APPENDIX A. BINDER AGING BIBLIOGRAPHY

The abstracts contained in this bibliography are, for the most part, taken primarily from the published papers or reports. Recent citations in this bibliography are work completed during NCHRP Project 9-36. Older citations are from a from a white paper written by Bahi, Anderson, and Christensen at The Pennsylvania State University as part of SHRP Project A-002A.

Abbott, F. P. and W. G. Craig (1960). "Determination of Age Hardening Tendencies and Water Susceptibility of Paving Asphalt." Highway Research Board **Bulletin No. 270**: 20.

This paper presents data on (a) progressive hardening and embrittlement of the asphalt cement with aging; (b) loss of adhesion of the asphalt cement to the aggregate with the resultant lower compressive strengths due to water displacement of the asphalt binder at the asphalt-aggregate interface; (c) progressive loss of water resistance of the asphalt cement as the asphalt: hardens; and (d) progressive loss of the ability of the asphalt binder to re-adhere to the aggregate after displacement by water. The action of effective anti-stripping additives in ameliorating these causes of road deterioration is shown to be in the direction of reducing the magnitude of the last three of these deteriorative factors.

Abu-Elgheit, M. A., C. K. Hancock, et al. (1969). "Effect of Selected Solvents on Viscosities and Oxygen Contents of Asphalts." Analytical Chemistry **41**(6).

Benzene (a), benzene-ethanol mixture (b), trichloroethylene (c), and I,I,I- trichloroethane (d) were used to determine their effects as solvents on series of six asphalt cements used in construction of bituminous pavements; magnitude of hardening (measured by viscosity at 25 C) increased in order (a) through (d); oxygen content was determined by neutron activation analysis in original and recovered asphalts; in general, recovered asphalts had lower oxygen contents than reference asphalts.

Airey, G. D. and S. F. Brown (1998). "Rheological Performance of Aged Polymer Modified Bitumens." Journal of the Association of Asphalt Paving Technologists **67**: 66-87.

The rheological and chemical changes associated with laboratory short term and long term ageing of unmodified, penetration grade, bitumens are well known and understood. However, these changes are not fully understood for polymer modified bitumens (PMB's). The rheological changes that occurred after ageing for three base bitumens and fifteen PMB's using conventional binder specification tests (Penetration, Softening Point and viscosity) and a dynamic mechanical test (Dynamic Shear Rheometer) were measured. The conventional tests were able to describe the effect of ageing on the rheological properties of unmodified bitumens but were limited in their ability to do so for PMB's. The PMB's showed different rheological responses to ageing compared with the penetration grade bitumens. The Dynamic Shear Rheometer results indicated that the changes that occur after ageing for EVA modified PMB's can be linked to a chemical change in the semi-crystalline copolymer with a shifting of the rheological characteristics of the aged PMB towards that of an unmodified bitumen. The rheological changes associated with the SBS modified PMB's can be linked to a breakdown of the molecular structure of the copolymer to form a lower molecular weight polymer substructure.

Alvarez, C. and M. R. Thompson (1994). Aging Phenomenon in Asphalt Concrete Pavements: A Literature Review. - Supplemental Report. Illinois Transportation Research Center Members, Edwardsville.; Illinois Univ. at Urbana-Champaign. Dept. of Civil Engineering.; Illinois State Dept. of Transportation, Springfield.**:** 42.

The properties of the asphalt cement binder in asphalt concrete (AC) significantly affect flexible pavement performance. These properties change as a function of service time. The GA airport performance and longevity part of this study confirmed the significant contribution of asphalt aging to the loss of flexible pavement serviceability. A comprehensive literature review was conducted to consider the various factors that influence asphalt aging and techniques for alleviating the problem. Two major effects dominate asphalt cement aging: (1) loss of volatile components and oxidation in the construction phase - primarily during mixing - (short-term aging) and (2) progressive oxidation of the in place mixture in the field (long-term aging). Many efforts have been directed to better understand the aging phenomenon and laboratory simulation of field asphalt cement aging. Laboratory aging studies have primarily been conducted with asphalt cement, ignoring the effect of the aggregate on the AC aging phenomenon.

Anderson, D. A., D. W. Christensen, et al. (1994). Binder Characterization, Volume 3: Physical Characterization. Washington, D.C, Strategic Highway Research Program, National Research Council.

Anderson, D. A., Y. M. L. Hir, et al. (2002). "Zero Shear Viscosity of Asphalt Binders." Transportation Research Record.

Anderson, D. A. and T. W. Kennedy (1993). "Development of SHRP Binder Specification (with Discussion)." Journal of the Association of Asphalt Paving Technologists **62**.

The new SHRP binder specifications and the measurements upon which they are based are designed to provide performance-related properties that can be related in a rational manner to pavement performance. To this extent, the new SHRP binder specifications are performance related. A major decision was made in the SHRP program when it was decided that the binder specification should be equally applicable to both plain and modified asphalt cements. Thus, the term asphalt binder as used in this paper refers to asphalt cement with or without the addition of a non-particulate organic modifier. Over the course of the SHRP program the binder specification underwent a number of changes. These changes were in response to the research findings reported by the various SHRP asphalt program contractors, refinements in the test methods that occurred during the course of the A-002A contract, "Binder Characterization and Evaluation", and input from the SHRP Binder Rheology and Specification Expert Task Group, SHRP staff, and others. The purpose of this paper is to update an earlier paper on the development of the binder specification and to provide a description of the final specification as developed within the SHRP program.

Anderson, D. A. and M. O. Marasteanu (1999). "Physical Hardening of Asphalt Binders Relative to Their Glass Transition Temperatures." Transportation Research Board.

Physical hardening (physical aging) is a process that occurs below room temperature in asphalt binders. Physical hardening causes time- dependent isothermal changes in the rheological behavior and specific volume of asphalt binders. The process is reversible: when the asphalt binder is heated to room temperature or above, the effect of physical hardening is completely removed. Physical hardening for amorphous materials is generally reported as occurring below the glass transition temperature, but this is not the case for asphalt binders, in which physical hardening is observed both above and below the glass transition temperature. The glass transition temperature of asphalt binders is measured by using three different techniques: dilatometry, differential scanning calorimetry, and rheological considerations (peak in the loss modulus versus temperature). These three techniques give roughly equivalent estimates of the glass transition temperature. The behavior of physical hardening in asphalt binders is somewhat different than that reported for polymers and other organic materials. This difference is explained in terms of the presence of crystalline fractions in the asphalt binder. Techniques for modeling physical hardening are described, and possible explanations for the anomalous behavior of asphalt binders are given.

Babu, D. R. and D. E. Cormack (1984). "Effect of Oxidation on the Viscosity of Athabasca Bitumen." Canadian Journal of Chemical Engineering **62, No-4**.

The effect of low temperature oxidation on the viscosity of Athabasca" bitumen was investigated over the temperature range 320 to 370K, and to extents of oxidation as high as 41.7 X 10^-3 kg-O2/kg-bitumen. Even at this relatively low extent of oxidation, the viscosity was observed to be more than two orders of magnitude higher than that of unoxidized bitumen. It was found that the Andrade viscosity model could adequately characterize the temperature dependence of the viscosity at all extents of oxidation. However, the pre-exponential constant in the model was observed to be a strong function of extent of oxidation. 8 refs.

Bahia, H., D. W. Christensen, et al. (1991). White Paper on Miscellaneous Topics Regarding Aging, The Pennsylvania Transportation Institute, The Pennsylvania Statte University.

Bahia, H. U. and D. A. Anderson (1995). "The Pressure Aging Vessel (PAV): A Test to Simulate Rheological Changes Due to Field Aging." ASTM Committee D-4 on Road and Paving Materials(STP 1241,; ASTM PCN: 04-012410-08).

The Pressure Aging Vessel (PAV) is an aging procedure proposed by the Strategic Highway Research Project (SHRP) to simulate long-term field oxidative aging of asphalt binders. The development of the PAV included evaluation of the factors affecting the PAV procedure as well as validation of the PAV as a procedure to mimic field aging of binders. In this paper the research done to evaluate the factors affecting the aging in the PAV and the selection of the operational factors is described. The changes in rheological properties that result from the PAV procedure are also presented and compared with changes resulting from field aging. The results indicate that temperature can be used effectively to accelerate aging in the PAV and that film thickness and time are important factors that need to be carefully controlled. The evaluation of the rheological changes indicates that aging changes the rheological type of asphalts by changing the shape of the master rheological curve while the temperature dependency, as measured by the time-temperature shift function, does not appear to change significantly as a result of aging. The results indicate that the PAV can be successfully used to mimic rheological changes that result from field aging.

Bahia, H. U., H. Zhai, et al. (1998). "Evaluation of Stability, Nature of Modifier, and Short-Term Aging of Modified Binders Using New Tests: Last, Pat, and Modified RTFOT." Transportation Research Record **1638**.

In a recent survey of users and producers of modified asphalts, stability and short-term aging were two of the main concerns regarding the use of modified asphalts. In an NCHRP project, a concentrated effort was put into development of revised or new testing procedures to better characterize the nature of modified asphalt and to solve some of the difficulties with using existing aging procedures developed for neat asphalts and modified asphalts. Three main procedures have been proposed to complement the existing Superpave procedures: the laboratory asphalt stability test (LAST), for measuring the storage stability of asphalt binders; the particulate additive test (PAT), for separation of particulate additives; and the modified rolling thin film oven test (RTFOT) for short-term aging. The background behind the development of these test methods is explained, and typical data collected for a number of modified asphalts are presented. The results indicate that these tests show high promise in covering characteristics not covered by the current Superpave binder specifications and in solving some of the problems with the existing aging methods. The results also indicate that the behavior of modified binder can be very complex and that the method of data interpretation is very critical.

Banu, N., M. Ciort, et al. (1996). Method for Accelerated Ageing of Bitumen. Eurasphalt & Eurobitume Congress.

The ageing of bitumen has an important influence on how long it is in service as a road coating. So, it is very important to have reliable methods to predict the time of ageing of bitumen. At the Romanian Research Institute for Petroleum Refining and Petrochemistry of Ploiesti a method of accelerated ageing has been developed. The testing should be carried out at 70°C in the presence of oxygen. There is a major difference between this method and other methods having the same goal. It does not use bitumen as it is produced but the residue resulted after thin film oven test (TFOT). To predict ageing, the penetration, viscosity, ductility, chemical composition, and IR spectrum are determinate before and after each stage of method. The bitumen characteristics obtained by this method are similar to those obtained testing the same bitumen extracted from sample of one-year old coating.

Barbooi, M. M., H. H. Ai-Soufi, et al. (1987). "Thermogravimetric Studies on Paving Asphalts." Journal of Petroleum Research **6, No. I**.

The thermal behavior of two asphalts of different origins, employed for paving in Iraq, was studied during mixing and laying conditions using dynamic thermogravimetry under air and nitrogen atmospheres. The asphalts were prepared in such a way that they would have the same penetration value. The main features of the TG curves were explained and correlated with the chemical composition, method of preparation and performance of the asphalts. Thermogravimetry can be used to aid the standard methods of asphalt testing. (Edited author abstract) 16 refs.

Behl, B. A., F. H. Scrivner, et al. (1969). "Oxidation of Asphalt Films Measured by Light Scattering." Indus & Eng Chem-Product Research & Development **8, No 4**.

The light-scattering technique is a reliable measure of the susceptibility of an asphalt to oxidation. The relation among the light-scattering ratio, relative film thickness, and time in minutes of exposure to ozone, is represented with acceptable accuracy by the equation given. There is a well defined relationship between hardening index (relative viscosity) and the light-scattering ratio of an asphalt.

Bell, C. A. (1989). Summary Report on Aging of Asphalt Aggregate Systems. Corvallis Oregon, Oregon State University.

Bell, C. A., M. J. Fellin, et al. (1994). "Field Validation of Laboratory Aging Procedures for Asphalt Aggregate Mixtures." Journal of the Association of Asphalt Paving Technologists **63**.

This paper is a summary of the validation of two Accelerated Laboratory Testing (ALT) procedures developed at Oregon State University (OSU) -- Short-Term Oven Aging (STOA) and Long-Term Oven Aging (LTOA).This paper covers both including: selection of the sites;

evaluation of the field data and/or cores; preparation, treatment and testing of the laboratory specimens; and comparison of field and laboratory data.

Bell, C. A. and D. Sosnovske (1994). "Aging: Binder Validation." SHRP-A-384: 1994.

This research was conducted as part of the Strategic Highway Research Program (SHRP) A-003A contract at Oregon State University to validate the findings of SHRP contracts A-002A and A-003B with regard to aging. One short-term and four long-term aging methods were used to simulate aging of asphalt-aggregate mixes in the field. Four aggregates and eight asphalts for a total of 32 different material combinations were tested using the different aging methods. Results of the aging studies are compared with the A-002A and A-003B studies of asphalt binder or asphalt mixed with fine aggregate. This research concludes that aging of asphalt mixes cannot be predicted by tests on asphalt binder alone since results show that aggregates have considerable influence on aging.

Bell, C. A., A. J. Wieder, et al. (1994). Laboratory Aging of Asphalt-Aggregate Mixtures: Field Validation. Washington, DC, National Academy of Sciences, Strategic Highway Research Program**:** 210.

The hardening or stiffening associated with heating asphalt has been researched since the first use of asphalt in the United States around 1900, but little research has been accomplished on asphalt-aggregate mixtures. This hardening is referred to as aging and occurs in two stages: "short-term" aging which occurs during mixture mixing and placement, and "long-term" aging which occurs throughout the life of the pavement. A portion of the Strategic Highway Research Program (SHRP) has been dedicated to developing Accelerated Performance Tests (APTs) for aging of asphalt-aggregate mixtures. Two test procedures developed at Oregon State University utilize oven aging at 135°C and 85°C or 100°C (275 ° and 185° or 212°F) to simulate short- and long-term field aging. This report presents the results of the field validation of these two procedures. The short-term procedure of 4 hours at 135°C (275°F) prior to compaction is adequate for the majority of the field mixtures evaluated and conservative for some mixtures. Long-term oven aging for 2 days at 85°C (185°F) or 1 day at 100°C (212°F) after compaction and in addition to the short-term treatment appears representative of "young" mixtures (0 to 3 years old), in the field. Long-term oven aging for 4 to 8 days at 85°C (185°F) or 2 to 4 days at 100°C (212°F) appears representative of "older" (older than 3 years) mixtures in the field and conservative for some mixtures. Use of long-term oven aging at 85°C (185°F) is recommended, since 100°C (212°F) may damage specimens and result in unreliable data. Continued analysis of the field sites used in this study and selection of additional sites is required to develop prediction models for all combinations of climatic region and asphalt grade. The continued study of the existing younger sites would require additional cores to be drilled, possibly 5, 10, and 15 years from now, to determine the field moduli at those times.

Bishara, S. and R. McReynolds (1996). "Laboratory Aging and Annealing of Asphalt Binders by Microwave Radiation." Transportation Research Record **1535**(ISBN: 0309059100 ISSN: 03611981).

A household microwave oven with a frequency of 2,450+/-13 MHz and an output power of 1000 W is used to simulate short- and long-term aging of asphalt, and for annealing, prior to sampling, to remove steric (isothermal) hardening. A quartz petri dish holds the asphalt during microwave treatment, at atmospheric pressure. To simulate thin film oven (TFO) aging, a 10-g

sample is microwaved for a total of 33 min. For 11 asphalts, the average difference in G*/sin delta, at limiting high temperature, between TFO and microwave aging is +/-0.68 kPa. Simulating rolling thin-film oven (RTFO) aging is possible by microwaving for a total of 63 min. For 18 asphalts, the average difference in G*/sin delta, at limiting high temperature, between RTFO and microwave aging is +/-1.19 kPa. Aging by RTFO + pressure aging vessel (PAV) and TFO + PAV is simulated by microwaving for a total of 158 min. Microwave aging marginally underestimates long-term aging. For 18 asphalts, the average difference in intermediate temperature obtained after RTFO + PAV versus microwave aging is -2.8 deg C; for TFO + PAV versus microwave aging, the average difference is -2.7 deg C. Annealing for 2 hr at 150 deg C in a convection oven (conductive heating) is simulated by microwaving for a total of 27 min. The average difference in G*/sin delta between the two methods is +/-0.24 kPa. Molecular size index (MSI, the ratio of first to second fraction from size exclusion chromatography) correlates with stiffness at low temperature. At intermediate temperature, tan delta remains practically unchanged until MSI reaches a minimum, then increases sharply. At limiting high temperature, G* does not correlate with MSI.

Bishara, S. W. and R. L. McReynolds (1995). "Effect of Microwave Energy on the Properties of Asphalt and Its Use as an Aging Tool." Transportation Research Record.(1995).

Microwave energy causes changes in asphalt properties. Unsymmetric organic molecules with dipoles, that is, with a permanent separation of positive and negative charges, undergo excitational rotation when they are subjected to microwave radiation. The excitational rotation depends on the material's dielectric constant. Because the radiation frequency is relatively high and the dielectric constant of asphalt is low, asphalt molecules cannot rotate as fast as the applied electromagnetic field, and an out-of-phase component of the dielectric constant, called dielectric loss, is dissipated as heat. Treatment of asphalt for a short time with low-power microwave radiation decreases the dispersitivity (D) and molecular size index (MSI) values obtained by high-performance size exclusion chromatography (HPSEC). Alternately, exposure for a longer time to a higher-power radiation increased both the D and MSI values for 12 asphalts studied. Microwave conditions (power level, treatment time, sample weight, and sample container material) were tailored to simulate the effects obtained after rolling thin film oven-pressure aging vessel (RTFO-PAV) aging of 18 asphalts. HPSEC gave comparable results for the two aging techniques: RTFO-PAV aging versus microwave aging. The difference in MSI amounted to +/-7.3 and +/-4.2 percent by using gravimetry and ultraviolet detection at 345 nm, respectively. The bending beam rheometer showed that microwave energy underestimates aging by a maximum of about 3 deg C in the limiting low temperature. Accelerated aging by microwave radiation is very simple and consumes less than 3 hr.

Bishara, S. W., R. E. Robertson, et al. (1999). "Rapid and Simple Method for Binder Oxidative Aging,"

This work describes a simple procedure for aging of road binder. In a single step, the neat (virgin),unmodified binder is irradiated by microwaves to give a product equivalent to that produced by both the Rolling Thin Film Oven Test (RTFOT) followed by the Pressure Aging Vessel (PAV).The one-step approach, besides simplicity, eliminates the need for solvent to clean the RTFOT vessels. At 147 °C and 3080 kPa air pressure, the microwave radiation simulates "RTFOT +PAV "aging in 4.5 hr (as opposed to 1.5 hr for RTFOT +20 hr for PAV,in addition to the time of transfer). Microwave aging allows aging and testing in the same day. The proposed method is therefore competitive with the aging techniques of ASTM:D2872-96 and AASHTO PP1. Microwave aging was tested on the eight SHRP core asphalts. According to the SUPERPAVE PG system, the aged binder should meet the specification limit of 5,000 kPa at the critical intermediate temperature, and meet the limit of 300 MPa for the low temperature stiffness, S, and 0.300 for the slope, m, at the critical low temperature. The difference between the critical intermediate temperature after “RTFOT +PAV ” and that obtained after microwave aging did not exceed ± 1.1 °C for the critical low temperature the difference did not exceed ± 1.6 °C. The relative total polarity for five out of the eight core asphalts aged by microwaves did not differ by more than 0.6 percent from those obtained after “RTFOT +PAV.” The height of the infrared absorption peak for the carbonyl group was practically the same regardless of the aging approach (microwave or “RTFOT +PAV ”). According to ASTM C670,the variation of six measurements of G*sin ä (expressed as a percent of their mean)for asphalt AAF-1 (4.9 percent)was much smaller than the acceptable range of variation (31.6 percent).For S and m,again the variation (3.2 and 1.7 percent)was smaller than the acceptable range of variation (12.8 and 5.6 percent, respectively).This reflects the high repeatability of microwave aging.

Bishara, S. W., R. E. Robertson, et al. (2000). Rapid Oxidative Aging of Binder Using Microwave Energy. An Improved Method. 2nd Eurasphalt & Eurobitume Congress.

This work describes a simple procedure for aging of road binder. In a single step, the neat (virgin), unmodified binder is irradiated by microwaves to give a product equivalent to that produced by both the Rolling Thin Film Oven Test (RTFOT) followed by the Pressure Aging Vessel (PAV). The one-step approach, besides simplicity, eliminates the need for solvent to clean the RTFOT vessels. At 147°C and 3080 kPa air pressure, the microwave radiation simulates “RTFOT + PAV” aging in 4.5 hr (as opposed to 1.5 hr for RTFOT + 20 hr for PAV, in addition to the time of transfer). Microwave aging allows aging and testing in the same day. The proposed method is therefore competitive with the aging techniques of ASTM: D2872-96 and AASHTO PP1. Microwave aging was tested on the eight SHRP core asphalts. According to the SUPERPAVE PG system, the aged binder should meet the specification limit of 5,000 kPa at the critical intermediate temperature, and meet the limit of 300 MPa for the low temperature stiffness, S, and 0.300 for the slope m, at the critical low temperature. The difference between the critical intermediate temperature after “RTFOT + PAV”and that obtained after microwave aging did not exceed ± 1.1 °C; for the critical low temperature the difference did not exceed ± 1.6 °C. The relative total polarity for five out of the eight core asphalts aged by microwaves did not differ by more than 0.6 percent from those obtained after “RTFOT + PAV”. The height of the infrared absorption peak for the carbonyl group was practically the same regardless of the aging approach (microwave or “RTFOT + PAV”). According to ASTM C670, the variation of six measurements of G*sinδ (expressed as a percent of their mean) for asphalt AAF-1 (4.9 percent) was much smaller than the acceptable range of variation (31.6 percent). For S and m, again the variation (3.2 and 1.7 percent) was smaller than the acceptable range of variation (12.8 and 5.6 percent, respectively). This reflects the high repeatability of microwave aging.

Bishara, S. W., R. E. Robertson, et al. (2003). "Rapid Microwave Aging of Modified Asphalts." Transportation Research Record.

A rapid method is hereby developed to simulate short- (RTFO) and long-term (PAV) aging of modified binders. The proposed method may be used for day-to-day quality assurance leaving RTFO + PAV for referee purposes. The original modified binder (66 g) is treated for 3 hr

and 10 min at 135°C in a scientific microwave unit under 3200 kPa (460 psi) of air pressure. Validity of the method has been established by measuring the intermediate-temperature loss modulus, G", the low-temperature stiffness, S, and the slope m at 60 sec, the master curves for the complex modulus, | G*|, and the phase angle, δ. Superimposing master curves of the microwave-aged product over those of the RTFO + PAV-aged product showed a good agreement. This applied well for five modified (PG 70-28) asphalt samples from FHWA. Ten other modified asphalt samples were collected from five refineries, with PG's ranging between 70-22 and 76-28; elastomer and plastomer modifiers were included. The rheological parameters measured after microwave aging generally agree with those obtained after RTFO + PAV aging. Repeatability of the aging procedure was tested by doing six replicate sample runs. For G", the percent variation of 23.1 percent between the six data points was well within the limit of 31.6 percent calculated according to AASHTO TP-5 and ASTM Practice C 670. The same was true for S and m, where the percent variation of 10.3 and 5.0, respectively, was within the acceptable range of 12.8 and 5.6 percent calculated according to AASHTO TP-1 and ASTM Practice C 670.

Bissett, J. R. (1962). "Changes in Physical Properties of Asphalt Pavement with Time." Proceedings, Highway Research Board: 211.

This paper reports the study of approximately 60 mi of asphaltic concrete pavement under actual traffic conditions. The pavements vary from 3 to 8 years of age and represent seven construction projects. Recovery of the asphalt cement was accomplished by a simplified Abson method. Check tests were made on this method to determine any effect it might have on Arkansas asphalts. Density, asphalt content, and gradation of aggregate of the pavements were determined. The asphalt cement recovered from the pavements were subjected to penetration, ductility, softening point, and ash content tests. In some cases the thin-film oven tests was also made. Generally, the results indicate a rapid reduction in the ductility of the asphalt with time. There is also a decided but less rapid reduction in the penetration of the asphalt. Samples of the pavement were heated, remolded, and tested by the Marshall method. Usually, the stabilities were quite high.

Bissett, J. R. (1969). Changes in Physical Properties of Asphalt Cement under Service Conditions, Arkansas Highway Department.

