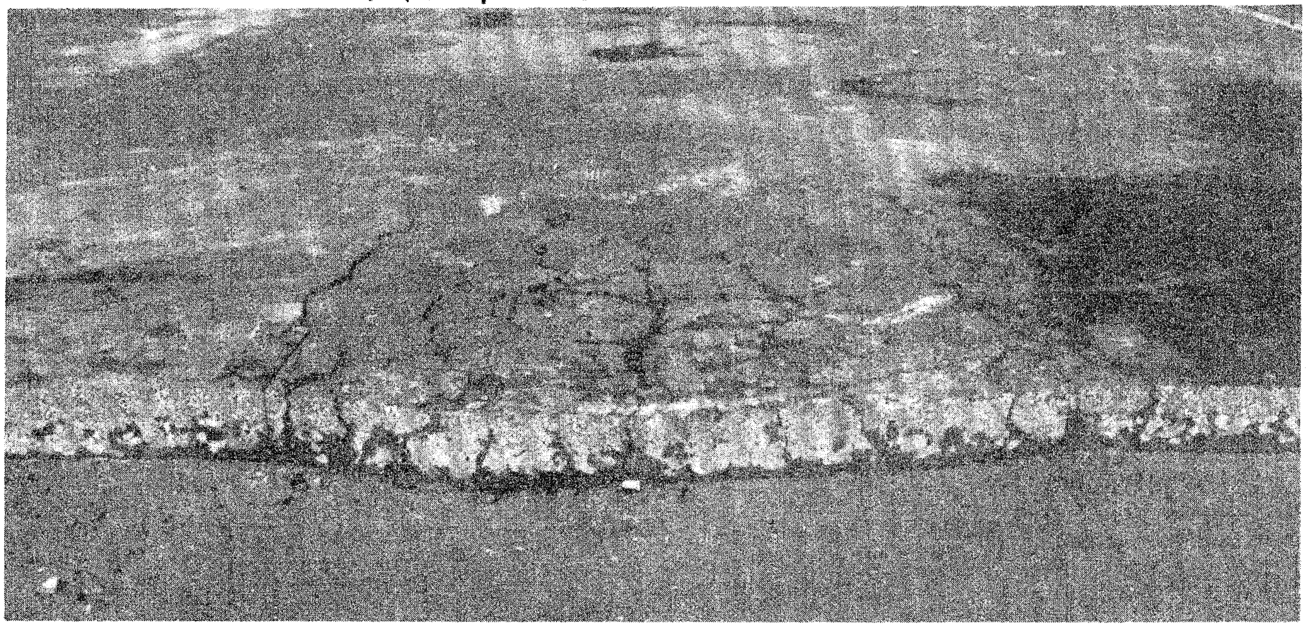

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FOREWORD

This state-of-the-art report is on the moisture susceptibility of asphalt mixtures used in highway pavements. Moisture damage in asphalt mixtures is a complex mechanism which is not well understood and has many interacting factors. The majority of State highway agencies report some problems with moisture susceptibility, primarily in the form of stripping, and use anti-stripping additives to increase durability. Stripping generally leads to potholes, raveling and/or rutting, but can also lead to cracking and bleeding. This report will be of interest to individuals concerned with any aspect of understanding and preventing the moisture susceptibility of asphalt mixtures.

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16. Abstract

This state-of-the-art report is on the moisture susceptibility of asphalt mixtures used in highway pavements. It addresses the known causes of moisture damage, methods for controlling damage such as antistripping additives, and moisture damage tests. Several current research studies are also given in the report. Moisture damage in asphalt mixtures is a complex mechanism which is not well understood and has many interacting factors.

This report is mainly concerned with dense-graded hot asphalt mixtures as most of the literature discusses these types of mixtures. Some information on chip seals and emulsion mixtures is also included.

One of the intents of this report is to indicate where data is lacking so that research can be performed in these areas. State-of-the-art reports often give the impression that more is known than is really known. More knowledge is needed in all areas dealing with moisture damage in asphalt pavements. How to develop moisture damage tests so that they relate to pavement performance needs to be addressed.

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Moisture damage, Stripping, Adhesion Moisture susceptibility, Antistripping additives, Hydrated lime, Amines, Retained ratio, Asphalt mixtures, Moisture sensitivity, Moisture conditioning

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

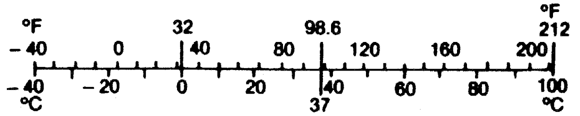
Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
in	inches	25.4	millimetres	mm
ft	feet	0.305	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km
AREA				
in^2	square inches	645.2	millimetres squared	mm^2
ft^2	square feet	0.093	metres squared	m^2
yd^2	square yards	0.836	metres squared	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	kilometres squared	km^2
VOLUME				
fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	litres	L
ft^3	cubic feet	0.028	metres cubed	m^3
yd^3	cubic yards	0.765	metres cubed	m^3

NOTE: Volumes greater than 1000 L shall be shown in m^3.

Symbol	When You Know	Multiply By	To Find	Symbol
MASS				
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg
TEMPERATURE (exact)				
°F	Fahrenheit temperature	5(F-32)/9	Celcius temperature	°C

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
LENGTH				
mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi
AREA				
mm^2	millimetres squared	0.0016	square inches	in^2
m^2	metres squared	10.764	square feet	ft^2
ha	hectares	2.47	acres	ac
km^2	kilometres squared	0.386	square miles	mi^2
VOLUME				
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m^3	metres cubed	35.315	cubic feet	ft^3
m^3	metres cubed	1.308	cubic yards	yd^3
MASS				
g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T
TEMPERATURE (exact)				
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F



* SI is the symbol for the International System of Measurement

(Revised April 1989)

TABLE OF CONTENTS

Section Page

CHAPTER 1: CAUSES OF MOISTURE DAMAGE 1

1. Type of Aggregate 4

a. Surface Energy Theories 5

(1) Spreading of a Liquid on a Solid 6
(2) Debonding or Stripping 14
(3) Conclusions of Surface Energy Studies 17

b. Chemical Bonding 18

(1) Degree of Acidity or pH 18
(2) Classifications Based on Chemical Composition 19
(3) Classifications Based on Mineralogical Composition 19
(4) Zeta Potential 19
(5) Conclusions of Chemical Bonding Studies 24

c. Mechanical Interlock 25
d. Classification According to the Degree of Visual Stripping 28

2. Type of Asphalt 31
3. Mixture Design and Construction 33
4. Environment 34
5. Traffic 36
6. Antistripping Additive Properties 36
7. Summary of Factors 36

CHAPTER 2: METHODS FOR CONTROLLING DAMAGE 39

1. Encapsulating the Aggregate 39
2. Precoating the Aggregate 39
3. Allowing the Aggregate to Weather 40
4. Washing the Aggregate 40
5. Altering the Mixture Design 41
6. Using Antistripping Additives 41

a. Traditional Liquid Additives 43

(1) Antistripping Mechanism 43
(2) Types of Traditional Liquid Additives 43
(3) Dosage 43
(4) Methods of Addition 44
(5) Factors Affecting Migration to Aggregate Surfaces 45
(6) Effects on Properties Other Than Moisture Susceptibility 46
(7) Overall Performance 47

TABLE OF CONTENTS (Continued)

Section Page

b. Metal Ion Surfactant 47
c. Hydrated Lime and Quicklime 48

  (1) Antistripping Mechanism 48
  (2) Types of Lime 49
  (3) Dosage 49
  (4) Methods of Addition 50

    (i) Hydrated Lime Slurry to Dry or Wet Aggregate. 51
    (ii) Dry Hydrated Lime to Wet Aggregate 53
    (iii) Dry Hydrated Lime to Dry Aggregate 53
    (iv) Dry Hydrated Lime to Asphalt 54
    (v) Quicklime Slurry to Dry or Wet Aggregate 54

  (5) Effects on Properties Other Than Moisture Susceptibility .. 54
  (6) Overall Performance 55

d. Silane Coupling Agents 56
e. Silicone.. 56

CHAPTER 3: MOISTURE DAMAGE TESTS 57

1. Additive Indicator Tests 62

a. Bottle Test 62
b. Color Indicator 63
c. Miscellaneous Tests 64

2. Aggregate Tests 64

a. Static Immersion 65
b. Dynamic Immersion 67
c. Boiling Water 67
d. Sodium Carbonate Immersion 68
e. Detachment Tests 68
f. Contact Angle, Peeling Tests, Tensile Tests on Films, and Heat of Immersion 69

3. Mixture Tests 69

a. Retained Ratios 70
b. Level of Mechanical Value 71
c. Visual Stripping 72
d. Compaction Methods and Air Void Levels 73
e. Saturation 78
f. Swell 80
g. Moisture-Conditioning Methods 81

TABLE OF CONTENTS (Continued)

Section | Page

- h. Number of Samples Required 82
- i. Types of Mixture Tests 82
  - (1) Boiling Water 82
  - (2) Dynamic Abrasion 83
  - (3) Immersion-Compression 85
  - (4) Marshall Immersion 87
  - (5) Hveem Stability 87
  - (6) Indirect Tensile Tests 88
  - (7) Elastic or Resilient Modulus 90
  - (8) Sonic 90

4. Chemical Analysis Tests 91

CHAPTER 4: EXECUTIVE SUMMARY 92

1. Causes of Moisture Damage 92
   - a. Types of Damage 92
   - b. Variables Which Influence Moisture Damage 93

2. Methods for Controlling Damage 95
3. Moisture Damage Tests 96
   - a. Additive Indicator Tests 97
   - b. Aggregate Tests 97
   - c. Mixture Tests 98
   - d. Chemical Analysis Tests 99

4. Conclusions 99

CHAPTER 5: CURRENT RESEARCH STUDIES AND ADDITIONAL STATE-OF-THE-ART REPORTS 100

1. Strategic Highway Research Program (SHRP) 100
2. Federal Highway Administration (FHWA) 100
3. Highway Planning and Research (HP&R) Studies 101
4. National Cooperative Highway Research Program (NCHRP) 101
5. Additional State-of-the-Art Reports 102

REFERENCES 103

LIST OF FIGURES

Figure Page

1. Interfacial tension diagram 8
2. Interfacial tension diagram in vector form 11
3. Equipment for double plunger compaction 75
4. Marshall hammer compactor 75
5. Kneading compactor 76
6. Gyratory compactor 77
7. Equipment for saturating compacted specimens or cores 78
8. Boiling water test 84
9. Specimen and apparatus for the immersion-compression test 86
10. Indirect splitting tensile test apparatus and the Marshall tester 89
11. Resilient modulus test apparatus 89

LIST OF TABLES

Table Page

1. Factors which influence moisture damage 3
2. Examples of interfacial tensions and work of separations 7
3. Typical chemical analyses of rocks in percentages 20
4. Typical mineralogical compositions of rocks in percentages 22
5. Degree of acidity of igneous rocks 23
6. List of rocks and minerals according to the degree of stripping associated with them 29

CHAPTER 1: CAUSES OF MOISTURE DAMAGE

The majority of studies on moisture or water damage in asphalt mixtures deals with an observed phenomenon called stripping. Stripping is the displacement of asphalt films from aggregate surfaces that occurs when the aggregate has a greater affinity for water than the asphalt. It has been speculated that an asphalt may be able to strip from an aggregate under dry conditions, especially after it has aged many years, but most losses of adhesion are attributed to the action of water. Stripping under dry conditions and the effects of changes in the amounts and types of the asphalt chemical functional groups adsorbed onto the aggregate surfaces with time have not been investigated to a significant degree. Also, in most cases, the effects of aging and moisture occur simultaneously in pavements.

Mechanical tests which evaluate the susceptibility of a compacted mixture to moisture damage measure reductions in strength due to a loss of cohesion and adhesion. In most moisture damage studies, adhesive failures are defined as those where the asphalt is debonded or stripped from the aggregate. Cohesive failures are defined as those where the bulk asphalt film flows, tears, or is weakened in some way. However, this is a limiting definition for cohesion, as the cohesional resistance of a mixture is reduced by losses in adhesion if these losses affect the frictional resistance between the aggregate particles or how the aggregate particles interlock. Cohesion in general terms is simply some measure of how the mixture holds together. In this report, the definition that cohesive failures are those where the bulk asphalt film flows, tears, or is weakened is used.

Water can cause cohesive and adhesive failures. Expansive materials, such as clays, caught in an asphalt can cause a cohesive failure when water is present without any adhesive failure. However, how water affects an asphalt within the film when clays are not present is not understood. Water at 140 °F (60 °C) used in laboratory tests for evaluating the moisture susceptibility of asphalt mixtures can damage a mixture with little or no evidence of visual stripping or expansive materials such as clays. There is evidence that water can diffuse into an asphalt and weaken the film, and this may be one reason.(1,2) The binder in this case is sometimes defined as an inverted emulsion. The extent to which this occurs in pavements is unknown.

It is possible that high pore pressures in a pavement due to water in the voids and the action of traffic can assist in causing some mixtures to ravel without visually stripping. This is another form of cohesive failure.

Moisture-related failures in pavements are also a function of any aggregate degradation due to processes such as freeze-thaw cycles, although moisture-related failures due to losses in aggregate strength seem rare.

The mechanisms by which water alone causes adhesive failures, as manifested by stripping, are also not clearly understood. Although stripping is the most commonly recognized form of moisture damage, as indicated by the previous information, it is not the only form of moisture-related damage that can occur. However, most of the literature deals with the adhesive failures, or stripping, and moisture or water damage is often equated to stripping.

Moisture damage generally starts at the bottom of an asphalt base layer or at the interface of two asphalt layers where the water content is the highest. Eventually, potholes are formed or the pavement ravels or ruts. With hardened binders, fatigue cracking (alligator cracking) may occur. Surface raveling or a loss of surface aggregate can also occur, especially with chip seals. Occasionally, binder from within the pavement will float to the pavement surface creating spots of bleeded asphalt. This process is sometimes referred to as the "emulsification of binder," but it has not been proven whether a significant quantity of asphalt is being emulsified, or if the asphalt is simply stripping off the aggregate and floating to the surface. There are cases where asphalts from caustic treated crudes have emulsified in the presence of water, but these cases are limited.(3)

The following factors influence the degree of moisture damage. These factors are further defined in table 1.

- Type of aggregate.
- Type of asphalt.
- Mixture design and construction.
- Environment.
- Traffic.
- Antistripping additive properties.

Table 1. Factors which influence moisture damage.

1. Aggregate

    - composition
        - degree of acidity or pH
        - surface chemistry
        - types of minerals
        - source of aggregate
    - physical characteristics
        - angularity
        - surface roughness
        - surface area
        - gradation
        - porosity
        - permeability
    - dust and clay coatings
    - moisture content
    - resistance to degradation

2. Asphalt

    - grade or hardness
    - chemical composition
    - crude source and refining process

3. Mixture Design and Construction

    - air void level and compaction
    - permeability and drainage
    - film thickness

4. Environmental

    - temperature
    - freeze thaw cycles
    - moisture vapor
    - dampness
    - pavement age
    - presence of ions in the water
      (including the effect of the pH of the water)

5. Traffic

6. Antistripping Additive Properties

1. Type of Aggregate

Studies that have been used to evaluate the effects of aggregates on the degree of damage are generally separated into three concepts: (1) surface energy theories, (2) the degree of chemical bonding, and (3) the degree of mechanical interlock. Adhesion, stripping, and even other forms of moisture damage are thought to be related to a combination of all three concepts, but the concepts have never been combined to form an overall coherent theory for them. When these different concepts are applied to a particular asphalt-aggregate combination, the conclusions from them regarding the potential of the mixture to undergo damage may conflict. Even the conclusions of various studies which deal only with only one concept often conflict with each other. Although the procedures and theories under all three concepts evaluate asphalt-aggregate-water interactions, most studies have been concerned with evaluating the effects of aggregates rather than the effects of asphalts. It is generally believed that the type of aggregate has a greater effect on moisture susceptibility.

Surface energy theories deal mainly with how materials reduce their surface free energies to obtain more thermodynamically stable conditions. Chemical bonding studies try to relate adhesion to the chemistry of the materials and the chemical reactions that occur. In both concepts, it is hypothesized, but not confirmed, that molecules in the asphalt interphase and at the interface can orientate themselves to improve adhesion. The interphase region of the asphalt is that part of the asphalt layer between the bulk asphalt and the interfacial region where the aggregate and asphalt contact and adsorption occurs. Both concepts evaluate the same bonding phenomena but in different ways. Surface energy concepts use phenomenological approaches, while chemical bonding studies use molecular approaches. However, surface energy studies make no assumptions regarding the nature of the molecular structures at the interface responsible for adhesion.(4) Studies concerned with the degree of mechanical interlock deal mainly with the physical properties of the aggregate which affect the physical strength of the composite material.

a. Surface Energy Theories

Surface energy theories state that molecules in the interior of a liquid or solid are closely packed and are in equilibrium with themselves, while surface molecules have unbalanced forces. These unbalanced forces cause the surface molecules to be attracted inward. For a liquid, this results in molecular counter-diffusion which sustains a layer of less dense liquid along the surface. This layer is in a state of tension, called surface tension. It is assumed that this tension is a constant in all directions.

For a solid, the molecules do not have the freedom to move, and thus reactions occur within the surface to balance the forces, and/or the surface adsorbs polar or polarizable molecules from the surrounding medium.(5) Factors which can lead to reactions in the surface structure which equalize the difference between the surface and interior molecules are: (1) polarization of surface ions, (2) distortion of surface structure, and (3) nonstoichiometric excess of anions over cations at the surface. A state of equilibrium generally cannot be obtained without adsorption and may never be fully achieved. A real surface tension can only occur in a solid if the surface molecules can move. Because movement is generally very limited even with the occurrence of reactions in the surface layer and/or adsorption, a surface tension which accounts for the effects of the unbalanced forces and the inward pull cannot be measured. Also, any surface tension that does exist will generally vary across the surface or from point to point.

Surface free energy (force x length) is the difference between the energy in the surface molecules and in the interior molecules. It is equal to the surface tension (force/length) times the surface area of the material. Surface free energy is the energy stored in the surface. Materials try to minimize the amount of surface free energy. A drop of liquid tends to remain in the form of a sphere because this shape has a minimum amount of surface area and thus surface free energy. Whether or not a liquid will increase its area to spread over a solid depends on whether this will reduce the total surface free energy of the combined materials. Any change in surface free energy due to any physical or chemical mechanism is defined as surface activity.(6) For two liquids having similar viscosities, the liquid with the lower surface tension will spread more readily on a solid than the liquid with the higher surface tension because it has a lower amount of surface free energy per unit area. In general, surface tension and surface free energy will decrease with an increase in temperature.

(1) **Spreading of a Liquid on a Solid.** Values for the interfacial tensions between some materials and air, and between some flat solid surfaces and drops of liquids in air, are shown in table 2.(2,7,8,9) The term "interfacial tension" is often used instead of "surface tension," because the surface tension of a liquid is often specified as the tension of the liquid in its vapor. A higher interfacial tension in the table means there is more surface free energy per unit area.

Some methods for determining the interfacial tensions between liquids and air and between two immiscible liquids are reported elsewhere although newer methods may exist.(2,4) In most reports, the asphalt-air and asphalt-water interfacial tensions are reported at 77 °F (25 °C). However, interfacial tensions with asphalt are difficult to determine at this temperature where the asphalt is a semi-solid. Thus, the interfacial tensions were generally determined at various temperatures above 77 °F (25 °C), where the asphalts were fluid, and the data at 77 °F (25 °C) was obtained through extrapolation.(2,9) The literature states that these interfacial tensions vary little with the source of asphalt, and in most cases, the asphalts may not have reached their true equilibrium positions of zero flow when the interfacial tensions were recorded.(2) If the equilibrium position has not been reached, then the surface tension is approximate or is the tension for some less than final condition. Procedures for determining the interfacial tensions between solids and air and between solids and liquids were not reported in the literature reviewed, except the procedure for asphalt-water interfacial tensions just mentioned. Although true surface tensions for solids do not exist, there are still unbalanced forces, whose effects were determined through some indirect means in these studies.

Figure 1 shows a drop of asphalt on aggregate in air. The "work of adhesion" is the change in the total surface free energy that occurs when the materials are combined, or the numerical sum of the energies for and against spreading. However, the work of adhesion is generally calculated using interfacial tensions. Thus the term "tension" can be confusing. For

Table 2. Examples of interfacial tensions and work of separations.(7,8,9)

Interfacial Tensions between Materials and Air	Dynes/cm
Free Water[1]	72
Asphalt[2]	21-39
Rocks, Minerals	
- Limestones	28-50
- Diabase	42-50
- Granites	52-73
- Quartz	74-85

Interfacial Tensions between Solids and a Drop of Liquid in Air		Dynes/cm
Solid	Liquid	
Asphalt	Water[3]	16-40; 30±5 at 77 °F (25 °C)
Glass	Tar	18.5
Quartz	Asphalt	14-20
Quartz	Water[4]	0

Work of Separation in Air	Dynes/cm
Rocks or minerals and Asphalt	
- Limestone and Asphalt	21-26
- Slag and Asphalt	23-26
- Sand and Asphalt	22-30
- Quartz and Asphalt	33
Rocks or minerals and Water	
- Limestone and water[5]	58-64
- Slag and water	63-68
- Silica sand and water	83
Asphalt and water	0-16
Sand and tar	40.5

---

[1] True surface tension of water in its vapor.

[2] Lower values are obtained at high temperatures.

[3] Lower values are produced by soft asphalts.

[4] Based on the assumption that the quartz has a thin layer of adsorbed water, which completely ties up the surface charges.

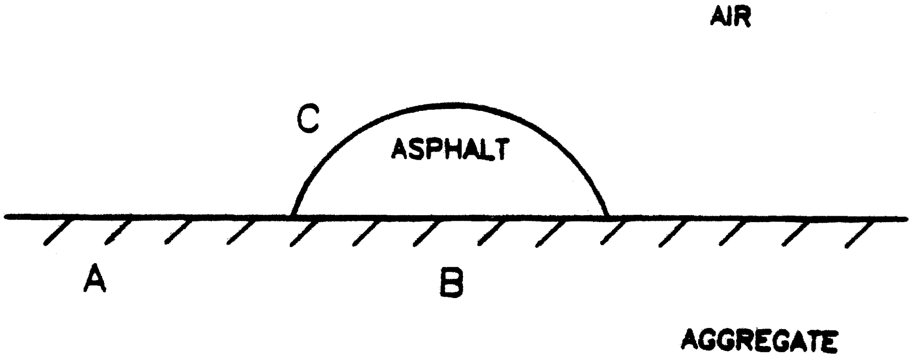
[5] Theoretically, these values should not be higher than the values given for the surface tension of limestone in air. No reason for this discrepancy was given.

a unit surface area, the interfacial tension and the surface free energy between two substances are numerically equal, although they do not have the same physical meaning. As stated previously, energy is force x length while tension is the force divided by length. Thus, multiplying a tension by a unit area gives an energy which has the same numerical value as tension. For practical purposes, tension is often equated to energy even though tension should be a vector requiring vector addition, whereas energies are the numerical sums of the energies for and against spreading. For vector addition, the directions and changes in the directions of the tensile forces must be considered. Thus it is often easier to calculate a change in energy for combined materials than a change in tension.

The work of adhesion is defined as:

$$\text{Work of Adhesion} = B - A + C. \qquad (1)$$

Often a coefficient is placed before the asphalt-air interfacial tension "C" to account for the difference between the change in the asphalt-air surface area and the changes for the other two surface areas during spreading.(9) The changes in the other two surface areas are equal.



A = Interfacial tension between aggregate and air.
B = Interfacial tension between aggregate and asphalt.
C = Interfacial tension between asphalt and air.

Figure 1. Interfacial tension diagram.

