Annotated Bibliography

This Bibliography below was developed in the early stages of the project by the original project team. Other excellent resources can be found on the website for the National Center for Pavement Preservation (www.pavementpreservation.org). Caltrans has also developed a technical advisory guide, which can be found at http://www.dot.ca.gov/hq/maint/mtag/ch6_fog_seals.pdf.

By Larry Schofield

I Aging and Hardening of Asphalt Pavements

1. Coons, R., Wright, P. "An Investigation of the Hardening of Asphalt Recovered from Pavements of Various Ages", AAPT

There is an increase of approximately 50% in the viscosity of the asphalt located in the top ¼ inch when compared to that found in the ¼ inch to ½ inch zone

There is a very thin film at the pavement surface which has a higher viscosity than the average viscosity of the top ¼ inch.

Increases in viscosity with age are more apparent in the top ½ inch. Little change occurs below this depth. In the upper ½ inch, asphalts with lower viscosities were found to increase more than asphalts with higher viscosities

When the top 1/16 inch of a ¼ section was removed, the average viscosity for the ¼ inch section decreased by 25%.

At a depth of about 1 ½ inches, no change in viscosity occurs with time.

2. Button, J., "Permeability of Asphalt Surface Seals and Their Effect of Aging of Underlying Asphalt Concrete", TRB 1535, pg 124

The objective of the study was to evaluate the relative aging abatement effects of a slurry seal, a micro-surfacing, or a chip seal on the upper ½ inch of an asphalt pavement. This was accomplished by conducting accelerated again on laboratory prepared specimens using two mixture types, with one mixture known to highly susceptible to aging. Essentially, half inch thick beams were compacted to between 10-15% air voids. One half of the beam was then sealed with an impermeable membrane (i.e. saran wrap) while the other half remained uncovered. Accelerated aging was then conducted, using three aging periods, by elevated temperatures, forced air movement, periodic water wetting, and UV light exposure. This allowed for comparison of the treated and untreated conditions. Permeability testing was also conducted on a laboratory prepared slurry seal, chip seal, and micro-surfacing to evaluate the water permeability. A constant-head permeameter was used for this testing.

By comparing laboratory aging data with existing field data on aged asphalt pavements, it was possible to make inferences regarding the number of years a surface seal would delay hardening of an underlying asphalt pavement.

The study indicated that surface seals relative abatement of aging effects only extends to a depth of about ½ inch. Testing indicated that surface seals retard aging 0 to 2 years. Most of the oxidative hardening in the uppermost surface occurs in the first four years. Therefore, for a surface seal to significantly impact the oxidative hardening, it must be placed within the first two years after overlay construction. It was reported that surface seals are applied to pavements to:

- Renew skid resistance
- Fill Ruts
- Retard Raveling
- Restore Ride Quality
- Reduce Intrusion of Surface Water
- Improve Appearance

The oxidative hardening depends upon on several factors: susceptibility of asphalt to aging, depth in pavement, air void content, permeability, asphalt content or film thickness, climatic conditions.

Asphalt was extracted from the beam specimens using conventional methods. The rheological properties of the extracted binder were measured using the dynamic shear rheometer.

Analysis of the change in oxygen content of the extracted asphalts was quantified using a Fourier transform infrared analyzer. Oxygen uptake was measured by the change in carbonyl peak height on infrared spectra.

The researchers estimated that UV light will only penetrate 2 microns into a film of asphalt. Therefore they surmised that UV has practically no effect on the asphalt viscosity, except on a micro layer near the surface. However, this micro layer may play an important role in initiation of thermal cracks.

It was reported that as the permeability of a material decreases, air permeability and water permeability asymptotically approach the same value.

From previous field testing it was found that micro-surfacings typically exhibit 20% air voids at the time of construction. Six months later, after considerable trafficking, the air voids reduces to approximately 10%.

Oxidation of asphalts in pavements covered by surface seals depends on diffusion of oxygen at slow rates or long periods of time because of the relative impervious nature of the seals. Changes in pavement temperature can promote more diffusion. That is, as pavements heat and cool, air enters and leaves permeable voids to maintain atmospheric pressure. This movement helps provide sources of oxygen.

The researchers assumed that since asphalt is a good UV absorber, that chemical reactions catalyzed by ultra-violet light (actinic light) could only be affected to a depth of 2 microns within the asphalt cement. However, the researchers cite a different study that suggested that UV aging of the asphalt binder formed water soluble products. It has been suggested that the natural weathering cycle of the pavements could erode these water soluble products. The researchers indicate that they believe this erosion process would be limited by the exposure of the aggregate materials as the binder was removed. Once the aggregate “armor” was formed, no continued erosion could occur.