The purpose of this study was to develop information on the hardening characteristics of asphalt cements used by the Arkansas Highway Department during hot plant mixing and during service in pavements. Asphalt cements from three sources within the State were used in thirteen paving contracts. Samples of asphalt and paving mixture were obtained from each job at the time of construction. Pavement samples representing these materials were obtained three to six months after construction and again after 21 to 42 months service. Extraction and recovery tests were made on the mixtures and pavement samples and the recovered asphalts were tested for penetration and ductility at 77F and 60F and viscosity at 140F. Paving mixtures loose and compacted and stored under water in the laboratory were tested to determine asphalt hardening. A laboratory study of the effect of mixing on hardening also was made. (BPR abstract)

Blokker, P. C. and H. V. Hoorn (1959). "Durability of Bitumen in the Theory and Practice." Proceedings, 5thWorld Petroleum Congress **6**: 16.

After a brief review of the physical hardening of bitumen, which is caused by a change in structure or by loss of volatiles, the more important phenomenon of chemical hardening, due to oxidation, is dealt with extensively. The rate of oxidation is much higher in the presence of light than in its absence, and the reactions are of a different type. Oxidation in the light is promoted mainly by the ultra-violet part of the spectrum, and hardening is restricted to a depth of about 4 microns. In the dark, hardening may occur down to depths of 3 mm or somewhat more, which is in good agreement with a theoretical interpretation. The consequences of hardening in the dark for road construction are discussed in considerable detail. It is shown that, since the cracking of road carpets is most likely to occur under the impact of moving traffic at low temperatures, the tendency to this type of failure should be judged from the increase in stiffness of bitumens at short times of loading and at low temperatures, rather than from the increase in viscosity. Data on the hardening of a large number of bitumens are given. An accelerated test procedure for assessing the ,aging characteristics of bitumens was investigated. The acceleration is affected by increasing the oxygen pressure; it is reproducible and fairly constant. Results of this test show a satisfactory correlation with hardening data obtained from road trials. A recently published test method using acceleration by increase of temperature appears to be practically equivalent to the present method except in the case of an experimental bitumen with a large content of volatiles, where the high-temperature test gives too high a value.

Blomberg, T., M. R. Haekkinen, et al. (1988). "Laboratory Investigation of Bitumen Aging Properties." Statens Vaeg-och Trafifinstitut **VTI/Meddelande-558**: 29.

Comparative laboratory investigations of the aging properties of bitumen using two standardized methods, TFOT (Thin Film Oven Test, ASTM D 1754) and RTFOT (Rolling Thin Film Oven Test, ASTM D 2872), have been performed. Forty-seven samples of bitumen produced at three refineries from six different crude oils have been examined before and after heating in accordance with TFOT and RTFOT respectively. The parameters investigated are penetration at 25 and 10 degrees C respectively, dynamic viscosity at 60 degrees C, kinematic viscosity at 135 degrees C and change in mass in TFOT and RTFOT respectively. The penetration index, retained penetration and viscosity ratio have been calculated.

Bocci, Maurizio, et al. (2000). "The Ultraviolet Radiation in Short-and Long-Term Aging of Bitumen." Eurasphalt and Eurobitume Congress 2000.

In this research the influence of ultraviolet radiation on short-and long-term aged bitumens has been studied, combining the SHRP tests (RTFOT,PAV)by means of a new UV standardized aging procedure. Thanks to this study it has been possible to quantify the influence of photochemical processes on rheological parameters of bitumens, and to value their percentage of incidence on the total long term aging evaluated by PAV. In particular it has been verified that the said incidence doesn’t seem to be constant, but rather depends on the nature of the asphalt binder. For these reasons the effect of the UV radiation by itself, which is a real contributing term in the in situ aging process, can’t be simulated by means of the standard oxidative-thermic treatments carried-out in the laboratory.

Bouldin, M., R. , R. Dogré, et al. (2000). A Summary of Preliminary Results for Refining the High Temperature PG Specification Parameter. Asphalt Binder ETG, May 2000.

Bright, R. and E. T. Reynolds (1961). " Effect of Mixing Temperature on Hardening of Asphaltic Binder in Hot Bituminous Concrete under Stated Conditions." Highway Research Board Abstracts **31**.

Plant mixes of hot bituminous concrete were made in the mixing temperature range of 250 to 400 F, corresponding to viscosity limits of approximately 400 to 15 Saybolt Furol seconds. The asphalt from samples of these mixes was recovered by the modified Abson method, and changes in the penetration, ductility, softening point, and absolute viscosity were measured. Asphalts from Venezuelan and East Texas crudes were used. The mixes used were base courses, binder courses, wearing surface, and certain city street mixes. The aggregates were varied and were either all granite or mixtures of granite, sand and mineral filler, mixtures of sandy limestone, sand and mineral filler, or mixtures of siliceous gravels, sand, and mineral filler. Some of the samples were cooled slowly, whereas others were cooled rapidly by quenching in water. The samples cooled slowly showed 65 to 75 percent penetration retained at 250 F with an additional 10 percent drop in percent penetration retained for each 50 F increase in mixing temperature. The samples quenched in water showed essentially no difference in hardening at 250 F from slowly cooled. No definite difference in hardening was found for different asphalts, different mixes, different aggregates or different type pugmills. Samples of paving mixture were found to harden appreciably on storage during the first 15 days; but thereafter the rate of hardening was very slow.

Bright, R., J. Steele, et al. (1966). "The Effect of Viscosity of Asphalt on the Properties of Bituminous Paving Mixtures. Part I. Hardening of Asphalt in Hot Bituminous Base, Binder, and Sand Mixtures." North Carolina State Univ., Raleigh. Highway Research Program. **ERD-110-L "Final Report"**: 96.

The purpose of this investigation was to study the effect of the viscosity of the asphaltic binder on the mixing, laying, and compaction of hot bituminous: base, binder, and sand asphalt mixes, and to observe the performance under traffic of test strips laid from these mixes. Four test strips were laid for each of the above mixes in which the mix viscosity of the asphaltic binder was varied from approximately 930 to 40 Saybolt Furol Seconds. Temperatures were measured in the pavement at four different elevations during rolling operations. Ross counts were made on the base and binder mixes as they left the mix box, laying characteristics of the mixes were observed, and densities were measured on the finished pavements. Samples of pavement were taken immediately after laying, after 10 months and after 21 or 22 months, and the asphalt extracted and recovered. Penetrations and viscosities were determined on the recovered asphalts. Ross counts and visual inspection showed incomplete coating of the aggregate for all mixes at the high mix viscosities. Base and binder mixes laid satisfactory at all mix temperatures but the sand asphalt showed some tearing at the higher mix viscosities. There was a slight tendency toward higher densities with higher mix temperatures. There was definitely greater hardening in the mix box with increased mix temperature. However, as the strips aged this relationship showed some change. The base and binder mixes made at 250F showed the least hardening after 10 months and 22 months service. Sand asphalt strips showed similar hardness after 21 months. The thicker pavement layers hardened more slowly than thin layers. (Author)

Brown, B. (1958). "Possible Effects of Hardening on Pavement Life." Proceedings of the Association of Asphalt Paving Technologists **27**.

This paper is a purely hypothetical discussion of the possible effects of the changes in composition of asphalt due to aging on several important physical properties of the asphalts. Some of the important points in which the author describes the mechanism of aging effects on properties of asphalts are as follows: (a) as the oxidation changes, the non-polar oils remain substantially constant, while the smaller resin molecules convert to the larger asphaltene molecules. Undoubtedly, asphaltenes further combine with resins or with themselves to form still larger asphaltenes. This size growth of the reactive molecules result in loss of hydrogen, which is converted to water. Such formation of water in the body of the road probably adversely affects the adhesion of the asphalt. Also, because of increase in size, per-se, a greater degree of physical entanglement of these complex species must result with increased resistance to the slippage of layers at the molecular level. Thus decreased freedom of movement shows an increase of consistency signaled by higher softening points and lower penetration; (b) big molecules respond reversibly to biased stress by reorientation of their configuration in space. Because substantial molecular masses and distances are involved, finite times are required for the action. By buildup of large molecules on the expense of smaller and more-mobile molecules, asphalt during aging would be expected to shift both toward higher consistency and toward accentuation of elastic response of the predominantly time-dependent type; (c) conversion of lower molecular weight polar resins to asphaltenes would leave the flow medium relatively richer in non-polar oil constituents with smaller temperature coefficients of viscosity. Thus, even though its over-all viscosity is greater, aged asphalt might be expected to be less susceptible than its unaged precursor; (d) aging of asphalt would be expected to favor failure by cracking under some lower level of maintained stress than for the fresh asphalt. For transient load of short duration and below some critical load magnitude, aged pavements would be expected to suffer less from distortion, because of better elastic response and higher specific viscosity; (e) aging makes asphalts more susceptible to fracture. Input energy can only be accumulated in elastic mechanisms, which tend to increase over the aging process, and may provide reservoirs of energy favorable to initiation and propagation of fracture failures. On the other hand, absence of such mechanisms would result in a material of less elasticity and, thus, of less negative shock-absorbing capacity.

Brown, R. A., R. W. Miller, et al. (1977). "Long-Term Effects of Heated Storage on Asphalt Concrete." International Journal of Hydrogen Energy **54**: 15.

Asphalt hardening in five bitumimous concrete mixes was studied after storing at elevated temperatures for periods of 18 to 24 hr in both inert gas and normal atmospheres. Asphalts extracted from the loose mixes before and after storage, and from compacted mixes at the time of placement and after up to 4 years of service, were tested for penetration (77 F), absolute viscosity (140 F) and kinematic viscosity (275 F).

Brown, S. F. and T. V. Scholz (2000). "Development of Laboratory Protocols for the Ageing of Asphalt Mixtures." 2nd Eurasphalt &Eurobitume Congress Barcelona 2000 –Proc.0053.uk.

Laboratory protocols for the long and short-term ageing of bitumen have been developed and are routinely used in practice. The ageing process, however, depends to an extent on the asphalt mixture in which the bitumen is placed and protocols for the ageing of mixtures have not been universally agreed. The manufacture of test specimens from compaction of bituminous

mixtures prepared in the laboratory is carried out using a wide variety of procedures. These depend on the facilities available and often result in storage of hot material causing short-term ageing of the binder which is not representative of full-scale production conditions. In order to determine a laboratory protocol which did reproduce field conditions, studies were conducted in conjunction with six contractors and in the laboratory through varying the ageing period at 135 °C. Both continuous and gap-graded materials were investigated. The stiffness modulus under standard conditions was used to judge the extent of ageing through the increase in stiffness caused by this process. By comparing results of laboratory and plant-mixed material compacted to the same void content, the hot storage period required in the laboratory was determined. This was shown to be mixture dependent and varied from 0 to 2 hours. A long-term ageing protocol was also assessed. This was intended to reproduce the in-service ageing that occurs over many years in the field. A range of mixtures was used and the protocol, involving exposure to a temperature of 85 °C for 120 hours, was shown to distinguish between mixtures normally regarded as durable (dense,gap-graded) and those likely to be susceptible to ageing (lean with high void content).

Buelt, J. L. and S. M. Barnes (1983). "Aging Test Results of an Asphalt Membrane Liner." 57.

The objective of the asphalt aging study described in this report was to determine the expected performance lifetime of a catalytically airblown asphalt membrane as a seepage barrier for inactive uranium mill railings. The study, conducted by Pacific Northwest Laboratory for the Department of Energy's Uranium Mill Tailings Remedial Action Program, showed through chemical compatibility tests that the asphalt membrane is well suited for this purpose. The chemical compatibility tests were designed to accelerate the aging reactions in the asphalt and to determine the accelerated aging effect. Higher temperatures and oxygen concentrations proved to be effective acceleration parameters. By infrared spectral analysis, the asphalt was determined to have undergone 7 years of equivalent aging in a 3-month period when exposed to 40 °C and 1.7 arm oxygen pressure. However, the extent of aging was limited to a maximum penetration of 0.5% of the total liner thickness. It was concluded that the liner could be expected to be effective as a seepage barrier for at least 1000 years before the entire thickness of the liner would be degraded. (ERA citation 08:043346)

Burgh, A. J. P., B. Van Der, et al. (1962). "The Aging of Asphaltic Bitumen." <u>Rijkswatersta at Communications</u> **3**.

The aging in the course of the years of asphaltic bitumen used in bituminous construction has various causes. One of these, the action of oxygen, is the subject of this publication, although in particular the investigation relates to the rate and intensity of aging caused by the action of oxygen under pressure and without the presence of light. The chemical reactions involved, however, are not dealt with. The investigations showed that of the various factors which could serve as the most suitable basis for a quantitative examination of the phenomena of aging, the penetration was preferable to the ring and ball softening point, the ether asphaltenes content, or the increase of weight. In evaluating the general results, attention is paid to the shape of the aging curves, and an attempt is also made to explain what happens when the aging procedure is interrupted and then resumed after remixing the batch. From the study it has been inferred that asphalts may be prepared which are much less liable to aging than normal ones of the same grade. The probability of parallelism between natural and artificial aging has also been shown by the results of some of the experiments. The experimental part of the investigation consisted of

keeping thin layers of various types of asphaltic bitumen in oxygen at 60 C and 20 arm for a varying number of days, and then measuring the changes in the penetration figure, the softening point and other similar characteristics. In addition, several practical experiments relating to the influence of the atmosphere were carried out (natural aging). The materials used were asphaltic bitumens, either as such or mixed with filler, oil or rubber. The results have shown that the characteristics measured, such as the penetration figure and the softening point, altered most quickly at the beginning of the experiments, but that those changes, and therefore the aging rates of the asphaltic bitumens, subsequently became slower and slower. Although the number of available data relating to experiments with natural aging is fairly small, it can be assumed that natural and artificial aging proceed in similar ways.

Button, J. W., M. Jawle, et al. (1993). "Evaluation and Development of a Pressure Aging Vessel for Asphalt Cement." Transportation Research Record **ISBN: 0309054621 ISSN: 03611981**(1391).

This study evaluates a pressure aging vessel (PAV) for asphalt cement, with the specific objectives of examining the safety of the procedure and the effects, on aging, of aging temperature, film thickness, vertical location within the PAV, and proximity of aging asphalt to other asphalts. Four Strategic Highway Research Program (SHRP) core asphalts (AAC-1, AAD-1, AAF-1, and AAG-1) were used in this study. An interlaboratory test program to establish the variability associated with the PAV conditioning procedure was conducted. The study indicated that the PAV operated at 71 deg C (160 deg F), 2.07 x 10^6 pascals (300 psi) air pressure for 144 hr, effectively simulates 2 to 10 years of pavement aging depending on the method used to measure hardening, air voids in the paving mixture, average ambient temperature, and other factors. Degree of oxidative hardening of asphalt increases with increase in temperature. For a given temperature and time of exposure, degree of hardening increases with decrease in asphalt film thickness. The vertical location of asphalt in the PAV and proximity to other asphalts had no effect on the extent of hardening. Different asphalts exhibited different rates of hardening at the same conditions of temperature and time. After this work was essentially completed, the SHRP PAV conditioning protocol was modified by increasing the temperature and decreasing the time of aging. This was done to accommodate the needs of state departments of transportation for an aging test requiring no more than 24 hr.

Bynum, D. and R. N. Traxler (1970). "Gel Permeation Chromatography Data on Asphalts before and After Service in Pavements." Proceedings, Association of Asphalt Paving Technologists **39**: 20.

Gel permeation chromatography was applied to nine asphalts investigated during a cooperative research conducted by the Texas Transportation Institute and the Texas Highway Dept on the serviceability of 1.5 in. thick hot mix bituminous pavement surfaces. Extracted and recovered asphalts were tested for viscosity in the same way as the original material to establish the extent of hardening developed in each asphalt during the preparation and construction of the hot bituminous pavement and at intervals of service in the pavement. 9 refs.

Campbell, P. G., J. R. Wright, et al. (1962). "The Effect of Temperature and Humidity on the Oxidation of Airblown Asphalts." American Chemical Society, Division of Petroleum Chemistry **Preprints 7, No. 3**: 123.

A direct comparison based on carbonyl index, of the effects of temperature and relative humidity on asphalts exposed in accelerated weathering machines for a fixed period of time is not possible because the oxidation rate of each asphalt varies with exposure time. The effect of temperature and relative humidity on asphalt oxidation as a function of exposure time showed that the rate of oxidation is dependent on both of these environmental factors. However, the effect may be shown during the induction period, in the slope of the oxidation-rate curve, or in the time required to produce film failure due to cracking. In general, asphalt durability varied inversely with the temperature and relative humidity, respectively. It is proposed that the effect of temperature and humidity on asphalt oxidation rates may be due to the formation and subsequent decomposition of an asphalt-oxygen-water complex. The outdoor exposure of a series of asphalts caused oxidation of about the same relative amount as that obtained indoors by exposure to carbon-arc irradiation.

Chappat, M., J.-E. Poirier, et al. (2000). "Appreciation by Rheological and Tensile Tests Methods of the Impact of Ageing of Polymer Modified Binders Towards Low Temperature Behaviour." Eurasphalt and Eurobitume Congress 2000.

In this communication are related the tests results describing the impact of ageing for pure and polymer modified binders towards low temperature behaviour. Bitumens are modified with SBS on the one hand, with a polymers blend chemically reactive with the bitumen on the other hand. Thermo-rheological methods (BBR,viscoanalysis) and tension test methods (DTT, binder tension test according French standard) are performed on fresh and aged binders. Only the tensile tests methods are relevant for low temperature performance. Aged SBS modified binders keep good performance at low temperature; performance is even improved in the case of the chemically reactive polymer modified binder. Pavement contracts more rapidly than the materials surrounding it. Section one is a summary of the state of the art in this field.

Chipperfield, E. H., J. L. Duthie, et al. (1970). "Asphalt Characteristics in Relation to Road Performance." Proceedings, Association of Asphalt Paving Technologists **39**: 79.

The behavior of the eight bitumens was studied in dense type hot mix wearing courses subjected to medium to heavy traffic in two European areas, one with a hot and dry summer, the other with a continental cold winter with much heavier rainfall. The paper describes the work carried out on both trails during the first 5 to 6 years in service. Test work included skid-resistance and deflection measurements. Laboratory investigations were conducted to study changes which have occurred in the chemical composition, rheological properties and general aging characteristics of the bitumens. 10 refs.

Chipperfield, E. H. and T. R. Welch (1967). "Studies on the Relationships between the Properties of Road Bitumens and Their Service Performance." Proceedings of Association of Asphalt Paving Technologists **36**: 67.

To assist in the development of significant specifications for road bitumens, two large-scale road trails have been laid in Europe involving eight bitumens of different physical characteristics within the 70/100 penetration grade range. The first trial was constructed in France in 1963 and the second in South Germany in 1964. One area chosen has a largely hot and

dry climate, the other has a cold winter. In each trial, two types of mix design, three binder contents for each type of mix, and two types of aggregate were used with each bitumen. Together with control sections, a total of 110 test sections were constructed for each road trial. To measure the extent of deterioration, inspections of the roads were made twice a year by panels of observers. The inspections indicated that there is only slight deterioration that cannot be attributed to bitumen types. Viscosity data on bitumens recovered from samples taken at different stages of construction indicate that much of the initial hardening really occurs during the laying/compaction operation. The different mix designs, in spite of widely different filler contents, did not have much influence on bitumen hardening during mixing. Chemical composition data show that the most significant change during the mixing/laying operation was an increase of n-heptane asphaltenes. After 20 months of service, there were no differences in viscosity increase between coarse- and dense-graded mixes. Viscoelastic properties of the recovered bitumens at loading times representative of traffic stresses were studied using a double cone microelastometer. At short loading times the loss tangent (tan/delta) was shown to be a good measure of the amount of structure of "gel character" in the bitumen as it is aged. A decrease in tan at a particular value of complex modulus will result in an increase of shear susceptibility. Plots of tan versus complex modulus are suggested to study the influence of aging on short time viscoelastic behavior of bitumens. At long loading times it was shown that an aging index based on viscosities before and after aging should be based on viscosities at constant shear stress, rather than at constant shear rate. It was shown that aging index based on viscosities at constant shear rate will vary with shear rate while an aging index calculated from constant shear stress data is reasonably independent of shear stress. Aging indices based on viscosities at constant arbitrary shear rates will tend to decrease with increasing shear rate. The validity of this concept will be fully tested by results emerging from the trials.

Chipps, J. F., R. R. Davison, et al. (2001). "A Model for Oxidative Aging of Rubber-Modified Asphalts and Implications to Performance Analysis."

Oxidative aging of asphalt binders is a primary cause of binder-related long-term road failures. Viscosity hardening is primarily due to the oxidative conversion of polar aromatics to asphaltenes; oxidation is indicated by carbonyl formation. The aging of unmodified asphalts yields a constant, aging-temperature independent "hardening susceptibility" (HS) relation between viscosity change and the growth of the infrared carbonyl peak. Crumb-rubber-modified asphalts (CRMA) exhibit superior aging characteristics, lower hardening rates, and, often, lower oxidation rates, throughout the aging simulation range. However, CRMA materials may exhibit a hardening susceptibility that varies with aging temperature, suggesting either enhanced diffusion resistance or a kinetic competition between the oxidation sites of the rubber polymer and the asphalt's polar aromatics. This evidence suggests that the commonly accepted high-temperature, high-pressure, long-term aging technique is of questionable value when applied to CRMA materials. The aging characteristics of CRMA were found to depend most heavily upon the curing method, the fractional content of the rubber, and the chemical composition of the binder. The curing method has a major effect on the material and chemical properties. Curing at lower temperatures and shear rates leads to a mere introduction of the rubber material into the binder, producing a swollen, gelatinous particle phase, the aging consequences of which are difficult to assess. Progressively higher levels of mixing shear and temperature partially degrade the long polymer chains and cross-link structures. Polymer chains freed by thermo-mechanical shear are integrated in the binder, shielding or altering by competitive means the oxidation of the binder.

Chiu, C. T., M. Tia, et al. (1994). "Investigation of Laboratory Aging Processes of Asphalt Binders Used in Florida." Transportation Research Record(1436).

A laboratory investigation was performed to evaluate a variety of aging processes used for simulating the long-term aging of asphalt binders. Four promising methods investigated in this study include an extended thin film oven test (TFOT), an ultraviolet (UV) chamber, the California tilt oven (CTO), and the pressure aging vessel (PAV). A few conventional asphalts commonly used in Florida and a few modified binders were subjected to these aging processes, and their aged residues were tested for comparison of aging severity. Because of the insensitivity of consistency measurements at lower temperatures, the most sensitive parameter for differentiating the aging severity was found to be the aging index at 60 deg C, which is the ratio of absolute viscosities at 60 deg C. On the basis of this parameter, the relative aging severities of aging processes were established. Various asphalts were found to exhibit different aging severities when subjected to different aging processes. Asphalts from different sources exhibit differentiable degrees of volatile loss when subjected to the extended TFOT. The UV chamber was found to be effective only in aging the surfaces of the binder samples. Low-viscosity asphalts were found to age more in the CTO process. Whereas low-volatile-loss asphalts show less aging in most aging processes, some high-volatile-loss asphalts could age less in the PAV process.

Chollar, B. H., J. A. Zenewitz, et al. (1989). "Changes Occurring in Asphalts in Drum Dryer and Batch (Pug Mill) Mixing Operations." Transportation Research Record.

The study was designed (a) to discover whether steam distillation of asphalt takes place in a drum dryer mixer, (b) to compare changes induced by various laboratory conditioning (aging) techniques versus those occurring in drum dryer mixers, and (c) to identify possible differences in asphalts subjected to drum dryer mixing versus batch (pug mill) mixing. Twenty-seven virgin asphalts were subjected to various laboratory conditioning experiments, including thin film oven exposure (TFO), rolling thin film oven exposure (RTFO), (small) steam distillation (SSD), forced air distillation (FAD), and rolling forced air distillation (RFAD). Various physical and chemical properties of these conditioned samples were measured. These properties were compared with those of the residues recovered from drum dryer operations for each asphalt. By comparing the laboratory conditioned residues to the recovered residues from the drum dryer operation, similarities between the variously exposed asphalts and asphalt recovered from drum dryer mixers were ascertained. This demonstrated that steam distillation does not take place in drum dyrer mixers. Eight matched asphalt pairs, one used in a drum dryer mix and one in a batch (pug mill) mix, were identified among 24 virgin asphalts from Georgia by statistically comparing various physical, thermal, compositional, and molecular size properties of the virgin asphalts. Asphalts were then recovered from the mixes in which each of the eight drum dryer-batch (pug mill) asphalt pairs were used. The recovered asphalts were analyzed, and the results show the asphalt residues extracted from drum dryer operations to be slightly harder than those extracted from batch operations.

Christensen, D. W. (1998). "Analysis of Creep Data from Indirect Tension Test on Asphalt Concrete." Proceedings of the Association of Asphalt Paving Technologists **67**: 458-489.