When placing a drop of asphalt on an aggregate, the aggregate-air surface area decreases, the aggregate-asphalt surface area increases, and the asphalt-air surface area increases. Thus, spreading of the asphalt over the aggregate is promoted by a higher interfacial tension "A" between the aggregate and air, a lower interfacial tension "B" between the aggregate and asphalt, and a lower interfacial tension "C" between the asphalt and air. The sign convention used in this report is that when a system loses energy, then energy is negative.(10) Thus spreading of an asphalt on an aggregate is more likely with a lower work of adhesion because this means more energy is given off by the asphalt spreading. A negative work of adhesion indicates that spreading should occur while a positive value indicates the asphalt should recede. Note that if the drop of asphalt is round, its surface area will initially decrease with spreading. Thus the work of adhesion for this limited case is:

$$\text{Work of Adhesion} = B - A - C. \tag{2}$$

However, at equilibrium the angle should always be less than 90° for aggregate-asphalt systems, where equation 1 is applicable.

The work of adhesion is a measure of the propensity of the asphalt to spread, but does not indicate how much area a drop will cover. The equations assume that the materials have reached their equilibrium positions and thus refer to equilibrium conditions only.

Of the four aggregates listed at the top of table 2, quartz has the highest aggregate-air interfacial tension "A." However, the aggregate-asphalt interfacial tension "B" is only given for quartz and thus the work of adhesions, or the various degrees to which an asphalt should spread on the four aggregates, cannot be calculated. Also, the references from which the data in table 2 were taken do not indicate how each of the interfacial tensions were obtained, such as those between the aggregates and air. Most of the data in the reviewed literature were taken from other, older reports, which are now not readily available and were not reviewed.

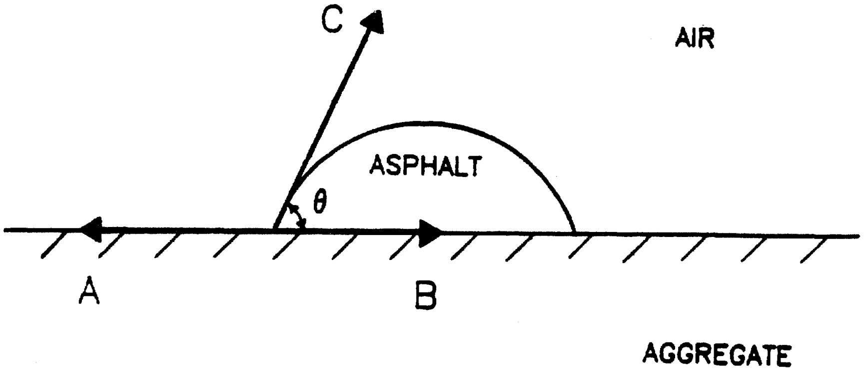
The work of adhesion can be calculated using the energy of immersion. When an aggregate is totally submerged in an asphalt, the change in surface free energy due to immersion, or the change in surface free energy due to the aggregate-air interface being replaced by an aggregate-asphalt interface, is "B - A." This difference is called the energy of immersion or adhesion tension and is often defined by the letter "F." Because energy is given off with asphalt-aggregate systems, it is a negative value.(2,11) The energy of immersion is often obtained by measuring the heat of immersion using a calorimeter, which actually measures the change in enthalpy or the heat released when the aggregate is immersed. Free energy is equal to the enthalpy minus the absolute temperature times the entropy. Entropy is a measure of internal disorder or the capacity of a material to undergo spontaneous change. As heat is given off, both the enthalpy and entropy are negative. Thus the effects of entropy on free energy opposes the effects of enthalpy. However, in most studies, free energy is equated to enthalpy and the entropy term is dropped. The heat measured by this test must be divided by the surface area of the aggregate to obtain the surface free energy per unit area. Determining the energy of immersion by a calorimeter only gives the difference between the two interfacial tensions "B - A" and not the individual tensions. However, it can be used along with the asphalt-air interfacial tension "C" and equation 1 or 2 to calculate the work of adhesion. Some other methods for measuring the quantity "B - A" are reported elsewhere, but they have not been used with aggregate-asphalt combinations.(2)

Vector notation can also be used to calculate the work of adhesion. The model in figure 2 shows the interfacial tensions in vector form. The convention used in this report is to evaluate spreading in the negative direction, so that the analysis using vectorial equations is consistent with the above equations based on energy. Using this convention, spreading occurs in the negative x-direction. The summation of the interfacial tensions in the x-direction along the aggregate surface is:

$$\text{Sum } x = B - A + C(\cos\theta).$$
$$\text{Sum } x = B - A + C(\cos\theta) = 0 \text{ at equilibrium.}$$
$$-C(\cos\theta) = B - A \qquad (3)$$

This equation is applicable to any angle. When the drop is round, or the angle is 180°, the summation in the x-direction will be the lowest possible negative value, which indicates the point at which the likelihood of spreading is the greatest. Generally, the angle will never stay at 180° because of the action of gravity and because there will always be some attraction between two materials. When spreading occurs, the angle decreases and the summation in the x-direction increases until equilibrium is reached. Equation 3 assumes that equilibrium can be reached, although equilibrium of the unbalanced forces on the surface of an aggregate may never be fully achieved. By substituting the term "-C(cos θ)" into equations 1 or 2, the work of adhesion can be calculated by measuring only the contact angle and the asphalt-air interfacial tension "C." Thus, the two common approaches for calculating the work of adhesion are to either measure the contact angle or the energy of immersion. Both give the quantity "B - A." The results from contact angle studies and energy of immersion studies can be compared using equation 3, but this was not done in any of the literature reviewed.

To determine the contact angle between aggregates and asphalts, cutback asphalts were often used. One reason for this is that during these studies, cutbacks were widely used in pavements. However, cutback asphalts were also used to replace semi-solid asphalts because semi-solid asphalts are very slow in reaching their equilibrium positions. The correctness of the measured data for semi-solid asphalts was often questioned. Thus a semi-solid asphalt was



A = Interfacial tension between aggregate and air.
B = Interfacial tension between aggregate and asphalt.
C = Interfacial tension between asphalt and air.

Figure 2. Interfacial tension diagram in vector form.

often cutback with solvent. However, a semi-solid asphalt will not have the same angle as the cutback as each has its own viscosity and its own interfacial tension with the aggregate. The kinetics of the system is a major problem with surface energy studies.(9) Different materials will reach equilibrium positions at different times, which depend on viscosity and thus temperature.

Methods for measuring contact angles are reported elsewhere.(4,10,11) The validity of an approach where contact angles have to be measured has been questioned because (1) the angles are difficult to measure, (2) angles can only be measured where spreading is low to moderate, and (3) an angle depends on whether the asphalt was advancing or receding before its equilibrium position was reached.(9,11) Also, the roughness of the aggregate must be quantified when measuring contact angles, or else the data has little meaning. An increase in roughness generally exaggerates the flow during either spreading or recession.(10) A material which flows easily will flow even more easily, and a material which does not flow easily will flow less easily. However, studies which have used smooth, flat surfaces to measure contact angles often do not indicate if the aggregate surfaces were polished to such a degree that the effects of surface roughness were eliminated, or whether the degree of roughness was factored into the experiment. When a significant amount of air is entrapped under the asphalt because of high roughness or porosity, studies concerned with measuring surface energies must be modified so they account for this air.(9)

Contact angles and interfacial tensions are also dependent on (1) the test temperature, (2) aggregate characteristics which affect roughness, such as the use of weathered versus polished surfaces and the degree of absorption, (3) the presence of water or contaminates on the surface and the degree of adsorption, (4) possibly the size of the liquid drop, and (5) possibly the atmospheric pressure. Some of these factors, such as the degree of asphalt absorption and adsorption, may be difficult to take into account.

Only a few works of adhesion are given in the literature for aggregate-asphalt combinations. These are presented later in this literature review. The literature states that asphalts should spread freely on an aggregate even if the aggregate is coated with a thin film of adsorbed water and/or dust, because spreading will still reduce the free surface energy.(2,8) The literature states that adsorbed materials such as water and dust will decrease both the aggregate-air interfacial tension "A" and aggregate-asphalt interfacial tension "B." If both are reduced proportionally, then there would seem to be no change in the work of adhesion or degree of spreading. However, the presence of water or dust will decrease the adhesive force by decreasing the contact area between the aggregate and the asphalt.(2,4,7,8) This conclusion is not explained in terms of surface energies. The literature also does not indicate whether the two interfacial tensions "A" and "B" are always reduced proportionally, nor are the effects of various types of adsorbed materials including antistripping additives on adhesion discussed in any detail. Because other surface energy studies generally indicate that aggregates have more affinity for water than asphalt, it appears that thin films of adsorbed water are of insufficient substance to prevent this spreading. With thick films of water, there will be no adhesion unless the system is chemically modified.

Spreading also depends on the viscosity of the asphalt, although the roles of viscosity and temperature are not clear in most surface energy studies. More viscous asphalts will spread less easily. Adjustments in the temperatures of the various asphalts can be made to obtain equal viscosities, but these adjustments will also affect the interfacial tensions.

As stated previously, a higher interfacial tension means there is more surface free energy per unit area. As shown in table 2, asphalt has a lower interfacial tension with air (21 to 39 dynes/cm) compared to free water (72 dynes/cm). Although the degree to which these two materials will spread on a solid also depends on the interfacial tension between the liquid and solid, the data appears to suggest that asphalt should spread more readily than water because it has a much lower interfacial tension with air. However, the energy that is needed to spread an asphalt at 77 °F (25 °C) far exceeds any interfacial energies which may promote spreading.(2,7) This is due to its high viscosity. The energy which causes a material to resist spreading due to its cohesiveness is defined as the work of cohesion. The work of cohesion goes against spreading and thus is positive energy. The work of adhesion must overcome the work of cohesion for spreading to occur. Thus, when the work of adhesion is added to the work of cohesion, the summation must be negative for spreading to occur, indicating energy is given off. This difference is often defined as the spreading coefficient.(2) None of the reports reviewed indicated how the work of cohesion was considered. Thus the results of surface energy studies must be viewed with caution.

(2) Debonding or Stripping. The degree of spreading when mixing an asphalt and aggregate is mainly a function of the amount of binder, the binder viscosity, the degree of mixing, the shape of the aggregate, and the degree to which the aggregate is dried. Thus the results of interfacial studies concerned with spreading, such as those previously mentioned, give little useful information for most applications. However, interfacial tensions can be used to study debonding or stripping.

The "work of separation" is the energy required to separate two materials when they are at equilibrium. In figure 1, when the asphalt rolls back into a bubble, the aggregate-air surface area increases, the aggregate-asphalt surface area decreases, and the asphalt-air surface area decreases, thus the work of separation is:

$$\text{Work of separation} = A - B - C. \qquad (4)$$

When energy must be applied to a system to obtain separation, the work of separation will be positive. Again, a coefficient may be placed before the interfacial tension "C" to account for differences in the changes in the three interfacial surface areas. This equation is the negative of the work of adhesion given in equation 1 and thus is determined in the same way, by measuring either the energy of immersion or the contact angle. As with studies on spreading, the effect of the cohesiveness of the asphalt on separation is generally not addressed in most studies.

Values for the work of separation for some materials are given in table 2. In some reports these are defined as the work of adhesion, as the absolute values of these two types of work are equal for an asphalt bubble which spreads by rolling and recedes by rolling back. However, as previously noted, contact angles can depend on whether the asphalt is advancing or receding before the measurement is recorded. This is a fundamental problem with using contact angles. In other reports the work of separation is called an adhesion tension, which makes the literature confusing as adhesion tension is also another name for the energy of immersion.

As previously stated, table 2 does not contain the necessary interfacial tensions to calculate the works of separation (or works of adhesion) and in many studies only the work of separation is reported. It is often difficult to determine from the literature how a reported work of separation was determined and at what temperature it was determined. Mathematical errors were found in a few reports concerned with the measurement of the work of adhesion and separation, which reduces the confidence in these studies. The reported works of separation in table 2 between rocks or minerals and asphalt are close, although the literature indicates they increase slightly with increasing aggregate polarity.

If the edge of the asphalt bubble in figure 1 detaches upward from the aggregate rather than rolls back, then the aggregate-air surface area increases, the asphalt-air surface area increases, and the aggregate-asphalt surface area decreases, all by the same amount. The work of separation needed to accomplish this is:

$$\text{Work of Separation} = A - B + C. \quad (5)$$

This is the amount of work that must be applied to the system when it is at equilibrium to cause a unit area of detachment. It is known as the Dupre equation.(4,10) The work of separation is greater for the detachment case compared to the case where the asphalt rolls back and thus it would seem less likely to occur. However, many aged asphalts are so stiff that they cannot roll-back, and thus detach.

The work of separation by detachment is the negative of the work of adhesion if adhesion were to be by attachment. (Equation 5 is also the negative of the work of adhesion given in equation 2 if a coefficient is not placed before the interfacial tension "C.") As with the case where the asphalt rolls back, it can be found by measuring the energy of immersion. For the case where the asphalt rolls back, the term "A - B" can also be obtained by measuring a contact angle. The literature does not indicate whether this approach physically applies to the detachment case. Although the literature is generally confusing on which equation is used to calculate a work of separation, it appears that equation 4 is generally used.

Figures 1 and 2 can also be applied to a drop of asphalt on aggregate which is then placed in water. Compared to the case in air, it has been stated in the literature that the work of separation in water is generally much lower, thus indicating a greater propensity for the asphalt to recede or strip when surrounded by water. However, little data is available to confirm this hypothesis. When placed in water, the interfacial tension "A" should significantly drop, the interfacial tension "C" should change very little, and the interfacial tension "B" should remain the same. A negative work of separation indicates the asphalt should recede. Some methods for directly measuring the work of separation for some oils on granular materials in water are reported elsewhere, but they apparently are not used and/or are not applicable to aggregate-asphalt combinations.(4) By subtracting the two works of separation (work in air minus the work in water), the change in the work of separation due to the water can be calculated and used as another parameter to determine the propensity for stripping. This has not been done.

Studies on asphalts indicate that water, which is highly polar, can strip asphalt from most aggregates because polar liquids are better able to reduce the surface energies of aggregates than nonpolar or partially polar liquids such as asphalt. As shown in table 2, the works of separation between aggregates and water are greater than between aggregates and asphalt. Thus water has a greater selective wetting power and should produce stripping. However, whether stripping will occur should be determined using the combination of asphalt and water, as the asphalt and water have their own interfacial tension. These values in table 2 appear to be computed using equation 4.

Polar molecules are those in which the centers of the negative and positive charges do not coincide. Water molecules being polar thus can satisfy both negative and positive charges (polar or ionic sites) on aggregate surfaces. Asphalts on highly polar aggregates such as quartz are most likely to strip while asphalts on weakly polar aggregates such as limestone are least likely to strip. The asphalts on the highly polar aggregates should have slightly higher works of separation in air but lower works of separation in water. Aggregates more prone to stripping should have high interfacial tensions. Whether or not some polar groups of an aggregate have a higher adhesive force with asphalt than other polar groups is generally not determined in surface energy studies. Only the overall total surface free energy is considered. Surface energy studies also have not accounted for any long-term, time-dependent chemical bonds if they occur.

Because surface energy theories indicate that most aggregates are capable of being stripped of asphalt to some degree, then most aggregates must be considered hydrophilic. Whether an aggregate is hydrophilic must be determined using the combination of asphalt and water, as the asphalt and water by themselves in air will spread differently. How water displaces an asphalt film on a completely coated aggregate, or moves it aside, is not clearly known. An inverted emulsion, where water penetrates through an asphalt, is possible.(1)

(3) Conclusions of Surface Energy Studies. The majority of researchers who have studied the causes of stripping hypothesize that interfacial energy relationships are primarily responsible for adhesion and stripping mechanisms. However, the literature indicates that surface energy theories of adhesion and concepts based on minimum surface free energy and contact angle have not adequately described the adhesive properties of asphalt-aggregate-water systems. Only generalized conclusions have been obtained from them.(4,8) Studies in these areas use numerous assumptions and oversimplifications compared to pavement mixtures, such as the use of smooth, flat aggregate surfaces. The literature also has poorly defined models for asphalt-aggregate systems, lacks explanations for many test results, and the terminology is not consistent from report to report. The models used in figures 1 and 2 are the simplest versions given in the literature and, like most models, can be expanded.(2,11)

One conclusion from surface energy studies is that aggregates that have more unbalanced forces may have a greater adhesive force with the asphalt. However, these aggregates will also have a greater tendency to strip because more forces will remain unsatisfied. Adsorbed foreign materials can have positive or negative effects on adhesion and stripping. The effects depend on if they are compatible with the asphalt.

b. Chemical Bonding

(1) Degree of Acidity or pH. Concepts and research on chemical bonds between asphalts and aggregates indicate that these two materials may form chemical bonds, such as water-insoluble covalent bonds, which affect adhesive strength.(4,8) Most studies on chemical bonding have been very simple such as those that indicate how asphalts and aggregates should bond according to their degree of acidity, or pH. The pH of a material indicates its hydrogen-ion activity. Values less than 7 represent increasing hydrogen-ion concentration and increasing acidity, while values greater than 7 indicate decreasing hydrogen-ion concentration and increasing alkalinity. A pH of 7 indicates neutrality.

Chemical bonding concepts based on measuring pH state that more bonds will be formed between an acidic material and a basic material than between two materials that are either both acidic or both basic, and the degree of bonding will be greatest between a strongly acidic material and a strongly basic material. Even though asphalts are amphoteric, or are capable of functioning as a base or an acid, they have generally been considered slightly acidic in most chemical bonding studies. Thus it is hypothesized that basic aggregates should provide good adhesive properties while acidic aggregates should bond poorly.(12) It was assumed in the chemical bonding studies which were reviewed that the reaction would produce water-insoluble chemical bonds, which may not be the case. The solubility of the bonds were not discussed.

Assuming that water has a pH of 7 and asphalt has a pH less than 7, then in chemical bonding studies, acidic types of aggregates are considered hydrophilic and should strip. Asphalt has a lower pH than water and thus the water should tend to displace most of the asphalt chemical groups and be adsorbed itself. A thorough discussion of this process was not given in the literature. Basic aggregates are lipophilic and should not strip. In this case, the lower pH of the asphalt compared to water is desirable. Some reports define basic aggregates as hydrophobic. However, very few aggregates are known to repel water. Either definition opposes surface energy concepts where most aggregates are considered hydrophilic. An additional complication is that through hydroxylation, partially stripped aggregates in contact with water can become more hydrophilic over time.(2)

(2) Classifications Based on Chemical Composition. Most types of aggregates have both basic and acidic characteristics, thus the degree of acidity must be determined on a percentage basis. One method of classifying rocks determines the ratio of acidic components, SiO_2 plus CO_2, to the basic components: Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, plus K_2O.(4,7) These classifications, based on chemical analyses, use cutoffs between acidic and basic aggregates of around 50 to 55 percent, and some define an intermediate range such as 55 to 66 percent. Below 55 percent is considered basic and above 66 percent is considered highly acidic in this case.(7) The reasons for these particular cutoffs were not given in the literature reviewed. Chemical analyses of some rocks are shown in table 3.(7,13) For most types of rocks, the degree of acidity can be based solely on the SiO_2 content.

(3) Classifications Based on Mineralogical Composition. Table 4 shows a mineralogical classification for rocks. Mineralogical classifications base the degree of acidity on the percentage of individual minerals in the rocks and the acidity of each mineral. Acidity in table 4 is often based on the percentage of quartz and orthoclase and plagioclase feldspars, which are considered acidic. The degree of acidity from mineralogical classifications may conflict with chemical classifications. Chemical analyses report compositions in terms of oxides, even if such oxides are not present in the rock.(7) Chemical analyses also do not account for the various molecular arrangements that exist. Neither analysis necessarily determines the degree of acidity for the composition at the surface, nor do they account for the various levels of acidity of individual chemical constituents or mineralogical types. For example, two rocks may have the same overall degree of acidity, but one rock may have a strongly acidic component and a strongly basic component, and the other rock may have a weakly acidic component and a weakly basic component. Even though they have the same rating, their bonding properties may be different. Elemental analyses are not useful at all. Table 5 shows another mineralogical classification for igneous rocks based mainly on the amount of quartz.

(4) Zeta Potential. Studies on the pH and zeta potentials of minerals and rocks indicate that various natural samples for any one type are rarely identical and their pH values and zeta potentials can vary.(22) Zeta potential is the difference in electrical potential across the interface

Table 3. Typical chemical analyses of rocks in percentages.(7,13)

Rock	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O	CO_2
IGNEOUS ROCKS										
Granite	68.3	14.8	1.3	2.7	0.8	2.3	2.7	5.0	1.1	...
Syenite	64.7	10.5	1.1	7.4	5.2	3.1	2.2	3.6	0.9	...
Granodiorite	59.9	16.4	3.0	3.7	3.1	6.3	4.1	2.5	1.1	...
Quartz-diorite	46.5	13.3	2.6	7.2	7.3	8.2	1.7	1.7	3.7	...
Diorite	52.1	16.4	3.7	6.0	4.1	7.3	3.7	2.3	1.1	...
Gabbro	44.9	15.4	2.3	12.4	10.9	7.5	3.0	0.5	0.8	...
Olivine gabbro	49.8	18.6	2.1	8.4	5.8	9.7	2.6	0.7	1.0	...
Granite porphyry	73.5	13.7	1.2	0.7	0.4	1.2	4.4	4.5	0.4	...
Syenite porphyry	64.5	16.8	2.1	1.0	0.6	1.4	6.1	5.7	0.8	...
Diabase	48.9	20.9	2.0	9.4	4.4	8.0	3.1	1.8	1.2	...
Rhyolite	74.3	12.9	0.8	0.5	0.9	0.9	2.5	4.7	2.1	...
Trachyte	66.0	18.5	2.2	0.2	0.4	1.0	5.2	5.9	0.9	...
Dacite	65.7	15.6	2.1	2.1	2.5	3.6	3.7	2.0	1.1	...
Andesite	61.4	16.6	2.1	3.1	2.7	6.2	3.8	1.3	1.7	...
Augite-andesite	63.5	12.4	6.4	1.3	1.3	4.2	4.9	1.8	2.9	...
Basalt	51.7	17.9	7.2	1.0	2.8	6.9	4.2	1.6	1.2	...
Olivine basalt	49.9	15.2	1.7	10.5	6.3	9.4	3.1	0.9	0.2	...
Obsidian	73.5	12.9	0.4	0.4	0.2	0.6	4.4	4.3	3.5	...
Pumice	68.6	14.2	1.4	1.5	0.8	2.4	5.2	2.5	3.3	...
Ash	64.5	14.7	2.7	0.8	0.3	4.0	2.6	3.3	5.7	...
Tuff	31.4	11.6	2.4	7.5	5.3	16.7	2.3	0.7	4.9	...
Breccia	46.7	12.8	0.5	...	2.6	5.4	3.7	6.9	1.2	...
METAMORPHIC ROCKS										
Quartzite	74.2	10.6	7.5	0.9	1.5	0.6	2.1	1.1	1.8	...
Feldspathic quartzite	73.7	11.1	7.2	0.8	1.5	0.4	1.7	1.7	...	...
Micaceous quartzite	...	...	...	...	...	...	...	...	...	...
Gneiss	70.2	13.9	1.1	3.1	1.3	3.1	3.3	2.7	0.7	...
Hornblende gneiss	48.7	14.4	4.0	10.1	6.3	9.2	2.3	0.5	2.5	...
Granite gneiss	66.9	14.9	0.9	3.4	0.3	1.2	5.6	5.0	0.5	...
Quartz gneiss	76.9	12.1	1.2	1.4	1.9	0.4	5.3	Tr.	0.5	...
Biotite gneiss	67.7	16.6	2.1	2.0	1.3	1.9	4.4	2.4	1.7	...
Mica gneiss	58.8	17.2	5.2	4.0	0.9	0.6	5.7	5.4	1.1	...
Schist	59.3	19.5	1.8	5.7	1.8	1.2	1.3	3.3	4.2	...
Hornblende schist	50.3	14.1	7.0	5.3	7.2	8.1	4.0	2.3	1.6	...
Biotite schist	62.4	17.4	1.0	7.1	2.1	0.5	0.7	4.1	3.1	...
Sericite schist	57.2	23.5	3.2	4.9	0.9	0.1	1.2	3.6	5.0	...
Mica schist	64.7	16.3	1.8	3.8	2.9	0.1	0.1	5.6	3.1	...
Talc schist	53.3	4.4	5.8	1.0	29.9	1.5	1.5		2.6	...
Slate	61.6	16.3	4.1	2.7	2.9	0.5	1.3	5.5	3.4	...
Calcareous slate	50.9	14.1	...	9.9	8.7	8.7	...	0.9	...	...
Siliceous slate	78.9	None	13.9	1.2	0.2	0.8	...	...	2.9	...
Marble	...	0.2		...	21.4	30.9	CO_2 = 46.7			...
Dolomitic marble	...	...	0.2	...	20.7	30.7	CO_2 = 46.7			...
Amphibolite	48.5	16.4	2.0	10.5	9.7	9.8	1.4	0.3	0.8	...
Serpentine	40.0	1.4	...	3.4	39.2	...	...	...	12.1	...