When a surface seal is placed, there may be some mixing of the binders at the interface with the underlying asphalt pavement. This may result in a lower viscosity asphalt cement at this interface.

Study Observations

- A slurry seal, micro-surfacing, or chip seal can delay oxidative hardening of the underlying asphalt concrete by 0 to 2 years.
- Most of the oxidative hardening that occurs in the upper stratum of the pavement occurs within four years of its construction.
- UV light only penetrates to a depth of 2 microns in asphalt cement
- Permeability to air and water in a seal coat is almost zero. The permeability of slurry seals and micro-surfacing after densification by traffic is on the less than 1 x 10 $^{-5}$ cm/sec. Chip seals were reported as essentially impervious.
- Since most aging occurs from the top down, and since thermal cracking initiates at the surface of a pavement, the researchers propose two additional benefits of surface seals not addressed in the study: (1) When a seal is placed, the surface is new and more crack resistant, and (2) there maybe some rejuvenation of the existing pavement at the interface with the seal.

3. Kandhal, P.S., Chakraborty,S., "Effect of Film Thickness on Short-and Long-Term Aging of Asphalt Paving Mixtures", TRB 1535, pg 83

The objective of this study was to quantify the relationship between film thickness and the aging characteristics of asphalt paving mixes so that an optimum film thickness for durable pavements can be recommended.

Literature Citations

The researches report on several previous research studies with the following results:

(1) Campen, et al: Presented relationship between air voids, surface area, film thickness, and stability for dense graded ac. They recommended that an average film thickness of 6-8 microns was sufficient for dense graded mixes. They also concluded that film thickness decreases as surface area increases. However, they found that the binder content did increase with increasing surface area but that the relationship was not directionally proportional.

(2) Goode and Lufsey: Related asphalt hardening to voids, permeability and film thickness. They defined a bitumen index that related the pounds of asphalt cement per sq foot of surface area. This term was used to avoid the implication that a uniform film thickness occurred on all aggregate particles. The study found that a combined factor of the ratio of the air voids to the bitumen index satisfactorily related to the asphalt binder hardening characteristics. They suggested a maximum value of this ratio of 4.

(3) Kumar and Goetz: This study suggested that the best indicator for predicting the resistance to asphalt cement hardening in a single sized aggregate mix was to calculate the ratio of the film thickness factor to permeability. The film thickness factor was defined as the ratio of the percentage of asphalt cement available for coating the aggregate. They indicated that, for dense graded mixtures, the concept of average film thickness was dubious at best if not totally inaccurate. For dense graded mixes the permeability was found to be the best indicator of resistance to asphalt cement hardening. However, at 4 percent voids or less, the permeability had almost no effect on hardening.

In this study, samples were prepared to a target air voids content of 8%. Samples were subjected to short term aging prior to compaction and then long term aging conducted using SHRP protocol. The prepared samples were designed to represent mixes with average film thicknesses ranging between 4 to 13 microns. Resilient Modulus and Tensile Strength were determined on the compacted specimens. Complex modulus and phase angle, penetration, and viscosity were measured on extracted binder. Only one aggregate and one binder were used in this study.

Study Observations

- A fairly good correlation was found between film thickness and resilient modulus of the aged asphalt mixtures. An optimum film thickness of 9 to 10 microns was found.
- Relationships between film thickness and viscosity, penetration, and complex modulus were also found with the optimum film thickness about 9 to 10 microns.
- The Goode and Lufsey ratio of a maximum of four seems to be a good indicator.

II Test Section Results of Spray Applied Sealers-Rejuvenators

Dense Graded Pavements

4. Vallergo, B.A., "Emulsified Petroleum Oils and Resins in Reconstituting Asphalts in Pavements", Highway Research Record 24, 1963 (Reprinted)

This paper is an excellent treatise on the aging of asphalt pavements. It essentially is the basis for the development of Reclamite the product. The paper describes the addition of suitable components at the appropriate time during the aging process to stop or reconstitute the weathered asphalts. The paper discusses both the laboratory investigation and three years of follow up investigations.

The Rostler analysis determines the following four principal fractions of maltenes: nitrogen bases (N), first acidifins (A1), second acidifins (A2) and paraffins (P). The influence of maltenes on the durability of asphalts as cementing agents has been shown to depend on the ratio of the four fractions of maltenes. The parameter (N a A1)/(P+A2), expressive of the ratio of the more reactive to the less reactive fractions, is a useful guide for predicting performance of an asphalt binder.