Christensten, D. W. (2002). Quarterly Progress Report to the National Cooperative Highway Research Program on Project NCHRP 9-31: Air Void Requirements for Superpave Mix Design. Washington, DC, National Highway Research Program, National Research Council.

Churchill, E. V., S. N. Amirkhanian, et al. (1995). "HP-GPC Characterization of Asphalt Aging and Selected Properties." Journal of Materials in Civil Engineering **7**(1).

The primary objective of this study was to examine compositional changes of AC-20 asphalt cements after 5, 14, and 24 hours of laboratory age hardening, as detected by high-performance gel permeation chromatography (HP-GPC). Testing of the selected physical properties and HP-GPC analyses were performed on the virgin and aged asphalt cements. HP-GPC profiles were partitioned into three, four, and 10 segments based on equal elution time. Long-term laboratory aging produced significant differences among HP-GPC parameters. Statistical analysis conducted on HP-GPC profiles also indicated that significant compositional differences existed among the AC-20 asphalt cement sources. Regression models were developed for predicting physical properties of asphalt cements based on HP-GPC parameters. Strong relationships were observed between four physical properties and HP-GPC partitions into tenths. A better resolution of the data prevailed when partitioning the chromatograms into 10 segments versus division into thirds and fourths.

Clark, R. G. (1956). "Asphalt Volatility and Weathering Tests." Proceedings of Association of Asphalt Paving Technologists: 417.

Data on a large number of paving asphalts from many sources are presented. Samples of hot mixtures were obtained in the field and brought to the laboratory for extraction of the bitumen and recovery by the Abson method. The recovered asphalt was tested for penetration and compared with the original penetration of the asphalt. These values were compared with the standard loss in weight test. The thesis is proposed that volatilization is the main cause for the initial hardening of an asphalt. It was found, in the cases of pavements showing considerable cracking, that the asphalt used was air-blown in the final stages of refining.

Clark, W. H., and J. J. Thomas (1968). "Early Hardening of Asphalt Cement." New York State DOT Report **RR-68-5**: 56.

To determine the effect of hardening of asphalt cement on pavement performance the rates and causes were investigated. Hardening of 46 pavements ranging in age up to 16 years was studied by recovering their asphalt cements by the Abson method and performing penetration testing on the recovered material. A brief review of the state of the art is presented in an appendix.

Coons, R. F. and P. H. Wright (1968). "An Investigation of the Hardening of Asphalt Recovered from Pavements of Various Ages." Proceedings of Association of Asphalt Paving Technologists: 37.

The purpose of this research was to obtain a precise measure of asphalt viscosity taken from various layers in existing pavement surfaces and to study pavement cores of various ages to measure the magnitude of asphalt hardening that occurs within these layers. The asphalt samples were obtained from 14 existing pavements in Georgia by extraction and recovery from cores. These cores are representative of ages from 4 months to 12 years. Viscosity testing was performed with the sliding plate microvisometer developed by Shell. Absolute viscosity was determined at a shear rate of 0.05 i/sec at 77 F in accordance with procedures proposed by Griffin, et al. Viscosity variations with depth were obtained from asphalt viscosity extracted from five 1/4-in layers of each core. The major increase in viscosity was observed to be in the first layer near the surface, and therefore the variation within that sublayer was further studied by thinner slicing. Increase in viscosity with each 1/4-in layer with age was studied. Also the relation between a relative increase in viscosity and the original viscosity was investigated. The data collected was statistically analyzed to determine major factors affecting viscosity changes. The following conclusions were indicated: (a) there is about a 50 percent increase in the viscosity of asphalt extracted from the top 1/4 in of a pavement over asphalt extracted from depths of 1/2 in; (b) within the top 1/4-in layer there is a greater viscosity immediately under the surface than lower in the layer; (c) viscosity in the upper 1/2 in increases with age, while little change with age occurs at greater depths; (d) at a depth of about 1-1/2 in below the pavement surface, there is little change in viscosity with age except for an initial increase during or before placing: (e) at a depth of about 1-1/2 in below the pavement surface, the relative viscosity is independent of original viscosity.

Corbett, L. W. (1970). "Relationship between Composition and Physical Properties of Asphalt." Proceedings of Association of Asphalt Paving Technologists **39**.

Corbett, L. W. and H. E. Schweyer (1973). "Viscosity Characterization of Asphalt Cement." ASTM STP **532**: 40-51.

Cotte, C. and C. Such (1996). Influence of RTFOT Ageing on the Rheological Behaviour of Polymer Modified Bitumen and Their Associated Phases. Eurasphalt and Eurobitume Congress.

Bitumen ageing is one of the main causes of the evolution of the rheological behaviour of a pavement. Even if changes are well known for pure bitumen when exposed to artificial ageing, such as the Rolling Thin Film Oven Test, it is not the case for polymer modified bitumen. The study of the dynamic rheological properties of blends (80/100 bitumen + EMA or SBS) and their associated phases, separated by high temperature centrifugation, will be presented here. From isochronal curves and the Black diagrams, it was shown that the thermal treatment affects both components of the mix: the bituminous phase's behaviour becomes more solid like due certainly to an increase of the molecular size, the polymer phase undergoes a slight modification of properties in the case of EMA and, in the case of SBS, a more fluid like behaviour is observed, most likely indicating a fragmentation of the initial molecular chain. Finally, these polymer phase evolutions through ageing could explain an improved resistance to ageing of polymer modified bitumen in comparison to pure bitumen.

Culley, R. W. (1969). "Relationships between Hardening of Asphalt Cements and Transverse Cracking in Saskatchewan." Proceedings, Association of Asphalt Paving Technologists **38**: 18.

Transverse cracking and related pavement performance are major problems with flexible pavements in Saskatchewan. An investigation into the causes of these problems was begun in 1963, and the most significant finding was a relationship between asphalt source or refinery and the amount of transverse cracking. This finding led to a new specification based on tighter viscosity limits for asphalt cement and also to an asphalt usage program based on viscosity criteria. To determine if asphalts produced under the new specifications still resulted in significantly different transverse cracking patterns, a second investigation was begun in 1966.

This program consisted of measuring penetration (at 77F) and viscosity (at 60 F and shear rate of 0.05 1/sec) changes and temperature and shear susceptibilities of asphalt, which were sampled at various locations in the transition from the storage tank to 12 months service on five projects. The results of this investigation showed three distinct phases in the hardening of all asphalts, namely, the pre-mixing phase, the mixing-laying phase, and the in-service phase. There is not, however, a significant effect on penetration or viscosity from the various handling procedures within any one phase. Different asphalts are not similar in their hardening behavior. Depending on factors such as environmental temperature range and air "voids content, some asphalts harden less during pugmilling than during service, whereas the reverse is true for other asphalts. The use of penetration at 77 F as a measure of hardening over the 12 month period does not show as significant a difference between the asphalts as does the use of viscosity at 60 F or 140 F. Also, viscosities at 140 F and 275 F haye little meaning with respect to in-service pavement behavior, therefore test data at 60 F is regarded as more meaningful. Little change in temperature susceptibility was observed as each of the asphalts passed from storage to 12 months of service. Data related to shear susceptibility shows two distinct changes, one during transition from tank to final mix and the other over 12 months of service. The increase in shear susceptibility follows trends of viscosity increase measured at 60 F and 0.05 1/see. Comparison of losses (changes in penetration and viscosity) from this film oven test with losses from actual pugmilling shows no valid relationship for the particular asphalts tested. Comparison of transverse cracking with hardening of asphalt shows no direct relation and suggests that transverse cracking is a complex phenomena that is probably more affected by the degree of compaction and environmental conditions than by changes in a single variable, such as penetration or viscosity, during handling or mixing.

Dickinson, E. J. (1980). "The Hardening of Middle East Petroleum Asphalts in Pavement Surfacing." Proceedings of the Association of Asphalt Paving Technologists **49**: 34.

This study examined the hardening of the bitumen binders that have been used in pavement surfacing in Australia for the last 15 years. These bitumens have been almost wholly derived from Middle East crude petroleums. A durability test based on an aging procedure developed by the California State Highway Department was used to age seven different asphalts used for seal coats and thin dense hot mix surfacing laid down at different time periods. The viscosity at 45 C and 0.005 1/sec of these aged asphalts were compared with the viscosity of recovered asphalts from field samples. Linear regression analysis was used to relate the durability test results to the viscosity of recovered asphalts from seal coats and to the viscosity of asphalts and air voids content of dense surface mixes. Different regression models were obtained for different ages of test sections. Improving the resistance to hardening in service by using antioxidants and lime, and by blending the bitumens or adjusting the refinery processing was also investigated. Analysis of the data and results of the testing indicated the following conclusions: (a) rate of hardening is dependent on the susceptibility of the bitumen to hardening by thermal reaction with oxygen, the degree of exposure to air, and the temperature regime; (b) the level of hardening at which distress will occur in a surfacing is dependent on the pavement temperature regime in the cold season. Although the rate of hardening is higher in a hot climate, the distress level will also be higher because of the warmer conditions in winter; (c) a durability test that determines the time for a thin film of bitumen maintained at 100 C and exposed to air (in the dark) to reach an arbitrary viscosity level (associated with pavement surfacing distress in temperature climates) was developed to assess the susceptibility to hardening by "Hermal" reaction with oxygen. This test correlated with the hardening observed for different bitumens in seal coats; (d) dense hot mix surfacing trial indicates that the rate of hardening depends on the thermal oxidation of a bitumen as indicated by durability test and the degree of exposure to air as indicated by air void ratio; (e) process hardening by blending precipitated asphalt with propane is preferred to high temperature air blowing. The blending process produces a bitumen with better durability but slightly inferior temperature flow properties; (f) antioxidant zinc diethyl dithiocarbonate decomposed after two years in service and was not an effective oxidation inhibitor. Hydrated lime or lime containing fillers could be effective for reaching the rate of hardening.

Dickinson, J. H., S. Nicholas, et al. (1958). "Physical Factors Affecting the Absorption of Oxygen by Thin Films of Bituminous Road Binders." Journal of Applied Chemistry **8**: 15.

The absorption of oxygen by bituminous road binders in the absence of light at temperatures normally encountered on the road was found to be a process controlled by diffusion, with the rate of absorption depending markedly on the viscosity of the binder and the thickness of the binder-film. The acceleration of absorption produced by increasing the temperature corresponded to an activation energy for the process of approximately 10 kcal/mol. Generally speaking, tars showed a higher rate of absorption than straight-run petroleum bitumens. Irradiation of the film with light in the wavelength range 3000-5000A was found to produce a marked acceleration of the reaction, but, because of the high degree of absorption of the light, it was probably effective only to a depth of 10 below the exposed surface. Light had no effect at film depths greater than 60 When the illumination was sufficiently intense, a relatively hard layer was formed on the surface, which retarded further reaction of oxygen with the underlying layers of binder. This surface skin is always produced by exposure to natural sunlight. With the bitumens examined, light produced a greater acceleration of the reaction than with the tars; the surface skin was also formed more rapidly on the bitumen films.

Domke, C. H., R. R. Davison, et al. (1998). "Effect of Oxidation Pressure on Asphalt Hardening Susceptibility." Transportation Research Board.

There are many methods to accelerate the aging process of asphalts to determine how susceptible the asphalt is to hardening. These tests use increased temperature and/or pressure, and assume that the properties after the accelerated test match those if aged at lower temperature and pressure. However, the slope of the logarithm of viscosity versus carbonyl area, known as the hardening susceptibility, does not easily correlate from high pressure to low pressure aging conditions. The hardening susceptibility (HS) is a strong function of the oxygen pressure at which the test is run. HS is a function of pressure because the two terms that comprise it, the asphaltene formation susceptibility (AFS) – which determines how susceptible the asphalt is to the production of asphaltenes - and d(%AS) d(ln h - which determines how the asphaltenes are affecting the viscosity of the asphalt - are functions of pressure. The pressure dependency is hypothesized to be due to oxygen diffusion on a molecular scale.

Domke, C. H., R. R. Davison, et al. (2000). "Effect of Oxygen Pressure on Asphalt Oxidation Kinetics."

The oxidation of asphalt is a major cause of pavement failure. At a given temperature and pressure, the asphalt oxidizes in two stages: (1) a rapid-rate period followed by (2) a long period with constant oxidation rate. The degree of oxidation that occurs in the constant-oxidation region

is asphalt-dependent and varies with oxygen pressure and with temperature. Using pavement temperature oxidation kinetics obtained for eight asphalts in this study, it has been determined that the activation energies for the constant-rate region are dependent on the oxygen pressure and can be related to the asphaltene composition of the asphalt. An oxidation kinetic model is developed to predict the rate of oxidation in the constant-rate region knowing an initial asphaltene composition variable for the asphalt.

Domke, C. H., M. Liu, et al. (1997). "Study of Strategic Highway Research Program Pressure Aging Vessel Procedure Using Long-Term, Low-Temperature Aging Experiments and Asphalt Kinetics." Transportation Research Record(1586).

An essential element of understanding and predicting long-term asphalt binder performance is understanding asphalt oxidative aging and its effect on physical properties. High-temperature, high-pressure laboratory kinetic studies, pressure aging vessel (PAV) aging, and aging at pavement conditions are compared. The consequences of running the PAV at conditions far from road conditions are examined. An aging model previously reported in the literature was used to describe the data. Important asphalt aging parameters include the pressure reaction order (alpha), activation energy (E), initial jump in carbonyl content, and hardening susceptibility. All of these parameters are asphalt dependent. PAV tests were performed on asphalts for which kinetic data were available, and the results were compared with the kinetic model and with results obtained after 135 days of aging at 333 K (140 deg F) and 1 atm of air. The high temperature and pressure used in the PAV test sometimes results in serious errors in the performance ranking of asphalts of different E and alpha. Nevertheless, the test often ranks asphalts remarkably well because of fortuitous cancellation of several effects of pressure and temperature and the dampening effects of diffusion. Diffusion slows the oxidation rates, and asphalts with higher rates harden at the surface faster, increasing the diffusion resistance and slowing the observed bulk rate. The relative hardening of different asphalts is affected by the choice of PAV time, temperature, and pressure.

Fair, W. F., B. H. R., et al. (1949). "Accelerated Weathering of Pitches and Asphalts." American Society for Testing and Materials, Special Technical Publication **94**: 109.

The present work confirms the findings of Streiter and Snoke regarding the formation of water-soluble products from asphalts by the action of ultraviolet light, heat, and air. Water-soluble materials are extractable to only a small extent from pitches following exposure to ultraviolet light, heat, and air. Both asphalts and pitches exposed in thin films to the action of ultraviolet light, heat, and air in a weather-o-meter with and without water immersion exhibit marked increases in softening points; addition of filler to pitches or use of pitches according to standard built-up roofing procedures greatly reduces this softening point rise. The softening point rise in asphalts is accompanied by the formation of water-soluble compounds supposedly resulting from oxidation. In the case of pitches, the softening point rise is accompanied by the extraction of much smaller amounts of water-soluble compounds. This rise in softening point is probably due mainly to evaporation caused by the high temperature in the weather-o-meter. Thodes and Gillander found evaporation to be the major factor in the weathering of road tar materials. Pitches show little solubility in water following exposure to the action of heat, ultraviolet light, and air and show no change in rate of solubility during the periods studied; the asphalts exhibited considerable solubility for the first several 5-week periods and then exhibited a decrease thereafter. Accelerated aging tests of the kind described cannot be expected to

duplicate long-time service performances because materials tested singly in the weather-o-meter behave differently than they do in service, when used in combination with other materials that partially eliminate or greatly retard the aging processes; however, important information may be obtained by accelerated tests if the results are judiciously evaluated and conservatively applied in comparing experimental and standard materials. The importance of the intelligent use of accelerated aging data for practical construction consideration cannot be overstressed.

Fink, D. F. (1958). "Hardening of Paving Asphalts; Research Studies and Procedures." Proceedings of Association of Asphalt Paving Technologists **27**: 8.

This article is a review of the research techniques that have evolved over the years for the study of the rate of paving asphalt hardening. The studies on asphalt hardening may be classified into three groups: (a) studies concerned with the mechanism of hardening, which showed that hardening is due to chemical reactions, including oxidation, polymerization, and condensation and/or due to physical processes, including volatile loss and structural change; (b) studies on the rate at which hardening occurs, which indicated that temperature, oxygen pressure, catalysts, and oxygen diffusion are factors affecting rate of hardening; and (c) studies on the effect of hardening on the mechanical properties of either the binder itself or its admixtures, which measured change by conventional consistency, viscosity, elastic modulus, and toughness and brittleness tests. During laboratory hardening, asphalt was exposed to hardening influences (air, temperature, and oxygen) in the bulk, in relatively thick films solution, and more recently in films only a few microns thick. The reasons for the trend of using thin films are because: they correspond to films existing in actual paving mixtures, hardening proceeds to a much greater extent in a given environment, and oxygen diffusion effects are minimized, permitting a closer approximation to actual reaction velocities. Under normal aging conditions, it has been observed before that oxygen diffuses only a few microns into the bitumen surface. Therefore, the desirability of using films a few microns thick seems well established. Simulation of the hot-mix operation is not a problem. Simulation of long-term aging in a procedure short enough in duration for investigation purposes poses more serious problems. Increase of temperature has been widely used, since most oxidation reactions approximately double in rate for each 10 C increase. However, it is not known whether all asphalts have similar temperature coefficients of oxidation rate and release volatiles to a similar degree; furthermore, there is a possibility that the mechanism of chemical reactions changes with temperature, producing changing effects on consistency properties. There is considerable argument as to which measure of consistency is an appropriate physical property that correlates best with actual road performance. Generally, change in response to rapidly applied stresses (such as stiffness at 10 sec) and change in response to slowly applied stresses such as ductility or viscosity measured, are used as a measure of hardening. Analysis of some field aging data suggests that stiffness at short loading times has a consistent relationship with viscosity (stiffness at long loading times). Since viscosity values are observed to be more sensitive to aging, it is suggested that an aging index based on viscosity values at normal field temperatures should prove a useful indication of overall hardening characteristics of asphalts.

Ford, W. G., H. R. Smith, et al. (2000). "Preliminary Results of the Accelerated Ageing of Modified and Unmodified Bituminous Binders Using the Pressure Ageing Vessel."

The Transport Research Laboratory in collaboration with road authorities in a number of developing countries is currently developing recommendations for the use of bitumen modifiers

in both hot mixed asphalt (HMA) and surface dressings. This project forms part of an extensive programme of research, funded by the Department for International Development (DFID), which has the final objective of producing a guide to design and construction of bituminous surfacings in tropical climates. A specific aim is to identify modified and unmodified bitumens which may have improved resistance to environmentally induced degradation. The effect of natural weathering on a range of modified and unmodified bitumens has been assessed in trials constructed in four tropical countries. The change in viscosity of bitumens used in these trials has been monitored over a two year period, to establish rates of hardening. Ever increasing numbers of bitumen modifiers are being introduced and it would be advantageous to have an accelerated laboratory technique for testing the effect of ageing on new products without the need for laborious field-testing. To do this a pressure ageing vessel (PAV), as used during the Strategic Highway Research Programme, has been used to simulate long-term weathering using the standard and two extended ageing procedures. Early results indicate that, under controlled laboratory conditions, the PAV can be used to estimate the rate of ageing of bitumens used for surface dressing. (a) For the covering entry of this conference, please see ITRD abstract no. E204151.

Francken, L., A. Vanelstraete, et al. (1997). "Long Term Ageing of Pure and Modified Bitumen: Influence on the Rheological Properties and Relation with the Mechanical Performance of Asphalt Mixtures." **Volume II**.

This paper presents a study of the behaviour of eight road binders (one reference bitumen and 7 modified bitumens) used in porous asphalt wearing courses of an experimental road built in 1985. The complex moduli as well as different other characteristics of the binders were determined on the original binders and mixtures. A relationship between the complex modulus of binders and that of the corresponding mixtures has been validated for the case of modified bitumens. The complex moduli as well as different other characteristics of the binders were determined after different exposure times in a laboratory simulated long term ageing test. For some of the binders, these results were compared with the results obtained on the binders extracted from cores on the mixes in service for 12 years. It was investigated whether the complex moduli of the aged mixes could be estimated on the basis of that of the aged binder, with the help of the relationship between the complex modulus of the binders and mixtures.

Galal, K. A., T. White, D., et al. "Second Phase Study of Changes in In-Service Asphalt. Volume I: Main Report and Volume II."

In response to the need to improve asphalt pavement performance, the Strategic Highway Research Program (SHRP) was initiated in 1987. Products from SHRP included performance-based specifications for asphalt binders and performance-based mix design tests and criteria for asphalt mixtures. The Superpave asphalt binder specification addresses performance of in-service pavements for given environmental and traffic conditions. During the 1985 paving season in Indiana, the original asphalt binder and hot mix asphalt (truck mix samples) from a number of pavements were sampled and retained. Cores were also taken from these pavements after seven or eight years of service. Condition surveys were performed on these pavements, prior to coring. The study objectives were directed toward characterizing the original and extracted/recovered asphalt binders from the field samples using Superpave test methods and equipment. Taking this approach provided an early opportunity to examine a number of features of the Superpave system, including short (RTFO, rolling thin film oven) and long-term (PAV,

Pressure Aging Vessel) aging. Results of this research documented the difference in stiffness between RTFO aged and asphalts extracted and recovered from loose mixtures; in addition to, the difference in stiffness between PAV aged and in-service aged asphalts, in Indiana. Additionally, asphalt stiffness was related to pavement performance. A poor relationship was found between the stiffness of RTFO aged asphalts and rutting. On the other hand, a good relationship was found between stiffness of in-service asphalts and cracking. Collected weather data from seven counties indicated agreement between calculated PG grades for these counties and recommended Superpave PG grade, based on the environmental conditions. Based on the results of this research, recommendations were made to further investigate the short- and long-term binder aging to better address variability and reliability of these procedures, to address storage conditions sometimes unavoidable for field samples, and to validate PG grades requirements for Indiana.

Galal, K. A. and T. D. White (1997). "SHRP PG Classification and Evaluation of In-Service Asphalts after Eight Years." American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA, 19428-2959, USA.

A study has been conducted on the changes to in-service asphalts. This study represents ongoing extensive research efforts at Purdue University to investigate the changes to in-service asphalts and to evaluate the recently developed Superpave asphalt binder specifications. During the 1985 construction season, samples from the original asphalt binders and the truck mix samples (original mixtures) were retained from a number of paving projects in Indiana. In 1992/1993, after 7 to 8 years in-service, cores from these pavements were taken. During the same period of time, distress surveys were conducted. In a later stage, six projects were selected for detailed analysis using Superpave binder test equipment and procedures. A major interest of this research was to characterize the changes in the asphalt binders in-service and to correlate these changes with the pavement distresses, mainly: permanent deformation (rutting), fatigue cracking, and low temperature cracking. Consequently, the performance grade (PG) binder specifications could be evaluated. The Superpave binder tests and associated criteria were used to determine the high, immediate, and low temperature characteristics (stiffness, (PA)) of the asphalt binders tested. The results compare the relation between the conditioned (aged) asphalt binders from the Rolling Thin Film Oven (RTFO) test and the asphalt binders extracted from the original mixtures and the relation between the asphalt binders conditioned in the Pressure Aging Vessel (PAV) to the asphalt binders extracted from the in-service (field) cores. The results indicate that the current Superpave RTFO conditioning does not simulate short term aging. Similarly, the results show that the PAV aging procedure does not correspond to the aging encountered after eight years in-service

Galal, K. A., T. D. White, et al. (2000). "Second Phase Study of Changes in In-Service Asphalt. Volume 1. Main Report. - Final Rept." **N/A; FHWA/IN/JTRP-99/07-V1**(0024).

In response to the need to improve asphalt pavement performance, the Strategic Highway Research Program (SHRP) was initiated in 1987. Products from SHRP included performance-based specifications for asphalt binders and performance-based specifications for asphalt binders and performance-based design tests and criteria for asphalt mixtures. The Superpave asphalt binder specification addresses performance of in-service pavements for given environmental and traffic conditions. During the 1985 paving season in Indiana, the original asphalt binder and HMA (truck mix samples) from a number of pavements were sampled and retained. Cores were

also taken from these pavements after seven or eight years of service. Condition surveys were performed on these pavements, prior to coring. The study objectives were directed toward characterizing the original and extracted/recovered asphalt binders from the field samples using Superpave system, including short (RTFO) and long-term (PAV) aging.

Galal, K. A., T. D. White, et al. (2000). "Second Phase Study of Changes in In-Service Asphalt. Volume 2. Appendices. - Final Rept." **N/A; FHWA/IN/JTRP-99/7-V2**: 354.