Table 3. Typical chemical analyses of rocks in percentages (continued).(7,13)

Rock	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O	CO_2
SEDIMENTARY ROCKS										
Conglomerate	59.2	19.2	Tr.	6.5	2.5	1.1	1.6	5.4	2.2	...
Sandstone	76.1	8.7	...	3.5	4.3	1.3	1.1	0.5	1.7	...
Argillaceous-sandstone	75.5	14.8	6.4		...	...	...	...	2.0	...
Calcareous-sandstone	54.2	7.4	0.5	1.4	3.3	14.6	1.7	1.7	1.5	...
Feldspathic-sandstone	...	...	...	...	...	...	...	...	...	...
Ferruginous-sandstone	49.8	5.2	29.2	0.4	1.0	2.4	0.8	0.5	10.4	...
Arkose	76.1	8.7	...	3.5	4.3	1.3	1.1	0.5	1.7	...
Shale	53.3	22.4	6.6		2.1	0.5	1.1	7.4	4.1	...
Calcareous shale	37.9	7.0	1.0	0.5	12.4	13.3	1.2	2.0	1.7	...
Siliceous shale	82.7	1.8	1.0	0.3	1.1	2.9	0.5	2.6	4.8	...
Chert	98.2	0.8		...	...	...	...	...	...	...
Limestone	3.8	1.0	0.4	...	1.2	51.3	...	...	...	41.6
Argillaceous-limestone	17.0	6.9	2.1	...	2.2	35.5	...	...	...	32.9
Dolomitic-limestone	16.2	3.2	0.9	...	$MgCO_3$ = 36.0		$CaCO_3$ = 54.5		...	$CaCO_3$ = 54.5
Ferruginous-limestone	28.8	1.3	1.0	37.4	3.6	0.7	...	...	0.7	...
Siliceous-limestone	27.5	1.7	2.0	...	$MgCO_3$ = 0.3		$CaCO_3$ = 63.8		1.9	$CaCO_3$ = 63.8
Limerock	0.3	0.3		...	$MgCO_3$ = 0.4		$CaCO_3$ = 99.0		...	$CaCO_3$ = 99.0
Dolomite	0.1	0.1	...	0.3	21.2	30.6	...	...	0.2	46.9
Argillaceous-dolomite	2.4	...	1.3	...	$MgCO_3$ = 41.1		$CaCO_3$ = 51.1		...	...
Siliceous-dolomite	8.3	1.8	0.2	1.1	16.7	29.0	0.1	1.1	0.4	41.6

Table 4. Typical mineralogical compositions of rocks in percentages.(7,13)

Rock	Quartz	Ortho-clase	Plagio-clase	Augite	Horn-blende	Biotite	Mus-covite	Epidote	Rock glass
IGNEOUS ROCKS									
Granite	30	41	8	...	...	3	3	1	...
Diorite	8	7	30	3	27	4	0.1	5	...
Gabbro	0.5	...	44	28	9	2	...	1	...
Diabase	...	...	44	46	...	...	...	...	2
Rhyolite	32	45	3	...	0.7	3	2	2	0.4
Trachyte	3	42	1	2	6	0.5	...	8	9
Andesite	0.6	...	48	14	3	...	...	3	13
Basalt	...	...	36	35	...	...	...	...	21
METAMORPHIC ROCKS									
Quartzite	84	3	...	...	1	2	2	2	...
Feldspathic-quartzite	46	27	1	...	...	2	5	1	...
Hornblende-gneiss	10	16	15	3	45	3	1	2	...
Granite-gneiss	37	32	3	...	...	7	11	2	...
Biotite-schist	34	13	3	...	1	38	3	2	...
Mica-schist	37	16	1	...	...	13	26	2	...
Slate	29	4	...	...	...	...	55	2	...
Marble	3	0.2	0.2	...	...	...	Calcite = 96		...
Amphibolite	3	1	8	...	70	1	0.2	12	...
SEDIMENTARY ROCKS									
Sandstone	79	5	0.3	...	...	0.2	1	...	...
Feldspathic-sandstone	35	26	2	...	...	0.6	2	1	...
Calcareous-sandstone	46	3	2	...	...	...	Calcite = 42		...
Chert	93	...	...	...	...	...	Calcite = 1		...
Limestone	6	...	...	...	Dolomite = 8		Calcite = 83		...
Dolomite	5	...	...	...	Dolomite = 82		Calcite = 11		...

Table 5. Degree of acidity of igneous rocks.

pH	Acidic <----------------------------------> Basic				
MINERALS	Quartz, %	> 10	0 to 10	Generally Absent, < 5	Usually Absent
	Type of Feldspar	Orthoclase	Orthoclase Na-Plagioclase	Na-Plagioclase (Albite usually)	Ca-Plagioclase (Labradorite usually)
	Other Major Minerals	Some Biotite, Hornblende, Muscovite	Some Biotite, Hornblende	Biotite + Hornblende + Pyroxene<40%	Biotite + Hornblende + Pyroxene + Olivine>40%
TEXTURE	Phaneritic Phaneritic-Porphyritic	Granites	Syenites	Diorites	Gabbros Peridotite Dunite Pyroxenite Hornblendite
	Aphanitic Aphanitic-Porphyritic Aphanitic-Vesicular	Rhyolites	Trachyte Dacite	Andesites	Basalts Augitite Dolerite/ Diabase Basaltic-Achondrite
	Fragmental	Tuff Breccia	Tuff Breccia	Tuff Breccia	Tuff Breccia
	Vesicular-Glassy	Pumice	Pumice	Scoria	Scoria
	Glassy	Obsidian Pitchstone Perlite	Obsidian Pitchstone	Obsidian Pitchstone	Basaltic-Obsidian
COLOR	Dark/Light	10/90	10/90	50/50	90/10

between a substance such as aggregate and the surrounding medium. It is caused by the presence of surface charges. Water is used as the medium in studies dealing with moisture damage. Zeta potentials can be determined for crushed and uncrushed minerals and rocks, and for natural surfaces and surfaces treated with materials such as antistripping additives. Thus the data can be used to evaluate surface effects. Studies concerned with the zeta potentials of aggregates try to relate the degree of chemical bonding to the zeta potential. For understanding adhesion, it is believed that measuring zeta potentials should be an improvement over just determining the degree of acidity or pH.

It has been determined that zeta potentials for rocks are not simple averages of the potentials of their mineral constituents. Interactions of the constituents and minor minerals appear to be very important. The source of the aggregate and variations within a quarry thus are factors which can influence the zeta potential.

In one study, both the zeta potential and the change in the pH of the water due to the mineral or rock were measured. The zeta potentials of the minerals and rocks were all negative, and they appeared to the authors to be more negative as the pH of the water deviated from neutral. They concluded that the zeta potentials were more negative at the low and high pH values, which ranged from 5.1 to 9.6.(22) However, the data was scattered and a relationship between zeta potential and stripping was not evident. In another study, higher zeta potentials appeared to indicate a greater propensity for stripping, but only five aggregates were evaluated.(23)

(5) Conclusions of Chemical Bonding Studies. As with studies concerned with surface energy theories, most past studies dealing with chemical bonding have only provided a few generalized conclusions concerning adhesion and debonding, and the chemical properties of the binder were generally treated as being far less important than the type of aggregate. However, the surface chemistries of aggregates have not been determined.

Support for concepts which state that chemical bonds are formed is given by some studies where the heat of reaction, or enthalpy, has been measured. For physical adsorption, the heat given off by the process should be very small because it is a condensation process. Chemical reactions should give off more heat because there is a heat of reaction.(2) The amount of heat given off in these studies indicates that chemical bonds are being formed. Most of these studies have been concerned with the effects of the chemical composition of the asphalt on moisture damage. See the section of this report entitled "**2.** Type of Asphalt."

c. Mechanical Interlock

The physical properties of the aggregate affect stripping, but how the effects of these properties along with surface energy and chemical bonding concepts can be combined to explain moisture damage is difficult to perceive.

Increased aggregate angularity and surface roughness increases the mechanical interlock, which may help to resist the effects of moisture damage. However, complete wetting and a uniform film thickness may be more difficult to obtain with aggregates having high angularities. Asphalt films at sharp edges may be very thin and more susceptible to breaking. Increased angularity and surface roughness also increase the surface area, or contact area, between the aggregate and asphalt. This may also increase the mechanical grip and asphalt demand, but any beneficial effects are confounded with the change and variability in film thickness.

The angularity of the aggregate and the contact area between the asphalt and the aggregate can be increased by crushing the aggregate, but changes in surface energy factors must also be considered. Crushing may increase the number of unbalanced forces, which may increase or decrease the susceptibility to moisture damage depending on the type of aggregate and asphalt. However, because reactions can occur within the surface of a solid to balance the surface forces and the surface can adsorb polar or polarizable molecules from the surrounding medium, some of the broken bonds from crushing may not be available for bonding. Surfaces of materials generally have unbalanced forces which leads to surface tension. Thus, these surfaces tend to attract various materials even from the air.(8)

Verbal reports indicate that crushing generally increases the susceptibility to stripping, while weathering generally has the opposite effect.

Weathering should decrease the interfacial tensions between the aggregate and other materials. This should reduce both the adhesive force and the potential for stripping, unless other factors which help to reduce the susceptibility to damage, such as mechanical interlock, are significantly lost in the process. However, there is little published data to verify this hypothesis. It is also hypothesized that over a long time period, adsorbed water molecules or loosely bound water may be replaced with oxides of iron, oils, fatty acids, or other organics more compatible with asphalt than water.(8,22)

The mechanical interlock and contact area between the asphalt and the aggregate can also be varied by manipulating the aggregate gradation. However, this manipulation can have a side effect. Fine and coarse aggregates used in a paving mixture often are not the same rock type since different types of aggregates are often blended together. Because moisture damage may be confined to only the coarse or fine fraction, or be more dominant in one fraction, an alteration of the blend could increase or decrease the potential for moisture damage. Also, while failure can be caused by damage in either fraction, damage in one fraction of an aggregate may be more detrimental than damage in another fraction if these fractions affect the mechanical properties differently. It has been hypothesized that stripping in the fine fraction may be more disruptive to the integrity of the mixture than in the coarse fraction. It is unknown if slight, routine adjustments in the percentages of the different aggregates may lead to some variations in moisture susceptibility. These adjustments often have to be made while the mixture is being produced at the plant.

A higher aggregate porosity generally increases the contact area and asphalt absorption, and thus possibly the mechanical grip. However, it also may be difficult to completely remove all water vapor from inside the pores. Furthermore, the effects of the long-term absorption of asphalt or specific asphalt chemical functional groups on the susceptibility to moisture damage are unknown. Thus, a higher porosity may or may not be beneficial. Studies to evaluate the role of porosity would be difficult to perform because it is hard to find a particular rock composition having various porosities. An evaluation of porosity would almost certainly be confounded with changes in the chemical composition of the rock.

The crystalline grain size of the aggregate can affect both surface roughness and porosity. Thus, it is also a factor. Glossy or cryptocrystalline surfaces are generally low in surface roughness and porosity.

Increased aggregate permeability is detrimental because water entering one point of an aggregate may diffuse through the aggregate to other points.

Dust and clay coatings must also be considered because they inhibit an intimate contact between the asphalt and aggregate and provide channels for penetrating water.(7,24) It has also been hypothesized that finely divided mineral matter may cause stripping by emulsifying small amounts of the binder when water is present, but this appears to be an insignificant factor if it does occur.(25) The agitation during mixing may remove some coatings from aggregate surfaces but it also may create additional dust.

An increase in the moisture content of the aggregate may also decrease adhesion if the water is not thoroughly dried from the aggregate surfaces or pores.(2,4) Even if the aggregates are thoroughly dried by the mixing plant, they still may have several molecular layers of adsorbed water, which will decrease the number of unbalanced forces on the surface of the aggregate. Most water is liberated upon heating to 212 °F (100 °C) but several molecular layers may be bound so strongly that temperatures exceeding 1832 °F (1000 °C) are required for liberation.(8) The effects of this strongly adsorbed water on adhesion and moisture damage are unknown but appear to be very low.(2,8) Adsorbed water can affect both surface energies and the degree of chemical bonding and the effects may depend on the type of aggregate.

Other molecular layers of materials may also be strongly adsorbed. As previously stated, these materials may increase or decrease adhesion depending on (1) the type of aggregate, (2) the types of adsorbed materials, and (3) the way the adsorbed materials affect surface energies and the degree of chemical bonding. The literature reports that oxides of iron, oils, fatty acids, or other organics may be adsorbed. Normal mixing temperatures and the agitation involved will not necessarily remove all of these materials.(26) Little or no research can be found concerning adsorbed materials and their effects on adhesion.

The hardness of the aggregate and its resistance to degradation may also be important because aggregates that degrade or break due to freezing or traffic loads may disrupt the asphalt film and expose new, uncoated surfaces. However, minerals of high hardness are often very hydrophilic.(10)

d. Classification According to the Degree of Visual Stripping

Table 6 lists various minerals and rocks according to the degree of visual stripping associated with them. This information was extracted from reports dealing with either surface energy theories, chemical bonding, or the effects of mechanical interlock. See references 4, 7, 14, 15, 16, 17, 18, 19, 20, and 21. Slight stripping is less than 10 percent; moderate stripping is from 10 to 30 percent, and severe stripping is in excess of 30 percent. Some minerals fall into more than one category, thus they often display various degrees of stripping. Because many minerals do not fall into a single category, it is not surprising that many rocks, which are made up of minerals, cannot be classified definitively.

Variations in the degree of visual stripping for a particular mineral or rock listed in table 6 are probably related to (1) the presence and types of adsorbed materials, (2) slight differences in mineralogical composition, (3) impurities, (4) the structure and degree of crystallinity, (5) the effects of weathering, and (6) other factors which affect the polarity of the surface. Factors such as the types of adsorbed materials and weathering show the importance of interfacial properties, and indicate that surface properties are more important than the overall composition of the aggregate. For example, hornblende and biotite are sometimes found to strip when used in their natural state, although freshly cleaved surfaces do not strip. These minerals are usually considered basic and not susceptible to stripping. Crystallinity is important because crystalline substances generally possess more unbalanced forces than amorphous materials. A rock may vary in mineralogical composition, impurities, and/or the degree of crystallinity even within a quarry.

Table 6 appears to indicate that most aggregates will strip to some degree. This may be due in part to the fact that more aggregates prone to stripping have been studied than those not prone to stripping. Highway agencies which have little problems with stripping do not publish reports

Table 6. List of rocks and minerals according to the degree of stripping associated with them.

MINERALS

Slight Stripping	Moderate Stripping	Severe Stripping
Biotite	Biotite	Biotite
Hornblende	Hornblende	Hornblende
Feldspars:	Feldspars:	Feldspars:
• Labradorite	• Oligoclase	• Oligoclase
• Bytownite	• Albite	• Albite
• Anorthite	• Anorthite	• Anorthoclase
Chlorite	Garnet	• Microcline
Sericite Muscovite	Quartz	• Perthite
Diopside	Muscovite	• Andesine
Olivine		Chalcedony
Pyroxenes		Quartz
Augite		
Calcite		

IGNEOUS ROCKS

Slight Stripping	Moderate Stripping	Severe Stripping
Gabbro	Biotite Granite	Granite
Basalt	Basalt	Biotite Granite
Greenstone (Basalt)	Olivine Dolerite with Analcite	Aplite Granite
Quartz Dolerite	Quartz Diorite	Pegmatite Granite
Diabase	Andesite	Soda Granite
Scoria, Slag	Diabase	Granite Porphyry
Peridotite		Granodiorite
		Obsidian
		Albitised Olivine-Diorite
		Diorite
		Rhyolite
		Trachyte
		Pumice
		Granite Porphyry
		Dacite
		Syenite

Table 6. List of rocks and minerals according to the degree of stripping associated with them (continued).

METAMORPHIC ROCKS

Slight Stripping	Moderate Stripping	Severe Stripping
Siliceous River Sand	Biotite Feldspar Gneiss	Quartzite
Siliceous Sand with Iron Oxide Coat	Feldspathic Quartz-Sercite Gneiss	Granitic Gneiss
Serpentine	Granitic quartz-Feldspar Gneiss	Quartz-Sericite Schist
	Biotite-Muscovite Schist	Feldspathic-quartzite
	Diabase-Hornfels	Biotite Schist
	Hornblende-Gneiss	Muscovite Schist
	Biotite Schist	

SEDIMENTARY ROCKS

Slight Stripping	Moderate Stripping	Severe Stripping
Limestone	Limestone	Iron Oxide-rich Arkose
Dolomite	Dolomite	Chert
Graywacke	Limerock	Flint
Limerock	Reef Coral	Breccia
	Calcareous Sandstone	Feldspathic Sandstone
		Sandstone
		Chalk
		Oolitic Limestone
		Argillaceous Sandstone

or perform a high amount of research on stripping problems, and thus their aggregates do not appear in reports on stripping. Also, data is not available to determine the number of times a mineral or rock falls into a particular category for stripping in table 6. Thus, even though a mineral or rock falls into more than one category, it may not fall equally into each category. Table 3 shows that the majority of aggregates have an SiO_2 plus CO_2 level above 50 percent, and thus some stripping with the majority of aggregates could be expected.

2. Type of Asphalt

The stiffness of an asphalt can have an effect on moisture susceptibility. The viscosity of the heated asphalt must be sufficiently low during mixing to allow complete coating and absorption. Mixing time is equally important. After coating, stiffer asphalts are generally harder to peel from an aggregate at ambient temperatures, or take longer to peel, and thus have more resistance to moisture damage. See references 2, 14, 16, 27, 28, 29, and 30. The strength or cohesiveness of a very stiff mixture may not significantly decrease even if a significant amount of detachment occurs. This is often shown by age hardened asphalts, such as those in 20-year old binder or base layers, where detachment from the coarse aggregate has occurred but the mixture remains intact. It is unknown if the increased resistance to moisture damage with increased stiffness is really due only to the stiffness or cohesiveness of the binder. Differences in the amounts of the various asphalt chemical functional groups being adsorbed also may play a role. Moisture susceptibility is a function of the grade of asphalt and age hardening.

Asphalt chemical composition has been connected to variations in the degree of moisture damage, although most problems have been attributed to and vary with the type of aggregate. See references 12, 15, 16, 27, 31, 32, 33, 34, 35, 36, 37, and 38. Studies concerned with the effects of asphalt chemical composition on moisture damage have been limited in scope and number. Most studies have been concerned mainly with the effects of the type of aggregate. The chemical composition of the asphalt was generally not considered. Most studies concerned with the effects of asphalts have only evaluated the effects of their rheological properties. However, all of these studies measured asphalt-aggregate-water interactions. In this report, the effects of the type of aggregate and the type of asphalt on moisture damage are separated even though they interact. The information in the literature is presented in this manner.

It has been shown that tars, which contain a relatively high amount of phenols, are more resistant to stripping than asphalts. However, under extreme conditions or with very poor aggregates, the differences between these two binders may be insignificant.(25,28,39)

Using Rostler-Sternberg fractional composition analyses, it has been stated that the resistance of asphalts to stripping decreases with a decrease in the ratio of the nitrogen bases (N) plus first acidaffin (A_1) fractions to the paraffin (P) plus second acidaffin (A_2) fractions, or with an increase in the asphaltene fraction.(33) Even though asphaltenes are polar, it is hypothesized that because their molecular species are strongly associated to form relatively rigid structures within the other asphalt fractions, they cannot satisfy the unbalanced forces on the surfaces of the aggregate. By itself, this explanation seems insufficient. How these conclusions explain or complement the conclusions from the studies on rheological properties was not given.

Other studies indicate that the asphalt chemical functional groups most easily displaced by water are carboxylic acids, anhydrides, and 2-quinolones, followed by sulfoxides, and total nitrogen. See references 37, 40, 41, 42, and 43. More difficult to displace are ketones, phenolic OH, and pyrrolic NH. Of particular note is that many of the functional groups which are most easily displaced, such as carboxylic acids and sulfoxides, are those which tend to be strongly adsorbed by the aggregate after mixing. No completed study concerned with chemical composition has evaluated asphalt-aggregate interactions and moisture damage mechanisms using a broad range of different asphalts and aggregates. Again, how these conclusions explain or complement the conclusions from the studies on rheological properties was not given. As with studies using surface energy theories, the effect of the cohesiveness of the binder is not adequately addressed.

The crude source of the asphalt and the refining process are important because the chemical composition of asphalts within a grade may be very different. Asphalts originating from the same crude source may even have different properties. The processes used to produce the asphalts may be different, or the asphalts may have been treated differently. Some suppliers may even add an antistripping agent to their asphalts.

3. Mixture Design and Construction

The air void level and the permeability of the mixture, which are influenced by the degree of compaction, asphalt content, and aggregate gradation, are important because they control the level of water saturation and drainage. See references 29, 44, 45, 46, 47, and 48. In general, the percentage of air voids which can be filled with water increases with an increase in permeable air void level. One exception is with open-graded mixtures where air void levels of 15 to 25 percent allow water to drain. However, the water must be able to completely drain from the mixture and not pond underneath. Therefore, open-graded layers should not be placed directly on rutted pavements. For dense-graded mixtures, the surface must allow any surface water to run off of it.(49) Sealing a pavement to prevent the entrance of water can be helpful. Any measure which prevents water from collecting and remaining in a pavement should be beneficial. Moisture damage often occurs in base layers and in permeable layers placed on nonpermeable bases, especially where subsurface drainage is poor.(3)

Increasing the asphalt content should decrease moisture damage because of the increase in film thickness and the decrease in permeability. Even if a coating appears to be complete, it may contain holes or discontinuities which can enlarge with time. See references 4, 7, 8, 25, 29, and 50. It may also be possible for water to diffuse through an asphalt by osmosis in quantities of significant substance regardless of the film thickness.(1) In this case, water may appear to be dispersed in the asphalt, which is considered an inverted emulsion (water in oil).(1) Diffusion may be due to (1) the development of blisters, where asphalt wraps around drops of water because of special interfacial energy mechanisms, (2) the presence of emulsifiers in the asphalt, (3) dusts and water soluble salts at the aggregate surface which attract water, and (4) the movement of water to aggregates because they are cooler.(8) The recommended method for increasing the asphalt content of a mixture, or the amount of coating, is to open up the gradation to increase the voids in the mineral aggregate (VMA).