Reclamite is a cationic maltene emulsion designed to combine with and reconstitute aged asphalt, thereby restoring its plasticity. It also acts as a "seal in depth" because after penetration it combines with and expands the asphalt. Permeability to both air and water is reduced.

Reclamite was designed to be used as a preventive maintenance treatment applied to structurally sound pavements as soon as it begins to show signs of aging or brittleness through the symptoms of dryness, surface pitting, raveling or shrinkage cracking. Generally these conditions develop in a 2 to 10 year period.

Laboratory Investigation

They used an ultra violet light to evaluate the depth of penetration into prepared plugs. During the lab phase, they found that certain fractions of petroleum oils and resins could not only be used to restore the original properties to ages asphalt but the same components could also make the reconstituted asphalt superior to the original.

Field Investigation
Edwards Air Force Base Test Sections
Lodi Test Sections

5. **Brown, E.R. "Preventive Maintenance of Asphalt Pavements", Paper for Transportation Research Board, 1988,**
6. **Brown, E.R., Johnson, R.R., "Evaluation of Rejuvenators for Bituminous Pavements", Air Force Civil Engineering Center, Tyndall Air Force Base, AFCEC-TR-76-3**

The TRB paper in 1988 essentially discusses the results of the 1976 study so both reviews are discussed as one report.

The purpose of a rejuvenator is to:

- Penetrate
- Rejuvenate
- Seal

A rejuvenator should be evaluated for:

- The ability to penetrate
- The ability to soften asphalt binder
- The ability to reduce the amount of surface cracking
- The ability to reduce the loss of fines through surface attrition
- The amount of surface friction loss resulting from application

The rate of oxidation is highly dependent upon air voids of ac. Void contents below 7 to 8% have significantly less oxidation. However, air voids need to be above 7 to 8% to allow for significant penetration.

The research evaluated five sealer/rejuvenators on three airfields. One Airfield was in the Desert in Arizona, one airfield was in Florida and one airfield was in Montana. The test section criteria consisted of:

- Pavement Approximately 10 yrs old
- Pavement that was relatively free of maintenance and would remain so for at least the next 3 years.
- Pavement section that could be closed to traffic for short periods

The tests performed on the rejuvenators consisted of:

- Consistency testing
- Temperature Susceptibility
- Safety and Heating
- Homogeneity
- Stability
- Amount of Residue

Testing Conducted on Existing AC pavements prior to Treatment Application:

- Aggregate Gradation
- Asphalt Content
- Density
- Asphalt Penetration

Testing Conducted on Field Test Sections over time:

- Skid Resistance (British Portable Tester)
- Penetration Testing on Extracted Asphalt
- Viscosity testing on Extracted Asphalt
- Distress Survey for Crack Extent and Severity
- Surface Texture Analysis using Sand Patch Test

Frequency of Evaluations and Core Retrieval:

- 48hrs
- 6 Months
- 1 Year
- 2 Years
- 3 Years

Observations from the Study

- Effect of Rejuvenator only extended to a depth of approximately 3/8 inch
- Skid data indicated that most materials reduced skid resistance for at least one year
- Suggested that Rejuvenators should not be place on Slurry Seals
- Although the total amount of cracking for all sections was approximately similar, the amount of cracking less than ¼ inch was less for three of the treatments
- The rejuvenators that softened the asphalt had more of an effect in the wheel paths where the kneading action of traffic existed than outside the wheel paths.
- All five treatments improved resistance to loss of fines.

7. **Predoehl, N.H., Kemp, G.R., "Binder Modifier Agents for Construction and Maintenance Seals", California Department of Transportation, FHWA-CA-TL-79-07, March 1979.**

This report is probably the best documented and evaluated test sections on surface sealers that has been conducted to date. The report describes the construction and evaluation of test sections at two locations in California. The report concluded that the main benefit of surface seals is to reduce raveling and heal, or cover, fine cracks. The report indicates that the skid properties are adversely affected by application of surface seals. It also demonstrates that only the top ¼ of the pavement is affected by the treatments.

The report categorized the surface seals by function into four groups: Hardening agents, softening agents, altering agents, and covering agents.

Hardening Agents: Hard base bituminous products which are used to coat the surface. Examples are Gilsabind, Astec Pavement Sealer, and Satin Black.

Softening Agents: Products containing resins, oils, or solvents which are applied to dilute the asphalt. Examples are Reclamite, SC-70.