In response to the need to improve asphalt pavement performance, the Strategic Highway Research Program (SHRP) was initiated in 1987. Products from SHRP included performance-based specifications for asphalt binders and performance-based mix design tests and criteria for asphalt mixtures. The Superpave asphalt binder specification addresses performance of in-service pavements for given environmental and traffic conditions. During the 1985 paving season in Indiana, the original asphalt binder and HMA (truck mix samples) from a number of pavements were sampled and retained. Cores were also taken from these pavements after seven or eight years of service. Condition surveys were performed on these pavements, prior to coring. The study objectives were directed toward characterizing the original and extracted/recovered asphalt binders from the field of the Superpave system, including short (RTFO) and long-term (PAV) aging.

Gallagher, K. P., H. U. Bahia, et al. (1996). "Influence of Air-Blowing on the Performance-Related Properties of Paving Asphalt." Transportation Research Record(Issue: 1535).

A comprehensive experiment was designed to compare the performance-related properties of a wide range of air-blown asphalt binders with those of straight run asphalt binders of similar viscosity grades. The binders were evaluated using the concepts of the Superpave binder specifications. In contrast to the prevailing perception in the industry, all performance-related properties of the air-blown binders were found to be as good as or better than conventional straight run asphalt binders.

Gallaway, B. M. (1957). "Durability of Asphalt Cements Used in Surface Treatments." Proceedings, Association of Asphalt Paving Technologists **26**: 151.

Eleven newly constructed roads widely distributed in Texas were surfaced with penetration grade asphalts from seven different producers. Data concerning the roads were obtained, and samples were obtained from each road after 1 and 2 yr service. The aged asphalt was extracted and tested in comparison with the original asphalt. Viscosity and degree of complex flow, component analyses, oxidation, and other special tests were made on the original and aged asphalts. The roads were carefully inspected after 1 and 2 yr and each evaluated for serviceability.

Gallaway, B. M. (1959). "Factors Relating Chemical Composition and Rheological Properties of Paving Asphalts with Durability." Proceedings, Association of Asphalt Paving Technologists **28**: 15.

This paper presents the second report on a series of surface treatment type pavements built in 1954 in various parts of the State of Texas. Samples of the asphalt cement used in these surfaces have been subjected to selected special tests as well as standard specifications requirement tests in an effort to evaluate durability characteristics. Testing agencies included on this project are: (1) Texas Transportation Institute, (2) The Texas Company, (3) The Bureau of

Public Roads, (4) The California Highway Department, Division of Materials and Research, and (5) The Texas Highway Department. A study has been made of the annual changes in the theological properties of the service aged samples. Also compositional changes as measured on solvent separated components of the asphalt have been investigated. Comparisons have been made of artificially aged samples and service aged samples. It is concluded from this research that: (1) Present standard specification requirements for paving grade asphalt cements do not adequately restrict the quality of this material. (2) Consistency requirements should include true theological measurements particularly in the range 40 to 140 degrees F. (3) Chemical composition should be restricted even though such a restriction may appreciably increase the cost of asphalt.

Gauthier, G. (2002). Fracture Testing of Asphalt Binders Using Notched Specimens in the Bending Beam Rheometer and the Direct Tension Device. Civil and Environmental Engineering. University Park, PA, The Pennsylvania State University.

Glotova, N. A., V. S. Gorshkov, et al. (1980). "Changes in Rheological Properties and Chemical Composition of Asphalts Upon Aging." Chemistry and Technology of Fuels and Oils (English Translation of Khimiya i Tekhnologiya Topliv i Masel) **16, No-34**.

Differences in the chemical composition of asphalts are responsible for differences in their colloidal and physical properties, particularly their rheological properties. The work reported in this paper represents a study of rheological properties to determine the relationship between changes in chemical composition and rheological behavior of asphalt during thin-film aging. Two grade BNK-5 asphalts were investigated, one from Romashkino crude and the other from Ust'-Balyk crude. Asphalt films with a thickness of 40-60 MUm were prepared and subjected to aging from April to October on a roof exposure rack under the climatic conditions of Moscow. The asphalts were investigated by rheological methods, group analysis, and microchromatography. Ten results are tabulated and evaluated. It is shown that the increase in concentration of the solid phase as a result of the appearance of new species and the evaporation of the oils leads no an increase in structurization and viscosity of the system. The asphalt viscosity varies directly with the content of asphalnenes, carbenes, and carboids, and inversely with the quantity of malthene components, 10 refs.

Glover, C. J., R. R. Davison, et al. (1989). "Evaluation of Oven Simulation of Hot-Mix Aging by an FT-IR Pellet Procedure and Other Methods." Transportation Research Board.

The long-established KBr pellet technique for IR analysis has been adapted for analyzing asphaltic materials. The procedure is highly reproducible and produces spectra that can be compared, with no normalization or other correction beyond normal background subtraction and baseline zeroing. Analysis of oven-aged and hot-mix asphalt samples by FT-IR, viscosity, penetration, and gel permeation chromatography provides comparisons for studies of asphalt aging. In a limited study, viscosity and penetration values for the hot-mix and for thin-film and rolling thin-film, oven-aged residues agreed quite well. However, the GPC and FT-IR analyses showed some significant differences.

Glover, C. J., R. R. Davison, et al. (2002). "A New Method for Simulating Hot-Mix Plant Asphalt Aging."

Because of deficiencies in the two standard tests for simulation of asphalt hot-mix aging, Rolling Thin-Film Oven Test and Thin-Film Oven Test, this project was designed to develop a new procedure for simulating asphalt short-term aging that occurs at a hot-mix asphalt cement plant. The Stirred Air-Flow Test (SAFT) was designed based on the fundamental studies of the process of air-blowing asphalt materials. Further testing of the SAFT apparatus to establish interlaboratory precision and consistency, introduction of the SAFT method for short-term asphalt binder aging and consideration for adopting the SAFT apparatus and procedure as a national standard are recommendations made by the researchers for expanded study.

Glover, C. J., R. D. Davison, et al. (2000). "Development of Stirred Air-Flow Test (Saft) for Improved HMAC Plant Binder Aging Simulation and Studies of Asphalt Air Blowing. - Research Rept." **RR-1742-2; FHWA/TX-02/1742-2**: 86.

In this work asphalt air blowing has been studied from two perspectives. First, the process itself was investigated in terms of the effect of air-blowing conditions on the properties of the asphalts obtained. It was found that according to the Superpave specification, very good grade asphalts can be produced by air blowing, and the blowing temperature does not seriously impact the grade span. Asphalt composition has a significant effect on the grade span. The materials with a higher concentration of asphaltenes and saturates have a higher performance grade span. In this work it is shown that the subsequent 88 degrees C hardening and oxidation rates are higher for materials blown at higher temperature, and this is not detected by Superpave specifications. The second part of this work deals with the development of a new procedure for simulation of asphalt short-term aging that occurs at a hot mix asphalt cement plant. The standard tests for simulation of asphalt hot-mix aging are the RTFOT (ASTM D 2872) and the TFOT (ASTM D 1754).

Goode, J. F. and L. A. Lufsey (1965). "Voids, Permeability, Film Thickness Vs. Asphalt Hardening." <u>Proceedings, Association of Asphalt Paving Technologists</u> **34**.

Five different combinations of aggregate containing crushed stone, natural sand, and limestone dust were used along with an 85 to 100 penetration grade asphalt for the mixtures of this study. Test specimens were molded by means of a motorized gyratory compactor employing a procedure that simulates the 50-blow Marshall density. At least three specimens of each mixture were prepared and tested for each of four aging conditions. Upon completion of aging, the specimens were tested for Marshall stability and extracted for tests on recovered asphalt, which included penetration, softening point, and ductility. Prior to the Marshall tests, and in a few cases prior to aging, selected groups of specimens were tested for air permeability using a new device developed by the Bureau of Public Roads. Additional determinations included the surface area for each aggregate combination, an index of asphalt film thickness for each mixture, and the density, air voids, and mineral voids for each set of specimens as molded. As was the case in an earlier study where gravel was used as the coarse aggregate, the results of this study indicate that 0.435 might be a better exponent for indicating maximum density than the 0.45 exponent used in setting up the Bureau of Public Roads gradation chart (1962 AAPT paper by the authors). Air permeability was found to be a function of aggregate gradation as well as air voids. The air permeability of mixes designed at about 4 percent air voids was a very low value regardless of gradation, and does not appear to be needed as a mix design criterion for dense-

graded mixtures. Air permeability or air void content, per se, do not appear to be factors affecting the rate of asphalt hardening. Air voids combined with asphalt film thickness, or with an asphalt coating index that is related to film thickness, does appear to be an important factor affecting the rate of asphalt hardening.

Gotolski, W. H., S. K. Ciesielski, et al. (1969). "Rates of Asphalt Hardening at in-Service Temperatures." Pennsylvania State Univ., University Park. College of Engineering. **Engineering Research B-100**: 56.

Rates of asphalt hardening at in-service pavement temperatures were studied in the laboratory to determine the effect of this factor on the durability of asphaltic concrete pavements. Samples of a sol, a sol-gel, and a gel asphalt, all within the penetration range 85 to 100, were tested at temperatures of 60, 100, 140, and 200 F, at four exposure-time intervals increasing from 0 to 28 days. Changes in asphalt consistency were measured by changes in apparent absolute viscosity and changes in percentage of asphaltenes. Tests results indicated that the rate of change of apparent absolute viscosity depends on temperature, regardless of asphalt type, and that the formation of asphaltenes, after a period of four or five days, is independent of asphalt type and temperature. Though the data for rate of change were similar for the three asphalts, a sol asphalt appears to have the best hardening characteristics for pavement durability. (Author)

Gotolski, W. H., R. W. Smith, et al. (1968). "A Study of Physical Factors Affecting the Durability of Asphaltic Pavement." Pennsylvania State Univ., University Park. Dept. of Civil Engineering.(report) **RR-IR-9**: 161.

The report is a summary of the results obtained, as of the reporting date, in a continuing study of the factors affecting in-service asphalt hardening and pavement durability. Among the factors considered are traffic density, mixture composition, aggregate type and gradation, pavement density and air voids, and asphalt consistency and chemical composition as determined by the Rostler method of analysis. Pavement durability is evaluated by periodic inspection. Asphalt hardening is evaluated principally by changes in composition, penetration, viscosity and ductility. The wearing courses in three pavement groups are studied. (BPR Abstract).

Green, E. L., W. J. Tolonen, et al. (1976). "Predictability Techniques for Asphalt Durability." Transportation Research Board.

A procedure is needed for predicting the durability requirements of asphalts. Development of this procedure should result in specifications for improvement of asphalt quality. First, testing techniques must be identified that will be sensitive to changes in asphalt quality. Second, these changes must be related to in-service changes in pavements. Third, the quality specifications must be imposed to curb the inevitable time-dependent changes to the degree desired. This study identified testing techniques that are sensitive to changes in asphalt quality by comparing the results of tests of (a) chemical composition, (b) vanadium content, (c) weatherometer exposure, and (d) rolling thin film oven aging to the durability of environmentally aged specimens. Durability is considered to be measured by the combination of viscosity and asphaltene increases with time. Rankings of each of these testing techniques are compared to actual environmental rankings to illustrate the techniques that best identify the durability changes. The major finding of the study is the high degree of correlation between the vanadium content and environmental rankings. If compositional considerations are such that any asphalt

imbalance or high volatility is a minimal factor, then the vanadium content is the best single parameter for predicting asphalt durability.

Greenfeld, S. H. (1953). "Effects of Thermal Shock on the Durability of Asphalt Coatings under Accelerated Test." American Society for Testing and Materials **Bulletin No. 193**: 46.

Three asphalts, representative of the major sources of coatings asphalt used in the manufacture of prepared roofings in the United States, were exposed, without stabilizer and with 30 percent and 60 percent of two mineral stabilizers, to accelerated durability tests. Four panels of each coating were subjected daily to 21 hr of exposure to the radiation from an enclosed, low-intensity carbon arc, with the introduction of a chilled water spray (40 F) for 3 min every 20 min (17-3 cycle). Two of the four panels with each coating were also exposed to air at -5 F for 2 hr daily. The use of the 40 F water produced results equivalent to those obtained when both the 40 F water and exposure to air at -5 F were employed. Exposure to air at -5 F had no significant effect on the durability or failure pattern of both stabilized and unstabilized asphalts under an accelerated test if the test included frequency cyclic thermal shocks.

Greenfeld, S. H. (1956). "The Effects of Mineral Additives on the Durability of Coating Grade Roofing Asphalts." Bitumen Material Series.

The effects of 14 mineral additives on the durability of coating made from three asphalts were evaluated in accelerated durability machines. It was found that while the durability of the coating is largely a function of the asphalt used, it increases, generally, with coating thickness and mineral additive concentration. Additives with flat, platelike particles finer than 75 microns in diameter (U.S. Standard Sieve No. 200) were most effective in producing coatings of increased durability. Complete dispersion of the additives in the base asphalts is necessary to produce consistent results.

Griffin, R. L., T. K. Miles, et al. (1955). "Microfilm Durability Test for Asphalt." Proceedings of Association of Asphalt Paving Technologists **24**: 32.

Methods used to accelerate the asphalt aging by various investigators were high temperatures, ultraviolet light, chemical oxidation agents and oxidation in solution under oxygen pressure. Many authors have agreed that it is best to work with thin films that approach the film thickness of asphalt in road carpets. Reaction with oxygen has been shown to be one of the principal factors responsible for the hardening of asphalts in the road. Rate of chemical reaction and rate of diffusion of oxygen have been shown to control aging. Therefore, aging may be considered as a chemical as well as a physical problem. Recently, a durability test in which asphalt is aged in films 5 microns thick and tested with a microviscometer has been developed. In this paper, the microdurability test procedure is used to measure the change in viscosity of 5 microns asphalt films aged in air in the dark. The effects of temperature, film thickness, and presence of light were explored. Also, the hardening due to loss of volatiles was determined by aging in an inert gas (nitrogen). Analysis or results of tests on various types of asphalts indicated the following points: (a) most asphalts are non-Newtonian, therefore comparing viscosity before and after aging should be done at the same shear rate; 5xl0 sec was chosen in this study. Some asphalts, especially after aging, show a slight yield point, however, at this shear rate the shear susceptibility curves have about the same slope and no correction is needed; (b) measurements of the viscosity of a non-Newtonian asphalt at different shear rates and different film thicknesses showed no effect of film thickness on viscosity measured by the sliding plate microviscometer at

25 C; (c) effect of film thickness on hardening of asphalts was observed to be significant. The ratio of viscosity before and after aging in the dark was observed to increase by about 25 percent when the film thickness was changed from 10 to 5 microns; (d) increasing the temperature increases the chemical reaction as well as the diffusion coefficient of oxygen due to the lowering of the asphalt viscosity. Temperature has great influence on aging rate; the same amount of hardening can be obtained by aging the asphalts 2 to 3 hours at 225 F as by aging 330 hours at 140 F. Increasing temperature does not have the same effect on various asphalts. (i.e. not all asphalts show same response to increased temperatures.); (e) comparing asphalts as aged in air and in nitrogen under the same conditions indicates that a large part of the hardening is due to loss of volatiles, especially for the asphalts that have high aging indexes. The loss in weight after aging correlates somewhat with the increase in viscosity when aged in nitrogen; (f) aging asphalts in very thin films should be done in the dark, otherwise light will have a significant effect on hardening. In the field, it is not expected that light will effect more than very thin layer surface.

Griffin, R. L., T. K. Miles, et al. (1955). "Microfilm Durability Test for Asphalt." Proceedings of Association of Asphalt Paving Technologists 1955.

A durability test for asphalt using the sliding plate (microfilm) viscometer is described as follows: a 5 micron film of asphalt is aged on glass plates for 2 hours at 225 F. The hardening which occurs is determined by measuring the viscosity of the asphalt before and after aging. The durability is reported as an aging index which is the ratio of the viscosity of the aged sample to that of the original, both viscosities having been determined at the same rate of shear (5 x minus 100 sec). A low aging index signifies a more durable asphalt. The original viscosity is obtained from a film prepared in the same manner but aged. Data were also obtained on samples aged in nitrogen. From the data obtained by aging in air and nitrogen, information is obtained concerning the relative effects of oxidation and volatilization.

Guin, J. A., C. W. Curtis, et al. (1988). "Coal-Based Synthetic Asphalt: Oxidative Aging and Testing of Compacted Bituminous Mixtures." **Transportation Research Record 1171**(ISBN: 0-309-04710-2 ISSN: 03611981).

An asphalt binder material, functionally equivalent to petroleum asphalt, has been produced by catalytic hydroliquefaction of coal. The synthetic coal-based asphalt, with approximately 3 percent polymer additive, meets all ASTM and AASHTO specifications for asphalt paving cements, with the exception of the optional thin-film oven test weight loss specification. Age hardening of the coal-based asphalt is primarily due to air oxidation rather than volatilization or polymerization. Marshall stability and immersion-compression testing show that the polymer-modified, coal-based asphalt produces compacted mixtures with good moisture resistance and high compressive strength compared with those of control samples prepared with petroleum asphalt of the same viscosity grade.

Halstead, J. and J. A. Zenewitz (1961). "Changes in Asphalt Viscosities During the Thin Film Oven and Microfilm Durability Tests." American Society for Testing and Materials **Special Technical Publication NO. 309**: 133.

The sliding plate microviscometer was used to determine the changes in asphalt properties during the thin film oven test and the microfilm durability test. The data presented include tests on 85 to 100 penetration asphalts from a wide variety of sources and methods of manufacture. Data on two groups of asphalts used in experimental construction are also included. Viscosity measurements for the 85 to 100 asphalts made at several temperature show significant differences in temperature susceptibility and degree of complex flow. Two types of behavior were noted: In one type, apparently typical of the majority of asphalts, the hardening in the microfilm is greater than the hardening in the thin film tests. This difference is not significant for values of aging index approximately 2 or lower but it increases rapidly as the hardening increases. In the second type of behavior, the hardening occurring during the two tests was essentially equal for all levels of resistance. These studies illustrate the value of the sliding plate microviscometer for obtaining theological information on asphalts not obtainable with the usual empirical methods. The differences in asphalts and the changes in relative rheological characteristics at different temperatures or values of stress emphasize the inadequacy of control of asphalt consistency by means of measurements at only one temperature. The need for further studies is clearly indicated.

Halstead, W. J. (1963). "The Relation of Asphalt Ductility to Pavement Performance." Proceedings, Association of Asphalt Paving Technologists.

Since its introduction in 1903 the ductility test for asphalts has been, and still is, controversial. Some asphalt technologists believe that the test is an indication of a necessary property of asphalt related somewhat to its adhesive properties or stickiness, while others consider the present laboratory test for ductility of no value for indicating the potential quality of an asphalt as a paving material. A review of the literature offers support for both of these divergent views. These contradictions suggest a need for a careful evaluation of the significance of the ductility test and its relation to other properties of the asphalt cement and a restudy of some of the available data to determine if there is a satisfactory explanation for the opposing viewpoints. This report, which is part of a general symposium on the properties of asphalt that affect pavement performance, emphasizes the advantages of considering the ductility-penetration relationship of an asphalt in evaluating the effect of the asphalt characteristics on pavement performance. When available data are analyzed on this bases, there is a strong indication that the consistency at which the asphalt begins to lose ductility rapidly and the temperature at which such consistency occurs is a significant relationship. It is also indicated that for some asphalts this point occurs at a sufficiently low penetration (or temperature) so that factors other than ductility, as measured in the laboratory test, control pavement performance. Hence, the conclusion is often reached that ductility is unimportant.

Hare, C. H. (2000). "Chemical Changes Occurring Within the Can--Part 1: Oxidizing Systems and Amino Crosslinking Systems." Journal of Protective Coatings and Linings. 2000/10.

This article examines the chemical changes that occur within a can of paint after manufacture. Chemical reactions and interreactions between raw materials can compromise the design and confound the application, curing, and therefore, service of a coating. The article reviews some of these troubles in oxidizing systems and considers thermally cured amino formaldehyde crosslinked systems. Certain acid-sensitive pigments may be subject to chemical change in oxidizing systems, which cure by the introduction of oxygen. With many such paints, the observed change is a deterioration in color. The postaddition of thixotropes during the pigment dispersion phase can reduce flow, and in many cases, decrease gloss. The polyamide resins may also lead to increased yellowing of films on aging. More recently, calcium sulphonate-based thixotropes have been introduced and are said to have less effect on gloss

reduction. The disadvantages of too much drier on long-term durability are not emphasized enough. As driers catalyze oxidative cure, they also encourage oxidative degradation in the applied film. This degradation accelerates the auto-oxidation reactions. These reactions cause crosslinking and loss of mechanical properties that naturally accompany the aging of all oxidizing films. Other aspects of aging include chain scission and the volatilization of low molecular weight fragments. Loss of drying ability in oxidizing systems after long storage intervals, especially at high temperature, can sometimes be traced to the pigment system used. At high temperatures, amino formaldehyde crosslinkers crosslink alkyds and other hydroxylated species, allowing both resin and crosslinkers to be packaged together as one-component systems. To conserve energy required for cure, catalysts may be added. These reduce conversions temperatures but may also decrease shelf life.

Heithaus, J. J. (1962). "Physical Factors Affecting the Weather Resistance of Asphalt Coatings." Industrial and Engineering Chemistry, Product Research and Development **1, NO -3**: 149.

Rheological measurements and accelerated weathering tests were made on a number of coating-grade asphalts. Performance in the weathering test did not correlate with viscosity, viscosity-temperature susceptibility, or elastic modulus measured on the original material. However, there was excellent correlation between weather resistance and the viscosity of the maltene phase of the asphalt. Asphalts with maltenes of high viscosity were most weather resistant. It is postulated that the rates of the reactions involved in the hardening of an asphalt coating are largely diffusion-controlled. A high-viscosity intermicellar liquid provides greater hindrance to diffusion, slowing down the hardening process.

Heithaus, J. J. and R. W. Johnson (1958). "A Microviscometer Study of Road Asphalt Hardening in the Field and Laboratory." Proceedings of The Association of Asphalt Paving TechnologisTs **27**: 18.

A series of asphaltic concrete test sections placed on a refinery entry road at Wood River, Illinois, provided a good opportunity for the study of asphalt hardening. They contained 18 different types of asphalts that represented four groups: vacuum reduced, cracked, semi-blown, and blends containing propane asphalt or lube extract. Two different types of surface course were in the field trails, one is a dense mix, while the other is an open graded mix. The objective of the study was to compare the properties of the asphalts extracted from the test sections with the properties of the same asphalts after aging in the laboratory. A review of tests used for assessing durability of asphalts indicated that several tests use unmixed asphalts. These tests are standard Loss on Heating Lewis Thin Film, Nicholson Blowing, Ebberts Oxidation, Anderson et al. Bomb. Other tests use asphalt-aggregate mix such as Shattuck test, and Shot Abrasion test. However none gave results in terms functionally related to pavement performance and, furthermore, not enough data exists that correlate these tests with actual field hardening. A recently developed Microfilm durability test that gives the results in terms of viscosity of the asphalt before and after aging is possibly the meaningful test so badly needed. Therefore, it was used in the study. The viscosity on the original, recovered, and laboratory aged asphalts was determined with a water bath model, parallel plate microviscometer at a shear rate of 0.05 1/sec. Asphalts were aged in a film 5 micron thick, at 225 F, for 2 hr. The viscosity was measured at 77 F. Analysis of results indicated the following points: (a) hardening during mixing and laying bears no close relationship to asphalt content or aggregate gradation; (b) there appears to be roughly a direct linear relationship between void content and binder hardening rate. Void content is a function of aggregate gradation, binder content and extent of compaction of mix; (c) the average viscosity increase during mixing and laying was found to be 140 percent of the Aging Index (ratio of laboratory-aged to original viscosity at 77 F, .05 1/sec). During 56 months service in addition to mixing and laying, the average viscosity increase amounted to 244 percent of that occurring in the Microfilm test; (d) different asphalts aged differently: times required for different asphalts to be aged in the Microfilm procedure to reach the same degree of field hardening were different; (e) the correlation coefficient between laboratory and field hardening indicated that type of mix has a significant effect. Asphalt content, open versus dense mix, and application of a prime coat to the base are the major factors. The correlation coefficient ranged between 0.13 and 0.99. Better correlation was obtained where hardening was greater, that is, in leaner, more open mixes and when hardening during both mixing and service are considered. Correlation was improved when the field data were corrected to the same void content. It is expected that an aging procedure of longer duration would give better correlations.