Other mixture design factors such as gradation have been previously discussed under the section of this report entitled "**c. Mechanical Interlock.**"

4. Environment

There are several environmental factors which can affect the degree of moisture damage besides the amount of rainfall and water in the pavement. Heat after a rainstorm can create blisters on aggregates at the surface of the pavement, which may leave a pit, if broken. These blisters are formed when warm asphalt moves from beneath a drop of water and spreads over it.(1,8) Low asphalt-water interfacial tensions should promote these types of blisters but retard pitting.(8)

Most blisters in asphalt pavements are formed primarily by the thermal expansion of entrapped water.(51,52) In some cases, bubbles coated with asphalt can be seen on the surface of the pavement, or the surface layer is pushed upward in small areas because of underlying expansion. Bubbles or raised surface layers caused by the expansion of entrapped water under the surface layer or in underlying layers may form holes or cracks if broken. If bubbles at the surface are caused by the expansion of water entrapped under the asphalt around the aggregates, then pits may be formed if the bubbles are broken. These mechanisms can speed up the moisture damage process. Besides water or water vapor, blisters have also been attributed, mainly through field observations, to salts, uncured steel slags, microbial action, and asphalt stripped from aggregate which makes its way to the surface along with entrapped air.(51) Other than the formation of blisters, the long-term effects of water vapor on a mixture are unknown.

Pressures and water movements due to freezing and thawing can rupture asphalt films and thus may promote stripping.(48) Cracks caused by low temperatures or fatigue stresses may promote stripping because they allow the entrance of water.

Temperature can also have an effect. Field experience has indicated that cool rainfalls and rapid drops in temperature while a pavement mixture is being placed or cured can have harmful effects on adhesion. Also, pavements placed in cool seasons may be more difficult to compact, and thus have higher air void levels and permeabilities than pavements placed in warmer weather. This may increase the susceptibility to moisture damage. During the life of the pavement, high temperatures may promote healing in dry weather, although in wet weather, the decrease in viscosity associated with the high temperature may decrease the resistance to moisture damage.(28)

Surface energies are a function of temperature. Changes in thermal vibrations caused by temperature fluctuations affect surface energies and thus the potential for moisture damage. However, little data is available on this subject.

Aging increases the stiffness of an asphalt and thus may decrease the susceptibility to moisture damage. As stated under the section of this report entitled "**2. Type of Asphalt**," the strength or cohesiveness of a very stiff mixture may not significantly decrease even if a significant amount of detachment occurs. However, aging also changes the chemistry of the asphalt and surface energies. The effects of these changes on moisture damage are unknown and are confounded with the increase in hardness and the fact that moisture damage is also time dependent. Whether a loss of adhesion can occur under dry condition with aging and how this interacts with moisture damage is unknown. There are no standardized or widely accepted aging methods to simulate the long-term chemical changes of an asphalt. Aging of an asphalt within a mixture is highly dependent on the climate and the amount of permeable air voids.

The pH of the water has been found to influence the degree of moisture damage and the effectiveness of antistripping additives. See references 4, 12, 23, 30, 32, and 53. Some of these studies show that a low pH helps the retention of acidic asphalts on acidic aggregates, while a high pH helps the retention of acidic asphalts on basic aggregates. This conclusion supports chemical bonding theories. The effectiveness of some antistripping additives appears to be affected by the pH of the water. In one study, it was stated that the effectiveness of liquid cationic antistripping additives on acidic aggregates may be improved by a low pH.(12) However, these studies have been limited in scope, and mechanisms for the reported conclusions were not given. Acidic rain may have an effect on damage, but this has not been investigated.

The presence of any ions in water could influence the degree of moisture damage. Thus, road salts may have an effect on damage, but this also has not been investigated.

5. Traffic

Asphalt which has partially stripped from an aggregate may re-adhere if the pavement dries except when the aggregate or asphalt is displaced by the action of traffic. See references 1, 4, 25, 27, 28, 45, and 49. Stresses from traffic and the effects of water interact to cause pavement failure.(2) Sharp, aggregate edges may be very susceptible to breaking because at these edges, the stress may be high while the film thickness may be low. Mechanical vibrations and pore pressures also may force water into asphalt-aggregate interfaces.(50) The extent that these two factors have on damage is unknown. Pore pressure is often hypothesized to be a major influence on the rate of damage. Traffic also wears and can scour the asphalt coating from aggregates on the surface of the pavement and can create cracks. However, decreased pavement air voids and permeability due to traffic may reduce the susceptibility to moisture damage in some cases.

6. Antistripping Additive Properties

The use of antistripping additives in mixtures can significantly affect the degree of moisture damage. Antistripping additives are discussed in chapter 2 of this report.

7. Summary of Factors

Adhesion should increase and moisture damage decrease when:

- The aggregate is thoroughly dried before the asphalt is added, because this liberates absorbed water and may increase the absorption of asphalt and thus the mechanical grip.

- The aggregate drying temperature is increased because higher temperatures liberate more water or water vapor.

- The aggregate is weathered because weathering decreases the number of unbalanced forces between the asphalt and aggregate. It is also hypothesized that during weathering, adsorbed water molecules or loosely bound water can be replaced with oxides of iron, oils, fatty acids, or other organics more compatible with asphalt than water.

- Dust coatings are removed because dust inhibits an intimate contact between the asphalt and aggregate and provides channels for penetrating water.

- The angularity, roughness, and absorption of the aggregate increase because these increase the mechanical interlock.

- The permeability and number of weakly bound planes in an aggregate decrease, because when this is not the case, water entering an aggregate at one point may diffuse to other points.

- The resistance of the aggregate to thermal, freeze-thaw, chemical, or other disintegration mechanisms increases.

- The grain size of the aggregate decreases because coarse-grained aggregates may be smooth and nonabsorptive.

- The percentage of balanced forces between the aggregate and the asphalt increases.

- The mixture air void level and permeability decrease.

- The asphalt film thickness increases.

- Drainage is improved.

- The level of traffic decreases.

- An effective antistripping additive is used.

Some of the above factors tend to contradict each other. Most weathered aggregates are extremely smooth and do not provide a good mechanical interlock. Crushing the aggregate will improve the mechanical interlock but may also increase the number of unbalanced forces. However, increasing the number of unbalanced forces can be beneficial if it promotes chemical bonding. Crushing also produces sharp edges which may only be thinly coated. Mixture air void levels and permeability may also increase with crushing if the mixture is more difficult to compact in the field. Increased aggregate porosity may increase the degree of asphalt absorption, but all interior water vapor may not be expelled during drying. High mixing temperatures may liberate strongly bound water molecules, but bound materials which are advantageous may also be liberated.

CHAPTER 2: METHODS FOR CONTROLLING DAMAGE

Methods that have been used to reduce the susceptibility of asphalt mixtures to stripping are:

- Encapsulating the aggregate.
- Precoating the aggregate.
- Allowing the aggregate to weather.
- Washing the aggregate.
- Altering the mixture design.
- Using antistripping additives.

These methods generally have been used to decrease the degree of visual stripping. Many test procedures use mechanical tests to evaluate moisture susceptibility. Even though mechanical tests measure reductions in properties due to both a loss of cohesion and adhesion, there are no specific treatments for preventing cohesive failures caused by water, unless the damage results from materials containing clays which can be removed. In cohesive failures, the water damages the binder and visual stripping is not evident or is low.

1. Encapsulating the Aggregate

Encapsulation of the coarse aggregate with materials such as epoxy can reduce stripping by preventing the binder from contacting the aggregate. The cost of this method is very high and generally there is a decrease in strength and stability because of a loss of surface texture.(54) The reductions in these properties are greatest when the aggregate initially has a high amount of texture. Epoxy to aggregate compatibilities should be considered because adverse reactions between the two have occurred.(14) Epoxy coatings also decrease the absorption and specific gravity of the aggregate and may create conglomerations. Encapsulation is not used in practice.

2. Precoating the Aggregate

Precoating aggregates used in applications such as chip seals with the binder (asphalt, cutback asphalt, asphalt emulsion, or tar) has been used with some success, although this method is often costly or impractical. Precoating reduces the amount of exposed aggregate, even though some of the binder will wear off due to traffic. Most evaluations of the effects of precoating or encapsulating aggregates on the degree of stripping have been laboratory studies rather than field studies. Precoating aggregates is a method occasionally performed.

3. Allowing the Aggregate to Weather

Aggregates can be weathered, although this method is often impractical. Weathering periods are generally not specified in practice. Differences between the effects of weathered and freshly crushed aggregates on adhesion are discussed in chapter 1 of this report.

4. Washing the Aggregate

Washing aggregates may be beneficial. Washing should always be performed when the aggregates contain clay, or the coarse aggregates have high dust coatings. Even dust coatings above one percent may cause problems. Aggregates should (1) be nonplastic using American Association of State Highway and Transportation Officials (AASHTO) Methods T 89 and T 90, or American Society for Testing and Materials (ASTM) Methods D 423 and D 424, (2) have less than one percent clay lumps and friable particles, and (3) have a minimum sand equivalent of 45 using AASHTO T 176 or ASTM D 2419.(55,56) Water is usually used to remove dust coatings. Washing aggregates with water is used in practice.

Washing aggregates with acid to remove coatings and strongly adsorbed materials may improve their resistance to stripping. However, this method may be costly and may abrade the aggregates, thus causing a loss of surface texture.(14,54) Whether an acid affects the surface chemistry of the aggregate by being adsorbed is not discussed in these reports. Acid washes are not used in practice.

Other combinations of treatments such as washing aggregates with acids and coating them with various oils or pitches have also been tried in the laboratory, but the results and mechanisms explaining how they affect the susceptibility of a mixture to moisture damage are not well documented.(4) These treatments are not used in practice and are costly.

5. Altering the Mixture Design

The degree of stripping may be reduced by altering the mix design, although some other additional form of treatment will probably be needed unless the degree of stripping is initially low. Increasing the VMA, which increases the amount of binder or average film thickness, may be advantageous. Using an asphalt with a higher viscosity is generally not a good approach for decreasing stripping because the advantages are often slight and usually any advantage will be offset by increases in other problems such as low temperature cracking or fatigue cracking. Increasing the VMA would seem to be a good method for helping to prevent moisture damage but it is generally not done.

6. Using Antistripping Additives

Antistripping additives or agents are used to increase the physicochemical bond between the asphalt and aggregate and to improve wetting by lowering the surface tension of the asphalt.(4,12,57) Some additives are added to the mixture by weight of the asphalt cement, while others are added by weight of the aggregate.

Most additives added to the asphalt cement are surfactants which primarily modify the aggregate surface. The interfacial tension between the aggregate and the asphalt is lowered through this modification. These chemicals generally consist of molecules having an oil-soluble, nonpolar tail which is attracted to oils and an oil insoluble polar head which attaches onto the aggregate. A portion may also attach onto some asphaltenes and thus not be effective.(4,57) Whether and how they promote chemical bonding is unknown. Other additives added to the asphalt cement may primarily reduce the surface tension of the binder to promote spreading. These would seem to be less effective as they would not be able to reduce the interfacial tension as much as those which modify the aggregate surface. Others may modify not only the surface chemistry of the binder, but the overall chemistry of the binder and even the aggregate surfaces. The literature is lacking in information concerning additives and the mechanisms for how they function.

Additives added by weight of the aggregate, such as hydrated lime, are generally added directly to the aggregate in order to modify the surface charges of the aggregate or modify the asphalt at its interface with the aggregate. As with additives added to the binder, most are used to modify aggregate surfaces. These additives are used primarily when the coarse aggregate fraction is susceptible to stripping because it is easier to coat coarse aggregates than fine aggregates.

The choice of an additive must be based on (1) the effects on adhesive properties, (2) the effects on other mixture properties, (3) the dosage needed, and (4) economy. Regardless of whether the additive is added to the binder or the aggregate, the end result is to decrease moisture damage. The long-term performances of many additives are often questioned, and with some additives, no long-term performance is available. It is generally assumed that laboratory tests used to evaluate moisture damage and the effects of additives predict long-term performance. However, these tests do not duplicate field conditions exactly and thus could give misleading results for some additives.

Additives that have been used in practice or tested in the laboratory include:

- Traditional liquid additives.
- Metal ion surfactants.
- Hydrated lime and quicklime.
- Silane coupling agents.
- Silicone.

By far, the traditional liquid additives and hydrated lime dominate the market in terms of use. The use of hydrated lime has increased greatly over the past 15 years.

a. Traditional Liquid Additives

(1) Antistripping Mechanism. Most traditional liquid additives are proprietary liquid chemicals containing a hydrocarbon chain and the amine group NH_2, which is structurally related to ammonia.(26,44) This amine group is the oil insoluble polar head which forms ammonium salts with hydrogen ions of the aggregate. Most are cationic (positive head) and thus should increase the adhesion between acidic aggregates and asphalts. It is hypothesized that the effects are greatest with asphalts that are higher in acidity because these asphalts will adhere more poorly with acidic aggregates. Other traditional additives reportedly are anionic, which promote adhesion to basic aggregates. Others are both anionic and cationic (amphoteric).

Most traditional liquid additives are considered surfactants. Some may affect the overall chemistry of the asphalt, but published research is limited in this area. There are also no chemical specifications for traditional liquid additives, which means that even the chemistry of a particular brand name product can be changed without the user knowing it.

(2) Types of Traditional Liquid Additives. Several chemical names for traditional liquid additives appear in the literature, such as amido-amines, imidazoline, fatty polyamines, fatty diamines, and fatty amines. However, there is no comprehensive report on these additives which gives their chemical composition, mechanisms for reducing moisture susceptibility, effects on other asphalt mixture properties, or their long-term field performance. Additives other than amines which fall into the traditional category, but may or may not be proprietary, include tall oil and fatty acids. Some of these may be blended with amines. There are a variety of other chemical names that appear in literature older than 25 years, such as cetyl pyridinium bromide and cetyl trimethyl ammonium bromide, but little or no data or information on their effectiveness is given.

(3) Dosage. Dosages range from 0.1 to 3.0 percent by weight of the asphalt cement although they are commonly 0.5 to 1.0 percent. The optimal dosage that should be used varies from asphalt to asphalt and from aggregate to aggregate. This optimal dosage can be determined in the laboratory by adding various dosages to the mixture and evaluating their effectiveness

for reducing moisture damage. Surfactants are known to build up layers of molecules on surfaces.(10) A monolayer of additive will increase adhesion by forming a layer where the oil-soluble head is toward the asphalt, while an additional amount of additive will reduce the effectiveness of the additive if it forms a second layer where the oil insoluble tails are now toward the asphalt. The oil-soluble portions of the molecules may attract to each other to form this double layer. Thus, dosage is important.

When excess dosages are used, the effectiveness of the additive may be reduced immediately. Losses of cohesion and stability due to excess dosages have been reported.(16) When an optimal dosage obtained through laboratory testing is used, and the blending of the additive, asphalt, and aggregate is thorough, it is unknown whether some of an additive still remains in the asphalt. It has been speculated that the long-term migration of excess additive from the asphalt to the aggregate surfaces may decrease the effectiveness of the additive or may even promote stripping after several years of good service. The excess additive is hypothesized to be dissolved and/or in micellar form in the asphalt cement. Excess dosages may also emulsify the asphalt in the presence of water.(1) Dosages are usually checked by using calibrated dispensers at the plant or simply by testing the mixture produced.

Liquid additives are supplied in 55-gallon (208-litre) drums or by tank truck. Many are slightly corrosive to steel.

(4) <u>Methods of Addition</u>. Traditional liquid additives are either blended with the asphalt in the asphalt storage tank for 15 to 30 minutes or in-line blended just before the asphalt is added to the mixing drum or pugmill. Liquid additives can also be added to the aggregate prior to mixing, although the additive must be dissolved in a solvent to increase its volume. With this method, most of the additive should remain at aggregate-asphalt interfaces, but this method is costly and may be impractical for most cases. This method is not used in practice. The use of water-soluble, cationic homologues that impart the same pretreatment effect has been suggested as an alternative to additives dissolved in solvents.(58) The water would be removed by drying. These types of chemicals are not used and are untested.

(5) <u>Factors Affecting Migration to Aggregate Surfaces</u>. In order to be effective, the additive must be able to migrate to aggregate surfaces. Migration is affected by (1) the heat stability of the additive, (2) the degree of interaction between the additive and asphalt chemical functional groups, (3) the efficiency of the blending operation, and (4) the blending time.

When an additive is not heat stable, it is hypothesized that it reacts with certain components of the asphalt to form inert salts, and thus is no longer an antistripping additive.(26,44) It is also possible that the additive may degrade in the asphalt or there may be some loss due to volatilization, but these hypotheses have not been tested. Additives which are stable at ambient temperatures for many years may become ineffective after a few hours at normal hot-mix temperatures. Reportedly, the heat stability of all the chemical names previously listed (amido-amines, imidazoline, fatty polyamines, fatty diamines, and fatty amines) are improved in some way. The literature does not indicate how they are improved. Storage temperatures for liquid additives should generally not exceed 200 °F (93.3 °C), and some do not have to be heated to be delivered from the storage tank to the asphalt.

With interaction between the additive and the asphalt, the additive is present but is attracted to certain asphalt components and thus does not migrate to the aggregate.(44) Additives also must not have a tendency to form micelles in the asphalt as this will also prevent migration.

An additive may be ineffective if not blended thoroughly with the asphalt, or if the viscosity of the mixture is not low enough for a sufficient period of time to allow migration. Normal plant mixing operations should be sufficient for most of the additive to migrate, but data in this area is lacking.

Additives can be tested for heat stability. Heat stability tests should account for temperature, storage time, haul time, and possible delays in construction including those caused by weather. The mixture with antistripping additive is tested for moisture susceptibility after the materials are put through the simulation process. Usually the asphalt with additive and then the mixture are kept hot in closed containers for periods of time. Heat stability tests will also account for any interaction between the asphalt and the additive. The rate of reaction or interaction between an additive and asphalt depends on time and temperature.

(6) <u>Effects on Properties Other Than Moisture Susceptibility</u>. Traditional liquid additives are occasionally diluted with fuel oils, kerosene, or aromatic oils, and thus are not 100 percent effective. These additions aid in blending the additive with the asphalt but they do not have antistripping properties themselves. Traditional liquid additives have a wide variety of physical and chemical properties, and new varieties frequently appear on the market while others are removed.

Large changes in asphalt binder properties, such as viscosity, loss on heating, temperature susceptibility, and aging have reportedly been caused by quantities of the additive at or slightly greater than the optimal dosage. See references 14, 16, 25, 59, 60, 61, and 62. When changes do occur, the viscosity generally decreases while the loss on heating increases. Decreases in the stiffness of the mixture have also been reported. A change in stiffness generally would cause some change in how the mixture compacts; however, these same reports state that density is often affected very little. Tests to determine the effects of an additive on asphalt binder properties are often not performed by highway agencies, as most dosages are so small that they are not expected to have any effect. However, as indicated above, they can have an effect.

Laboratory research studies concerned with the effects of liquid additives on asphalt binder properties often do not list the brand names of the additives, and thus the results are often of limited value. In some cases, chemical analyses are given and those familiar with the additives can recognize them. In most cases, even when the brand names are given, chemical analyses of the additives are not performed. The only guidance given concerning the effects of additives on asphalt binder properties is that the additive should not make the properties of the binder go out of its specifications for grade. Overall, there is limited information concerning how additives may affect the chemical and physical properties of an asphalt, and what highway agencies should do about these effects.

In some cases, the effects of an additive on the properties of the asphalt have been attributed to the diluents added to the additive. In other cases, the effects have been attributed to a lack of heat stability. This provides another reason for determining heat stability.

(7) Overall Performance. Many agencies report that the performances of traditional liquid additives in the field are not always as good as laboratory performances. The literature indicates that this may be due to (1) a lack of heat stability, (2) improper blending of the additive and asphalt, (3) inadequate test procedures, (4) the use of wet aggregates, (5) an improper choice of additive type or dosage, and/or (6) the long-term migration of excess additive from the asphalt to aggregate surfaces. However, it also may be caused by laboratory-to-field differences in either the mixture composition or the additive. Changes in mixture composition are known to occur but are often not taken into account. There is no discussion in the literature if there are ever any differences between the additive evaluated in the laboratory and the one supplied to the job site. It appears that little or no verification of an additive is done, although some agencies test the field mixture for its susceptibility to moisture damage.

In many cases, the durability against stripping is vastly improved by traditional liquid additives, while with some aggregates, little improvement is obtained. The main problems with these additives are: (1) there are numerous brand names; (2) many have poor heat stabilities; (3) many lack long-term field performance data, and (4) an additive is often chosen simply from an approved list of additives rather than based on testing the additive in the mixture. The costs of these additives vary widely, but most highway agencies do not use those which increase the cost of hot-mix by more than a few dollars per ton. Many increase the cost by less than one dollar per ton.

b. Metal Ion Surfactants

The antistripping properties of metal ion surfactants are similar to traditional liquid additives in that they primarily modify the aggregate surface and the effects are highly dependent on the type of aggregate and asphalt. However, mechanisms for how they reduce moisture damage and what defines a compound as being a metal ion surfactant are not indicated in the literature. It appears that in most cases, metal ion surfactants consist of cations with at least two valances.(2) One valency attaches onto the aggregate surface while the other attaches onto an organic anion of the asphalt. Metal ions that have been used include those of iron, chromium, lead, copper, zinc, sodium, calcium, potassium, and aluminum, although sodium and potassium themselves only have one valency. Both organic and inorganic forms of compounds containing these metal ions have been used, but data is lacking which indicates whether one form is better than another.

Compounds which have been found to be effective are sodium dichromate, potassium dichromate, and ferric naphthenate.(1,14) Usually a 2-percent solution by weight of the aggregate is added to the aggregate, with the solids in this solution less than 0.05 percent by weight of the aggregate. The solution of additive generally contains around 2.5 percent solids. Other compounds which have provided antistripping properties with some aggregates are aluminum sulfonate, and various compounds containing metals which are then dissolved in sodium oleate solution.(12,63) However, there is very little data on these compounds. Some metal ion surfactants have been combined with traditional liquid additives containing amines.

The majority of studies on metal ion surfactants have been laboratory studies concerned only with their effects on moisture susceptibility. Whether these surfactants have any adverse effect on other mixture properties has not been determined. The heat stabilities of these additives have also not been addressed. There is little to no data on field performance.

The more effective metal ion surfactants are generally more expensive than traditional liquid additives, but costs have not been addressed. Costs would have to consider not only long-term effectiveness, but also handling costs. More data is needed on these additives before they can be recommended.

c. Hydrated Lime and Quicklime

(1) Antistripping Mechanism. Research indicates that lime neutralizes acidic aggregate surfaces in two ways: (1) by replacing or coating acidic compounds and water soluble salts on the aggregates, mainly those containing hydrogen, sodium, and potassium, and (2) by reacting with long-chained organic acids in the asphalt containing either the carboxylic acid or 2-quinolone group. Surface-active calcium salts such as calcium naphthenate and calcium phenate are formed by the lime on the aggregate surfaces, and the number of bonds with water resistant nitrogen groups in the asphalt is increased. See references 2, 25, 40, 60, and 67. This mechanism has also been reported for many metal ion surfactants, although in less detail and with little data presented. The mechanism indicates some dependence of the effectiveness of lime on the type of asphalt as these functional groups vary in amount from asphalt to asphalt. However, it has not been determined if the antistripping properties of lime are significantly dependent on the type of asphalt.

(2) <u>Types of Lime</u>. Both hydrated lime and quicklime are used. Hydrated lime, which is also called slaked lime, is generally the Type S calcium form $Ca(OH)_2$, but Type N dolomitic hydrated limes, such as $Ca(OH)_2MgO$ and $Ca(OH)_2Mg(OH)_2$, have also been used.(69) Dolomitic limes may be as beneficial as nondolomitic types.(70) Quicklime is CaO.

Hydrated lime and quicklime are usually thought to be more beneficial than limestone dust, calcium salts, portland cement, and fly ash, especially if the aggregate is cold and wet when treated. However, the use of and research on materials other than hydrated lime and quicklime appear to be limited based on the amount of available literature, and in one study, portland cement was rated better than hydrated lime.(68) All of these materials are used as powders which pass the #200 (or 75 micron) sieve screen, although some limestone dusts and hydrated limes may have up to 25 percent material retained on the #200 sieve. The apparent specific gravity of lime averages approximately 2.4 with a range of 2.2 to 2.8.