Altering Agents: Products containing substances such as rubber, etc. which are used to alter the asphalt properties after they are mixed. Examples are Petroset A.T. and Reclamite X.M.

Covering Agents: Products that are sprayed on to "dress up" a surface or help bind loose material. Examples include SS-1h.

The test sections were placed at two different climatic regions in California and one pavement site represented a very tight pavement surface while the other represented was quite open. Skid testing with time, viscosity testing with time, penetration testing with time, and both air and water permeability testing were conducted with time at both of these sites.

The products tested were Gilsabind, Satin Black, Astec P.S., Petroset A.T., Reclamite, Reclamite XM, and SS-1

The following findings were reported:

- None of the binder modifier products should be applied to a new traveled way for a minimum of one year after construction so that any bleeding areas can become visible prior to any subsequent treatment applications.

- All of the studied binder modifier products caused a reduction in friction of the surface.

- All of the studied binder modifiers products reduced raveling as compared to adjoining untreated sections.

- With one exception, none of the studied binder modifier products appeared to affect the hardening or softening below the top ¼ inch of the pavement.

- None of the products evaluated appeared to have any significant effect on the structural integrity of the treated pavement.

- It was the opinion of the researches that a well-constructed asphalt concrete overlay pavement built with good materials should not ordinarily need a surface treatment with any of the studied binder modifier products until such time that surface deterioration has actually begun, as evidenced by dryness, fine cracks, or slight raveling.

8. **Wood, K.L., "Asphalt Pavement Surface Sealers", Colorado Department of Highways, Report Number CHOH-DTP-R 85-5**

This report evaluates the effectiveness of four surface seals that were in use by the Colorado Department of Highways at that time: Reclamite, GSB 78, CSS-1h, MC-70, and Gilsabind. The four products were used on two different overlay projects that experienced raveling shortly after construction. The report describes two principal reasons for using surface seals in Colorado, late fall paving and asphalt pavement moisture susceptibility. Skid testing was conducted at several intervals up to about 6 months. Both projects experienced raveling which very well could have influenced the actual skid values with time.

The report concluded that the Reclamite performed best. Although the skid numbers dropped after the application of all sealers, the Reclamite recovered the quickest. The results indicated that the reduction in skid number would be on the order of 20% to 50% with the application of Reclamite. The report further noted that the Gilssonite product wore off the surface in the wheel tracks.

9. **ASI-Runway Preservation System, Presentation on May 16, 2000 US Army Waterways Experimental Station, Vicksburg, Mississippi. Authors unknown.**

The presentation material describes a product known as ASI-RPS, a cationic emulsion of Gilsonite ore plus plasticizers. Describes the sealer application as typically 0.08 to 0.15 gal per sq yd. and can be sanded. The typical cure time is 2 to 8 hours. Presentation provides an ecological analysis of the product use on such items as global warming, acidification, cancer, etc.

Indicates that 60 regional airports have used this product, with most applications being taxiways. A life cycle analysis of different application is provided. The analyses use a cost of $0.50 sq yd as the product cost. The presentation provides three years of skid data for the Logan County Road 154 in Ohio. Data suggests that at the time of application, the pavement friction lost approximately 8% of its skid value but regained most of the original skid properties within 14 days.

Presentation lists the following goals for ASI-RPS:

- Prove that ASI-RPI is an effective pavement preservation system
- Prove the ASI-RPI can be effectively used on critical areas

10. Sebaaly.P.E., "Evaluation of the GSB-Repave System", Unpublished, May 23, 1997.

The report evaluated the use of three binders for application in cold recycling: GSB Repave, Reclamite, and HFMS-2S. The report concludes that the GSB-Repave system provided resilient modulus, tensile strength, and stability values which are equivalent to hot mixed asphalt mixtures. In addition, the GSB system exhibited better aging characteristics than both the HFMS-2S and the Reclamite.

These treatments were evaluated using Resilient Modulus, Hveem Stability and AASHO T-283 for moisture damage.

11. Pickett,J.E., "Evaluation of Seal Coat Runway 16-34 Lajes Field, Azores, US Army Geotechnical Laboratory, Waterways Experiment Station, March 1983

Provided an early assessment of the change in properties of the existing pavement materials after the application of Reclamite to a runway. Both penetration testing at 77 degrees and absolute viscosity testing at 140 degrees were conducted on treated and untreated sections. Cores were retrieved and the top 3/8 inch removed for binder recovery and evaluation. The results indicated that the penetration increased an average of 194% after treatment, while the viscosity decreased 94% after treatment.