Höbeda, P. (2000). "Testing the Durability of Asphalt Mixes for Severe Winter Conditions." Eurasphalt and Eurobitume Congress 2000. Book I –1029 ENGLISH

In Sweden, pavements are very often subjected to severe winter conditions, with cycles of freeze-thaw and action of de-icing salt. Degradation of asphalt bound layers also mainly occurs during the late winter and early spring. However, a test that takes into account such conditions is lacking and testing the sensitivity for water is not sufficient. A new test, based on experience from forensic studies, is presented. It has been observed that cores, taken up wintertime and that are saturated with de-icing salt, may swell and disintegrate when put into water, obviously through an osmotic action. This is especially the case with layers that are rich in voids, under the surfacing layer. In the field, such “osmotic softening ”has been observed and heavy traffic loading can cause rutting and also corrugation in the most extreme conditions. This is because of salt solution being pumped away from the stressed areas under tyres, inside the voids of the mix and even a secondary void network can be formed. Also layer interfaces may form weaknesses.(The upper layer of the unbound base seems also to be involved, but here focus is put only on asphalt mix).When the temperature drops low enough, both the rutting and longitudinal unevenness are temporary fixed. However, they disappear rapidly by evaporation in late winter, with dry and milder weather. This field experience has resulted in a new “winter conditioning ”test, involving a double “osmotic ”immersion of the test specimens, first in saturated NaCl solution and then in distilled water. Finally, freeze-thaw cycling is performed. The resilient modulus of the test specimens has been monitored using the indirect tensile strength, but it is also possible to test the tensile strength instead of the modulus value. Tests are reported with a base mix, studying the influence of different aggregates. A rather soft bitumen (B 180)has been used. This “winter conditioning ”can reduce the resilient modulus of a marginal mix to such an extent that such “osmotic softening ”, that has been observed in field conditions, can be understood. Surprisingly good results have been obtained with some anti-stripping additives, even at high voids content and low bitumen content. It seems possible, using the new test method, to optimise the composition of an asphalt mix and choose the right additive for a particular aggregate-bitumen combination. Limited work, done with surfacing asphalt mixes, shows that dense mixes can be “immune ”against this “winter conditioning ”.On the other hand, porous asphalt cannot stand up to freeze-thaw cycles in a saturated condition. In practice, a lateral drainage must occur inside the mix and in this case, testing should be stopped after the “osmotic ” conditioning and the resilient modulus determined.. Hopefully, a new test has been developed that takes in account the most severe winter conditions. Using this test, substantial cost savings of asphalt pavement maintenance should be possible as the lifetime of asphalt bound layers can be prolonged.

Horváthné, F., Erika and J. Lvey (2000). "Structure Analysis of Road-Building Bitumens the Effect of Aging for the Structure Road Building Case Study with Modified Bitumen." <u>2nd Eurasphalt &Eurobitume Congress, Barcelona</u>.

The characteristics of road-building bitumens highly depend on their chemical structure. Different methods can be used to determine their structure. These methods are based on the difference in solubility of the different chemical groups of the bitumen. The traditional method is the column chromatography, the new method is based on the Thin-Layer Chromatography with Flame-Ionisation Detection (TLC-FID). Bitumens consist of four different groups. In the colloidal bitumen structure, depending upon the resin content of the bitumen, the asphaltene micelles are present either as fine or rough dispersion. These micelles are dispersed in the oily parts of the bitumen. The oily parts are the saturated and aromatic components. The asphaltene parts are surrounded by resins. Peptising agents are resins. If these groups of bitumens can be measured easily, one can get more information about their structure. The TLC-FID method is used to determine the chemical structure of bitumens and to determine the changes in the structure of bitumens during different bitumen producing technologies. The traditional bitumen producing technology is fluxing and blowing. We modellised these technologies in laboratory during the production of road building bitumens. The changes in the structure could be observed well. Several kinds of bitumen were aged in RTFO and in PAV and the change in their structure was measured. The aging indexes were calculated. At the end a case study is shown in which a road building bitumen is presented from its production until its building up into the road.

Huang, S.-C., J. F. Branthaver, et al. "Effect of Film Thickness on the Rheological Properties of Asphalts in Contact with Aggregate Surface."

The effect of the interaction between aggregate and asphalt on asphalt mix properties has been a subject of many studies. However, studies using compacted mixtures cannot isolate the pure effects of the asphalt-aggregate interactions, while studies using mixtures of asphalt and fines cannot determine the asphalt rheology at the interface. In this study, direct measurement of asphalt rheology at the interface is being investigated using the sliding plate geometry with machined aggregate plates. Significant differences in behavior of asphalts in contact with aggregate plates have been observed, especially at low shear rates. One asphalt shows substantial aggregate surface-induced structuring while another asphalt shows essentially none. In addition, the film thickness effect on the rheological properties of asphalt binders and asphalt aggregate mixtures were investigated. The results strongly show that thin films of asphalt on an aggregate surface have substantially changed rheological properties that are asphalt composition dependent, and that asphalts which are graded alike as bulk materials do not have the same rheological properties as thin films, i.e., in this service environment.

Huang, S. C., R. E. Robertson, et al. "A Study of the Steric Hardening Effect of Thin Asphalt Films in the Presence of Aggregate Surface."

The interaction between asphalt and aggregate surfaces before and after low temperature storage (reversible and/or irreversible) at various film thicknesses was investigated by means of the sliding plate geometry with standard Pyrex glass plates and machined aggregate plates. The

study of storage and setting in thin films of asphalts on aggregate surfaces indicates that asphalts interact differently and unpredictably with aggregate surfaces. The phenomenon of steric hardening in thin films appears to be retarded (compared with the same phenomenon in bulk asphalts) during short storage times but is enhanced in contact with aggregate surfaces after several weeks storage.

Huet, J. (1952). "Contribution to the Study of the Chemical Aging of Bitumen." Raport de Recherche **57**: 72.

The aging of bitumen is caused by diffusion of oxygen into the material, accompanied by oxidation and polymerization, which may be induced by peroxides. Laboratory tests of 12 months duration on 4 bitumens in the absence of light showed that most aging occurs in the first 20-30 weeks; then there is a trend towards equilibrium, when the materials is more stable than the original. Aging affects a thinner layer more than indicated by accelerated tests. High-sulfur bitumens are more resistant to oxidation than the low sulfur ones. 64 references.

Huh, J. D. and R. E. Robertson (1996). "Modeling of Oxidative Aging Behavior of Asphalts from Short-Term, High-Temperature Data as a Step toward Prediction of Pavement Aging." Transportation Research Record(1535).

The oxidative aging data collected during the Strategic Highway Research Program have been analyzed in terms of kinetics of viscosity change with time and temperature. Changes in viscosity have been used as the measure of the progress of aging. The objective is to model viscosity increases accurately enough to be able to predict aging (in terms of viscosity changes) at pavement temperatures from short-term test data acquired at high temperature. This involved constituting a mathematical model, based on oxidative reactions, and a nonlinear regression of the data to test predictability of the proposed model. Clearly, there is a point beyond which viscosity change becomes independent of time, but no data were collected to that extent. Separately, it has been shown that oxidation of aliphatic sulfide to sulfoxide and oxidation of benzylic carbon to carbonyl are the principal chemical reactions that contribute to an increase in viscosity. The data fit the proposed equation sufficiently well to allow calculation of rate constants of viscosity increases for both reactions, and, hence, allow development of an Arrhenius temperature relationship. Finally, it is hoped that the proposed equation will provide reasonable estimates of rates of oxidative aging of asphalts at pavement temperatures from short-term, high-temperature oxidative aging data measured in a laboratory.

Hunter, J. B., F. C. Gzemski, et al. (1949). "A New Method for Evaluating Failure of Bituminous Materials Due to Weathering." American Society for Testing and Materials, Special Technical Publication **94**: 144.

A photographic technique is described for evaluating the characteristic failure patterns of bituminous coatings undergoing accelerated weathering. This method offers (a) extreme simplicity, (h) a permanent record of the failure pattern, and (c) rate of failure data. This last feature allows a comparison to be made between the weathering characteristics of various asphalts at a higher degree of failure as well as in the initial stages of one percent or less. Reproducibility tests show beyond question that this method of failure detection and evaluation constitutes a useful tool for carrying out investigations where the weathering characteristics of non-conducting coatings is an important factor.

Hveem, F. N., E. Zube, et al. (1963). "Proposed New Tests and Specifications for Paving Grade Asphalts." Proceedings of the Association of Asphalt Paving Technologists **32**: 247-327.

Ishai, I. "Long-Term Laboratory and Field Behavior of Ppa Asphalt Cement Blends." Association of Asphalt Pavement Technologists **64**: 306-330.

Ishai, I. (1987). "Suggested Methodology for the Analysis of Asphalt Age-Hardening." Journal of Testing & Evaluation **15, No 3**.

This paper discusses a suggested approach for utilization of rheological aging curves for prediction of in-service age-hardening of asphalt which can affect pavement durability. The standard 'one point' evaluation of laboratory aging of asphalts is quite limited with regard to a meaningful, rational, and comprehensive evaluation of asphalt aging with respect to pavement durability. On the other hand, the temperature-time domain should be characterized and investigated by aging curves over a wide range of two-parameter coordinates. An interpretation of asphalt-aging curves in the temperature-time domain is presented that can lead to a reliable calibration of laboratory aging on the basis of actual field aging. The suggested approach and methodology are believed to provide the proper correlation (for a certain asphalt) between laboratory and pavement asphalt aging that can be obtained in almost any of the thin-film or microfilm oven tests.

Jimenez, R. A. (1968). "Viscosity and Durability of Asphalts for Paving Mixtures." N Mex Univ, Proc 6th Paving Conf Dec 12-13: 14.

The report is concerned with measurements of viscosity and durability of asphalt cements used in Arizona to relate their values to the production and performance of asphaltic paving mixtures. The data on asphalt durability were obtained by Shell Oil Co Aging Index procedure. The druability measurements show large differences in the resistance of aging by oxidation of the asphalts tested.

Jimenez, R. A. and B. M. Gallaway (1961). "Laboratory Measurements of Service Connected Changes in Asphaltic Cement." Proceedings of the Association of Asphalt Paving Technologists **30**.

The investigation reported herein concerns the changes which have occurred in asphalt cements recovered from test roads during six years of service. Results of standardized tests and special tests performed on the asphalts are shown to compare the initial properties of the asphalts with subsequent changes in physical and chemical properties. Different testing instruments and methods were used to determine their desirability for evaluating fundamental and empirical properties of the asphalts used in the test roads. The trend of changes in asphalt occurring with age is presented and tentative recommendations are suggested for the specification of asphalts in order to improve or to make better use of certain fundamental properties of asphalts. This constitutes the final report of a cooperative study with the Texas Highway Department. Earlier progress reports on this research have been given before this Association.

Jones, D. R. (1993). SHRP Materials Reference Library: Asphalt Cements: A Concise Data Compilation. Washington, D.C., Strategic Highway Research Program, National Research Council.

Julio, D. R. (1991). Asphalt Cement Aging under Accelerated Laboratory and Service Conditions. Civil and Environmental Engineering. University Park, PA, The Pennsylvania State University.

Juristyarini, P., R. R. Davison, et al. (2003). "Development of an Asphalt Aging Procedure to Assess Long-Term Binder Performance." Transportation Research Record.

Asphalt oxidation is a major contributor to pavement failure. Previous studies have shown that ductility at 15 °C correlates well with road cracking. Moreover, when the ductility decreased to about 3 to 5 cm, road cracking began to occur. A linear correlation between log ductility at 15 °C, 1 cm/min and the dynamic shear rheometer (DSR) function, G'/(ç '/G'), at 15 °C, 0.005 rad/s exists below a ductility of 10 cm. A ductility of about 3 cm corresponds to a DSR value of approximately 0.003. Nine asphalts, including seven SHRP asphalts and two Texas asphalts, were aged at elevated temperatures between 60 to 110 °C, and pressures ranging from 0.2 to 5 atm oxygen. The DSR functions for aged and unaged samples were obtained. It was found that for all aging conditions AAF-1 was the first to reach the critical value of 0.003. Each aging condition was ranked and calibrated against environmental room aging (60 °C, 1 atm air), used to simulate road aging. PAV thin-film aging at 90 °C, 20 atm air for 32 hours best represented environmental room aging.

Kandahl, P. S. and S. Chakraborty (1996). "Effect of Asphalt Film Thickness on Short and Long Term Aging of Asphalt Paving Mixtures." **NCAT 96-1**.

This study was undertaken to quantify the relationship between various asphalt film thicknesses and the aging characteristics of the asphalt paving mix, so that an optimum film thickness desirable for satisfactory mix durability could be established. Mixes prepared with asphalt binder film thickness ranging from about 4 to 13 microns, were subjected to accelerated aging using Strategic Highway Research Program (SHRP) procedures to simulate both short and long term aging. Both the aggregate (RD) and the asphalt cement (AAM-1) used in this study were obtained from the SHRP Materials Reference Library. The aged, compacted mix was tested for tensile strength, tensile strain at failure and resilient modulus. The aged asphalt cement was recovered and tested for penetration, viscosity, complex modulus and phase angle. Aging indices were obtained from these tests, and the relationship between film thickness and the aged mix/aged asphalt cement properties were determined using regression analysis. For the particular aggregate/asphalt cement combination used in this study, it was found that accelerated aging would occur if the asphalt binder film thickness was less than 9 - 10 microns in a asphalt paving mixture compacted to 8% air void content.

Kandhal, P. S. and W. C. Koehler (1984). "Significant Studies on Asphalt Durability: Pennsylvania Experience (Discussion)." Transportation Research Board.

Because a widely accepted laboratory durability test for asphalt does not exist, many agencies including the Pennsylvania Department of Transportation (DOT) have resorted to controlled field experiments to evaluate and characterize those physical properties of the asphalt binder that are associated with aging and their relationship to pavement performance. Three asphalt durability projects undertaken by the Pennsylvania DOT are summarized in this paper: 1961-1962 test pavements, 1964 test pavements, and 1976 test pavements. The study was limited to the evaluation of dense-graded asphaltic concrete wearing courses in which a different asphalt source or type was used. Except for the 1961-1962 test pavements, the only significant variable

was the asphalt type. Mix composition and construction techniques were held reasonably constant. After construction, periodical core samples were obtained from these pavements to determine the percentage of air voids and the rheological properties of the aged asphalts. It has been observed that aging of the pavements results in progressively lower penetration and higher viscosity, which exhibit a hyperbolic function with time. However, the accompanying decrease in low-temperature ductility after the penetration falls below 30, and the rate of gain in shear susceptibility relative to increase in viscosity at 77 °F, have been found to be important factors that affect the pavement performance. Lower ductility values were associated with a higher incidence of load-associated longitudinal cracking. High stiffness modulus of the asphalt cement at low temperatures and a 20,000-sec loading time contributed to nonload-associated transverse cracking. In the discussion, Davis notes that his own experience supports the authors contentions and he proposes that the ductility test could serve as a viscometer if stress levels were recorded.

Kandhal, P. S., D. B. Mellott, et al. (1986). "Durability Study of Viscosity Graded AC-20 Asphalts in Pennsylvania." <u>FHWA report</u> **FHWA/PA-84/009**: 79.

This long term asphalt durability project was constructed in September 1976 using six AC-20 asphalts from different sources with the following objectives: (a) to study the changing asphalt properties on aging, (b) to determine the effect of theological properties of asphalts on the pavement performance and durability especially at low temperatures, and (c) to develop suitable specifications for AC-20 asphalt cements to insure durable pavements.

Kandhal, P. S., L. D. Sandvig, et al. (1973). "Asphalt Viscosity - Related Properties of In-Service Pavements in Pennsylvania." <u>American Society for Testing and Material</u> **Special Technical Publication No. 532**.

Research has indicated that absolute viscosity alone cannot specify the complete rheological behavior of paving-grade asphalts, and other parameters such as shear susceptibility or temperature susceptibility or both are needed. Hence, to study these suggested viscosity-related parameters in relation to the performance of the in-service pavements, six viscosity-graded asphalts from different sources were used in the construction of pavements sections. Tests to determine the viscosity-related properties of the original asphalts, as well as the asphalts recovered from time to time for pavements in service, have been conducted. Evaluation of the performance of these test pavements was carried out using a rating method which reflects effect of aging on pavement condition. The aging index based on viscosity at 77 F (25 C) (.05 1/sec shear rate) was rounded to conform to the pavement performance rating and thus seems to be more meaningful to indicate the comparative aging and life expectancy of the test pavements. The viscosity at 77 F (after mixing in the pug mill), measured using the sliding microviscometer designed by Shell, was found related to the capability of pavements to compact under traffic. Viscosity at 140F using the Carmen Manning Vacuum Viscometer did not show such relation. Shear susceptibility at 77 F of the six aged asphalts was determined after 30-, 42-, and 78-month periods. Very good correlation was obtained between aging indexes (based on viscosity at 77 F) and the shear susceptibility values, which indicates that shear susceptibility is one of the major factors affecting the pavement performance. Data on temperature susceptibility of the asphalts in three temperature ranges (39.2-77 F, 77-140 F, and 140-275 F) for the original and aged asphalts were collected. A decreasing trend of temperature susceptibility was observed with aging in the first two temperature ranges, whereas the increase in the 140 to 275 F range is not appreciable. It appears that the temperature susceptibility parameter may have more significance in the case of low viscosity asphalts. There was an absence of any crack pattern on these test pavements, which can be attributed to temperature susceptibility.

Kemp, G. R. (1972). "Asphalt Durability Tests and Their Relationship to Field Hardening." ASTM Special Technical Publication **532**: 23.

A total of 24 asphalts in 8 test sections are being evaluated relative to their change in viscosity with time. The test sections are located in different climatic areas in California. Statistical correlations are presented covering various laboratory test methods for predicting asphalt durabilitywith 30 and 50 months of pavement service life. The laboratory test methods employed for predicting asphalt durability involve the concept whereby the asphalt is weathered by heat and air in a thin film. The amount of heat and thickness of the film varies, but the end result is basically volatization and oxidation to cause hardening of the asphalt. Additional correlations are presented using original voids and chemical procedures involving the Rostler analysis and Heithaus procedure. This report discusses the findings to date; additional pavement service life will be required before final conclusions can be drawn. 17 refs.

Kemp, G. R. and N. H. Predoehl (1981). "Comparison of Field and Laboratory Environments on Asphalt Durability." Proceedings of the Association of Asphalt Paving Technologists: 46.

This asphalt durability study involved the weathering of carefully controlled and fabricated briquettes in four distinctly different field environments for four years. The purpose of the study was to compare the effects of various field environments on asphalts in briquettes to the effects produced on the same asphalts by various laboratory accelerated weathering procedures. The controlled variables included three different asphalts representing high, high moderate, and low temperature susceptibilities; three void ranges, 5-5, 7-9, and 10-12 percent voids; and two aggregate sources representing absorbent and nonabsorbent characteristics. All of the briquettes were weathered in identical trays at each weathering site. In addition, a correlating test road was later studied, using one of the study asphalts in a desert site in the vicinity of the briquette desert weathering site. Laboratory testing of the briquettes was programmed to occur on original, 1-, 2-, and 4-yr-old specimens. Recovery of the asphalt was accomplished using the Abson recovery procedure (AASHTO-T170) prior to testing. Some of the briquettes were tested to determine their resilient modulus (MR) when this procedure became available. Also, a portion of some of the briquettes were sawed into slices to determine hardening with depth. The micro-recovery procedure (California Test 365) was used to recover the small samples of asphalt. Tests on asphalts recovered from briquettes included penetration at 77 F (0.1mm), softening point, ductility at 77 F, absolute viscosity at 140 F, kinematic viscosity at 275 F, and micro-viscosity at 77 F at .05 1/set shear rate. Several laboratory aging procedures were performed on the asphalts used in this study; Rostler finger printing, asphaltenes dispersions (Heithaus Method), and vanadium content are the compositional types of tests used. The accelerated weathering procedures used in this study were: RTF (5 hr at 325 F), RMF-C at 210 F for 48 hr, Ohawa sand mix weathering at 140 F for time periods up to 1200 hr, weathering plate durability test (California test 347) at 210 F for 24 hr, actinic light weathering test 95 F, 18 hr, 1000 MW/CM of 3660 angstrom actinic radiation, and a new California tilt-oven asphalt durability test. Important findings of the study are: (a) high average air temperature (thermal oxidation) is the most significant factor affecting the rate and amount of asphalt hardening in hot climates. Voids and aggregate porosity are also contributing factors but are dependent upon the type of asphalt and average temperature. The effect of voids is similar among all asphaltswhile the effect of aggregate porosity varies among the more volatile asphalts; (h) results from the field test road indicated that briquette weathering per unit time is slightly more severe than actual road weathering; (c) testing of the 2-yr sampling of weathered briquettes indicated that with the exception of the California tilt-oven test, none of the laboratory durability tests can adequately predict the effect of asphalt weathering at field sites. The California tilt-oven tests, however, could be used to predict the asphalt hardening with a good level of accuracy. Tests on the residue from this accelerated weathering procedure could be used with a hot climate specification to control asphalt hardening. Minimum penetration at 77 F of 15, a maximum absolute viscosity at 140 F of 100 kilpoise, and a minimum ductility of 20 cm at 77 F (5 cm/min) are _he specification limits on residue properties proposed for hot desert areas; (d) it is recommended that to improve asphalt durability, the voids should be reduced, absorbent aggregates should not be used, the softest grade of asphalt consistent with curing and stability should be used, and the insulation of the asphalt concrete mat with a cover such as a reflective chip seal in hot areas is desirable; (e) the minor study of hardening with depth indicated _hat, generally, the surface slice showed more hardening due to the effect of actinic hardening. Change of hardening with depth was similar for all types of mixes; (f) effects on temperature susceptibility indicates that, except for the site with the highest average temperature, the effects were negligible. For that one site, the temperature susceptibility decreased continuously with time. Softening point measurements showed a general increase with time. Shear susceptibility as measured by (California Test 348) increased continuously with time but at a lower rate at longer lives. Microductility at 77 F decreased with time at varying rates depending on the site. The most dramatic changes in properties were always seen at the site with the highest average temperature, which indicates the importance of this factor.

Kim, O.-K., C. A. Bell, et al. (1987). "Development of Laboratory Oxidative Aging Procedures for Asphalt Cements and Asphalt Mixtures." Transportation Research Record **1115**.

An evaluation of an oxidative aging procedure for asphalt materials is described. Test results and the effectiveness of the aging device used are presented. The study also involved laboratory tests on field core samples as well as laboratory mixture samples and asphalt cements used in three projects constructed in Oregon. The procedure selected for aging involved the use of a pressure oxidation bomb (POB)- a sealed container in which asphalt mixture or asphalt samples, or both, were subjected to pure oxygen at 100 psi pressure at 60C for periods of up to 5 days. Resilient modulus and fatigue tests were performed to measure the properties of cores and laboratory mixtures (before and after aging). The asphalt samples were aged on a Fraass plaque to achieve minimum disturbance of the sample, and the degree of aging was assessed by changes in the Fraass breaking temperature. The results of this study showed that the POB was an effective means of producing measurable changes in both mixtures and asphalt samples. However, the mixture properties were substantially different from those measured for the field core samples, whereas the asphalt Fraass breaking temperatures were the same. The resilient modulus ratio and the Fraass breaking point are found good indicators of the aging of mixtures and asphalt cements, respectively. The aging ratio of mixtures varies with the air voids content (higher ratio with higher air voids content). Asphalts aged in the POB for 5 days had compositions comparable to those of recovered asphalts that were from 5 to 10 years old. The laboratory aging period that is equivalent to field aging may vary with the grade and source of asphalt cement as well as mixture properties (particularly air voids and asphalt film thickness), and environmental conditions. Higher pressure or temperature, or longer exposure times, or all

three, could be applied to accelerate the aging process. To effectively evaluate mixture aging, representative mixtures must be tested, and if possible these should be core samples obtained shortly after construction rather than laboratory-compiled mixtures that may not represent field mixtures.

Kim, Y.-R., D. N. Little, et al. (2002). "Use of Dynamic Mechanical Analysis (Dma) to Evaluate the Fatigue and Healing Potential of Asphalt Binders in Sand Asphalt Mixtures." Proceeding of the Association of Asphalt Paving Technologists.

King, J. D. and Q. Ni (1994). "Magnetic Resonance for in-Situ Determination of Asphalt Aging and Moisture Content." Transportation Research Board: 19.

This Innovations Deserving Exploratory Analysis (IDEA) project investigated the feasibility of using nuclear magnetic resonance (NMR) technology for in-situ determination of aging and moisture content of asphalt in pavements. The combination of NMR and electron paramagnetic resonance (EPR) techniques was shown to be an effective tool for assessing asphalt condition in pavements. Field verification of the system will be required for the IDEA product transfer. The recommended system design configuration and specifications, as presented in Appendix A, incorporates both NMR and EPR in an integrated, trailer mounted configuration using a common magnet.