Because lime can carbonate or harden, it may be beneficial to specify that in order for a lime to be used, it must have less than some maximum percentage of carbonated lime, or $CaCO_3$, such as 10 percent.(71) A firm, recommended percentage has not been established.

(3) <u>Dosage</u>. One half to 2 percent hydrated lime by weight of the aggregate is generally used. Lower percentages of quicklime by weight can be used compared to hydrated lime because the volume of quicklime when added to water increases by approximately 20 percent. When added to water, quicklime becomes hydrated lime. This process is called slaking. Thus, quicklime will provide 20 percent more hydrated lime than an equal weight of lime bought in the hydrated form. However, it must be used in the form of a slurry.

Hydrated lime is often used in slurry form. Slurries are usually formed by combining 30 percent hydrated lime with 70 percent water by weight, and can be produced continuously or batched in a tank which is continuously agitated. A greater percentage of water could be used with quicklime because the volume of lime will increase when it reacts with the water. Regardless of the form of lime, the optimal percentage for a mixture should be established through laboratory testing. The effect of lime on the moisture susceptibility of a mixture generally increases with dosage and then levels off.

Lime can be obtained in bags or in bulk form. It is usually transported by tank truck and stored in a silo.(69)

(4) Methods of Addition. The four methods for introducing hydrated lime into a mixture are to add: (1) lime slurry to dry or wet aggregate, (2) dry lime to wet aggregate, (3) dry lime to dry aggregate, and (4) dry lime to asphalt. See references 73, 74, 75, 76, and 77. Some users believe that the first two methods are better methods based on performance, but there is insufficient data to firmly rank the methods. The last method is generally accepted to be the most inefficient method.

The first two methods are considered wet methods, while the latter two are considered dry methods. Dry methods are easier to perform. However, they may require additional lime. Dry lime can easily be vibrated off the dry aggregate during production using the third method.(69) A greater percentage of the lime is caught in the bulk asphalt and is not at the interface using the fourth method. The disadvantages with wet methods are that they generally require additional drying processes or reduce the plant production rate mainly because additional drying time is required. This increases the initial cost per ton of mixture. Dry lime, which is used in three out of four methods, is more easily proportioned compared to a lime slurry. Quicklime is always added to water, where it then becomes a hydrated lime slurry. Life cycle cost analyses of the different methods were not given in the literature.

Based on the literature, the best overall method for incorporating hydrated lime (slurry or dry) into a mixture is by thoroughly mixing it with the damp, raw aggregate in the plant pugmill or in a specially added premixing pugmill. In drum plants, a small premixing pugmill added to the end of the headchute gives good results. However, many highway agencies are satisfied with other methods, and through experience have reduced many of the problems associated with them. One study concluded that there are a number of satisfactory systems for adding lime and a best method could not be determined.(69) Calibration of feeding and proportioning systems is as important as the method chosen.(69)

Guidelines for adding lime are listed below.(69) Most of these guidelines are also applicable when using other types of antistripping additives.

- The user agency should approve the lime introduction method.
- The method must deliver the lime within 10 percent of the target value.
- The lime must be uniformly distributed on the aggregate.
- The loss of lime inside and outside of the plant must be minimal.
- The flow of lime must be monitored to verify that it is being delivered.
- The lime consumption must be checked by a positive means.
- The lime should be added to mixtures in the laboratory in a way that mimics the process that will be used at the plant. All mixture design criteria must be met.
- The performance of the lime must be checked at the plant using a test for moisture susceptibility.

The advantages and disadvantages of the common methods of adding lime are given below. Excluded is how easily the feeding and proportioning systems can be set up as this could not be established. Also, some of the most inefficient systems are the most easy to set up. Photographs illustrating many of these systems and detailed discussions on them are given elsewhere.(69,76,77)

(i) Hydrated Lime Slurry to Dry or Wet Aggregate. The advantages and disadvantages of this method are listed below for each part of the mixing plant operation where lime can be added. Slurries are generally not added directly to a batch plant pugmill or weighbox, or directly to a drum mixer plant.

Advantages	Disadvantages
• PRIOR TO STOCKPILING:	
- High loss of moisture. - Coordination between the slurry production and asphalt mixture production is not needed. - The lime can cure; this may or may not improve its effect. (Laboratory tests can be performed to determine if curing is beneficial.)	- Chance of carbonation. (There are no tests to determine the amount of carbonation after stockpiling.) - Additional aggregate handling is required. - Some cementing of the stockpile may occur. - Chance of a loss of lime due to runoff or rainfall.
• UNDER THE COLD FEED BINS OF EITHER A BATCH OR DRUM MIXER PLANT:	
- May be good for treating specific poor aggregates rather than all aggregates.	- Poor coating and mixing, although scalping screens and plant mixing action should help improve coating. - Clogging of scalping screens may occur if they are used, but this appears to be a very rare problem as the screen openings are generally very large. - A high amount of water must be removed by the plant.
• ON THE COLD FEED CONVEYOR BELT OF A DRUM MIXER PLANT:	
- None.	- Poor coating and mixing. - A high amount of water must be removed by the plant.
• IN A PREMIXING PUGMILL OF EITHER A BATCH OR DRUM MIXER PLANT:	
- Good mixing and coating. - Some loss of moisture may occur here. - Minimizes the loss of lime.	- Cost of additional pugmill. - A high amount of water must be removed by the pugmill.

(ii) Dry Hydrated Lime to Wet Aggregate. In this method, dry hydrated lime is either added to wet aggregate, usually containing 3 to 5 percent water, or added to dry aggregate and then sprayed with water. The advantages and disadvantages are usually the same as for a hydrated lime slurry unless the water content is low, where the advantages and disadvantages associated with the dry hydrated lime to dry aggregate method (listed below) may be encountered. Wetting the aggregate first is generally the better method if a pugmill is not used. Both methods are probably equally effective when using a plant pugmill or a specially added premixing pugmill.

(iii) Dry Hydrated Lime to Dry Aggregate. The advantages and disadvantages of this method are as follows:

Advantages	Disadvantages
• PRIOR TO STOCKPILING:	
- None.	- Chance of carbonation.
	- Poor coating and mixing.
	- Possible loss of lime due to segregation, dusting, and rainfall.
	- Some loss into the asphalt cement if the lime is poorly mixed with the aggregate.
• UNDER THE COLD FEED BINS OF EITHER A BATCH OR DRUM MIXER PLANT:	
- May be good for treating specific poor aggregates rather than all aggregates.	- Poor coating and mixing although passing the materials through a scalping screen can improve the degree of coating.
	- Some loss due to dusting especially if a scalping screen is used.
	- Some loss into the asphalt cement.
• ON THE COLD FEED CONVEYOR BELT OF A DRUM MIXER PLANT:	
- None.	- Poor coating and mixing.
	- Some loss due to dusting.
	- Some loss into the asphalt cement.

- IN A PREMIXING PUGMILL OF EITHER A BATCH OR DRUM MIXER PLANT:

- Good coating and mixing.	- Some loss due to dusting. - Some loss into the asphalt cement. - Cost of additional pugmill.

- IN THE BATCH PLANT PUGMILL OR WEIGHBOX PRIOR TO ADDING THE ASPHALT:

- Good coating and mixing. - Only a small loss due to dusting.	- Some loss into the asphalt cement.

- IN THE DRUM MIXER PLANT PRIOR TO ADDING THE ASPHALT:

- None.	- High loss due to dusting unless specialized equipment is used or the baghouse fines are returned. - Some loss into the asphalt cement.

(iv) Dry Hydrated Lime to Asphalt. This method is not used to a significant extent because it is usually not as effective as adding lime to the aggregate. The use of this method is not recommended.(74,76)

(v) Quicklime Slurry to Dry or Wet Aggregate. Quicklime (CaO) can be used instead of hydrated lime. Quicklime costs the same as hydrated lime per unit weight, but provides 20 percent more hydrated lime when slaked. However, it can burn a person's skin and is more difficult to handle because it spatters when it contacts water. Thus additional safety precautions must be taken and personnel must be properly trained. The exothermic reaction temperature of 180 °F (82.2 °C) which occurs when quicklime is added to water may help drying. The advantages and disadvantages for a hydrated lime slurry apply to quicklime.

(5) <u>Effects on Properties Other Than Moisture Susceptibility</u>. The effects of lime on the mechanical properties of a mixture vary even if the lime is substituted for aggregate dust (minus #200) by volume.(14,64) This may be due to differences in the physical properties of the two dusts, such as gradation, and/or how the dusts extend the asphalt. Often, lime is simply added to the mixture, which increases the amount of dust and the stiffness of the mixture. In this case, the effects of this increase in mixture stiffness on moisture susceptibility should be considered, because other less costly fillers or dusts may also provide similar benefits. Regardless of how the lime is incorporated, the lime must be considered in the mixture design.

An additional benefit of lime may be that it reduces oxidative hardening. Lime may reduce the formation of oxidation products and viscosity-building components in asphalt by removing (1) some materials which tend to oxidize and cause hardening and (2) some reactive polar molecules which tend to interact with the oxidation products to cause additional hardening.(72) The effects of lime on oxidation and distresses such as fatigue cracking have not been verified in the field.

Research also indicates that the number of hydrogen-bonding bases in asphalt increases with oxidation. These bases interact with acidic aggregate surfaces to form pseudo-polymeric structures which increase the hardness of the binder. Hydrated lime may reduce this hardening process by neutralizing the surfaces of the aggregates. Lime coatings may also partially act as acidic surfaces themselves, thus partially offsetting the benefits. However, the degree of acidity and the effects of this on bonding capabilities are unknown. It is also unknown whether lime affects polymerization processes other than those associated with the formation of hydrogen bonding bases during oxidation.(67,72) Again, how this property of lime translates to improved pavement performance is unknown.

(6) **<u>Overall Performance</u>**. The antistripping properties of lime are often excellent, although like other antistripping additives, there is a dependence on the type of aggregate employed, and with some aggregates, lime will not be effective.(14,64,65,66) Some highway agencies have orally indicated that for a given mixture, the antistripping properties of lime are less sensitive to routine adjustments in the mixture composition at the hot-mix plant compared to traditional liquid additives. The main concern when using lime is how to incorporate it into the mixture. Lime increases the cost of hot-mix up to $4.00 per ton with an average increase of approximately $2.00 per ton.(69)

d. Silane Coupling Agents

Silane coupling agents have been tested in the laboratory on a limited basis and found to act as antistripping additives.(68,80,81,82,83) It is hypothesized that the inorganic parts of the silane coupling agents condense with acidic components of an aggregate, such as those containing hydroxyl groups, which tend to cause stripping.(83) The aggregates were pretreated with aqueous solutions of the silane coupling agents in these studies.

Only a few silane coupling agents have been evaluated out of a large group of existing agents. One is a low viscosity liquid aminoalkyl functional silane with the formula $(CH_3O)_3SiCH_2NHCH_2CH_2NH_2$ (N-(beta-aminoethyl)-gamma-aminopropyltrimethoxysilane), and marketed as Dow-Corning Z-6020.(68,82) Another is a diaminosilane with the formula $NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$, and marketed as Union Carbide A-1120.(38) A third is gamma-methacryloxypropyltrimethoxy silane, and marketed as Union Carbide A-174.(83,84) The effects are dependent on the type of aggregate, and they appear to work best with those containing silicon. Whether the effects are dependent on the type of asphalt has not been established. The costs of these additives were not given in these reports, but they tend to cost the same as traditional liquid additives. Optimal dosages for these coupling agents have not been firmly established. These additives can not be recommended at this time. More research is needed to prove their cost effectiveness.

e. Silicone

In drum mixer plants, a silicone is often added to the asphalt cement in order to control foaming caused by the evaporation of water. Generally, one to two parts silicone per million of asphalt cement are used. Other than the decrease in surface tension that silicones provide, the effects of these trace amounts on reducing the potential for stripping appear to be nonsignificant.(78) However, the decrease in surface tension may allow the asphalt to wet the aggregate more easily. Mechanisms for how silicones should reduce raveling or stripping are not given in the literature. Silicones may simply coat or encapsulate the aggregates. The effects of silicones at higher dosages are unknown, but a few agencies have used them for controlling moisture damage. The use of silicones is not recommended because of a lack of data.

CHAPTER 3: MOISTURE DAMAGE TESTS

Numerous tests are available to determine the moisture susceptibility of a mixture and additive need, dosage, effectiveness, heat stability, and presence, but no laboratory test currently correlates to a high degree with field performance.(33,63,85) Because of the many factors which effect moisture damage, listed in table 1, it is not possible to develop a test which is reliable 100 percent of the time. The test method which is chosen should be reliable for most cases, or correctly order the generalized performances of various mixtures, although an exact reliability for any existing test is unknown. As a minimum, the test should indicate the propensity for damage over the life of the pavement, and should be sensitive to the effects of various additives and their dosages.

Because moisture damage is related to many environmental and mixture variables, it is generally accepted that a test method must simulate field conditions and should be performed on compacted mixtures meeting the mixture design.(44,86) However, it must also be an accelerated test which means that some factors, such as the environmental conditions and possibly the air void level, have to be altered to cause accelerated damage. The test should also probably be slightly severe because the costs due to underpredicting the degree of moisture damage are higher than the additional mixture costs arising from overpredicting the degree of moisture damage. However, no economic studies have been performed in this area. To develop a test, the test conditions needed to duplicate field conditions, and those needed to accelerate the procedure must be balanced. Because of the difficulty in doing this, time-consuming studies are needed to develop or improve tests.

The most difficult problem encountered when choosing or developing a test is determining the number of years for which the test predicts. Most comparisons between laboratory predictions and actual pavement performances have only been carried out on a short-term basis. Also, there is no single value of field performance, as the performance of a mixture is a variable which depends on factors such as environmental conditions, air void level, and traffic.

All tests for measuring the susceptibility to moisture damage have been developed for new, undamaged mixtures. There are no standardized procedures for evaluating pavement samples which are damaged, either to determine quantitatively how much damage is present or to predict the future condition of the pavement. Generally, the current condition of a pavement is determined simply by splitting cores in half and estimating the percent visual stripping. The cores can first be vacuum saturated with water because this process may help to remove loose asphalt coatings from the aggregates. It also puts the core in a saturated state which should be its worst condition. Cores should be split as soon as possible after they are removed from a pavement because mixtures can heal. If cores are tested for some mechanical property, the faces and/or sides may have to be ground or prepared in some way to provide smooth testing surfaces.

The majority of tests have been developed for mixtures containing asphalt cements; and with older tests, for cutback asphalts. There has been very little test development for emulsion mixtures and often tests for moisture susceptibility are not performed on them.

It is difficult to develop laboratory tests that predict pavement performance with a high level of confidence because of the following reasons:

- Field performance for any given mixture is a variable because performance is affected by factors such as the amount of rainfall, drainage, healing in the mixture, traffic level, and air void level.

- Pavement mixture properties may not match the mixture design criteria. Large differences between the two may make the results of predictive tests invalid.

- Pavement mixture properties may depend on the season when the pavement is placed because the season or weather can affect factors such as the degree of compaction and initial densification under traffic.

- Pavement composition often varies from point to point and even slight differences in some properties such as the asphalt content or the air void level may significantly influence the degree of damage. Only optimal mixtures, with expected initial or ultimate air void levels, are generally tested in the laboratory.

- Stress, temperature, and possibly even the properties of the asphalt, such as viscosity, vary with the depth of the pavement.

- Pavement properties such as strength and stiffness vary daily and seasonally. The mechanical properties of cores obtained during the summer and then during the following winter may differ by 50 percent, even if they are tested at the same temperature. Cores taken at the end of the winter may be harder. The mixture may then soften after the next summer. These variations are independent of moisture damage and long-term age hardening.(62,87) They may be related to short-term steric hardening in the asphalt which is at least partially reversed during hot weather. No studies have been performed to verify this hypothesis.

- The degree of damage in a pavement may fluctuate during the year because stripped asphalt may re-adhere to the aggregate during hot, dry weather. Simple tests cannot duplicate these fluctuations, therefore damage must be based on either some form of average damage or the worst condition obtained during the year.

- Long-term pavement properties are affected by traffic and climate. No current laboratory test reflects changes in these properties. A decrease in the air void level by the action of traffic over time may decrease the amount of moisture damage that can occur. However, traffic also provides stresses and pore pressures. Possibly, tests could be developed which consider some number of axle loadings, but this has not been studied. Changes in the chemistry of the binder with age may affect properties such as strength, stiffness, fatigue, and adhesion. If a test is developed to predict moisture susceptibility for a certain number of years, such as a 10-year period, an aging method must also be developed for a matching period. However, it may not be possible to age and moisture condition specimens at the same time; and if not, the effects of years of interacting mechanisms cannot be evaluated.

- Moisture damage may be related at least partially to other forms of damages and their interactions. For example, the degree of stripping may be related to the degree of low temperature cracking or fatigue cracking because cracks allow water to enter the pavement. However, no test combines all of these mechanisms. The healing of these cracks may also be a factor which affects the degree of moisture damage.

- Assessing the degree of damage in the field is difficult. In many cases, the degree of damage is determined subjectively through visual observations, which do not account for losses of cohesion in the binder film. However, many moisture damage tests measure losses in both adhesion and cohesion. Also, what one highway agency considers a severe problem may only be a moderate problem to another highway agency, so qualitative assessments must be viewed with caution.

- The amount of damage a pavement has undergone is difficult to determine quantitatively because the properties of the pavement in an undamaged state are unknown. Yet, most quantitative tests which measure mechanical properties use damaged to undamaged property ratios as the measure of damage, therefore undamaged properties are needed. Cores tested immediately after a pavement is placed will not be damaged, but they also will not reflect the large changes in properties that will occur with aging or with seasonal variations. These changes in properties with time can vary significantly from pavement to pavement for a given mixture. Mechanical properties, such as tensile strength, for cores taken immediately after placement may be less than those of slightly damaged (stripped) cores obtained at a later time because the damaged cores have also age' hardened. There are also no procedures for aging compacted cores or specimens in the laboratory. Thus undamaged properties are often determined from damaged cores. Various methods have been tried to heal stripped cores such as drying them in ovens or in desiccators.(88,89) Desiccation at 77 °F (25 °C) may require more than 8 weeks.(88) Cores may be tested at various times to obtain peak properties, but even with this approach, some mixtures will not heal unless placed at elevated temperatures such as 140 °F (60 °C). Damage is then expressed as the ratio of the damaged mechanical property to the undamaged mechanical property of the healed cores. The predictive test method using laboratory prepared specimens is then developed to produce a similar ratio even though the specimens are not aged. A complication is that the mechanical properties of the damaged cores may vary with the amount of water in it (natural or induced), although the cores can be saturated to obtain the worst condition. Additional complications are that the moisture damaged cores may also be damaged due to other mechanisms, and with severely moisture damaged pavements, intact cores may not be possible to get. In some cases, some cores may be intact while others are not intact. An alternative method may be to heal all cores, if possible, and develop the test based on the amount of visual stripping in the pavement, although visual estimates are highly subjective.

- Damaged to undamaged property ratios determined through mechanical tests vary with the test temperature and rate of loading. However, the visual estimates of damage for these specimens may not change even though the ratios change. The algebraic difference between the ratios of two different mixtures may also vary with the temperature and load rate. Thus, it is difficult to choose the optimal testing procedures.

- Pavement failure may not be linearly related to the percentage of visual damage. For example, a smooth aggregate may produce a failure with a lower percent visual stripping than an angular aggregate. Stripping in one fraction of aggregate, such as the fine aggregate fraction, may be more detrimental than stripping in another fraction, such as the coarse aggregate fraction.

- The testing procedure must be practical and quick for acceptance. However, a practical and quick test cannot measure the effects of moisture on all mixture properties, cannot consider interacting failure mechanisms, and can only duplicate field conditions very generally. Most procedures using mechanical tests generally only measure one property, which itself cannot predict pavement life.

- Inherent test variability is usually high.

Tests can be separated into the following four groups. The majority of tests performed at the present time fall into the mixture test category.

- Additive indicator tests.
- Aggregate tests.
- Mixture tests.
- Chemical analysis tests.

1. Additive Indicator Tests

The following additive indicator tests have been used:

- Bottle test.
- Color indicator.
- Miscellaneous tests.

These tests generally only determine qualitatively the presence of some antistripping additives in asphalts.(44) Additive indicator tests cannot determine the dosage of additive needed or the effectiveness of the additive. They are not always reliable and are very rarely used. Reportedly, a few can determine quantitatively the percentage of amines in an asphalt before it is used in a mixture. However, the literature gives no data to support these claims. No method can determine the amount of additive in a mixture.

a. Bottle Test

Ottawa sand and a semi-solid asphalt cement which is cutback with naphtha or a similar diluent are placed into a container filled with distilled water. After 20 to 30 seconds of vigorous shaking, the material is poured out and examined.(90,91) If an additive is present in the asphalt, the asphalt will completely coat the sand. This test does not indicate whether or not an additive will prevent stripping, nor does it indicate how much of the additive is present at aggregate-asphalt interfaces. In one case, the test indicated the presence of additive when no additive was used.(92) This test has only been used with traditional liquid additives. The quantities of sand and cutback asphalt used in this procedure have been varied. There are no standardized quantities.

b. Color Indicator

In this test, a small amount of asphalt cement, usually 1 gram, is placed in 40 ml of isopropyl alcohol (2-propanol).(93) A control sample of 40 ml of alcohol is placed in a second beaker. Both samples are warmed on a hot plate until small bubbles appear and the sample containing the asphalt shows a slight discoloration. This discolored solution is then transferred to a clean beaker and tested. Drops of bromophenol blue indicator, at a concentration of 0.2 percent in isopropyl alcohol, are added to this sample and to the control. When the control turns yellow, the test is complete. The solution with asphalt will be green or dark blue if an antistripping additive containing an amine is present; it will remain at the original color if no additive is present. Modifications of this procedure, various other color indicator tests, and a chromatographic indicator procedure have also been developed but are rarely used.(44) How well each of these procedures work is not given in the literature.

Reportedly, one color indicator test based on ASTM D 2074 can determine the percentage of amines in an asphalt which contains an amine-based additive, but no data is given to support this claim.(44,94) A solution of about 20 gms of asphalt in isopropyl alcohol is first prepared at 160 °F (71.1 °C) to 180 °F (82.2 °C), then filtered at room temperature to remove insoluble particles, and finally titrated at 150 °F (65.6 °C) using a 0.2 N solution of hydrochloric acid in isopropanol containing 0.2 percent bromophenol blue as the indicator. The solution is blue to yellow color at the end of the titration. The volume of the solution at the end of the titration (mm) times the normality of the hydrochloric acid times the combining weight of the additive divided by the weight of the asphalt cement (gm) is used to obtain the percentage of amines in the asphalt. The combining weight of the additive, which means the weight of the amine portion of an additive to the weight of hydrochloric acid, is obtained from the manufacturer. A calibration using known dosages of additive has to be established to determine any change in dosage due to reactions with the asphalt, degradation in the asphalt, or volatilization.

c. Miscellaneous Tests

High-performance gel permeation chromatography can be used to determine the effect of some antistripping additives on the molecular size distribution of an asphalt.(44,95) The results may be useful as an additive indicator test, or may indicate when an asphalt and an antistripping additive are not compatible. Research has been very limited in this area and the usefulness of the procedure has not been established.

A procedure based on ASTM D 2073 reportedly can also be used to determine the percentage of polyamines in an asphalt.(94,96) It uses an acid-base titration procedure, which compares the additive-asphalt basicity to that of a known standard. It is a potentiometric titration procedure. This procedure has recently been developed and has not been used in practice. The procedure needs to be verified.

2. Aggregate Tests

The following tests have been used to rate aggregates:

- Static immersion.
- Dynamic immersion.
- Boiling water.
- Sodium carbonate immersion.
- Detachment tests.
- Contact angle, peeling tests, tensile tests on films, and heat of immersion.