12. Kennedy,J. "Demonstration Project Report on CRF & Reclamite", Waco District Texas Department of Transportation,

This project was conducted in two phases. Phase one, conducted in October of 1997, consisted of placing seven 6 inch diameter test spots to determine the optimum dilution rate and application rate. Two additional application areas which were 3 yards wide by 7 yards long were also used; one for a CRF test area and one for a Reclamite test area. Phase II, constructed on June 10, 1997, consisted of placing three test areas. One area was designated as the control section, one section, 14 ft by 800 ft, had CRF applied, and the third section, 14 ft by 675 ft, had Reclamite placed. Both the CRF and Reclamite sections were allowed to cure for 30-45 minutes and then were blotted with approximately 3lbs per sq yard of dry washed crusher sands. The sand was drag broomed, rolled and then swept prior to opening to traffic.

Cores were retrieved in July 1998 and in January 1999. Testing conducted on the cores consisted of water permeability, % asphalt determination, viscosity testing and penetration testing.

Observations from this project include:

- CRF and Reclamite both appear to provide sealing of the surface and this effect last for at least six months. The difference in sealing between CRF and Reclamite was minimal.

- The CRF and Reclamite both appear to reduce the viscosity and increase the penetration of the pavement at the surface. This effect probably is only present in the top ½ inch.

13. Pannuto,B.J. "Report on Reclamite Usage", Department of the Navy Western Division, Naval Facilities Engineering Command, 1973

The study evaluated the application of Reclamite on three test roads as part of a road repair contract. Periodic inspections were performed at four month intervals, beginning in April of 1969 and ending in August 1970 (i.e. approximately a 1 ½ year evaluation period). The inspections consisted of retrieving cores, conducting sliding plate micro-viscosity testing on extracted binder, conducting Airfield cone penetration testing to a depth of 1/8 inch in the surface, and taking photographs of the pavement surface. In addition to the three test roads reported on in this study, a follow-up report of Reclamite used as a construction seal is included at the end of the study. The three road sections subsequent construction seal application is described as:

- G-2 Tower Road. A one-inch overlay that was placed 27 months before the Reclamite was placed in 1969.
- Pole Line Road. A two-inch overlay had been placed on this road approximately 26 months before application of the Reclamite test section in mid 1969.
- Area L Road. A one-inch overlay had been placed 25 months prior to the application of the Reclamite test sections.
- A freshly laid 1 ½ inch overlay had Reclamite used as a construction seal in November 1971. The evaluation period was approximately 1 ½ years.

Observations from this study include:

- In the top ¼ inch of the pavement, Reclamite achieves its maximum affect (i.e. viscosity change) within the first month. For the ½ to one inch depth, the largest increase occurs within the first month, but at two of three of the test sections, change continued to occur throughout the evaluation period.
- Cracks existing in the pavement before treatment tended to close up after treatment due to the softening of the asphalt and kneading action by traffic.
- A difference in surface texture was noticed between the control sections and the treated sections at all sites. This affect was observable after just five months at one location.
- At the location where Reclamite was used as a construction seal, it was observed that there was a noticeable difference in surface texture between the treated and untreated sections. It was also noted that the reflected cracks that came up through the overlay were tighter in the treated section.
- The report refers the readers to another Naval report "Technical Report No R690 "Reclamite as a Life Extender for Asphalt Concrete Pavements".

Open Graded Pavements

Surface Treatments

14. Keane,E.G. "Rejuvenation and Sealing of Flexible Pavements", Utah Department of Transportation, Research Study Report 943,1989

Rejuvenators and sealers are applied for the following reasons:

- To arrest pitting and raveling
- To reduce shrinkage tendencies

- To close shrinkage cracks
- To decrease permeability
- To improve durability
- To Extend the period between application of surface treatments

The Purpose of the Study was to:

- Determine the Pavement Conditions where a rejuvenator can be applied
- Identify Effective Agents
- Generate Procedures to Develop Optimum Application Rates
- Develop strategies for using rejuvenators to extend pavement life

The functions of two major asphalt constituents:

- Asphaltenes-provide stiffness
- Maltenes-provide adhesive and ductile properties
- Problem is asphaltenes remain in place while maltenes dissipate to the surroundings

The study used a different approach for chip seals than for plant mix seals. Chip seals need to have the "lock" restored. The lock is complemented by adding what, in essence, is an asphalt grout. Plant seals respond to penetration with maltenes.

Originally 8 test sections were to be constructed. Five of them were not completed or meaningfully evaluated. Three sites were essentially evaluated.