Kleinschmidt, L. R. and H. R. Snoke (1959). "Effect of Light and Water on the Degradation of Asphalt." Journal of Research **63 C**.

Coatings prepared from two blown petroleum asphalts in a thickness range of 0.002 to 0.04 inches were exposed to accelerated test conditions and outdoors. When exposed to light only, a surface film, insoluble in common asphalt solvents, was formed. The formation of this surface film was accompanied by a gain in weight of the coatings, apparently due to an oxygen pickup. This surface film retarded further degradation of the maltenes during the exposures made to light only. When the coatings were immersed in water after exposure, or sprayed with water during exposure, or exposed outdoors, they lost weight. These decreases in weight were found to be in part due to the extraction of water-soluble, light-degraded material. Their magnitudes were dependent upon the asphalt exposed, the thickness of the exposed coatings, and exposure conditions. The relationship between the losses in weight and water-soluble material, when considered in conjunction with the oxygen content of the asphalts and the water-soluble materials, indicated that volatile degradation products were also formed. When the surface skin formed by the action of light was partially removed by washing with water, percentage decreases were noted in the water-white oils, dark oils, and asphaltic resins. Since these decreases were unequal in magnitude and since the losses in weight were dependent on the thickness of the coating, it was concluded that light-degradable components of the asphalt had migrated to the surface to replace degraded materials that had been washed away.

Knorr, D. B., Jr., R. R. Davison, et al. (2002). "Effect of Various Aging Techniques on Asphalt Low-Temperature Properties." Transportation Research Record(1810).

The effects of various aging techniques on asphalt low-temperature properties were investigated in three phases. In Phase I, it was shown that 38 days' aging of a 1-mm-thick asphalt film at 60 deg C and 1 atmosphere of air is approximately equivalent to 20 h in the pressure-aging vessel (PAV) of a 3.2-mm-thick film at 100 deg C after both have been rolling thin-film oven test aged. Low-temperature properties of the samples were found not to vary significantly between the PAV and environmental room-aged material. In Phase II of this work, a correlation was developed from the high-temperature parameter G*/sin(delta) at 58 deg C and 10 radians/s to correct the low-temperature performance grade when it is desirable to skip the long-term aging procedure. In Phase III of this study, it was shown that as asphalts are aged for extended periods, their relative ranks with respect to Strategic Highway Research Program low-temperature specifications may change. Furthermore, as asphalts are aged for extended periods, the low-temperature grades move from being limited by stiffness at short aging times to being limited by m-value (creep rate) at longer aging times.

Knotnerus, J. (1972). "Bitumen Durability-Measurement by Oxygen Absorption." Industrial and Engineering Chemistry - Product and Research Development **11, No-4**: 12.

The absorption of oxygen by bitumens in the light and in the dark was measured at ambient temperature with stirred solutions in an indifferent solvent to avoid problems owing to diffusion effects. The rate of absorption was considerably increased by light (fluorescent lighting) and by traces of certain metals. All chemical-type fractions prepared from bitumens by chromatographic separation oxidized in the light, but only the asphaltenes and resins absorbed oxygen in the dark; this reaction was probably initiated by the stable free radicals present in bitumens. The concentration of reactive components in dark-colored bitumens is higher than in light-colored ones, but in practice the dark color acts as a protection against excessive oxidation in the light. Few of the compounds known to inhibit oxidation reactions appeared to affect bitumen oxidation. Those that were active accelerated oxygen absorption in the light but had hardly any effect in the dark. The effects found with these substances in the light experiments were checked with weather-o-meter experiments.

Korsgaard, H. C., J. Blumensen, et al. (1996). Accelerated Ageing of Asphalt in Pressure Ageing Vessel. Eurasphalt & Eurobitume Congress.

This paper describes the long-term ageing properties for different asphalt mix designs after ageing in a Pressure Ageing Vessel (PAV). In connection with the SHRP project, the PAV has been developed for the examination of long-term ageing properties for pure bitumens. The ageing is performed under a constant pressure and temperature for 20 hours. In this project the PAV is applied for ageing of asphalt cores with varying mix design. The purpose of this project is to examine the influence which formula changes have on the long-term ageing properties of the asphalt. The ageing in the PAV is performed on Gyratory compacted cores of GAB-S (a base course asphalt mix) with varying mix designs. The ageing time in the PAV has been fixed in proportion to the ageing of the pure bitumen. The results show that the ageing of asphalt cores in a PAV requires about four times as much time as the ageing of standard bitumen. Moreover, when reducing the thickness of the bituminous aggregate cover, as expected an accelerated ageing is observed. We expect that when comparing data from PAV ageing of asphalt with data from Gyratory compacting and Nottingham Asphalt Tests, mix designs cannot only be optimized in relation to the mechanical properties of the asphalt but possibly also in relation to the ageing properties.

Lau, C. K., K. M. Lunsford, et al. (1992). "Reaction Rates and Hardening Susceptibilities as Determined from Pressure Oxygen Vessel Aging of Asphalts." Transportation Research Board.

Many attempts have been made to simulate road aging with laboratory tests. These have generally not been successful. One reason is that other causes of road failure, such as heavy traffic or construction deficiency, can obscure the effect of the asphalt binder. But other reasons are that an adequate model relating laboratory-measured properties to changes in the road is not available and that the oven test temperatures that have been used may be too high to relate oven aging to road aging. Use of the lower-temperature pressure oxygen vessel offers promise of approximating road conditions. It is shown that no test run at a single elevated temperature can be used to simulate road aging and that at road temperature the rate is still too low for practical testing. It is also shown, however, that the oxidative aging mechanism is constant at temperatures up to 82.2 deg C and that it approximates aging of the asphalt binder in laboratory cores. If this is borne out with road cores, extrapolation of higher temperature data may provide more accurate predictions of road aging.

Lee, A. R. and E. J. Dickinson (1950). "Full Scale Experiments in Road Research, with Special Reference to Thin Carpets." The Institution of Civil Engineers, Road Paper.

An account is given of some of the full-scale experiments on bituminous road materials that have formed part of the research program of the Road Research Board. Reference is made to many of the problems investigated by these experiments, which include the assessment of the factors that affect the durability of surface dressings, the design of durable non-skid, open and medium-textured carpets for rural and city roads, and the relative performance of different road bases and surfacings used in the construction of new roads. Consideration is given to the principles involved in the planning and execution of road experiments, the degree of control required in such work, and the relation between road experiments and laboratory investigations. The limitations of circular-track and similar road-testing machines are discussed. As the deterioration of a road surfacing arises from the combined action of weather and traffic, misleading conclusions may easily be drawn from the results of experiments that omit or exaggerate unduly either one of these factors. The great influence of weather on the behavior, in early life, of surface dressings requires that experimental work on this type of road maintenance should consist largely of full-scale road experiments. Recent investigations have been directed to methods of overcoming the destructive action of wet weather, and they have shown how surface-active chemicals may be used successfully for this purpose. The problems raised by the popular demand for open-textured bituminous carpets may be solved with the help of full-scale road experiments in which a series of different surfacing materials are laid, with systematic regular changes being made in the aggregate grading, while with each grading a series of mixtures are laid covering a wide range of binder contents. Quantitative conclusions can be drawn from these experiments only if the limits of composition of each sub-series are so adjusted as to produce premature road failure. A description is given of the Colnbrook bypass experiment carried out in 1939, involving the use of granite and gravel aggregates and tar and bitumen binders. Definite conclusions can be drawn regarding the aggregate gradings and binder contents necessary for producing durable non-skid surfacings. The economic advantages of the successful use of local aggregates and binders has led to the repetition of this type of experiment in different parts of the country. These experiments have demonstrated the predominating influence that the type and quality of bituminous binder have on the life of the surfacing, and have indicated that adjustments in grading and binder content are required for different aggregates. Further adjustments are required according to the traffic and the climatic conditions. They provide a means of checking the results of laboratory investigations of the weather-resisting and adhesive properties of road tars and bitumens and the properties of aggregates. They also give a basis for the correlation of laboratory tests with road performance. Similar types of road experiments have been carried out with dense, impervious mixtures on city streets, with the object of finding mechanical tests suitable for designing compositions that will successfully resist deformation under heavy traffic. The establishment of laboratory techniques for measuring the weather-resisting properties of road tars and bitumens and the mechanical properties of road mixtures is the outstanding need in the field of bituminous materials. Until these objects have been achieved, the full-scale road experiments offer the only reliable method of investigation.

Lee, A. R. and E. J. Dickinson (1954). "The Durability of Road Tar with Special Reference to Its Use in Tarmacadamwearing Surfaces." Road Research Paper **31**: 35.

This paper summarizes the work carried out at the British Road Research Laboratory to determine the reason for the deterioration of open-textured road surfacings and to improve the quality of tars to make them suitable for this type of surfacing. It is shown that resistance to atmospheric oxidation is an important property required by the tar binder used in an open-textured carpet. A laboratory test has been developed with which it is possible to assess this property, and an upper limit has been given, which should not be exceeded if a durable tar is to be ensured. Two methods are suggested for improving the resistance of certain tars to atmospheric oxidation: the phenolic constituents are removed in one method by washing with aqueous caustic soda, and in the other by oxidizing them in the tar before it is used on the road. The practical value of these processes has yet to be proved. Further work is in progress to establish whether some major structural change occurs with time when tar in the form of a very thin film is in contact with a mineral aggregate. Two appendices are included: (a) Experimental Methods for Examining Tars and (b) Theory of the Diffusion-Controlled Reaction of a Gas with a Thin Film of Viscous Liquid.

Lee, D. (1968). "Development of a Laboratory Durability Test for Asphalts." Highway Research Board Record **231**.

A laboratory test procedure for evaluating the durability of paving asphalts is proposed that recognizes and is intended to simulate the two-stage hardening of asphalt during mixing processes and subsequent pavement service life. The test consists of first subjecting the asphalt to the thin film oven test (TFOT) and then treating the residue in oxygen at high pressures. The TFOT at 325 F is to simulate the changes that may occur in asphalt during hot-mixing and the pressure-oxidation process at 150 F is to simulate the changes that may occur in asphalt during pavement service life. A 1/8-in film thickness is used in both treatments. The effectiveness of the proposed test in accelerating the hardening and other changes of asphalt, the ability of the test to differentiate asphalts with respect to changes (both physical and chemical), and the effects of time and oxidation pressure were demonstrated by the results of the proposed durability test on five 85 to 100 penetration grade asphalt cements and one of 120 to 150 penetration grade. The properties measured to indicate changes include penetration, softening point, absolute viscosity, asphaltene content, and percent oxygen. The major conclusions from this study are that (a) the approach of the proposed durability test is sound, and the procedure is reproducible; (b) the procedure is capable of accelerating the hardening of asphalt in a relatively short period of time; (c) differences exist among asphalts in hardening during the pressure-oxidation procedure, and therefore the procedure can distinguish between asphalts that are susceptible to hardening and those that are not; (d) the hardening in the pressure-oxidation process is a hyperbolic function of time, which suggests that a definite correlation can be established between field hardening and the proposed laboratory durability test; and (e) continued study into the next phase of the durability test investigation is necessary and warranted so that the information obtained can be put into useful and applied form in asphalt paving design and quality control.

Lee, M. G., M. Tia, et al. (1997). "Comparison between the Aging Processes for Asphalt Mixtures and Those for Asphalt Binders." American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA, 19428-2959, USA.

The Strategic Highway Research Program (SHRP) has proposed a short-term oven aging (STOA) process to simulate the aging effects of hot mixing and construction process on asphalt mixtures, and a long-term oven aging (LTOA) process to simulate the effects of additional aging of asphalts mixtures in service for 5 to 10 years. In the SHRP Superpav Binder Specifications, the conventional Rolling Thin Film Oven (RTFO) Test is used to simulate the effects of the hot-mix process on a binder, and the Pressure Aging Vessel (PAV) is used to simulate additional aging of the binder in service. This study evaluated the effects of the SHRP STOA and LTOA by comparing their effects on the asphalt binders with those produced by the RTFOT and the PAV processes.

Letters, K. (1957). "Investigations on Artificial Aging of Bituminous Binders and the Relations to the Properties of Their Films." Bitumen, Tere, Asphalte, Peche **8**: 37.

The author's previous work on tar and bitumen films is followed up by tests on films 0.1mm thick on glass. The periodical course of artificial aging is observed on 16 road tar and bitumen samples. Results of the test series in 3 alternating variables--water storage, u.v. irradiation, heating to 50 C and cooling to -20 C--are presented in detail for individual materials with supporting photographs. Visual observation indicates surface changes. Scratch tests give an estimate of crack and pit formation, depth effects, progress of hardening or oil separation, and changes in adhesion to the glass. Road tars show surface changes with crack formation generally earlier than bitumen, especially with longer water stressing, and show generally some contraction tendency. Bitumen-tar mixtures have higher plasticity, better adhesive power, and smaller tendency to crystallization; advantages are only effective in weak solar irradiation. In tar-bitumen mixtures with small tar additions, thick films give retarded aging with low strengths. Results of further experiments--supported by photographs--show that surface changes with crack formation do not occur with bitumen as rapidly as with tar under long water and heat stressing. In the water stage of stressing, the picture is reversed insofar as an intensified surface change with formation of bright hardened islands and broad oily canals, with a decrease of adhesive power after water storage, appear.

Lewis, R. H. and W. J. Halstead (1946). "Behavior of Asphalts in Thin Films." Public Roads, Us Bureau Public Roads. 1946/04.

The report covers the results of tests on the residues of asphalts from many sources that were obtained in the Thin- Film Oven test (50 gram sample, approximately 1/8 inch thick heated at 325 F for 5 hours in the standard volatilization oven). Ductility, softening point and penetration tests were made and on the basis of results obtained, recommendations for specification requirements for the thin-film oven test were suggested.

Lin, Y.-Y., L. L. Anderson, et al. (1974). "Coal Tar Autoxidation--Kinetic Studies by Viscometric and Refractometric Methods." Preprints of Papers - American Chemical Society, Division of Fuel Chemistry **19 No-5**: 31.

Results are presented of an experimental program which was carried out to investigate the kinetics of coal-tar autoxidation. The measurement of viscosity and refractive-index change were regarded as the most convenient ways to determine the extent of coal-tar autoxidation; hence, both of these methods were used in this study. Present-day theory of autoxidation is employed to explain the different mechanisms involved in the autoxidation of whole tar, neutral oils, tar acids, and tar bases respectively, under ambient storage conditions. Extensive experimental data are plotted and evaluated, 10 refs.

Linde, S. and U. Johansson (1992). "Thermo-Oxidative Degradation of Polymer Modified Bitumen." ASTM STP **1108**.

Lottman, R. P. and A. M. Rao (1966). "Durability Characteristics of Asphaltic Materials." Ohio State Univ., Columbus. Engineering Experiment Station. **EES-259-2**: 89.

The conclusions are: (1) The constant-power calculated viscosities of the oven aged asphalts increased more rapidly with increasing oven temperature than with oven time; (2) The aging index values of the asphalt differed at a given viscosity test temperature and for a given asphalt and aging, the aging index increased with decreasing test temperature; (3) Using viscosity-shear plots, the asphalts were shown to have different degrees of non-Newtonian characteristics. Generally, non-Newtonianism increased as aging increased and as test temperature decreased; (4) The percent asphaltene content increased with oven aging, being highest for the most non-Newtonian asphalt and lowest for the least non-Newtonian asphalt; (5) As aging increased, the change in intrinsic viscosity of aged asphalt solutions in benzene increased. Excepting asphaltenes from the least non-Newtonian asphalt, the asphaltene intrinsic viscosity increased at a greater rate beyond a 'critical degree' of aging for each asphalt, indicating that the asphaltenes increase in size weight rapidly above some aging severity; (6) Molecular weights of asphaltenes were determined indirectly by calculations using Staudinger's equation with the intrinsic data. Due to the equation, molecular weights increased with aging in the same manner as intrinsic viscosity did, weights ranged from 900 to 1400 grams per mole; (7) Limited glass transition temperature data were obtained. It was found that by using the glass transition temperatures and log viscosity versus reciprical temperature plots obtained for the asphalt, plots of the unaged and aged asphalt samples could be shifted by use of the Williams-Landel-Ferry equation to a 'reference' plot. (Author)

Lund, J. W. and J. E. Wilson (1986). "Field Verification of Asphalt Aging in Hot Mix Plants." Proceedings of the Association of Asphalt Paving Technologists **55**.

As a measure of aging in the mixing and placement process, the following formula was used to determine the percentage of the expected change in asphalt viscosity at the time of aging:

$$C = \left(\frac{R-A}{B-A}\right) x100\%$$

where A-absolute viscosity of original asphalt, B-absolute viscosity of the asphalt residue after rolling thin film over aging, and R-absolute viscosity of the asphalt recovered from the mixture. Asphalt concrete pavement tenderness, due to inadequate aging or unexpected soft consistency of asphalt, has caused problems such as rutting, surface flush stripping, ravelling, and segregation on Oregon highways for the past 10 years. In order to identify the causes of pavement tenderness, data were gathered from 29 different projects in Oregon from 1981 through July, 1983. A total of 111 samples were collected for determining "C" based on field observation. Paving problems were not experienced when "C" was above 50 percent, there were some problems when "C" values were 30 to 50 percent, and problems were always experienced when "C" values were less than 30 percent. In 1985, "C" values were analyzed again to see if any changes had occurred. The comparison of results between the 1981-83 data and the 1983-85 data indicated that "C" value still appears to be a good measure of asphalt properties relating to the tenderness of asphalt paving mixes, especially during the initial placement time.

Maccarrone, S. (1987). "Flow and Deformation Properties of Bitumens Service Weathered to Near Distress Level." <u>Research Memorandum, Australian Road Research Board</u> **28**: 34.

A study was carried out examining the flow and deformation properties of service weathered bitumens and their corresponding road performance. Bitumen from 39 spray seals was recovered from the cover stones and tested for the range of temperatures and stressing rates experienced in pavement service. A viscosity test conducted at 45 C and a creep test conducted at 0 C both gave information on the response of bitumen under very low rates of stressing. The dynamic data, after being superimposed, gave information on the response of bitumen over a large range of frequency and temperature. The hyperbolic equations of Dickinson and Witt successfully described the frequency dependence of the modulus and phase angle. For weathered bitumens the WLF equation with coefficients derived from this study described the variation of viscosity with temperature in the range -10 to + 60 C. The viscosity result (45 C) was a very good indicator of bitumen modulus at low temperature (0 C) and low rates of stressing (thermal contraction) but not at fast rates of stressing (fast moving vehicle). Bitumen viscosity at 45 C is adequately correlated with its service performance and as such it is a suitable parameter for evaluating the field performance of bitumens. However, bitumen modulus calculated at conditions representative of lowest site temperatures and traffic stressing was a marginally better indicator of its service performance. Further studies should be undertaken to confirm the conditions critical to bitumen performance.

Mack, C. (1965). "An Appraisal of Failure in Bituminous Pavement." <u>Proceedings of Association of Asphalt Paving Technologists</u> **34**.

Failure in bituminous pavements consists, in general, of the formation of cracks that result from external forces being greater than the cohesive forces of the asphalt. Based partly on experimental evidence, it has become customary to relate loss in cohesive forces of weathered asphalts with an increase in consistency as determined by viscosity, penetration, and ductility tests. Weathered asphalts at constant temperature have flow properties that vary with the magnitude of shearing stress. At low stresses up to a certain limit, the viscosity is constant and the shear stress is proportional to the shear rate. Beyond this stress limit, the flow in non-Newtonian and the shear stress is proportional to the shear rate raised to the power of b. It requires, therefore, three constants to characterize the flow properties of non-Newtonian asphalts in the described stress range. It is suggested to compare the viscosities at a given shear rate of an asphalt before and after weathering as a measurement of durability without taking the flow properties into consideration. It is shown that this disregard can lead to wrong interpretations of the tests and can lead, under certain circumstances, to lower viscosities and higher penetrations of the weathered asphalts than those of the originals. Flow properties at low stresses are difficult to measure, but based on the behavior of asphalts in pavements, a large amount of weathering is accompanied by a large decrease in the value of the parameter b, which can be easily obtained from viscosity as well as penetration measurements. The significance of ductility is discussed in the light of present knowledge, and it is shown that a decrease in the ductility of an asphalt after weathering is also accompanied by a decrease in the value of the parameter b. A great change in the flow properties of a weathered asphalt is not the cause but the effect of failure in a pavement. Failure is due to the presence of large residual stresses in the asphalt film, which are mainly caused by the considerable difference in the coefficients of expansion of mineral aggregate and asphalt. This phase is discussed on the basis of the total energy present. It is demonstrated that residual stresses can be reduced and the durability of the pavement improved by proper selection of the mineral aggregate.

Majidzadeh, K. (1969). "Rheological Aspects of Aging-2." Nat Acad Sciences-Nat Research Council-Highway Research Rec **273**.

Effect of aging of asphaltic binder on theological response of sand-asphalt mixtures is studied; experiment and method of analysis follow procedures outlined in earlier report indexed in Engineering Index 1968 p 2651; Creep response of sand-asphalts at various temperatures and aging were analyzed, and viscoelastic model parameter and overall response were related to asphalt aging index; analysis of activation energy was carried out. 14 References

Martin, K. G. (1966). "Influence of Stabilizers on Bitumen Durability." Journal of Applied Chemistry **16**.

Combinations of 8 asphaltic bitumens and 12 selected antioxidants have been examined for susceptibility to oxidative hardening. Bitumen films 40 microns thick were oxidized at 300 psi in the dark and by simple exposure to solar radiation. Subsequent changes were determined with the sliding plate microviscometer. Many combinations exhibited improving stability and their behavior is discussed in relation to the current theory of autoxidation of hydrocarbons.

Mcgennis, R. B., S. Shuler, et al. (1994). "Background of Superpave Asphalt Binder Test Methods. Final Report." FHWA-SA-94-069.

This manual represents the first formal training document that embodies the complete series of SUPERPAVE asphalt binder test equipment and procedures. These tests and procedures represent the results of the Strategic Highway Research Program (SHRP) 5-year research effort to investigate and improve asphalt cement technology. This manual was developed under the Federal Highway Administration's National Asphalt Training Center. Students attending the center utilize this manual to obtain a better understanding of the underlying theory behind asphalt cement testing, as well as how to perform each of the new procedures.

Mcmullen, B. J., W. R. Vavrik, et al. (2001). "Effect of Short Term Oven Aging on Volumetrics and Selection of N-Design." Transportation Research Board.

This report presents findings on the effect of conditioning time on the volumetric properties of Superpave Gyratory Compactor (SGC) prepared asphalt mixtures. Field mixtures were sampled from the producing plants and then recreated in the laboratory following 3 different short-term conditioning procedures to measure the effect on the N-design value of the mixture. The projects selected represent three different N-design levels, have different nominal maximum aggregate size, aggregate sources, and asphalt binder types. Bulk Specific Gravity (Gmb) samples were aged at compaction temperature for 1-hr, 2-hr, and 4-hr. Maximum Specific Gravity (Gmm) samples were also aged at compaction temperature for 0-hr, 2-hr, and 4-hr. The short-term aging times are based off of Illinois Department of Transportation aging procedures, current National Center for Asphalt Technology recommendations, and the original Superpave conditioning specifications. It was observed in this study that increased conditioning time has a greater impact on the volumetric properties of polymer-modified binder mixes than on neat binder mixes. Also, noticed is that the presence of polymers in the binder appears to have greater effect than the higher temperatures used for conditioning polymer-modified HMA.

Migliori, F. and J.-F. Corte (1998). "Comparative Study of RTFOT and PAV Aging Simulation Laboratory Tests." Transportation Research Record(1638).

Tests were performed on unmodified asphalts of 35/50 grade penetration produced by French refineries to determine whether a prolonged pressure aging vessel (PAV) test would provide similar results to those obtained using the Strategic Highway Research Program coupled aging procedure, rolling thin film oven test (RTFOT) and PAV. Asphalts subjected only to PAV tests and identical samples after RTFOT and increasing PAV time were compared on the basis of (a) conventional consistency tests, penetration at 25 deg C, ring and ball softening temperature; (b) asphaltene content; (c) creep rheological tests at low temperature with bending beam rheometer; and (d) complex modulus tests with the Metravib dynamic rheometer. The results show that a hypothesis of equivalence between the effects of (a) RTFOT and 5 hr of PAV aging at 100 deg C and under 2.1 MPa and (b) RTFOT + 20 hr of PAV and 25 hr of PAV under the same conditions seems acceptable for the category of asphalts investigated.