Aggregate tests are usually performed on certain aggregate size fractions coated with a standard amount of binder. They ignore the effects of the other aggregate fractions and design parameters such as air void level and optimal asphalt content.(19,25,26,44,97) Aggregate sizes other than those used in the test can have slightly different stripping potentials because the various sizes may have different degrees of coating in a pavement mixture. Also, the sizes have different physical properties such as surface area. The coarse aggregate fraction, or an intermediate size fraction of a particular gradation, is generally tested. Stripping is usually visually or microscopically estimated, although some quantitative methods for determining the percent stripped aggregate have been used.

None of these tests determine the effects of moisture or water on the quality of a pavement because they do not test pavement mixtures. They also cannot determine the amount of antistripping additive needed when only specific size fractions of the aggregate are tested because dosage depends on the surface area of the aggregate. Correlations with field performance are often poor as should be expected. These tests are used most efficiently to rate aggregate types, to supplement tests on compacted mixtures, and in research studies to investigate stripping mechanisms. They should not be used to predict pavement performance.

a. Static Immersion

A standardized test method is given in AASHTO Method T 182, or ASTM Method D 1664.(55,56) The 3/8 in (9.5 mm) to #4 sieve (4.75 mm) fraction of a coarse aggregate is coated with 5.5 percent semi-solid or cutback binder by weight of the aggregate and immersed in distilled water at 77 °F (25 °C). For emulsions, 8 percent is used. After 16 to 18 hours, the degree of coating is estimated to be either above or below 95 percent. A sample fails if it has a visual rating below 95 percent. The standardized method has different procedures for preparing samples depending on whether the aggregate is wet or dry during mixing, and whether the binder is a cutback asphalt or tar, semisolid asphalt or tar, or an asphalt emulsion.

Nonstandardized modifications include changes to the binder content, test temperature, aggregate particle size, and immersion time, and the inclusion of curing periods.(4,19) Even though the sample is subjected to an overabundance of water compared to the amount of water which can enter a compacted specimen, static immersion tests generally underestimate the stripping potential of materials.(2,15,17) The poor performance of this test is probably related to the low immersion temperature used and the lack of mechanical action which is needed to remove loose films. In a recent evaluation of six aggregates which are known to strip in pavements, the standardized test produced no damage.(98) All six aggregates passed. No visual stripping was observed even after one week of immersion. Paving mixtures meeting job mix formulas for four of the aggregates were also tested using the same conditioning procedure. Again, no visual stripping was observed. Based on these data, this method is not recommended.

The percent stripping is estimated visually, or measured using tracers which react with exposed aggregate surfaces. See references 17, 31, 102, 103, and 104. Various dyes, salts, and radioactive materials have been used as tracers. Lithium chloride is advantageous because its chloride is neutral, or will not affect the pH of water, and lithium usually is not present in aggregates or asphalts. The coarse aggregate is impregnated with the lithium salt, then coated with asphalt.(102,104) After moisture conditioning the sample, the concentration of salt in the water is determined by flame photometry. The concentration is also determined for uncoated, impregnated aggregate subjected to the same conditioning process. This concentration is equivalent to 100 percent stripping. Effects caused by the diffusion of salt through the asphalt and to nonuniform impregnation appear to be low, although it is not known if the tracers themselves affect adhesive properties.(17,102) The percent stripping measured using tracers may differ significantly from visual estimates if there is a loss of binder to aggregate contact but the binder still surrounds the aggregate. In this case, the visual method would give a lower percent stripped area. Tracer methods have also been used with compacted mixtures, but only to a very limited degree because of the long period of time that the moisture damage test including the tracer method requires.(104)

A variation of static immersion tests, called the freeze-thaw pedestal test, subjects a small compacted specimen to continuous freeze-thaw cycles until cracks are visible.(38,99,100,101,141) The specimen is placed on a pedestal so that it can crack. Various asphalt-aggregate combinations are compared based on the number of cycles to cracking. Selected sand-sized aggregate fractions are tested rather than an actual gradation used in a paving mixture. The specimens are heated to 140 °F (60 °C) after each freezing period. One freezing period plus one heating period is considered a cycle. One cycle requires either 24 or 48 hours depending on which version of the test is used. The test generally requires at least one week to perform. The effect of heating versus freezing on damage is unknown. Air void levels are not controlled and are unknown. It is also unknown if the results are more dependent on adhesion or cohesion. This test has only been used in research studies.

b. Dynamic Immersion

Dynamic immersion procedures are similar to the previous static immersion procedures for loose samples, except that after soaking, the sample is agitated rapidly for 5 to 30 minutes by rotation or shaking.(4,26,35,140) The sample is then washed to remove loose coatings. The extent of stripping is estimated visually or by weighing the sample before and after the test. However, these two methods of estimating stripping may not give the same result. It is unknown whether agitation increases the extent of stripping or simply removes loose asphalt films, but it appears that it simply removes loose films because the process is very short. A 90 to 95 percent retained coating is generally required for accepting a sample. Dynamic tests, like static tests, may produce results which do not correlate well with field performance.(19) Because the soaking processes of most dynamic tests are at room temperature, these tests are not recommended.

c. Boiling Water

Boiling water tests are similar to static immersion tests except that the loose sample is either placed in boiling water or water at ambient temperature which is then brought to a boil. The amount of coating is estimated after one minute of boiling.(25,105,106) This test has been criticized for the extremely high temperature used. High temperatures could influence the effectiveness of a liquid antistripping additive if it promotes the migration of the antistripping additive to the aggregate surfaces. The viscosity of the asphalt could also be more important at 212 °F (100 °C) than at normal pavement temperatures, but this has not been investigated. The effect of the boiling action on stripping, or the bumping caused by the bubbles, is also unknown.

This test is rarely used because it is just as easy to test a complete paving mixture. The poor performance of the boiling water test for complete paving mixtures indicates that the boiling water test for evaluating aggregates should not be used.

d. Sodium Carbonate Immersion

Tests in which chemicals are used to evaluate stripping are generally termed chemical immersion tests. In these tests, sodium carbonate was the most prominently used chemical. The most widely used procedure is as follows. Sand-sized particles of aggregate, which are coated with binder, are put into test tubes or beakers containing successively stronger aqueous solutions of sodium carbonate (Na_2CO_3).(4,18,19,25) The samples are then boiled for 1 minute. The strength of the sodium carbonate solution at which stripping is first observed is used as a measure of adhesion. Ten concentrations are usually employed, ranging from zero (distilled water) to 1.0 molar. Variations include increasing the number of concentrations, using larger-sized aggregate, and using less than the boiling temperature.

This test is now rarely used because the processes do not resemble naturally occurring ones. In one study, fair correlations with pavement performance were obtained with materials containing no additives but the effects of additives could not be determined.(19) Overall, correlations with pavement performance are lacking. Because the processes do not resemble naturally occurring ones, this test is not recommended.

e. Detachment Tests

In these tests, a certain number of coarse aggregate particles are pressed into a film of asphalt.(4,107,108) In some procedures, a certain weight of aggregate is used. The samples are then placed in water, often after some period of curing. The aggregates are checked daily for evidence of detachment. Loose stones are removed and a percent detachment value (number or weight of detached stone divided by the total number or weight of stone) is computed. These tests are generally used with chip seal surfaces, and some require up to 30 days. One variation of this test is to dislodge and whip off the aggregates by placing the sample in a centrifuge.(36) In another variation, called the Vialit Adhesion Test, the board containing the aggregates and asphalt is turned over and struck to dislodge any loose aggregates.(109) Neither of these processes resemble pavement conditions. Various methods of abrasion have also been used to dislodge aggregates. Correlations with pavement performance are lacking, although some form of a detachment test should be useful for predicting the performance of chip seals.

f. Contact Angle, Peeling Tests, Tensile Tests on Films, and Heat of Immersion

These tests generally employ elaborate types of equipment and use smooth, grounded aggregate surfaces or specific aggregate particle sizes in order to use theoretical adhesion principles.(4,110,111) These tests do not duplicate actual stripping processes in pavements and have produced unsatisfactory correlations to pavement performance.(4,18) They are mainly used in research studies to investigate stripping mechanisms.

These tests either measure contact angles between the asphalt and smooth aggregate surfaces with and without water, peel or scrape asphalt from a surface, or determine the tensile strength of a film between two flat surfaces.(2,4) Heat of immersion tests are used to try to relate the degree of adhesion between asphalts and aggregates to the change in enthalpy, or the heat released when they contact. See references 37, 40, 42, 43, 44, and 112. A microcalorimeter has been used to measure the heat of immersion between asphalts and certain sand-sized fractions of aggregates. Tests generally have been performed at 140 °F (60 °C). The aggregates are dropped into the asphalt and the heat given off is measured. The effect of test temperature on bonding has not been established.

3. Mixture Tests

The following mixture tests have been used:

- Boiling water (loose mixtures).
- Dynamic abrasion.
- Immersion-compression.
- Marshall immersion.
- Hveem stability.
- Indirect tensile tests.
- Elastic or resilient modulus.
- Sonic.

These methods use the entire mixture and test the effects of the coarse and fine aggregate, filler, asphalt cement, additives, and film thickness. These tests, excluding the boiling water and dynamic abrasion tests, indicate quantitatively a loss in a mechanical property due to a change in both the adhesion of the binder to the aggregate and cohesion, or any effects water may have on the binder. Losses in mechanical properties are also a function of any losses in the strength of the aggregate due to conditioning processes such as freeze-thaw cycles. The boiling water test, like most of the aggregate tests listed in the last section of this report, only evaluates the degree of visual stripping. Abrasion tests generally measure a loss in surface aggregates by weight due to both moisture damage and the abrasive action.

All of the tests, except the boiling water test, are performed on a compacted mixture, which accounts for mixture design parameters such as air void level and the VMA. Tests on compacted mixtures better simulate inservice mixtures, but they are difficult to develop, most have many modifications, and their between laboratory precisions or reproducibilities are often poor. The measured amount of moisture damage in a compacted mixture is a complex function of the type of mechanical test, the air void level, the amount of water in the air voids, and the conditioning processes used to try to induce moisture damage.(85)

Before discussing the tests, the following topics which apply to most mixture tests are reviewed: retained ratios, level of mechanical property, visual stripping, compaction methods, saturation, swell, and moisture-conditioning methods.

a. Retained Ratios

Quantitative tests which measure some mechanical property, such as strength or stability, are useful because the conditioned (wet) mechanical property, the unconditioned (dry) mechanical property, and the ratio of the wet to dry mechanical properties can be evaluated. These ratios are often called retained ratios or indices of retained strength. However, quantitative procedures are usually more time consuming than tests which are only qualitative.

Pass/fail acceptance ratios, or minimum allowable wet to dry retained ratios, usually vary between 70 and 80 percent and depend on the type of test and the highway agency using the test. No pass/fail ratio for any laboratory test correlates to a high degree with field performance, and as with any test where a pass/fail criterion is used, mixtures slightly above the criterion and slightly below the criterion may perform similarly. There are virtually no long-term studies which have related the retained ratios to years of pavement life, even though some tests have been developed using pavement performance.

When performing mechanical tests, the wet specimens must be tested in the wet state because partially stripped specimens which are allowed to dry may produce properties which approach the dry control specimens even if there is little or no healing.(4) This indicates that the water in the specimen has a lubricating effect.

b. Level of Mechanical Value

The level of the mechanical property, such as the level of strength or stability, should be considered because the moisture conditioning process may produce an acceptable retained ratio but an unacceptable wet mechanical property. The wet property may go below a minimum acceptable level, such as minimum stability, used to control other forms of distress. However, wet mechanical properties are poor indicators of the degree of moisture damage, and minimum allowable properties based solely on moisture damage cannot be developed.(85) This is because the wet mechanical properties of moisture-damaged mixtures can be greater than the dry mechanical properties of other undamaged mixtures. For example, one mixture may have a wet tensile strength of 100 psi and a dry tensile strength of 150 psi, which gives a retained ratio of 66.7 percent. Another mixture may have both a wet and dry tensile strength of 80 psi, which gives a retained ratio of 100 percent.

Tests for moisture damage fix the moisture conditioning process. Therefore, the retained ratios indicate some rate of loss in a mechanical property, or are a relative comparison of mixtures at some point in time under equal environmental conditions, rather than an endpoint. The wet properties do not indicate the properties at the end of the life of the pavement, but are the properties after some particular length of time. The pavement could fail before this time or last longer. The severity of a test, or the length of time for which it predicts, can be changed by changing the moisture conditioning process. Therefore, simply evaluating the wet mechanical values is insufficient. No test has actually been developed based on the performances of pavements at equal ages, or any other method which uses the lives of pavements. Thus, it can be expected that any correlation between current test results and the life of a pavement should not be very high.

Antistripping additives can affect both the wet and dry mechanical properties. Currently, mixtures with and without additive are treated as separate mixtures. Each has its own retained ratio computed from its own dry and wet mechanical properties. One study has suggested that the retained ratios of mixtures with additive should be calculated using the wet strengths of these mixtures divided by dry strengths of the mixtures without additive. However, in another study this did not provide better correlations with field performance and was not recommended.(85,113) Problems with evaluating only the retained ratios are evident though, especially when the additives affect the dry mechanical values.

c. Visual Stripping

Even when retained ratios are computed, the amount of visual stripping is important and should be considered in the evaluation. Visual damage may not agree with the retained ratios because the retained ratios are a function of (1) changes in both adhesion and cohesion, (2) the characteristics (sizes, angularity, etc.) of the aggregate fraction that has stripped, and (3) possibly other characteristics such as the maximum aggregate size used.[1] The visual examination is also very subjective. Black and white rating patterns, or boards with various colored aggregates and various degrees of stripping, have been used in some cases to help determine the amount of visual stripping.(30) A value of 10 percent or greater visual stripping has been suggested as indicating susceptibility to damage for most tests which use compacted mixtures.(85) For the boiling water test, greater than 5 percent visual stripping is used to indicate a susceptibility to moisture damage.

Most additives which improve the resistance of a mixture to moisture damage decrease the amount of visual stripping as desired, and increase the retained ratio by increasing the wet mechanical property. However, as indicated previously, additives can affect either the wet or dry mechanical properties, or both, and consequently have various effects on the retained ratios. These effects may or may not agree with the changes in visual stripping.(85) Therefore, for a complete evaluation of moisture susceptibility, the retained ratios, visual stripping, and the wet and dry mechanical values may have to be evaluated. The problem with this approach is the difficulty of including all of these factors, especially visual stripping, in a specification.

The time at which the visual evaluation is performed is important. For most tests, stripping may continue after testing is completed because of the presence of films of water. For tests where high temperatures are used before the visual examination, such as the boiling water test, recoating may occur quickly if the hot mixture is placed in air. This is due to the low viscosity of the binder at high temperatures. However, for samples tested or evaluated at room temperature, recoating may not occur or may require several weeks. It is recommended that the evaluation be performed immediately after the specimen or sample has been tested or the next day. The time chosen should be consistent. Placing the conditioned and unconditioned specimens or samples under water can assist in determining the percent visual stripping. Compacted specimens must be broken in half to evaluate the damage.

d. Compaction Methods and Air Void Levels

In most mixture tests, the specimens are compacted; then they may or may not be partially saturated with water by use of pressure or a vacuum, and finally they are moisture conditioned to try to induce moisture damage using processes such as soaking them in hot water. In some reports, the use of pressure or a vacuum to partially saturate specimens is considered part of the moisture-conditioning process, but in this report they are not. The most widely used compaction methods are:

- Marshall hammer.
- Kneading compactor.
- Double plunger.
- Gyratory compactor.

Any of the above compaction methods, which are shown in figures 3 through 6 can be used to obtain the required mixture air void level. Usually a 6 to 8 percent air void level is used because (1) this level permits saturation by water, (2) is equivalent to average actual inservice air void levels obtained after a pavement is placed, and (3) may accelerate the test. The use of air void levels higher than the design level also decreases the likelihood of underpredicting moisture damage because actual pavement air void levels are not known until the pavement is placed. Because the effects of the level of air voids on the retained ratio can be highly significant with some mixtures, one study concluded that specimens should be prepared at different air void levels and the mechanical properties at the required air void level, such as 7 percent, be obtained algebraically or graphically.(113) Some methods control the level of compaction rather than the air void level. Whether one method is more appropriate than the other has not been determined.

If specimens are compacted to the same air void level using different compaction methods, the results of moisture damage tests performed on the sets of specimens may or may not be slightly different.(44,114) The effect of compaction has not been clearly established. A change in the method of compaction will affect the results if it significantly changes the amount of permeable air voids or the mechanical properties. The air voids of a mixture generally contain some percentage which are enclosed and not permeable to water. Mechanical properties can be affected by aggregate orientation, which may vary with the compaction method. Some test methods specify a single method of compaction, while others allow the user to choose a method. In the latter case, most highway agencies use the compaction method which they normally use for designing a mixture. A consistent method should be chosen.

Tests for measuring the susceptibility to moisture damage have generally been developed for use during the mixture design process. There are no standardized procedures for evaluating pavement cores which may have air void levels significantly different than those required by a test. As stated previously, a certain air void level may be one test parameter which accelerates the test. If a pavement has a low air void level and the test is based on the use of a higher level, then the test results from cores may not truly predict or estimate future pavement performance.

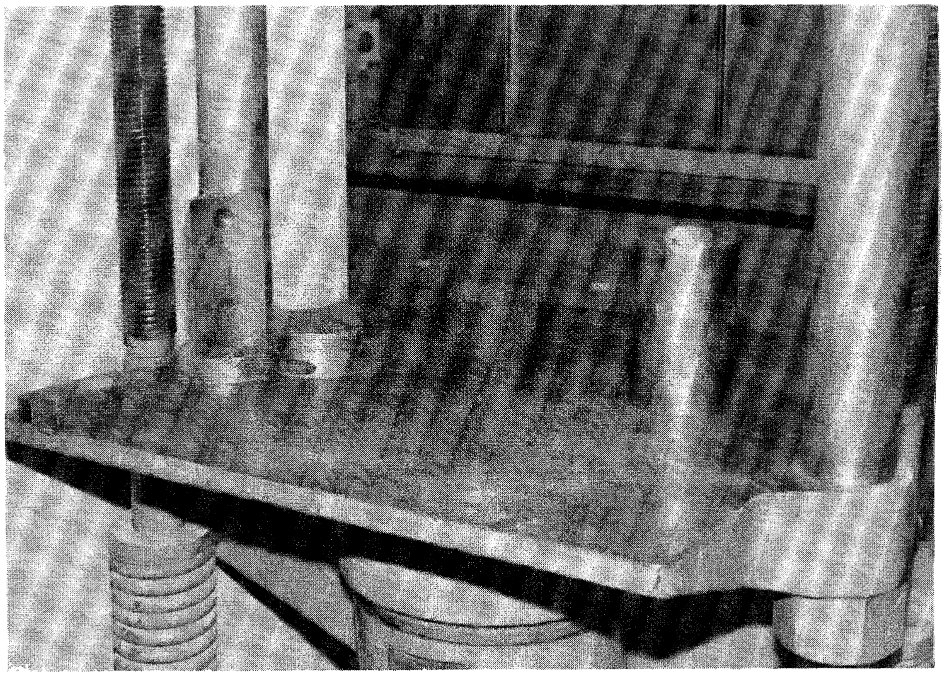


Figure 3. Equipment for double plunger compaction.

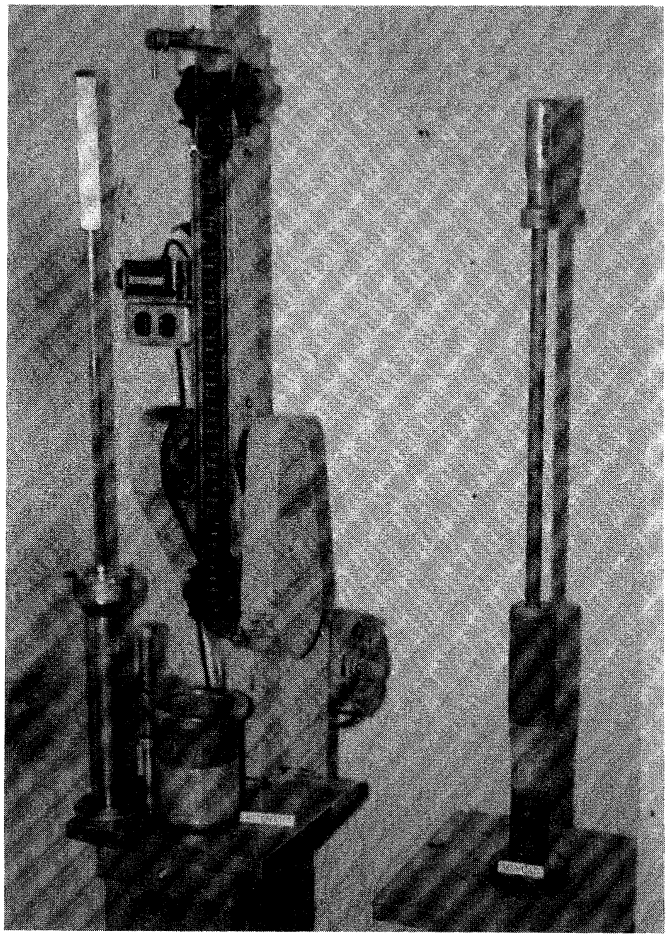


Figure 4. Marshall hammer compactor.

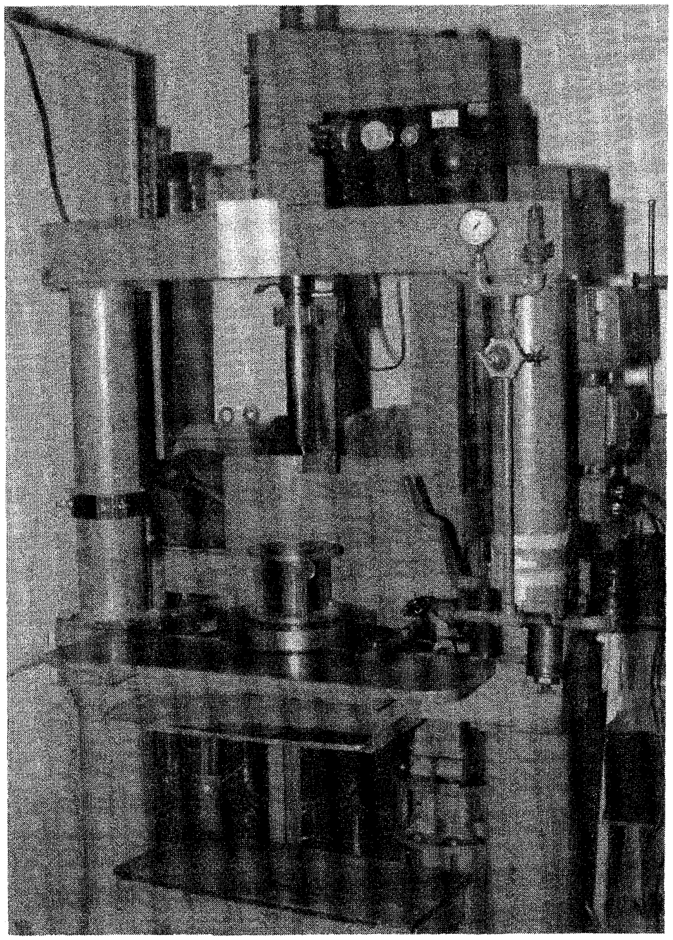


Figure 5. Kneading compactor.