Date Placed	Location	Surface Type
1984	I-80	Plant Mix Seal
1986	US 95 & U-276	Chip Seal
1987	US 89	Chip Seal

Products Evaluated Included:

- Reclamite
- CRF
- GSB Emulsion
- Cyclogen ME
- Penetrating Emulsion Prime

Study Observations

There was a marked difference between the control sections and treated sections in the filling of hairline cracks. No difference in filling of 1/8 inch or larger cracks.

III The Origin and Properties of Asphalt Pavements

15. Robertson, R., "Chemical Properties of Asphalts & Their Effect on Pavement Performance", TRB Circular No. 499

Origin of Asphalt

Petroleum is formed by algae that are converted to a "kerogen", a consolidated organic mineral matrix that has little or no solubility in organic solvents. The kerogen is then pressure cooked into petroleum. The deposit temperature increases with depth and therefore the material will vary based on years of "pressure cooking" and location of pressure cooking. (Technical term for pressure cooking is diagenesis of organic material (dead algae) into petroleum).

During the process of forming petroleum, the organic liquid migrates through the rock from its original deposit to another rock area that is more porous and serves as a reservoir. This migration is analogous to filtering the crude source at the molecular level; hence additional variability is induced by this filtering.

Some higher plant forms also contribute to formation of petroleum. Sometimes the plant cuticle (i.e. the water resistant layer of the leaf) survives and becomes part of the crude. This material is a waxy substance and produces waxy crudes which is yet another variable.

The chemical nature of the crude source strongly affects the in-service behavior.

Chemistry of Petroleum Asphalt

Chemistry at Molecular Level

Numerous types of organic compounds are found in petroleum asphalt. Organic compound means a molecular species made up of at least one carbon atom and at least one other atom except carbon dioxide and mineral carbonates.

Covalent bonds are thermally stable and are typically formed by the sharing of electrons by different atoms.

At the molecular level, much of the mass of the neat asphalt is a mixture of a wide variety of high boiling hydocarbons. Some are aliphatic (i.e. oily or waxy), some are aromatic. Aliphatic have no double bonds.

Aromatics have double bonds and are flat and hence can be stacked efficiently. Aliphatic chains are zigzagged shaped.

In general, boiling point increases with increasing molecular weight.

Certain types of carbon in asphalt are particularly susceptible to oxidation.
Oxidation products formed upon aging are polar and further contribute to the polarity of the asphalt. It takes more energy to separate polar molecules than non-polar molecules.

Chemistry at the Intermolecular Level

Polar molecules have a tendency to attract each other and form clusters of molecules. Molecules that have both acidic and basic sites present are called amphoterics. Amphoterics self assemble easily and have a profound effect on viscosity enhancement. Covalent bonds are strongest. When covalent bonds are broken, totally new molecules are formed.

You can predict the physical properties of an asphalt from ion-exchange chromatography composition data. This readily allows selection of additives to alter physical properties predictably.

Size Exclusion Chromatography (SEC): Separates asphalt by apparent molecular size

SEC and molecular weight analysis are both rapid tests.

Ion Exchange Chromatography (IEC)

Supercritical Fluid Chromatography

Oxidation

* The principal species in asphalt that oxidize under road service conditions are benzyl carbon and sulfide sulfur. Organic sulfides generally oxidize faster than benzyl carbon, even at fairly high pavement temperatures. This means sulfides consume most of the oxygen in the early stages and hence inhibit oxidation of benzyl carbon in the early life of a roadway. The differences in oxidation rates of sulfide versus benzyl carbon are important because sulfoxides generally cause minor increases in asphalt stiffness where as ketones formed from oxidation of benzyl carbon typically cause major increases in stiffness.

Speculation on Relationship of Chemistry to Pavement Performance

At Low Service Temperatures the more neutral materials, like waxes, also organize into a more crystalline-like material imparting further stiffness. This is a special case of steric hardening.

Aging

There are two types of aging:

1. Steric Hardening: hardening that takes place as a result of prolonged standing. Steric hardening is the process where polar molecules of asphalt slowly align themselves (self-assemble) into the most stable state (lowest energy). (It is reversible.) This results in the best intermolecular structure and hence greatest stiffness. However, since the intermolecular association is no more than low energy bonds, both heat and stress can break the bonds.

   At low service temperatures the more neutral materials, like waxes, also organize into a more crystalline-like material imparting further stiffing. This is a special case of steric hardening.