Miller, R. W. and K. S. Dodge (1979). "Effects of Heated Storage on Asphalt Concrete." NYSDOT, FHWA report **NYSDOT-ERD-79-SR-65; FHWA/NY/SR-79/65**.

Asphalt hardening in three bituminous concrete top-course mixes was studied after storing at elevated temperatures for periods of 18 and 48 hours in inert gas, and 24 hours in a normal atmosphere. Asphalts extracted from loose mixes before and after storage, and from compacted mixes at the time of placement and after up to 7 years of service, were tested for penetration (77 F), absolute viscosity (140 F), and kinematic viscosity (275 F). The consistency of asphalt in the three mixes was not altered by storage, but delayed hardening was measured in one mix after 1 year of service, the second after 3 years, and the third after 6 years. These differences after once appearing have persisted but have not been reflected in pavement performance. The cause of the delayed hardening is unexplained.

Mirza, M. W. and M. W. Witczak (1995). "Development of a Global Aging System for Short and Long Term Aging of Asphalt Cements (with Discussion)." Journal of the Association of Asphalt Paving Technologists **64**: 393-418.

One of the major issues in the development of the performance based specification for asphalt pavements is the binder characterization and its relationship to pavement performance. Among the various factors used for binder characterization, the durability or hardening property of asphalt binder is one of the key factors. This paper describes a series of sequential analytical models that have been developed to predict the aging (viscosity increase) characteristics of conventional "S" type asphalt cements due to both short and long term effects. These models were developed from a statistical analysis of results in a Master Data Base comprised of asphalt consistency results and synthesized from 40 field projects throughout North America and Europe. The data base contained over 2300 separate line entries relating to consistency information obtained at either a given time and/or depth within the asphalt pavement layer from a particular field project.

Moavenzadeh, F. and J. R. R. Stander (1967). "Effect of Aging on Flow Properties of Asphalts." Highway Research Board Record: 29.

The effect of aging on the flow properties of three asphalts of different origins was studied at different temperatures. The variables considered included the type of asphalt, the degree of aging, the temperature, and the shear rate. The flow of asphalts was measured by three different viscometers: a sliding plate microviscometer that covered a shear rate change of 0.00001 to 1 reciprocal seconds and a temperature range of 5 to 60 C, capillary viscometers, and a coaxial cylinder type of viscometer. Aging was done with a modified thin film oven with rotating tilted shelves. A limited study was performed to determine the change in the average molecular weights of asphalts and their asphaltene and maltene components. The results of this study showed that for the three asphalts studied and for the method of aging used, aging may result in the following changes: (a) aging increases the degree of non-Newtonian flow behavior. The change in the free energy of activation may be used as a measure of this influence:; (b) aging increases the maximum temperature at which non-Newtonian flow behavior is exhibited; (c) as the aging progresses, the asphalt becomes more strongly bonded and less temperature susceptible in the low temperature region (below the softening point temperature); (d) in the higher temperature ranges, however, the situation is quite different. The aging process reduces the size of the large molecules, and their ability to trap the small oily molecules is restricted so that they are more loosely held. Increasing the test temperature can more easily release these molecules, and therefore the asphalt is more susceptible in the higher temperature range after it is aged; (e) the softening point increases with aging. A significant change takes place in the asphalt flow behavior within a narrow range of temperature, and the ring and ball softening point is within this range; (f) the aging of the asphalt to any significant degree does not seem to change the average molecular weight of the asphalt substantially; (g) flow data obtained by different viscometers are consistent, and different viscometers can be used to obtain shear data over a wide range of shear rate or shear stress. The principle of reduced variables can be used to further extend this range by reducing the data obtained at different temperatures to an arbitrary base temperature; (h) aging increases the proportion of asphaltenes in each asphalt. Some breakdown of the complex asphaltene units may be taking place.

Moavenzadeh, F. and E. B. B. Sendze (1965). "Effect of Degree of Aging on Creep and Relaxation Behavior of Sand-Asphalt Mixtures." Highway Research Board Record **104**.

Previous work on the study of aging was reviewed. The creep parameters of mixture viscosity and modulus of recovery developed by Wood and Goetz were selected for comparing creep characteristics of aged and unaged mixes. Mixes comprised (by wt of aggregate) 9, 12, and 15 percent asphalt content (60-70 penetration grade) and Ottawa sand (maximum size, No. 16) with gradation corresponding to ASTM D 1663-59T. Mixes were aged at 77 (unaged), 140, and 225 F for 1 week. Specimens, 3.5 cm in diameter, 7 cm high, were tested in creep and relaxation. Maximum creep strain was limited to 1.2 percent and the relaxation strain was 1.4 percent. The rate of creep generally showed a decrease with the increase in aging. With higher asphalt content, the difference in the creep rates was less marked. Maximum relaxation load increased with aging. Semilog relations were developed showing the variation of mixture viscosity with degree of aging and the relation of maximum relaxation load to degree of aging.

Moavenzadeh, F. and R. R. Stander, Jr (1966). "Durability Characteristics of Asphaltic Materials." OSU report **EES-259-I; 0573**: 247.

The work included: (a) The rheologic analysis of the flow behavior of three asphalts under different shear rates and at various temperatures. (h) The use of three viscosity measuring instruments to obtain rheologic properties over a wide range of temperature and shear rate. (c) The aging of the asphalts to different levels and the determination of their flow behavior. (d) The application of various rheologic models, including especially the hyperbolic sine model, to the flow of asphalt. (e) The chemical separation of the asphalts into asphaltene and maltene components and the determination of aging effects on these components. (f) The measurement of intrinsic viscosity of the aged and unaged asphalts and their components to determine the effects of aging on composition and molecular weight. (g) A limited study of tests such as glass transition and direct molecular weight.

Moavenzadeh, F. and R. R. Stander (1966). "Durability Characteristics of Asphaltic Materials." Research Report EES-259 **259-1**: 236.

Relations between the mechanical variables and the degree of aging of asphaltic materials were studied to determine the effect of aging on such a relationship. Rheologic analysis was made of the flow behavior of three asphalts under different shear rates and at various temperatures using three viscosity measuring instruments. Asphalts were aged to different levels and their flow behavior determined using various rheologic models, including the hyperbolic sine model. The intrinsic viscosity was measured of the aged and unaged asphalts and their components to determine the effects of aging on composition and molecular weight. Glass transition and direct molecular weight tests were studied. It is concluded that flow data obtained by different viscometers are consistent when adjusted for errors of the geometry of the instruments, and the temperature dependency of viscosity requires that viscosity variation with temperature at fixed shear be larger than that at fixed shear rate. An examination of the applicability of Eyrings hyperbolic sine relation to the analysis of the flow of the three asphalts used reveals that: 1. For these three asphalts there exist critical shear stresses, beyond which the hyperbolic sine relations fails to represent the flow behavior of each material, and 2. When these critical shear stresses are within the experimental range, the flow results cannot be represented by such a relationship. The degree of aging influences the non-Newtonian response of the material, and the change in the free energy of activation may be used as a measure of this influence. The aging of the asphalt to any particular degree does not seem to change the average molecular weight of the asphalt substantially.

Montepara, A. and F. Giuliani (2000). "Performance Testing and Specifications for Binder and Mix Comparison between Ageing Simulation Tests of Road Bitumen." Department of Civil Engineering University of Parma,Parma,Italy.

The present work gives a contribution to the evaluation of the effectiveness of ageing simulation tests in road bitumen. In particular,a comparison between the effects produced on two different natural bitumens by ageing laboratory techniques, such as Rolling Thin Film Oven, UV-Ray, Pressure Ageing Vessel is presented. By varying the duration of exposition and, in general, the magnitude of ageing action, the equivalence of certain effects produced on bitumen through the different techniques is reported. The results of the experimental investigation allows an analysis of the variation of chemical composition of bitumen and of its performance specifications with the magnitude of ageing action. The comparison between ageing simulation tests has been stimulated by the concluding debate during the recent Eurobitumen Workshop,held in Luxembourg. During the Workshop in fact, the necessity of researching new techniques and of implementing the existing ones for short-and long-term ageing simulation of road bitumen has clearly emerged.

Morrison, W. R. (1969). "Laboratory Investigation of Aging Characteristics of Asphalt Cements Used in Membrane Lining Construction." **CHE-91**: 47.

Laboratory test results are given for an oven aging test and thin film oven test for determining the aging characteristics of asphalt cements used in membrane lining construction. Hardening is allied to penetration, ductility, and an increase in softening point. (Author)

Mouillet, V., J. Lamontagne, et al. (2003). "Development of a New Methodology for Characterization of Polymer Modified Bitumens Ageing by Infrared Microspectrometry Imaging." Performance Testing And Evaluation Of Bituminous Materials PTEBM '03. Proceedings Of The 6th International Rilem Symposium Held Zurich, Switzerland, 14-16 April 2003. 2003.

This paper presents the results of a study of the ageing of different polymer modified bitumens (PmBs) containing either saturated plastomers or unsaturated elastomers. Firstly, PmB's ageing throughout its whole service life could be simulated by applying conventional ageing tests, RTFOT, for the mixing process and laying of asphalt concrete, and PAV for in service ageing. Changes in the bitumen properties before and after ageing were thus recorded. Secondly, an ageing cell specially designed to fit the FTIR microscope was developed to study directly and continually the PmB's oxidation by FTIR microscopy imaging. The results obtained by following simultaneously both phases evolution, allow to propose a method to measure changes in PmB's chemical composition. These changes are both bitumen and polymer dependent. Finally, the kinetics study shows that RTFOT and PAV can be simulated in the ageing cell in a quicker way. In conclusion, the design of an ageing cell associated to the FTIR microscope appears to be a very effective tool to observe and chemically study the microstructure of PmBs during ageing. It also gives some insights to evaluate PmB's durability. For the covering abstract see ITRD E117423.

Neppe, S. L. (1951). "Durability Properties of Asphaltic Bitumen, a Review of the Literature." South African Institute of Civil Engineers **1**.

Literature on the hardening of bitumens is reviewed, with particular reference to critical penetration and ductility limits as affecting the disintegration of road surfaces. A critical survey is given of the methods for the evaluation of binder durability, covering the action of heat on thin films, oxidation, and sunlight, with special emphasis on ultraviolet and infrared radiations. Certain anomalies leading to incorrect interpretation of results in the graphical representations of experimental data by certain other investigators are pointed out, and the author illustrates the practical value of his conception of "true penetration." The term "percentage drop in penetration," as used in most bitumen specifications, is shown to be fundamentally unsound, and should be replaced by the more logical "percentage drop in log true penetration." 107 references are given.

Neppe, S. L. (1952). "Durability of Asphaltic Bitumen as Related to Rheological Characteristics." Trans., S. African Institute of Civil Engineers **2**: 103.

An extensive study is reported, covering the durability of asphaltic bitumen as related to theological characteristics. Six new methods for evaluation that have been evolved by the author are described and discussed. These are: (a) viscosity number - relating viscosity at any one of three temperatures 140, 158, and 176 F, to bitumen penetration at 77 F, (b) softening point number - relating R and B softening point to penetration, (c) softening point viscosity number - relating viscosity at 140, 158, 176 F to softening point; (d) fluidity characterization factor - based on absolute viscosity vs. temperature relationships over a wide range of temperatures from 77 to 275 F or higher, (e) penetration susceptibility factor - the temperature range over which penetration changes from 100 to 10, (f) ductility susceptibility factor - the temperature range over which ductility changes from 100 to 1. The data given amply support the author's concept of softening point number as a measure of bitumen stability. Softening point number is a rheological characterization index read directly from a chart and relating standard penetration at 77 F with softening point. It is shown that under identical conditions of exposure, the most drastic changes in characteristics invariably occur in bitumens of low softening point number. The higher this index, the longer is the life of the bitumen under the action of heat and weathering.

Noureldin, A. S. (1995). "Oxidation of Asphalt Binders and Its Effect on Molecular Size Distribution and Consistency." ASTM Committee D-4 on Road and Paving Materials(STP 1241,; ASTM PCN: 04-012410-08).

This paper presents a study in which the changes in molecular size distribution and consistency, of a given asphalt, caused mainly by oxidation during the thin film oven test (TFOT) are investigated. Samples of asphalt cement with the same consistency were exposed to various levels of oxidation (specific periods of time during the TFOT) and then characterized by means of consistency tests (penetration and viscosity). These samples were also characterized employing the high pressure liquid chromatography in the gel permeation mode referred to as the high pressure gel permeation chromatography (HP-GPC). It was concluded that the artificial weathering of the asphalt cement binder (used in this study) resulted in a significant increase in large molecular size (LMS) percentage associated with a significant decrease in medium molecular size (MMS) and small molecular size (SMS) percentages. Regression analyses provided relationships between the asphalt binder consistency (penetration and viscosity) and the relative percentages of LMS, MMS, and SMS.

Oakes, D. T. (1969). "Oxidation Cracking of Asphalt Pavement." Mississippi DOT report **RR-3**: 25.

The report presents a study of weathering effects of fluids on a compacted asphalt aggregate mixture and the mechanisms of deterioration in such a system. Deterioration is measured by changes in sonic modulus, 'Young Modulus' (stiffness), and in permeability (as an indicator of pore channel sizes and distribution of asphalt in the system). The weathering variables include air, water, and temperature. (BPR)

Oft, W. P. V. (1956). "Durability of Asphalt: Its Aging in the Dark." Industrial and Engineering Chemistry **48, No -7**: 6.

According to the literature, the action of oxygen is one of the principal factors responsible for the occurrence of aging phenomena. When asphalt is exposed to atmospheric oxygen, a slow autoxidation occurs, the chemical nature of which depends to a very large extent upon the temperature. At temperatures above 100 C dehydrogenation takes place, as is evident from the water produced. Some carbon dioxide is also formed. At lower temperatures e.g., 25 or 50 C, the oxygen involved in the oxidation is quantitatively bound in the bitumen and no water or carbon dioxide is formed. The overall rate of oxygen absorption was found to be not only determined by the chemical nature of the asphalt, but also by the physical transport of the oxygen from the surrounding atmosphere to the interior of the material. Therefore, it is also a physical problem, one of diffusion in particular. Measurements were made on asphalt in thin films at temperatures between 20 C and 70 C in the absence of light. Seven types of asphalts were studied. Several grams of each asphalt were made into a thin film (5-10 microns) by mixing grains of sand, as nearly as possible of uniform size, with the asphalts in a heated mixer, which could be provided with an inert atmosphere. The oxygen absorbed, as measured by a conventional volumetric method, by the different asphalts at 22 C in the dark for 50 weeks is presented. The change in viscosity after exposure of the asphalt was also measured with a specially developed micro technique. The rate of absorption and the rate of hardening were observed to decrease with time. The absorption process was not complete at the end of one year. Different asphalts showed significantly different rates. A theoretical model of oxygen absorption is proposed. The model permits the calculation of the total oxygen absorbed by whole layer from the knowledge of film thickness, time, a diffusion coefficient, a reaction coefficient, and other constants. Some experiments were carried out to ascertain the assumptions on which the model was based. The experiments indicated that assumptions made are valid. Other experiments to study factors affecting the absorption mechanism indicated that pressure of oxygen, temperature, and film thickness are the major factors affecting absorption. Lower pressure, lower temperature, and increased film thickness result in decreased absorption. Also, as the viscosity of asphalt increases (or penetration decreases), the coefficient of diffusion of oxygen decreases. The diffusion coefficient was found to depend on the concentration of chemically bound oxygen. As the later increases the coefficient decreases.

Oliver, J. W. H. (1984). "An Interim Model for Predicting Bitumen Hardening in Australian Sprayed Seals." Proceedings of Australian Road Research Board **12**.

A number of sprayed seal road trials to monitor bitumen hardening has been laid in different areas of Australia over the past 14 years. Previous analyses have been confined to relating the viscosity of bitumens recovered from the seals to single variables such as durability test result. Sufficient data now exist to develop a multi-variable model of bitumen hardening. Analysis has indicated that the equation log n = -3.34 + .0394 YMMT (t^0.5) - .023 D (t^0.5) explains 93 percent of the observed variance in log viscosity in 152 sets of test results, where n is the viscosity (Pc.s) of the extracted bitumen, YMMT (C) is the yearly mean of the maximum daily air temperature at the site, D (days) is the ARRB durability test result, and t (years) is the period of seal service. There is insufficient data from pavements near the distress condition for an accurate prediction of viscosity in this region. It is important that the trial sections continue to be sampled to obtain this information as well as information on the bitumen viscosity levels associated with distress in different climatic regions. Once this information has been obtained it should be possible to predict maximum seal life based on durability test result and meteorological parameters for the particular site.

Oliver, J. W. H. And P. F. Tredrea (1996). "The Change In Properties Of PMBs With Simulated Field Exposure." ARRB Transport Research Ltd, 500 Burwood Highway, Vermont South, Victoria, 3133, AUSTRALIA (30$A).

To determine whether the properties of commonly used polymer modified binders (PMBs) changed substantially during pavement service, thin films of PMB were exposed for up to 116 days in an oven at 70 degrees Celsius. The samples were tested using a dynamic shear rheometer (DSR) before and after exposure. Special test techniques were developed which permitted exposed samples to be treated without the heating stage normally required to mould DSR specimens. Oven exposure resulted in large changes in the rheological behaviour which reduced the advantage in performance in service which fresh PMBs have over unmodified bitumens. A secondary aim of the work was to develop a test procedure suitable for routine use. Rolling Thin Film Oven (RTFO) equipment was modified to permit testing of PMBs. The treatment produced similar rheological changes to the long-term exposure for all the binders except the EVA binder at low loading frequencies. A need for tests to indicate both high temperature resistance and long-term oxidation resistance was identified.

Oliver, J. W. H. and P. F. Tredrea (1997). "The Change in Properties of Polymer Modified Binders with Simulated Field Exposure (with Discussion)." Journal of the Association of Asphalt Paving Technologists **66**.

The aims of the study were to: (i) develop a method for dynamic shear rheometry (DSR) measurement on undisturbed samples subjected to a laboratory aging procedure which realistically simulated field exposure, and to thus determine whether the properties of polymer modified binders (PMBs) changed during pavement service; (ii) modify Rolling Thin Film Oven (RTFO) test equipment so that it could be used for PMBs; and (iii) determine whether an extended form of the modified RTFO test could be used to indicate the long term oxidation resistance of PMBs. It was found that long term laboratory exposure at a temperature below the maximum encountered in pavement service resulted in large changes in the rheological behavior of the PMBs and that these changes were likely to reduce the advantage which fresh PMBs have over unmodified asphalts in service. In the fresh state there were considerable differences in properties between the different PMBs but these differences were reduced after exposure. Simple modifications were made to RTFO test equipment so that RTFO treatment could be used with PMBs. Extended RTFO treatment was found to produce similar rheological changes to simulated field exposure for all the binders except an ethylene vinyl acetate (EVA) binder at low loading frequencies.

Page, G. C., K. H. Murphy, et al. (1985). "Asphalt Binder Hardening - Causes and Effects." Proceedings of the Associationof Asphalt Paving Technologists **54**.

To identify the relationships between binder hardening and certain variables, data from hour temperature-reduction projects in Miami were analyzed to evaluate the hardening trends. Each project contained test sections with two different mix temperatures. Penetration, absolute viscosity at 60 C (140 F), and apparent viscosity at 25 C (77 F) were determined for original and TFOT residue. The same test parameters were also obtained for asphalts recovered by the Abson procedure from samples at the pugmill, paver, and at different time intervals from the in-service

pavements. Air void contents were also determined for samples (cores) taken from the pavements. Based on results of the analyses and asphalt hardening trends the following conclusions are derived: (a) the TFOT is considered representative of the hardening which occurs in the hot mix plant for the AC-20 grade asphalt cements used in this study. A high degree of correlation was obtained between the difference in asphalt viscosity (TFOT minus original) and the recovered asphalt viscosity after eight years of service. Asphalts that are susceptible to greater TFOT hardening may also produce greater hardening in the plant mixing process as well as greater in-service age hardening; (b) the effects of age and air void content on asphalt binder hardening are not clearly distinguishable because of changes in air void due to traffic densification. However, when considering air void content at some selected age, the recovered asphalt viscosity or penetration usually indicates harder asphalts for high air void content samples; (c) simulation of in-service hardening appears to be feasible by using asphalt in mixtures compacted to different air void contents and then subjected to heating in an oven at 60 C (140 F) for 12 hours; (d) certain asphalts harden substantially at the high plant mix temperatures whereas other asphalts are unaffected by changing plant mix temperature. The value of TROF or RFT tests may be enhanced by altering test procedures to accommodate a series of test temperatures (e.g. 275 F, 300 F, 325 F, 350 F, and 375 F). The viscosity and/or penetration of these residues 'would aid in identifying the amount of hardening that could occur at a specific plant.

Pauls, J. T. and J. Y. Welborn (1952). "Studies of the Hardening Properties of Asphaltic Materials." Proceedings, Association of Asphalt Paving Technologists **21**: 48.

The rate of hardening of asphaltic mixtures is an important factor in the service life of bituminous pavements. In this study of the hardening properties of a large number of asphaltic materials, a test method was developed in which molded Ottawa-sand asphalt specimens were weathered in an oven at 325 F for different periods of time and then tested for compressive strength without lateral support. The basis for this procedure is the knowledge that the compressive strength of moded mixtures of asphalt and Ottawa sand, when tested without lateral support, is a measure of the hardness of the asphaltic binder. Oven weathering of the compression test specimens produced wide differences in the compressive strength of mixtures containing asphalts from various sources and produced by different methods of refining. Tests on the asphalts recovered from these weathered mixtures showed that the compressive strength was closely related to the consistency of the contained asphalt. Exposure of the asphalts to the thin-film oven test at 325 F produced changes in the asphalt similar to those produced by the oven weathering of sand-asphalt mixtures. It was thus further demonstrated that the thin-film oven test does indicate the relative resistance of asphaltic materials to hardening. Since the test procedure is relatively simple, the thin-film oven test should prove highly useful in evaluating this important property of asphaltic materials.

Pauls, J. T. and J. Y. Welborn (1953). "Studies of the Hardening Properties of Asphaltic Materials." Public Roads **27**: 187.

Experimental work by the authors led to the following conclusions: (a) bitumens of different crude origin have different hardening properties, (b) hardening properties depend upon method of manufacture, (c) cracked bitumens become hard and brittle more rapidly than distilled bitumens; on weathering, they also develop a higher degree of hardness and brittleness, the rate of hardness increasing with the degree of cracking, (d) increase in hardness, measured by

decrease in penetration, is accompanied by increase in softening point and decrease in ductility and solubility. During the course of the work, 2 new methods, the abrasion test and the weathering strength test, were developed, involving the measurement of the change in physical properties on exposure to heat and the atmosphere, of standard sand-asphalt mixtures. The thin-film oven test was found to be a more speedy and simpler test of measuring these hardening properties.

Periasamy, R., J. R. Newsome, et al. (1992). "Gas Permeability Measurements on Asphalt Using the Electrodynamic Balance. In: American Chemical Society Symposium on Chemistry and Characterization of Asphalts, August 1990, Washington, D.C." Fuel Science & Technology International. 1992/05.

A novel experimental method developed for the measurement of the transport properties such as the diffusion coefficient, D, solubility, S, and permeability, P, for oxygen into asphalt materials using an electrodynamic balance is described. Both unaged and aged rolling thin-film oven test (RTFOT) asphalt particle samples in the 12 to 62 micrometer size range were suspended contactless and weighted in the balance to measure D, S, and P in the temperature range 17 degrees Celsius to 66 degrees Celsius. Volatilization rate data were obtained from the particle mass measurements made prior to the start of the sorption experiments. Sorption curves obtained in this study for unweathered asphalt samples showed a non-Fickian, two-stage type sorption behavior indicating the possibility of an additional mechanism other than diffusion. Analogous behavior in sorption was observed for weathered samples.

Petersen, J. C. (1984). "Chemical Composition of Asphalt as Related to Asphalt Durability: State of the Art." Transportation Research Board.

The literature on asphalt chemical composition and asphalt durability has been reviewed and interpreted relative to the current state of the art. Two major chemical factors affecting asphalt durability are the compatibility of the interacting components of asphalt and the resistance of the asphalt to change from oxidative aging. Historically, studies of the chemical components of asphalt have been facilitated by separation of asphalt into component fractions, sometimes called generic fractions; however, these fractions are still complex mixtures the composition of which can vary significantly among asphalts of different sources. The reaction of asphalt with atmospheric oxygen is a major factor leading to the hardening and embrittlement of asphalt. The hardening phenomenon is primarily a result of the formation in asphalt of polar oxygen containing functional groups that increase asphalt consistency through strong molecular interaction forces. The identification and characterization of the chemical functional types normally present in asphalt or formed on oxidative aging that influence molecular interactions afford a fundamental approach to relating asphalt composition with asphalt properties and thus the performance of both asphalts and asphalt-aggregate mixtures. In addition to the polar chemical functional groups formed on oxidation, asphalt properties can also be significantly altered by molecular structuring, sometimes called steric hardening. This potentially reversible phenomenon, although highly elusive and difficult to quantify in asphalt pavement mixtures, may also be a major factor contributing to pavement embrittlement.