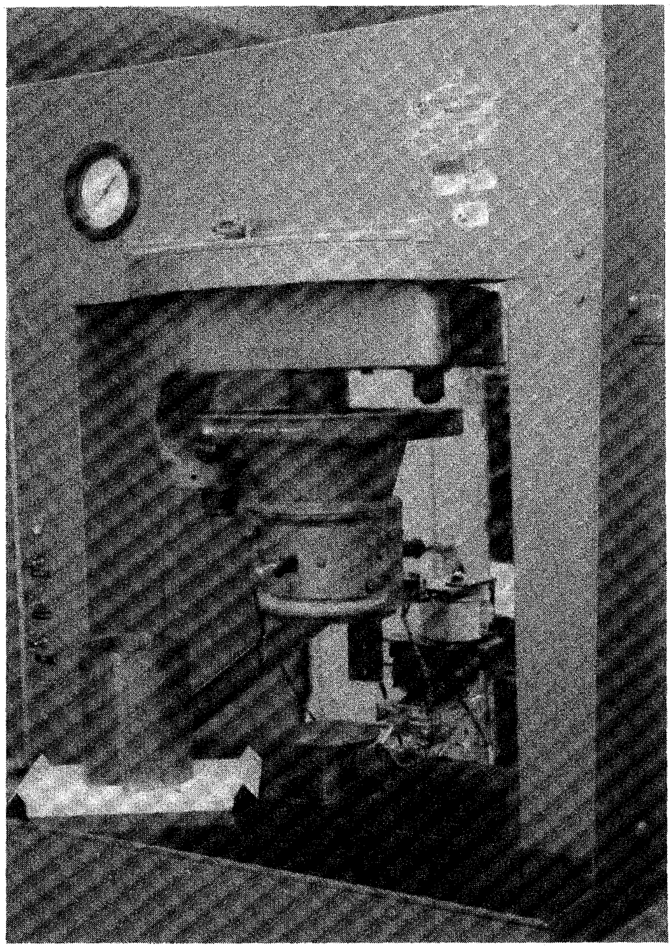


Figure 6. Gyratory compactor.

e. Saturation

The three methods of saturating specimens are:

- Pressure.
- Vacuum.
- Static soak.

Some procedures require that the specimens be saturated with water to a certain level, thus pressure or a vacuum must be used to partially saturate them before they are moisture conditioned. Other procedures require no forced saturation and depend on the water entering the specimens while they are submerged during the moisture conditioning process. This is called static soaking. In almost all procedures, water will enter the specimens during the static soak, even if they are initially partially saturated. The need for vacuum or pressure processes depends on how much water can enter the compacted specimens during the moisture conditioning period. Water must enter the specimen to evaluate the potential for moisture damage. An apparatus used to vacuum saturate specimens is shown in figure 7.

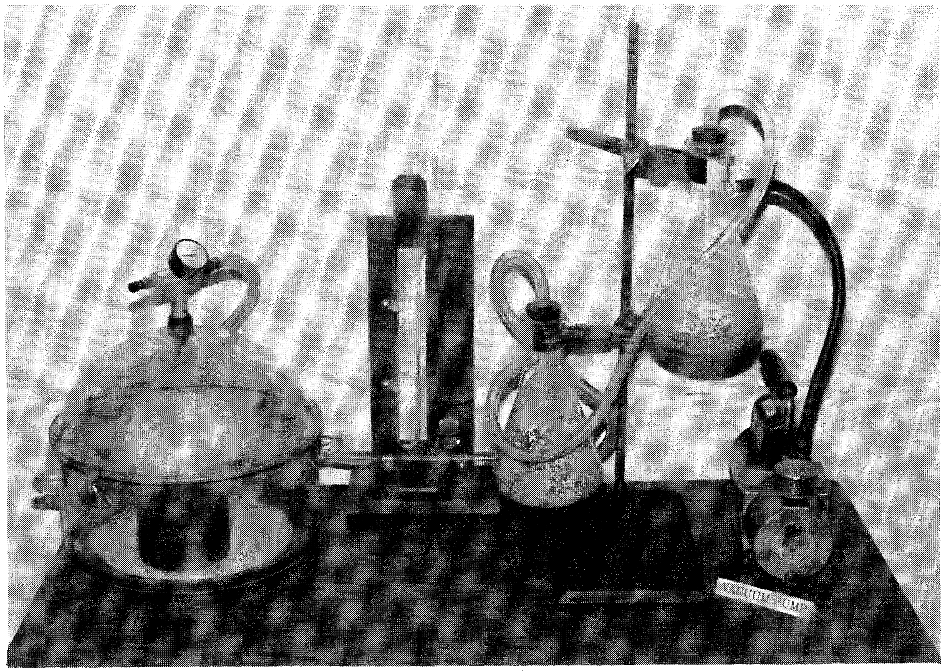


Figure 7. Equipment for saturating compacted specimens or cores.

The degree of water saturation of compacted specimens can be determined after they are partially saturated using pressure or a vacuum, and after they are soaked during the moisture-conditioning process. Saturation is the amount of water in a specimen and is generally calculated as the percent air voids filled with water. Without some minimum level of water in a specimen, damage due to moisture will be nil or low.

Saturation can also be calculated as the percent volume of water per specimen volume. This accounts for differences in air void levels from mixture to mixture by basing saturation on the amount of water in the specimens. For a saturation level of 50 percent based on the percent air voids filled with water, a specimen with 8 percent air voids has twice as much water as a specimen with 4 percent air voids. At the 8 percent level, the additional water and thinner asphalt coatings should lead to more damage, although no generalized relationships between the amount of water in specimens and damage has been established for various air void levels. Most test procedures control the air void level or compaction effort and therefore basing saturation on the air void level is appropriate. However, the term "level of saturation" can be misleading when comparing the results of various test procedures which use different air void levels. If the air void levels do vary by more than 1 percent, even for various mixtures tested by a single procedure, then it is recommended that saturation be based on the sample volume.

Vacuum levels and pressures must be carefully controlled because excesses may cause specimens to deform and lose strength. These losses of strength are unrelated to stripping processes and are not affected by antistripping additives. The results of some tests have poorly correlated with field performance where the specimens have been vacuum or pressure saturated to more than 100 percent based on the percent air voids filled with water, or where the saturation period was very long.(73,88,97,115) In ASTM Method D 4867, (discussed later in this report) the level of saturation after vacuum conditioning is maintained between 55 and 80 percent, although the saturation level after moisture conditioning may be above 100 percent.(44,56,85) Oversaturation after moisture conditioning is generally due to capillary action and expansion of the specimen. It occurs with a high amount of stripping and therefore is probably not detrimental because it is caused by the water alone. The effects of slightly oversaturating specimens during the vacuum or pressure saturation process may not lead to reductions in the mechanical properties of every mixture. The effects also may be dependent on the level of air voids. However, controlling the level of saturation prevents the occurrence of damage due to these processes. As a result, calculating and controlling saturation levels can be beneficial.

For a given mixture, a saturation level of 50 percent may produce a different result compared to 80 percent. However, a fairly large range must be allowed because mixtures will have different percentages of permeable air voids. Some mixtures and pavement cores may be difficult to saturate more than 60 percent, while others will saturate to 80 percent relatively easily, even though both groups have around the same total air void level. For most mixtures, a constant vacuum or pressure saturation period, such as 5 minutes, can be used to get within the required range of saturation. Therefore, the saturation period used for most mixtures can be fixed.

Because certain saturation levels are required by test procedures, it should not be inferred that these same levels are needed to fail pavements. Laboratory specimens must contain sufficient water in order to accelerate damage. Damage may occur in pavements at lower saturation levels and at low air void levels because of the long-term process involved.

f. Swell

The degree of swelling of compacted specimens can also be determined after vacuum or pressure saturation, if they are used, and after moisture conditioning. The percent swell is based on the change in height or volume of the specimen due to these processes. In most mixtures, the degree of swelling even after moisture conditioning will be very low (less than 2 percent). Where high degrees of swelling occur after moisture conditioning, the specimens generally have saturation levels well above 100 percent and are severely damaged.(85)

Swelling and a subsequent loss in the mechanical properties may occur even if a specimen does not strip. This is usually attributed to the expansion of clay or clay-containing materials. Where swelling caused by stripping and expansive materials occurs simultaneously, it may not be possible to differentiate the two mechanisms. However, measuring the degree of swell can give useful supplementary information concerning the nature of a mixture.(44,85) Procedures to measure both swell and saturation are simple and quick and therefore should be included with mechanical tests.

g. Moisture-Conditioning Methods

Moisture-conditioning processes attempt to accelerate processes occurring in the field. Static soaking methods provide conditions where damage will be caused by water and temperature only. Most tests use a static soaking process as the basic process for accelerating damage. Other processes, such as freeze-thaw cycling, thermal cycling, and pulsating pressures, can cause losses in mechanical properties unrelated to stripping, but may be useful because in-service processes of these types will increase stripping if they rupture asphalt films. These processes are generally incorporated with the static soaking process. The problem with including these supplemental processes is that it is unknown if they truly represent inservice conditions. If they are unrelated to inservice conditions, then mixtures with low susceptibilities to moisture damage may fail the test. Antistripping additives may also fail the test even if they would prevent stripping in pavements. On the other hand, a test may not be severe enough without the additional processes.

Static soaking procedures often use temperatures of 120 °F (48.9 °C) or 140 °F (60 °C). These temperatures should be reduced if they are not encountered in the field and the viscosity of the binder is low at these temperatures. A variation of the static soaking method is to place the sample in moisture vapor.(31)

Tests for emulsion mixtures often use a 77 °F (25 °C) static soaking process. Many emulsion mixtures fail consistently if a temperature of 140 °F (60 °C) is used. Whether it is justifiable to use a lower temperature so that emulsion mixtures are better able to pass is unknown. These mixtures are often used on low volume roads which are subjected to less traffic. The degree of curing significantly affects the results and various curing temperatures and times have been employed. Standardized test procedures for compacted emulsion mixtures have not been established.

Curing specimens containing semi-solid asphalts before they are moisture conditioned by exposing them to heat for a certain period of time, are used in some test procedures. Curing generally hardens the binder and increases its resistance to moisture damage. There is no universally accepted curing procedure.

Distilled water is used in most tests because ions in the water may affect the degree of damage and the effectiveness of some additives.(4,12,30,32) The use of a pH level other than close to neutral, or 7.0, may be beneficial in some cases, but the pH of the water has rarely been altered. No guidelines are available for altering the pH and therefore this practice is not recommended. In some cases, the pH of the water may change during the test because of the degradation of the specimens or a loss of hydrated lime when used as an additive. The addition of 0.1 percent hydrated lime by weight to the water has reportedly increased the resistance of some mixtures to stripping.(38) The effects of ions on moisture susceptibility, especially those which do not affect the pH, are unknown.

h. Number of Samples Required

The boiling water test is often performed on a single sample. Most tests which compute retained ratios require three dry and three wet specimens. However, the minimum number of specimens should be based on the sample variance, the difference between the dry and wet means, and the expected importance of the results.(144) Some tests, such as dynamic abrasion, elastic or resilient modulus, and sonic, can use the same specimens to obtain both the dry and wet properties. Thus three specimens as a minimum are needed.

i. Types of Mixture Tests

(1) **Boiling Water**. This test is similar to the boiling water test for single-sized aggregates, except that a complete paving mixture is tested. A standardized procedure, based on a 1-minute boiling time, is given in ASTM Method D 3625.(56) ASTM is in the process of changing the standardized procedure from 1 minute of boiling to 10 minutes. Ten minutes is generally used by highway agencies. This test only visually determines the degree of stripping, and coatings of 95 percent or greater are usually required.

Modifications include various methods of stirring the mixture, various sample sizes, and various procedures for decanting the water.(30,116) The boiling test is shown in figure 8.

The problems with the boiling water test for single-sized aggregates also apply to the test for mixtures. The test uses an extremely high temperature. A high temperature could influence the effectiveness of a liquid antistripping additive if it promotes the migration of the antistripping additive to the aggregate surfaces. The viscosity of the asphalt could also be more important at 212 °F (100 °C) than at normal pavement temperatures, but this has not been investigated. The effect of the boiling action on stripping, or the bumping caused by the bubbles, is also unknown. The boiling process does not resemble pavement conditions.

The success of this test has been mixed, but it often fails to predict performance. See references 44, 85, 99, 116, and 117. The results from this test should be compared to the results of a test which has a better relationship to pavement performance, such as those based on the indirect tensile test. If the results of the two tests agree, then the boiling water test can be used as a quick field test for checking mixtures. As a primary test for determining moisture susceptibility, this test should not be used.(85)

(2) <u>Dynamic Abrasion</u>. In most of these methods, moisture-conditioned compacted specimens are abraded under water for a specified time. See references 4, 26, 31, 104, 118, and 119. Bouncing solid rubber balls or brushes are generally used to abrade the specimens. The reported moisture-conditioning processes, abrasion times, and testing temperatures vary. Damage is proportional to the loss of weight that occurs. Correlations to pavement performance are lacking, and therefore these tests are not recommended.

These tests determine the degree of stripping which will occur at the surface of a pavement. The degree of stripping within the mixture is not determined. Most abrasion tests are easy to perform but may require one week. More sophisticated tests which can indicate the degree of stripping in lower pavement layers, and not just surface abrasion, include the use of a circular test track or other wheel-tracking tests. See references 4, 19, 25, 35, 120, and 121. The results of these tests have been reported as both good and

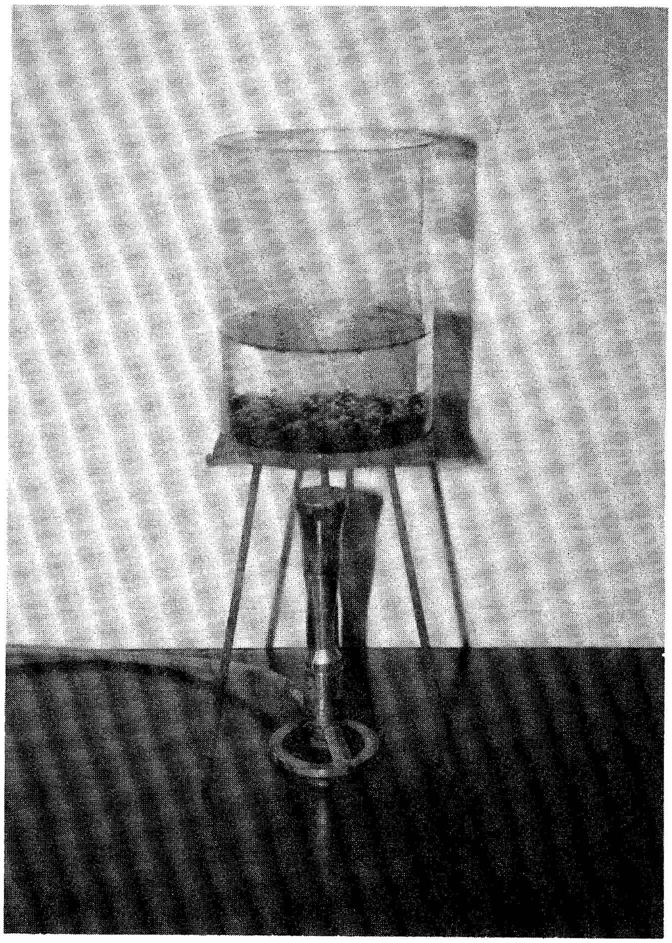


Figure 8. Boiling water test.

poor.(19,35,120) These sophisticated tests cannot be used for routine testing because they may require several months.

(3) Immersion-Compression. Standardized test procedures for the immersion-compression test are given in AASHTO Method T 165 and ASTM Method D 1075.(55,56) Cylinders, which are 4 in (10.2 cm) in diameter by 4 in (10.2 cm) in height, are compacted by the double plunger method and a standard level of compaction of 3000 psi (20.7 MPa) for 2 minutes. Specimens to be conditioned are soaked in distilled water at 120 °F (48.9 °C) for 4 days or at 140 °F (60 °C) for 1 day. The specimens are then tested at 77 °F (25 °C) in compression using a rate of 0.05 in/min/(in of height). A group of unconditioned (dry) specimens are also tested at the same time and temperature. Specimens are grouped so that both the dry and wet groups have approximately equal bulk specific gravities and air void levels. As with most tests which evaluate stripping using a mechanical measurement, moisture damage is based on the retained ratio. A retained ratio equal to or above 70 percent is usually required for acceptability. Equipment for this test is shown in figure 9.

Nonstandardized modifications include compaction using a kneading compactor, vacuum saturation, and grouping specimens on a random basis. Another modification is controlling the level of air voids rather than the standard compaction effort.(85) A 6 percent air void level is recommended. The immersion-compression test was originally developed along with a mixture design procedure based on compression, where the asphalt content was chosen to produce approximately a 6 percent air void level using the standard level of compaction of 3000 psi (20.7 MPa). Currently, mixtures are designed by other procedures and the air voids can vary from mixture to mixture in the immersion-compression test using this standardized level of compaction.

Standardized immersion-compression procedures do not contain a vacuum or pressure saturation process. During the development of the procedure, it was found that including a vacuum saturation process made the test too severe. Today some highway agencies believe the test is not severe enough. Comparisons to field experience have been found to be poor to good. See references 19, 66, 85, 116, and 122. Possibly, vacuum saturation is now needed.

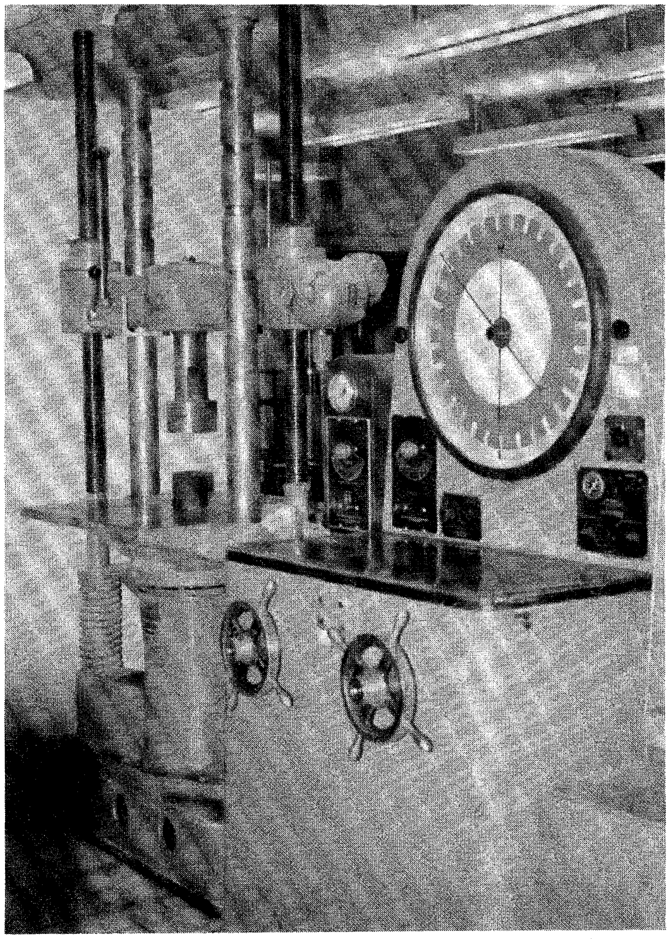


Figure 9. Specimen and apparatus for the immersion-compression test.

This test has also been criticized for producing retained ratios near or greater than 100 percent even when visual stripping is evident.(15,85) This has been attributed to (1) an increase in internal pressure and aggregate friction during testing resulting from water replacing the air in the voids and (2) the insensitivity of compression to properly measure losses in adhesion. If the severity of the conditioning process is increased, the wet compressive strengths and the retained ratios will eventually decrease because of damage. Other mechanical tests used for measuring moisture damage, such as Marshall stability, Hveem stability, indirect tensile strength, and resilient modulus, can also produce ratios above 100 percent even when visual stripping is evident. This has also been attributed to an increase in internal pressure and aggregate friction during testing resulting from water replacing the air in the voids. Therefore, the criticism can also be applied to these tests. However, the insensitivity of the compression test to properly measure damage means that this test should not be used to test mixtures for interstate and primary highways.

(4) <u>Marshall Immersion</u>. This test is similar to the immersion-compression test except that it uses the Marshall test apparatus and Marshall specimens, which are 2.5 in (6.4 cm) in height by 4 in (10.2 cm) in diameter.(139) The 1-day 140 °F (60 °C) static soaking method of moisture conditioning is generally employed. Modifications include compaction by the double plunger method, using a vacuum or pressure saturation process, and conditioning saturated specimens in a 140 °F (60 °C) air bath. Tests using Marshall specimens are practical because specimens can be fabricated at the job site to check mixtures.

Specifications for mixture design tests, such as the Marshall and Hveem stability tests, include minimum acceptable values. Therefore, both retained ratios and the levels of the dry and wet stabilities can be checked when using these tests. However, one evaluation of two similar Marshall-Immersion procedures showed that they both correlated poorly with pavement performance and no other better procedures are known.(85)

(5) <u>Hveem Stability</u>. Samples are compacted by a kneading compactor and tested using the Hveem stabilometer. Procedures are similar to those for the Marshall Immersion and immersion-compression tests. The ability of the test to predict moisture susceptibility is unknown, and therefore this method is not recommended. Tests based on Hveem stability are rarely used for determining moisture susceptibility.

(6) **Indirect Tensile Tests**. The majority of the most recently developed tests for determining moisture susceptibility use an indirect tensile test and Marshall-sized (or Hveem-sized) specimens. One method uses a pulsing pressure process to saturate and stress the specimens, a 122 °F (50 °C) hot-water soak, and a double punch, indirect tensile strength test.(68,115,143) In the double punch test, the Marshall-sized specimen is punched through the top and bottom by 1-inch cylindrical steel punches, causing it to split along the weakest radial plane. Most methods use a vacuum saturation procedure, a 140 °F (60 °C) hot-water soak, and the indirect diametral tensile test. See references 26, 44, 85, 88, 117 and 123. Numerous modifications have been developed including the use of thermal or freeze-thaw cycles.(88,124,125,126) Computer programs for predicting the life of a pavement using the retained ratios are also being developed.(114,127,128,142) However, they are only in their initial stages of development and very little performance data is available for their development. As with the immersion-compression test, strength may increase due to the stiffening effect of water in the voids.(110)

Cohesion, or shear resistance, and adhesion influence the results of indirect tensile tests, although it is hypothesized that the results of these tests are more dependent on adhesion than stability or compression tests. Therefore, these tests are more promising. However, the different variations of these tests often give widely different results, and correlations to pavement performance have given mixed results.(41,85,116,129) Procedures based on indirect tension appear to be better than those based on most other modes of failure.(85)

Standardized procedures are AASHTO T 283 and ASTM D 4867.(55,56) These two procedures are slightly different. The Marshall testing apparatus and the indirect splitting breaking head generally used in these tests are shown in figure 10. The indirect splitting breaking head is substituted for the Marshall breaking head.

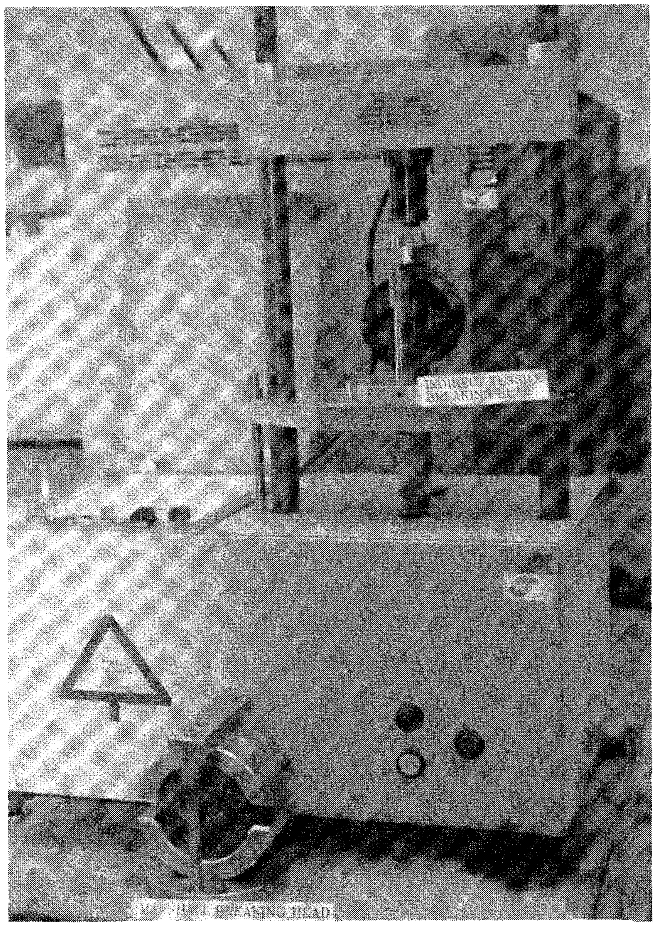


Figure 10. Indirect splitting tensile test apparatus and the Marshall tester.