2. Chemical Oxidation hardening: hardening that results from chemical oxidation of asphalt from exposure to air. This results in permanent hardening. The effects of steric hardening are minor compared to this, and the use of rejuvenator to disassociate the oxidization is required to soften it.
   - Aggregates also have an effect on this process.
   - The oxidative aging of asphalt eventually levels off. However, the viscosity at which one asphalt levels of may be many times higher than another asphalt of the same grade but from different crudes.
   - There may be a need for a specification for an upper limit of increase in viscosity, especially in hot climates.
   - The property of shrinkage and formation of a brittle asphalt is expected to be most closely related to the compositional features of aliphatic/aromatic ratio when all other characteristics are equal. Aliphatic and aromatic ratios can be determined by nuclear magnetic resonance. The differential scanning calorimetry may be useful.

Moisture Damage

Adhesion arises because of the interaction of the polars in asphalt with the polars in aggregate. But polarity alone may not be sufficient to achieve good adhesion in pavement, because asphalt is affected by its environment.

Asphalt has the capability of incorporating and transporting water. Absorption of water, like all other behavior, varies with asphalt composition.

Monovalent (singly charged) cation salts, such as sodium or potassium salts of carboxylic acids in asphalt, tend to be removed from aggregates quite easily. These are surfactants and combine with traffic to scrub the asphalt off the aggregate.

Divalent salts of acids (double charged) such as calcium from lime are more resistant to the action of water.

It would behoove the user to ensure the acids in asphalts are neither free nor in the form of monovalent salts.

Aged or oxidized asphalts, which have a greater amount of polars (oxidation products) tent to incorporate water to a greater extent than new pavements.

From a chemical viewpoint, the action of water is like is somewhat like the dilution of asphalt with a low molecular weight solvent.

16. Kim, Y.R., Whitmore,S.L., Little, D.N. "Healing in Asphalt Concrete Pavements", Transportation Research Record 1454,

A number of researchers have demonstrated that the relationship between the number of cycles until failure and tensile strain obtained from laboratory fatigue testing grossly under predicts field fatigue life. This discrepancy is generally accounted for by the shift factor employed between laboratory and field data. This discrepancy has been attributed to the causes shown below:

- Difference in loading conditions, including rest periods, multi-level loading, and sequences of loading
- Reactions or frictional forces between the AC and the unbound base material
- Residual stresses caused by the plasticity of the pavement layers
- Dilatancy stresses from the expansion of paving materials under load
- Complicated environmental conditions in the field.

When an ac pavement is subjected to repetitive multi-level loading and various rest periods, three major mechanisms occur:

- Fatigue or damage accumulation
- Time Dependent Behavior related to the visco-elastic behavior of ac
- Chemical healing of AC across macro and micro faces during rest periods

This paper evaluates three techniques for evaluating the chemical healing that occurs in ac pavements during rest periods between load applications

- **The nonlinear viscoelastic correspondence principle.** This approach was developed by Schapery in 1984 and the procedure reduces a (time dependent) visco-elastic to a (time independent) elastic procedure. This process employs pseudo strains to make some of the transformations. Using this technique the propensity of different mixtures for healing micro-cracks can be determined by measuring the difference in areas under the stress-pseudo strain curve before and after a rest period and normalizing it by the stress-pseudo strain area before the rest period. This technique is useful for modeling damage growth and healing in ac under complex loading conditions.

- **The Impact-Resonance Method described in ASTM C215**. In this testing, the elastic and shear moduli are independently determined. Healing ratios are then determined as the moduli ratio obtained from the before and after heating. This technique is a laboratory tool for evaluating modulus increases after rest periods at higher temperatures.
- **Wave Propagation Techniques**. This technique determines the elastic modulus from any one of three wave propagations (i.e. longitudinal wave, shear wave, or elastic shear wave) by determining the wave speed. The stress-wave method measures the stiffness of the ac in a glassy (i.e. purely elastic) region. Because of the impact loading, the modulus is not affected by the time dependent relaxation. Therefore the increase in modulus after a rest period could be the result of micro-crack healing. This technique is useful for field application.

IV The Permeability of Asphalt Pavements and Seal Coats

V Spray-Applied Asphalt Pavement Sealer-Rejuvenator Products

VI Friction Testing

17. Henry, J.J., "Evaluation of Pavement Friction Characteristics", NCHRP Synthesis 291, National Academy Press, 2000

This report presents the state-of-the-practice on the measurement and evaluation of roadway frictional characteristics. It discusses the importance of both macro texture and micro texture in relationship to frictional properties. It describes the current equipment used for measuring pavement friction and how each of the devices is influenced by the micro and macro texture.

Fatal Accidents occur on wet pavement at a rate of from 3.9 to 4.5 times the occurrence as on dry pavements. This is the reason that field testing is performed using water to simulate this condition. Wet pavement friction at low speeds is predominantly influenced by micro texture, whereas wet pavement friction at high speeds is predominantly influenced by macro texture.

Roadway friction cannot be represented from a single number. The same value of friction measurement can be obtained on two pavements that have significantly different frictional characteristics. It is important to provide both micro texture and macro texture parameters to assure appropriate frictional characteristics on wet pavement. Since micro texture cannot currently be measured at highway speeds, the International Friction Index (IFI) combines both a friction measurement and texture measurement to account for the influence of both micro and macro texture on frictional properties. By using the IFI, test results from different devices result in similar answers.

It should be remembered that friction decreases with increasing speed. Therefore, the friction value measured by devices that use different slip speeds produce different values of friction. The friction curve developed by the Rado model includes a steep increase in friction from zero, the static condition, until some maximum or peak value is achieved. Once the peak value is achieved, the friction decreases with increasing slip. The shape of the curve prior to the peak value is dependent upon the vehicle characteristics. The shape of the curve after the peak value is dependent upon the roadway characteristics. Anti-lock brakes attempt to operate before the peak of the curve to maximize the frictional properties.

Field Measurement Equipment

There are four basic types of full-scale friction measuring devices: Locked wheel, side force, fixed slip, and variable slip.

Locked Wheel: Simulates emergency braking without anti-lock brakes. Locked wheel systems produce a slip speed of 100% of the test speed. This device can be used with both a ribbed tire and a smooth tire. Measurements made with the ribbed tire are insensitive to macro texture and therefore measure the influence of micro texture predominantly. Most common device is the ASTM Locked Wheel Skid trailer. Measurements are taken at discrete locations. Usually five tests are taken. Test Procedure is ASTM E-274.

Side Force: Measures the ability to maintain control in curves. The slip speed for these devices is low even though they travel at highway speeds, so they predominantly measure the influence of micro-texture. They can make continuous measurement throughout a test section. Most common devices are: Mu-Meter and SCRIM.

Fixed Slip Method: Relates to braking with anti-lock brakes. Fixed slip devices operate at a constant slip speed, usually between 10 and 20%. These devices also measure low speed friction. No ASTM procedures exist for these devices.

Variable Slip Method: Relates to braking with anti-lock brakes. The variable slip devices are similar to the fixes slip except they allow several slip speeds to be used. Test procedure is E-1859

La**boratory Methods of Measuring Friction**

British Portable Tester: The slip speed is typically assumed to be about 6 mph. Because the slip speed is so low, the BPT is influenced predominantly by micro texture and can be used as a surrogate for micro texture. Test procedure is ASTM E 303.

Japanese Dynamic Friction Tester (DFT): The DFT has the advantage of being able to measure the friction as a function of speed over the range of zero to 55 mph. The DF tester value at 12 mph together with a texture measurement provides a good estimate of the IFI.

Macro Texture Measurement

Traditionally, macro texture has been measured by the sand patch test. Other methods for measuring macro texture include laser based systems that operate at highway speeds, the outflow meter, and the Japanese Circular Track Meter (CTMeter). The CT Meter, when used in conjunction with the Japanese DFT, can provide both the friction values and texture values for input into the IFI equation.

Tests to Consider for FHWA Sealer/Rejuvenator Research:

1. Size Exclusion Chromatography- separates asphalts by apparent molecular size

2. Ion Exchange chromatography-used to show the more neutral molecules very between crude sources.
3. Supercritical fluid chromatography- used to show the more neutral molecules very between crude sources.
4. Nuclear Magnetic Resonance has been used to show that neutral materials in asphalt become rigid solids (i.e. steric hardening)

*The chemical properties of asphalt can be used to predict the expected amounts of hardening of asphalts.

*The aliphatic/aromatic ratios can be determined by solution nuclear magnetic resonance, a common and fast analytic technique, but it is probably more practical to either measure shrinkage directly or predict it from very rapid DSC measurements. (pg36)

*In some but not all asphalts, a very strong acidic material appears with oxidation. This was first detected with non-aqueous potentiometric titration (NAPT)….. There is no doubt though, that using NAPT and acidity measurements of water washed samples of oxidized asphalts, that some (not all) asphalts show this phenomenon.

Use of the Fourier Transform Infrared Analyzer can be used for measuring the oxygen content of the extracted asphalt. Oxygen uptake was measured by the change in the carbonyl peak height on infrared spectra.