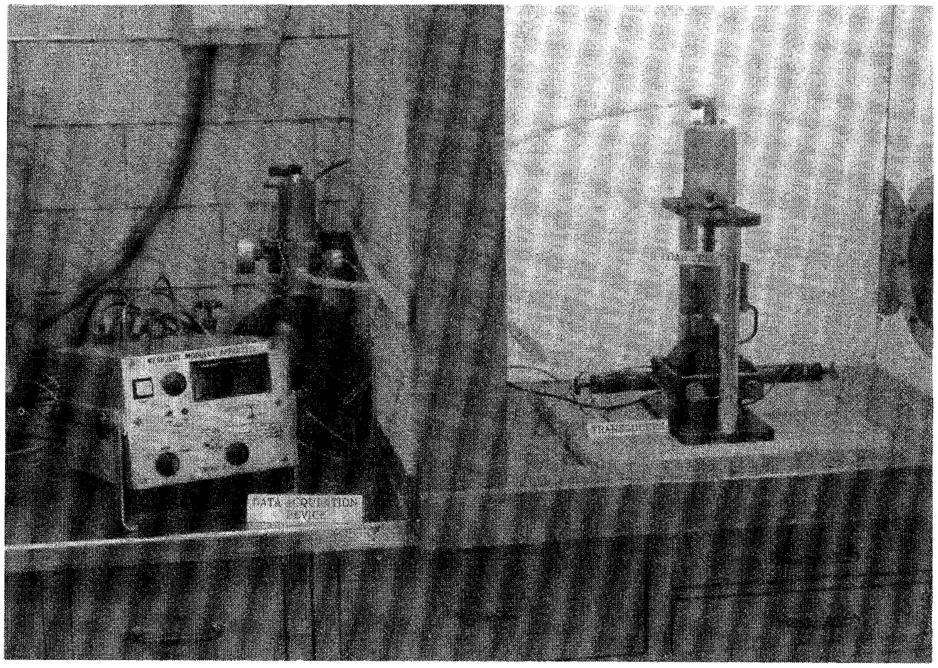


Figure 11. Resilient modulus test apparatus.

(7) Elastic or Resilient Modulus. In these tests, moisture damage is based on the retained ratio calculated from moduli.(66,85,88,130) Both static and repeated load modulus tests have been performed. In static tests, the modulus is taken from the initial linear portion of the stress-strain plot produced by a strength test, such as the indirect diametral tensile strength test. This is often defined as an elastic modulus, although it not a true elastic modulus. Therefore, strength tests can produce retained ratios based on both moduli and strengths.

Specimens and moisture-conditioning procedures for repeated load tests are generally the same as those used for the static tests. Moduli from repeated load tests are generally defined as resilient moduli, although they are generally total moduli which are based on the total amount of strain and not just the resilient strain. Often the indirect diametral tensile configuration is used. If repeated load tests are performed at a limited number of cycles and at low levels of deformations (below 100 microinches for the indirect diametral tensile configuration), then they are nondestructive and the specimens can be used for other purposes. For example, indirect diametral tensile strength retained ratios can then be obtained.(85) In one study where antistripping additives were evaluated, some specimens were tested statically while others were tested to failure using repeated loads, but the various results were not compared because of the limited amount of data.(125) One apparatus for measuring the repeated load-resilient modulus of specimens in the indirect diametral mode is shown in figure 11.

Retained ratios based on static moduli, repeated load moduli, or strength tests do not necessarily agree, even if one testing mode such as the indirect diametral mode is used. Whether the retained ratios from one correlates better to pavement performance has not been established. In one study, the retained ratios from the diametral repeated load test were lower than those of the diametral tensile strength test, but the two tests ranked the mixtures similarly. Both gave better correlations to performance than tests based on other modes of failure.(85)

(8) Sonic. The progressive deterioration of mixtures can be determined through the use of an audio oscillator.(4,131,132) Sonic vibrations are applied to the specimens, usually cylinders or beams. Elastic constants

(Young's modulus of elasticity, dynamic modulus of rigidity, and Poisson's ratio) can then be calculated from the resonant frequency and certain physical properties of the specimens (shape factors and weight). Retained ratios can be calculated although the constants have little physical significance for asphalt mixtures because the relationships use the laws of elasticity and frequencies over 100 cycles per second. Moduli obtained from these tests may be an order of magnitude higher than those from repeated load tests performed on asphalt mixtures.

Sonic tests are advantageous because they are nondestructive, and specimens can be retested many times. However, the results may be significantly affected by the surface flaws of the specimen.

A standardized method, which is generally used to monitor the freeze-thaw resistance of portland cement concrete, is given in ASTM C 215.(133) Although three vibrations can be applied to a specimen, namely, longitudinal, transverse, and torsional, the preferred method is to use transverse vibrations at room temperature. Sonic methods were not effective for evaluating cutback asphalts due to the compounding effects of long-term solvent evaporations.(134) This may also be true for emulsions, where water is lost, but this is unknown. Overall, correlations to pavement performance are lacking, and therefore sonic methods are not recommended at this time.

4. Chemical Analysis Tests

Chemical analyses are used to determine which asphalt components are strongly or weakly adsorbed onto aggregate surfaces, which are most easily removed by water, and the interacting effects of the composition of the aggregate. Therefore, the analyses are used to determine how the various asphalt functional groups and the aggregate components relate to adhesion and stripping. A chemical analysis of both the asphalt and the aggregate can be determined. See references 37, 40, 42, 43, 44, and 112. Chemical analyses are used in conjunction with the results of aggregate or mixture tests for moisture damage. In most studies, chemical analyses have been combined with a calorimetric method for determining the heat of immersion, the freeze-thaw pedestal test, and/or the indirect tensile test for mixtures to investigate stripping mechanisms. They have only been used in research studies.

CHAPTER 4: EXECUTIVE SUMMARY

This state-of-the-art report is on the moisture susceptibility of asphalt mixtures used in highway pavements. It addresses the known causes of moisture damage, methods for controlling damage such as antistripping additives, and moisture damage tests. The report is mainly concerned with dense-graded, hot-asphalt mixtures since most of the literature discusses these types of mixtures. Some information on chip seals and emulsion mixtures is also included. One of the intents of this report is to indicate where data is lacking so that research can be performed in these areas. This summary contains additional information compared to the separate FHWA Technical Summary issued with this report.

1. Causes of Moisture Damage

a. Types of Damage

The majority of studies on moisture or water damage in asphalt mixtures deals with an observed phenomenon called stripping. Stripping is the displacement of asphalt films from aggregate surfaces that occurs when the aggregate has a greater affinity for water than the asphalt. It has been speculated that an asphalt may be able to strip from an aggregate under dry conditions, especially after it has aged many years, but most losses of adhesion are attributed to the action of water. Stripping under dry conditions and the effects of changes in the amounts and types of the asphalt chemical functional groups adsorbed onto the aggregate surfaces with time have not been investigated to a significant degree. Also, in most cases, the effects of aging and moisture occur simultaneously in pavements.

In most moisture damage studies, adhesive failures are defined as those where the asphalt is debonded or stripped from the aggregate. Cohesive failures are defined as those where the bulk asphalt film flows, tears, or is weakened in some way. However, this is a limiting definition for cohesion, because the cohesional resistance of a mixture is reduced by losses in adhesion if these losses affect the frictional resistance between the aggregate particles or how the aggregate particles interlock. Cohesion in general terms is simply some measure of how the mixture holds together. How water causes either adhesive or cohesive failures is not completely understood. Moisture-related failures in pavements are also a function of any losses in the strength of the aggregate by processes such as freeze-thaw cycles. Most of the literature deals with the adhesive failures or stripping, and moisture or water damage is often equated to stripping.

Moisture damage generally starts at the bottom of an asphalt base layer or at the interface of two asphalt layers where the water content is the highest. Eventually, potholes are formed or the pavement ravels or ruts. With hardened binders, fatigue cracking (alligator cracking) may occur. Surface raveling or a loss of surface aggregate can also occur, especially with chip seals. Occasionally, stripped binder from within the pavement will float to the pavement surface creating spots of bleeded asphalt.

b. Variables Which Influence Moisture Damage

Moisture damage problems are related to many interacting variables. These variables are complex, and studies dealing with specific variables have generally been performed. However, the interacting effects of the excluded variables are important, and the conclusions of these studies are often either very general or give rise to many questions about their usefulness.

Moisture damage problems are related to the following variables, none of which are completely understood: (1) type of aggregate, (2) type of asphalt, (3) mixture design and construction variables, (4) environment, (5) traffic, and (6) antistripping additive properties. (See table 1 on page 3 for more details.)

Studies that have been used to evaluate the effects of aggregates on the degree of damage are generally separated into three concepts: (1) surface energy theories, (2) the degree of chemical bonding, and (3) the degree of mechanical interlock. Adhesion, stripping, and even other forms of moisture damage are thought to be related to a combination of all three concepts, but the concepts have never been combined to form an overall coherent theory for them. Although the procedures and theories under all three concepts evaluate asphalt-aggregate-water interactions, most studies have been concerned with evaluating the effects of different aggregates rather than the effects of different asphalts. It is generally believed that the type of aggregate has a much greater effect on moisture susceptibility.

Surface energy theories deal mainly with how materials reduce their surface free energies to obtain more thermodynamically stable conditions. Chemical bonding studies try to relate adhesion to the chemistry of the materials and the chemical reactions that occur. Both concepts evaluate the same bonding phenomenona but in different ways. Surface energy concepts use phenomenological approaches, while chemical bonding studies use molecular approaches. Studies concerned with the degree of mechanical interlock deal mainly with the physical properties of the aggregate which affect the physical strength of the composite material.

Surface energy theories of adhesion and concepts such as minimum surface free energy and contact angle have not adequately described the adhesive properties of asphalt-aggregate-water systems, and only generalized conclusions have been obtained from them. Studies in these areas use numerous assumptions and oversimplifications compared to pavement mixtures, such as the use of smooth, flat aggregate surfaces. The literature also has poorly defined models for asphalt-aggregate systems, lacks explanations for many results, and the terminology is not consistent from report to report. In the past 20 years there has been little or no advancement in these areas.

As with studies concerned with surface energy theories, most past studies concerned with chemical bonding have only provided generalized conclusions, and the chemical properties of the binder were generally treated as being far less important than the properties of the aggregate. More is known about the effects of mechanical interlock and how the physical properties of aggregates can affect moisture damage because of observations in the field, but the effects have not, and possibly cannot, be quantified or modeled.

Although the viscosity of the asphalt can affect the degree of moisture damage, the effects of other asphalt properties on moisture susceptibility, such as its chemistry, are unclear because limited research has been performed. The effects of mixture design properties, aggregate moisture content, drainage, construction, environment, and traffic on moisture damage are more well documented. However, these factors are complex, interact, and often cannot be controlled or predicted prior to construction. Antistripping additives can have a significant impact on performance, but the information on how they function chemically is very limited.

When considering all factors that influence stripping, it appears that any type of aggregate is capable of stripping and it is difficult to rank aggregate types according to their potential for stripping. No aggregate type always strips or never strips. Aggregate gradation, aggregate source, and asphalt characteristics are also unreliable for predicting the potential for moisture damage by themselves. Air void level, drainage, the moisture content of the aggregate, environment, and the level of traffic are extremely important, but precise levels for these factors cannot always be determined before construction.

2. Methods for Controlling Damage

Methods that can be used to reduce the susceptibility of asphalt mixtures to stripping are: (1) encapsulating the aggregate with materials such as epoxy to prevent asphalt-to-aggregate contact, (2) precoating aggregates used in applications such as chip seals with the binder, (3) allowing the aggregate to weather, (4) washing the aggregate, (5) altering the mixture design, and (6) using antistripping additives. All of these methods are generally used to decrease moisture damage as manifested by visual stripping. Many test procedures use mechanical tests to evaluate moisture susceptibility. Even though these procedures measure reductions in properties due to both a loss of cohesion and adhesion, there are no specific treatments for preventing cohesive failures caused by water, unless the damage is due to materials containing clays which can be removed. In cohesive failures, the water damages the binder and visual stripping is not evident or is low.

By far, the use of antistripping additives is the most common method of preventing damage. Additives that have been used or tested in the laboratory include: (1) traditional liquid additives, (2) metal ion surfactants, (3) hydrated lime and quicklime, (4) silane coupling agents, and (5) silicone. The most commonly used additives are hydrated lime and the traditional liquid additives, which generally consist of a hydrocarbon chain and the amine group NH_2. Traditional liquid additives are generally added to the asphalt cement, while hydrated lime is generally added in a slurry form to dry or wet aggregate, or in a dry form to wet aggregate. All additives should be considered in the mixture design process because they can affect binder and mixture properties.

3. Moisture Damage Tests

Numerous laboratory tests are available to determine the moisture susceptibility of a mixture and additive need, dosage, effectiveness, heat stability, and presence. However, the results of most tests for moisture susceptibility either correlate poorly with field performance or have not been correlated to performance. Because of the many factors which effect moisture damage, it is not possible to develop a test which is reliable 100 percent of the time. The test method which is chosen should be reliable for most cases, or correctly order the generalized performances of various mixtures. As a minimum, the test should indicate the propensity for damage over the life of the pavement, and should be sensitive to the effects of various additives and their dosages. An exact reliability for any existing test is unknown.

Because moisture damage is related to many environmental and mixture variables, it is generally accepted that a test method must simulate field conditions and should be performed on compacted mixtures meeting the mixture design. However, it also must be an accelerated test which means that some factors, such as the environmental conditions and possibly the air void level, have to be altered to cause accelerated damage. The test should also probably be slightly severe because the costs resulting from underpredicting the degree of moisture damage are higher than the additional mixture costs arising from overpredicting the degree of moisture damage. However, no economic studies have been performed in this area. To develop a test, the test conditions needed to duplicate field conditions and those needed to accelerate the procedure must be balanced. Because of the difficulty in doing this, time-consuming studies are needed to improve tests.

The most difficult problem encountered when choosing or developing a test is determining the number of years for which the test predicts. Most comparisons between laboratory predictions and actual pavement performances have only been carried out on a short-term basis. Also, there is no single value of field performance, because the performance of a mixture is a variable which depends on factors such as environmental conditions, air void levels, and traffic.

Tests can be separated into four groups: (1) additive indicator tests, (2) aggregate tests, (3) mixture tests, and (4) chemical analysis tests. The majority of tests performed at the present time fall into the mixture test category.

a. Additive Indicator Tests

Additive indicator tests include the (1) bottle test, (2) color indicator tests, and (3) miscellaneous tests such as high-performance gel permeation chromatography. These tests generally only determine qualitatively the presence of some antistripping additives in asphalts. Additive indicator tests cannot determine the dosage of additive needed or the effectiveness of the additive. They are not always reliable and are very rarely used. Reportedly, a few tests can determine quantitatively the percentage of amines in an asphalt before it is used in a mixture. However, the literature gives no data to support these claims.

b. Aggregate Tests

Aggregate tests include (1) static immersion, (2) dynamic immersion, (3) boiling water, (4) sodium carbonate immersion, (5) detachment tests, and (6) miscellaneous tests including contact angle, peeling, tensile tests on films, and heat of immersion. Aggregate tests are usually performed on certain aggregate-size fractions coated with a standard amount of binder. They ignore the effects of the other aggregate fractions and design parameters such as air void level and optimal asphalt content. Aggregate sizes other than those used in the test can have slightly different stripping potentials because the various sizes may have different degrees of coating in a pavement mixture, plus the sizes have different physical properties such as surface area. The coarse aggregate fraction, or an intermediate size fraction of a particular gradation, is generally tested. Stripping is usually visually or microscopically estimated, although some quantitative methods for determining the percent stripped aggregate have been used.

None of these tests determine the effects of moisture or water on the quality of a pavement because they do not test paving mixtures. They also cannot determine the amount of antistripping additive needed when only specific size fractions of the aggregate are tested because dosage depends on the surface area of the aggregate. Correlations with field performance are often poor as should be expected. These tests are used most efficiently to rate aggregate types, to supplement tests on compacted mixtures, and in research studies to investigate stripping mechanisms. They should not be used to predict pavement performance.

c. Mixture Tests

Mixture tests include (1) boiling water (loose mixtures), (2) dynamic abrasion, (3) immersion-compression, (4) Marshall immersion, (5) tensile splitting, (6) resilient modulus, (7) Hveem stability, and (9) sonic evaluations. These methods use the entire mixture and thus test the effects of the coarse and fine aggregate, filler, asphalt cement, additives, and film thickness. These tests, excluding the boiling water and dynamic abrasion tests, indicate quantitatively a loss in a mechanical property caused by a change in both the adhesion of the binder to the aggregate and cohesion, or any effects water may have on the binder. Losses in mechanical properties are also a function of any losses in the strength of the aggregate due to conditioning processes such as freeze-thaw cycles, although losses in aggregate strength are rare during testing. The boiling water test, like most of the aggregate tests previously mentioned, only evaluates the degree of visual stripping. Abrasion tests generally measure a loss in surface aggregates by weight caused by both moisture damage and abrasive action.

All mixture tests, except the boiling water test, are performed on a compacted mixture, which accounts for mixture design parameters such as air void level and the VMA. Tests on compacted mixtures better simulate inservice mixtures, but they are difficult to develop, most have many modifications, and the between laboratory precision or reproducibility is often poor. The measured amount of moisture damage in a compacted mixture is a complex function of the type of mechanical test, the air void level, the amount of water in the air voids, and the conditioning processes used to try to induce moisture damage.

In most mixture tests, the specimens are compacted; then they may or may not be partially saturated with water by use of pressure or a vacuum, and finally they are moisture conditioned, using processes such as soaking them in hot water, to try to induce moisture damage. Data that can be evaluated from mechanical tests are (1) the retained ratio, or the ratio of the conditioned to the unconditioned mechanical property, (2) the individual conditioned and unconditioned mechanical properties, (3) visual stripping, (4) saturation, and (5) swell. The majority of the most recently developed tests for determining moisture susceptibility use an indirect tensile test and Hveem or Marshall-sized specimens. The results of these studies indicate that tensile tests are better methods for measuring losses in adhesion than other forms of tests such as compressive strength and stability.

d. Chemical Analysis Tests

Chemical analyses are used to determine (1) which asphalt components are strongly or weakly adsorbed onto aggregate surfaces, (2) which are most easily removed by water, and (3) the interacting effects of the composition of the aggregate. Therefore, they are used to determine how the various asphalt functional groups and the aggregate components relate to adhesion and stripping. Chemical analyses are used in conjunction with the results of aggregate or mixture tests for determining moisture susceptibility. They have only been used in research studies.

4. Conclusions

Moisture damage in asphalt mixtures is a complex mechanism which is not well understood and has many interacting factors. Unlike most adhesives, asphalt is not a scientifically developed material and is rarely applied to surfaces which are completely clean or dry. Although it may not be an ideal adhesive, bonding can be adequate for the design life of the pavement using proper construction procedures, mixture designs, and antistripping additives. More knowledge is needed in all areas dealing with moisture damage in asphalt pavements.

CHAPTER 5: CURRENT RESEARCH STUDIES AND ADDITIONAL STATE-OF-THE-ART REPORTS

1. Strategic Highway Research Program (SHRP)

The National Research Council's Strategic Highway Research Program (SHRP), Washington DC, has several contracts which address moisture damage in dense-graded asphalt mixtures. As part of SHRP A-003A, entitled "Performance Related Testing and Measuring of Asphalt-Aggregate Interactions and Mixtures," tests for evaluating the susceptibility of asphalt mixtures to moisture damage are being evaluated and modified if needed. The effects of aging on moisture damage are being considered. A literature review which includes descriptions of current tests, their usefulness, and proposed modifications for the SHRP contract work, has been published.(135)

As part of SHRP A-003B, entitled "Fundamental Properties of Asphalt-Aggregate Interactions Including Adhesion and Absorption," the following areas concerning adhesion are being investigated: (1) the compatibility of asphalts and aggregates in terms of their ability to form chemical bonds, (2) the effects of aging on asphalt/aggregate chemistry, and (3) the chemistry and influence of modifiers or additives on adhesion. This work is also evaluating the effects of adsorption and absorption of asphalt on mixture properties. Literature reviews will be available for these topics. Fundamental properties concerning adhesion obtained from this study will be used in SHRP A-003A.

As part of SHRP A-004, entitled "Asphalt Modification," the effects of modifiers including antistripping additives on the asphalt/aggregate bond and on the susceptibility of asphalt mixtures to moisture damage are being investigated.

2. Federal Highway Administration (FHWA)

The Federal Highway Administration's (FHWA) Office of Implementation, McLean, VA, currently has contracts entitled "Evaluation of Asphalt Stripping Tests" with four State highway agencies (Indiana, New Mexico, Montana, and Oregon) to evaluate AASHTO T 283, "Resistance of Compacted Bituminous Mixture to Moisture Induced Damage," and ASTM D 4867, "Effect of Moisture on Asphalt-

Concrete Paving Mixtures," which are based on the indirect splitting tensile test.(55,56) The objective of this study is to encourage more widespread use of these tests. This study is an extension of past work performed by the FHWA, which is documented in reference 85.

The FHWA Office of Engineering and Highway Operations Research and Development currently has a contract entitled, "Study of AC Stripping Problems and Corrective Treatments," to determine the most effective methods of introducing lime into asphalt mixtures and to improve the reliability of laboratory test methods used to evaluate moisture susceptibility. This study is an extension of the work performed for the FHWA and reported in references 69, 77, and 85. The final report is being reviewed.

3. Highway Planning and Research (HP&R) Studies

Several State highway agencies are evaluating tests for moisture susceptibility. Missouri is currently evaluating the ASTM D 4867 procedure along with their standard immersion-compression under a Highway Planning and Research (HP&R) Study No. 88-3, entitled "Evaluation of Moisture Damage in Asphalt Mixtures by Tunnicliff & Root Procedure (NCHRP 274)." Louisiana is evaluating the boiling water, freeze-thaw pedestal, and splitting indirect tensile tests for asphalt mixtures under HP&R Study No. 85-1B, entitled "Compatibility of Aggregate, Asphalt Cement, and Antistrip Materials." South Carolina under HP&R Study No. 545 is investigating how to recycle stripped mixtures.(136)

States currently evaluating antistripping additives under the HP&R program are Maryland (Study No. AW088-332-046, "Evaluation of Antistrip Additives for Bituminous Concrete"), Mississippi (Study No. 95, "Use of Silane to Reduce Stripping in Asphalt Pavements"), and Texas (Study No. 3-9-86-441, "Treatment of Asphalt Mixtures with Lime and Antistripping Agents"). Colorado (Study No. 1481A, "Pretreatment of Aggregate") is evaluating the effects of pretreating aggregates with materials such as kerosene, reclamite, and emulsions.

4. National Cooperative Highway Research Program (NCHRP)

The National Cooperative Highway Research Program (NCHRP) under Project 10-17, entitled "Use of Antistripping Additives in Asphaltic Concrete

Mixtures," is evaluating liquid antistripping additives in pavement sections. This is a continuation of the work given in reference 44. In NCHRP Project 20-5, Topic 19-09, entitled "Moisture Damage in Asphalt Concrete," a synthesis is being written concerning current practices to control moisture damage and the extent of moisture-related damage in pavements. The final report is being reviewed.

5. Additional State-of-the-Art Reports

Additional state-of-the-art reports and additional details on some test procedures are given in references 4, 21, 26, 135, 137, and 138. References 26 and 44 also give state-of-the-practice information, which indicate what tests and types of additives are currently being used by highway agencies, and other experiences such as how stripping problems are identified in pavements and what aggregate types are most likely to strip. This information will be updated by the NCHRP synthesis currently being written.

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