Petersen, J. C. (1989). "A Thin Film Accelerated Aging Test for Evaluating Asphalt Oxidative Aging." Proceedings of the Association of Asphalt Paving Technologists: 220-237.

An accelerated laboratory aging test is described in which asphalt is oxidatively aged as a thin film at elevated temperatures in a rolling thin film oven bottle to simulate the level of oxidative age hardening that typically occurs during extended pavement aging. The test is a modification of the Schmidt rolling microfilm (RMF-C) test. The sample size has been increased from 0.5 g to 4.0 g to provide sufficient sample for chemical and rheological evaluation of the aged asphalt. In the test, volatile loss, the level of chemical oxidation, and the increase in viscosity are similar to those which occur during field aging.

Petersen, J. C., J. F. Branthaver, et al. (1993). "Effects of Physicochemical Factors on Asphalt Oxidation Kinetics." Transportation Research Board.

Oxidative aging of asphalt is a primary cause of asphalt hardening in pavements, thus contributing to various forms of pavement cracking. Although the changes in asphalt physical properties on oxidative aging are primarily the result of the formation of oxygen-containing functional groups in the asphalt, the sensitivity of an asphalt to these oxidation products varies widely with asphalt source (composition). An understanding of the kinetics of oxidation in the pavement temperature range is confounded by both the complex composition of asphalt and its thermally reversible microstructure. To better understand the mechanisms of age hardening, the kinetics of asphalt oxidation were investigated from the pavement temperature range [60 deg C (140 deg F)] through the higher temperature range of commonly used accelerated laboratory tests [130 deg C (266 deg F)]. It was found that asphalts with different component compatibilities may exhibit similar age hardening kinetics at the low end of the pavement temperature range, but quite different kinetics at the high end of the range. This is because the aging kinetics become highly dependent on how temperature affects the molecular microstructure. A new microstructural model of the age hardening of asphalt cement is presented that proposes that the kinetics of aging in the pavement temperature range is largely governed by physicochemical factors related to the state of dispersion of the molecular microstructure rather than the inherent reactivity of the molecular components with oxygen. The model is supported by results of past and present research..

Petersen, J. C. and P. M. Harnsberger (1998). "Asphalt Aging: Dual Oxidation Mechanism and Its Interrelationships with Asphalt Composition and Oxidative Age Hardening."

The kinetic data and chemistry of asphalt oxidative age hardening suggested a sequential, dual mechanism for asphalt oxidation. The dual mechanism rationalizes conflicts between earlier mechanistic investigations and explains the hyperbolic-like, time-versus-property plots characteristic of asphalt oxidative aging. The oxidation kinetics provide further confirmation of the asphalt microstructural model. It is proposed that the rapid initial oxidation rate of asphalt results from reaction of oxygen with limited amounts of highly reactive hydrocarbons. Final oxidation products of this initial reaction are sulfoxides and, most likely, ring aromatization. During this initial reaction, a slower oxidation reaction of asphalt benzylic carbons is initiated; final products are ketones and sulfoxides. The ratio of ketones to sulfoxides formed and the rate of age hardening were found to be dependent on temperature and oxygen pressure. Low-temperature oxidative aging, as occurs in pavements, was found significantly more sensitive to variations in temperature and asphalt composition than 100 deg C pressure vessel aging.

Peterson, J. C. and P. M. Harnsberger (1998). "Asphalt Aging: A Dual Oxidation Mechanism and It's Inter Relationships with Asphalt Composition and Oxidative Age Hardening." Transportation Research Record.

Phromsorn, C. J. and T. W. Kennedy (1995). "Evaluation of Laboratory Methods Simulating Aging Effects of Asphalt Binder." Transportation Research Record(1488).

The effects of short-term and long-term aging are important when evaluating the properties of asphalt binder. Thus, the properties of asphalts aged for the short term and the long term are considered in the Superpave binder specification. The most practical way of predicting the effects of aging within an asphalt binder is through laboratory simulation methods. For many years the thin film oven test (TFOT) method and the rolling thin film oven test (RTFOT) method have been used to simulate short-term aging. To simulate long-term aging the pressure aging vessel (PAV) method was developed within the Strategic Highway Research Program. However, the Superpave binder specification uses only the RTFOT method for short-term aging and uses RTFOT along with the PAV method for long-term aging. For a short period of time AASHTO considered the use of either the TFOT method or the RTFOT method and then the PAV long-term aging procedure for short-term aging. Unfortunately, few published data address this issue. The test data from a testing program conducted to evaluate these laboratory procedures for short-term and long-term aging with different asphalt binders are presented. The effects of aging are evaluated by dynamic shear stiffness, measured by using the dynamic shear rheometer at three intermediate temperatures. The data indicate that there are no significant differences at the 95% confidence interval between the properties of RTFOT-aged residues and those of TFOT-aged residues after exposure to the PAV procedure. The differences before aging by the PAV procedure, however, still exist. It is recommended that only one short-term aging procedure be used for the Superpave binder specification and that work be conducted to develop or improve the short-term aging procedure.

Planche, J.-P. (2002). Personal Communication. D. A. Anderson. Paris, France.

Poulikakos, L. D., M. B. Sayir, et al. (2003). "A New High-Frequency Torsional Rheometer for Bituminous Binders." Proceedings of the 6th International RILEM Symposium held Zurich, Switzerland,.

When a rod is performing torsional vibrations at one of its resonance frequencies, any interaction with a viscoelastic medium will change both its resonance frequency and its damping characteristics. By measuring this change, modulus, phase angle, elastic and viscous constants of a bituminous binder can be obtained. The new High-Frequency Torsional Resonance Rheometer (HFTR) developed at ETH Zurich and presented in this study is based on this principle. In comparison to prevailing rheometers, the HFTR is inexpensive and has various technical advantages. It can be embedded in the binder or placed on its surface and is suited for laboratory and field measurements. High frequencies in the 1 to 60 kHz range allow the measurements to be unaffected by traffic induced low frequencies, which makes it ideal for field measurements. The HFTR can also be used for continuous monitoring of binder aging effects or as a portable fingerprinting tool for materials characterization in the laboratory. In addition, it allows continuous measurements during binder production. This study focuses on the measurement technique using the HFTR for laboratory experiments involving conditioning of bitumen in a high temperature oven. Furthermore measurement uncertainties and practical examples are discussed. For the covering abstract see ITRD E117423.

Ramamurti, K., G. P. Jayaprakash, et al. (1984). "Microbial Biodeterioration of Asphalt and Related Hydrocarbons- A Literature Review." FHWA Report **FHWA/KS-84/I**: 51.

A survey of the literature related to microbial biodeterioration of asphalt and related hydrocarbons revealed European reports as early as 1895. U.S. studies related to microbial utilization of hydrocarbons date back to about 1910. Later many studies demonstrated microbial utilization of asphalt and related hydrocarbons, particularly the petroleum hydrocarbons. These studies show a fairly large number of microorganisms capable of utilizing asphalt and related hydrocarbons. The microorganisms are normal inhabitants of the soil and often belong to the following genera: Pseudomonas, Micrococcus, Flavobacterium, Mycobacterium, Corynebacterium, etc. The intensity of microbial attack depends on the types of microorganisms, moisture, temperature, oxygen, pH, composition of asphalt, etc. Under favorable conditions, microbial activity could cause rapid oxidation of hydrocarbons but usually any effect on roads would take decades. Several investigators gave specificities relating to bacterial types and described the type of asphalt used in the study. There is some indication that microbial activity can cause changes in the theological characteristics of asphalt. Bacteria are adaptive, hence bacterial infestations are hard to suppress. The literature surveyed did not reveal any universal panacea for suppression.

Reese, R. (1997). "Properties of Aged Asphalt Binder Related to Asphalt Concrete Fatigue Life." Proceedings Association of Asphalt Paving Technologists **66**: 604-630.

The proposed Strategic Highway Research Program (SHRP) asphalt binder specification includes a parameter that is represented as a fundamental binder property that contributes to pavement fatigue life. However, it has been the observation of some that the fatigue parameter, G* sin delta, does not correlate adequately with field performance data. There has also been some concern expressed that the parameter may actually allow the use of binders which, in previous experiences, have been used in pavements that have exhibited very poor fatigue life. Thus, a study was conducted to compare binder properties with the fatigue life of mix containing various binders, including some with "extreme" properties, for which documented performance data exists. The evaluation of the binders in a controlled laboratory mix "failure" test was considered a necessary tie between the binder properties and the field performance data. The laboratory fatigue test provides for better control of variables, while the field data are a necessary reality check on the performance ranking. A part of this tie is the degree to which the laboratory failure test simulates field conditions, such as aging. While it was intentioned to address this in the fatigue testing in the SHRP research, time limitations precluded this task. Thus, for this study, the binders were all aged using binder accelerated aging procedures prior to their incorporation into a mix. This approach was chosen over long-term oven-aging of mix because, currently, the binder aging procedure has been correlated specifically with the appearance of premature fatigue cracking in the climate where the performance data exists (the desert) on some of the binders used in this study.

Richard, B., A. Justice, et al. (1966). "The Effect of Viscosity of Asphalt on the Properties of Bituminous Paving Mixtures. Part II. Early Hardening of Asphalt in Hot Bituminous Paving Mixtures." North Carolina State Univ., Raleigh. Highway Research Program. **ERD-100-L**: 82.

The investigation was a study of the hardening of the asphaltic binder that occurs in the early life of hot bituminous concrete pavements and in compacted samples cut from the pavements. The rate of hardening was established in hot bituminous wearing surfaces during the first 30 to 60 days of the pavement life. Asphalt of 85-100 penetration grade from four different supply sources and one 170 penetration grade asphalt was used. The hardening of the asphalt in compacted pavement samples was determined when stored at 9F, room temperature, and 140F. The effect of sealing the samples from the air and storing under water was investigated. The effect on the hardening of the rate of cooling of the hot samples was studied. The hardening in the road and in compacted samples varied with the different asphalts used. Hardening occurring in the first 10 days of service was often greater than that occurring in the mixing operation. The hardening of the compacted pavement samples during laboratory storage was very much dependent on temperature. For some of asphalts a sample stored for 20 days at room temperature lost 13% of its penetration. Storing samples under water or at 9F maintained samples close to their original hardness. Sealing samples from the air with thin asphalt layers was not effective in retarding hardening. Rate of cooling had measurable effects on the hardening that occurred. Hardening that had occurred in a few old roads was determined. The asphalt in surface courses of two pavements 15 to 17 years of age showed recovered penetrations of 15 to 18. For other pavements 5 years of age the penetrations of the asphalt varied from 18 to 24. (Author)

Rigden, P. J. and S. H. Kuhn (1959). "The Measurement of Viscosity of Very Small Samples of Bituminous Binders for the Study of Weathering on the Road." Proceedings, Association of Asphalt Paving Technologists **28**.

A method for measuring the viscosity of small samples (40-80 mgs) of bituminous binders is described. It consists essentially of compressing a small sphere of the binder under a known load and measuring the deflection as a function of time. The instrument used in the work measures viscosities in the range of 107 to 1012 poises. The ball viscometer has been used to follow increases in viscosity produced by weathering of binders on the road and a method for the sampling of weathered binders from a surface treatment and for the preparation of the sample for viscosity measurement is described. The accuracy of this method has been shown to be sufficient for measuring the large changes in viscosity procedure by weathering on the road. The results of tests on a full-scale surface treatment experiment are given as an illustration of the use of this method.

Roberts, J. M. and W. H. Gotolskl (1975). "Paving Asphalt Properties and Pavement Durability." Transportation Research Record **544**.

Thirteen asphalt concrete pavements built in Pennsylvania were studied from September 1961 to March 1973. As a result of an extensive sampling and analysis program, considerable information has been gained on the durability of asphaltic pavement. Based on physical test data (penetration, viscosity, and ductility) and percentage of asphaltenes, all of the asphalts used in the various pavements hardened with time

Romero, P., J. Youtcheff, et al. (1999). "Low-Temperature Physical Hardening of Hot-Mix Asphalt." <u>Transportation Research Board</u>.
A study was conducted to determine if low-temperature physical hardening, which has been reported to be exhibited by asphalt binders, also affects hot-mix asphalt. Two asphalt binders, designation AAM-1 and AAM-2 of the Strategic Highway Research Program, which are known to show the effects of physical hardening, were used to prepare asphalt mixtures with different mineral fillers. The asphalt mixtures were compacted into slabs from which cores were obtained and tested at low temperatures in the thermal stress restrained specimen test. Before testing, the cores were cooled unrestrained to -15 deg C and held isothermally for 1 h or 24 h. After conditioning, the specimens were restrained and held at a constant length while the temperature was dropped at a rate of 15 deg C per hour until the specimens fractured. The temperature at which the specimens fractured, the stress at the time of fracture, and the slope of the temperature-stress curve were measured and analyzed using several statistical techniques. The results showed that the mixture made with asphalt binder AAM-2 was affected by conditioning time. The mixture made with asphalt binder AAM-1 was not affected by conditioning time. Other factors, such as mineral fillers and air voids of the mixtures, had a greater influence on the results than did physical hardening.

Rostler, F. and K. S. Rostler (1981). "Basic Considerations in Asphalt Research Relating to Durability." <u>Proceedings Association of Asphalt Paving Technologists</u> **50**: 582-619.

Rostler, F. S. and R. M. White (1962). "Composition and Changes in Composition of Highway Asphalts, 85-100 Penetration Grade." <u>Proceedings of the Association of Asphalt Paving Technologists</u> **31**.
Comprehensive data on physical characteristics of 119 specimens representative of this grade of asphalt available in various regions of the country were presented and discussed. The present paper is an attempt to enlarge on the information made available by Welborn and Halstead by providing data on chemical composition and changes of composition during aging for the same asphalts. The 119 asphalts, investigated by Welborn and Halstead, were analyzed at three states: (1) as received, (2) after mixing with Ottawa sand, (3) after aging of the asphalt-Ottawa sand mixtures. Abrasion resistance of the asphalt-Ottawa sand mixtures before and after aging was used as an indication of quality and criterion for durability. The first part of the paper is devoted to explaining the fractional chemical analysis used in defining asphalts and to demonstrating the specific influence of the fractions on asphalt performance. The second part of the paper demonstrates the value of complementing data for physical characteristics of asphalts with those for chemical composition on the asphalt specimens previously investigated by Welborn and Halstead. The results obtained in the investigation and presented in the form of a progress report reveal a significant trend for the relationship between composition and performance of the asphalts, which relationship appears to be valid for a wide variety of asphalts. The analytical method employed holds promise as a means of predicting the performance of highway asphalts from their chemical composition.

Rowe, G. M., J. A. D'angelo, et al. (2002). <u>Use of the Zero Shear Viscosity as a Parameter for the High Temperature Binder Specification Parameter</u>. Rheology Conference, San Antonio.

Ruth, B. E., D. Bloomquist, et al. (1995). "Development and Evaluation of a Testing Device for Accelerated Age Hardening of Bituminous Materials. Final Report."

Equipment was designed, constructed, and modified to spray a thin film of asphalt onto the inside surface of Pyrex (Trademark) glass cylinders and to process the coated cylinders in a special forced draft oven system at process temperatures of 85 deg C and 110 deg C. The spray coating unit yielded film thicknesses of 3 to 5 micrometers. The age hardening device circulated hot air through the cylinders while rotating the cylinders to minimize flow and change in film thickness. Other test methods (e.g., TFOT, RTFOT, PAV, and CTO) were used for aging. Their viscosity results were compared to those from the age hardening device. The test results indicated that the PAV and accelerated age hardening device were more effective in producing age hardened asphalt than the other methods. It was recommended that the age hardening device could be substituted for the PAV since it produced hardening only slightly less than the PAV after 20 hours of aging.

Schmidt, R. J. (1973). "Laboratory Measurement of the Durability of Paving Asphalts." Symposium on Viscosity Testing of Asphalt and Experience with Viscosity Graded Specifications, American Society for Testing and Materials **Special Technical Publication No. 532**: 21.

The objective of this study was to develop a practical laboratory test to measure reliably the relative durability of paving asphalts. An approximate test must harden a wide variety of asphalts in the same order as for field exposure. The studies reported demonstrated that current asphalt durability tests do not properly relate to field hardening because they exaggerate unrealistically the volatile loss to obtain sufficient oxidative hardening. Four asphalts with widely different hardening properties were used in the study. Asphalt concrete (4 C) specimens using the same aggregates were prepared and exposed in a 140 F oven. At appropriate intervals, specimens were removed, asphalt was recovered, and microviscositics (at 77F, under a uniform stress of $167 g/cm^2$) were measured. These results were assumed to represent field hardening. Asphalt specimens were then used in running durability tests under different conditions, and the results compared to those of the extracted asphalts from the aged AC specimen. The rolling microfilm oven test (RMFO) was conducted on each asphalt to study the effect of the following: (a) mineral filler and temperature, (b) extra air circulation, (c) capillary venting, (d) simulating hot-mix hardening prior to test, and (e) increasing exposure time. Best correlations were found when using exposure of a 20 μm film at asphalt deposited on the walls of an RTFO bottle (vertical through a .04 lid diameter, 2-in long capillary tube) in an RTF circulating oven for 48 hours at 210 F. No effects of fillers were observed. Comparison of the new RMFC test results on asphalts used in the Zaca-Wigmore and the life of the test sections at 10 percent cracking shows a better correlation than that obtained using the RMFO test results. Comparison of RMFC exposure with hardening in recent California Division of Highways field tests also indicated that this test is useful in ranking asphalts in the same order as they harden in the field. The comparison indicated that asphalts will harden differently in each location and in each different kind of mix. Each different field condition would berepresented by an individual curve on a log viscosities chart.

Schmidt, R. J. (1973). "The Rolling Thin-Film Circulating Oven- an Improved Rolling Thin-Film Oven Test." ASTM Special Technical Publications. 1973/06.

The thin-film oven test (TFO), ASTM D 1754-69, is well established and functional; however, it requires 5 h exposure time. The rolling thin-film oven test (RTFO), ASTM D 2872-70 is also functional. Its precision is better, and it is faster to do. Unfortunately, the two exposures differ enough so they should not be used interchangeably without separate specification limits for each test. A good solution to this dilemma would be another oven exposure which has the advantages of the RTFO (that is short exposure time and high precision) and which, at the same time, affects asphalts in the same way as the TFO. This has been substantially accomplished by converting the RFT oven from a conventional oven to a forced-draft oven. The added circulation causes more volatile loss to occur. This rolling thin-film circulation (RTO-C) oven test not only gives exposures very close to the well-accepted TFO; but it is just as fast as the RTFO to perform. It is suggested that this new oven exposure be considered as a replacement for the RTFO and interchangeable with the TFO in specifications. (Author)

Shaw, J. M. (1953). "Aging Characteristics of Certain 50-60 Penetration Asphalt Cements -an Interim Report." Proceedings, Association of Asphalt Paving Technologists **22**: 21.

Aging of asphalt at room temperature was evaluated by (a) ductility after 7 and 28 days, (b) penetration after 14, 28, and 365 days, (c) a special cavitometer test at 2 hr, 7 days, and 28 days, (d) ball pressure to cause rupture at 3 hr, 7 days, and 28 days, (e) Schweyer stain number, (f) film hardening at 325 F for 1 hr, and (g) an index based on softening point, ductility, and penetration. Data were obtained on airblown and P O and FeCI catalytically blown asphalts. Results showed definite differences for asphalts from different manufacturers and methods of processing.

Shiau, J. M., M. Tia, et al. (1992). "Evaluation of Aging Characteristics of Asphalts by Using TFOT and RTFOT at Different Temperature Levels." Transportation Research Board.

The aging characteristics of 20 asphalts were investigated by using the thin film oven test (TFOT) and rolling thin film oven test (RTFOT) at three temperature levels. Infrared absorption spectroscopy and the Schweyer rheometer test as well as penetration and absolute viscosity tests were used to evaluate the characteristics of the asphalts before and after the TFOT and RTFOT. Data from the field were also used to compare with the laboratory results. On the basis of percent penetration retained and absolute viscosity ratio, the RTFOT was found to be a more severe aging process than the TFOT for oven temperatures of 285 deg F and 325 deg F. However, the two processes were not significantly different at an oven temperature of 365 deg F. On the basis of carbonyl ratio, a ratio of infrared absorbance at 1700/cm and 1600/cm used to express the level of oxidation in an asphalt binder, the effects of TFOT and RTFOT are not significantly different at oven temperatures of 285 deg F and 325 deg F. However, at 365 deg F, the TFOT is a more severe aging process than the RTFOT from the standpoint of carbonyl ratio. On the basis of low-temperature constant power viscosity, the effects of TFOT and RTFOT are not significantly different at any of the three levels of temperature. As a rough estimate, the TFOT or RTFOT procedure performed at 365 deg F, 3 months of natural weathering of compacted Marshall specimens, and 6 to 9 months of aging in a pavement would result in approximately the same hardening effects on a typical paving grade asphalt used in Florida. From the results of this study, it appears feasible to use TFOT or RTFOT at higher temperature to simulate the aging process on the asphalt binder in asphalt paving mixtures in service, as well as that of the hot-mixing process.

Simpson, W. C., R. L. Griffin, et al. (1960). "Correlation of the Microfilm Durability Test with Field Hardening Observed in the Zaca-Wigmore Experimental Project." American Society for Testing and Materials **Special Technical Publication No. 277**.

Examination of the asphalts used in the Zaca-Wigmore project by means of the microfilm durability test gave ratings of the relative durability to be expected of asphalts when all are used under the same conditions. The actual order of occurrence of failures in the test road is in agreement with the predictions of this relatively simple and rapid laboratory test. Progressive hardening of the asphalts in the road over a period of several years was found to parallel that found in the microfilm durability test in a few hours (ratio of viscosity at 77 F before and after exposure of a 5 yr film to air at 225 F for 2 hr). In the first road construction, where pavement deflections were about 0.015 in to 0.025 in under a 15,000 lb axle load, failures developed when the asphalt viscosity entered the range of 10^7 to 10^8 poises. In the second test road construction where deflections are about 0.010 in under the same load, the first distress was noted in an asphalt which reached a viscosity at 77 F of about 10 poises. Recovery of asphalt from slices of pavement cores showed that hardening of asphalt is greatest at the top and decreases with increasing depth in the pavement. Pavements with high air void content were found to harden more rapidly than those with low air voids. Hardening during the asphalt aggregate mixing operation was about twice as great during period 1 as this construction as during period 2 and this difference in hardening in the mix plant is still evident after several years in the road. Hardening by loss of voltaic matter is an important fraction of the total hardening observed in these asphalts. It is shown that this can be controlled by proper selection of crude oil or by application of distillation and blending techniques so as to keep the 10 percent distilled point of the asphalt at or above 400 C (converted to atmospheric pressure).

Sirin, O., C. T. Shih, et al. (1998). "Development of a Modified Rotavapor Apparatus and Method for Short-Term Aging of Modified Asphalts." Transportation Research Board.

An alternative laboratory asphalt aging process that could be used to simulate the aging effects of hot mixing on modified asphalts was developed and evaluated. The rotavapor apparatus, which has been used for recovery of asphalt from solution, was modified to work as an aging device for asphalts and modified asphalts. The rotavapor apparatus was modified such that the vacuum connection was replaced by an air pump with a controlled air flow. To reduce the variation of aging condition due to variation of the temperatures in the oil bath of the rotavapor apparatus, an insulated covering for the oil bath was constructed and used in this aging process. Evaluation results indicate that the aging severity of the modified rotavapor aging process is affected by variables such as process temperature, duration, and sample weight. All these factors could be adjusted to achieve the desirable level of asphalt aging. Because of the flexibility in controlling these variables in the modified rotavapor process, it appears that this method could be used to simulate the aging effects of hot mix plant process effectively.

Sisko, A. W. and L. C. Brunstrum (1968). "The Rheological Properties of Asphalts in Relation to Durability and Pavement Performance." Proceedings of Association of Asphalt Paving Technologists **37**: 28.

There have been many studies on the changes in asphalt consistency with aging. However, viscoelastic properties have been neglected. This paper reports on the use of a modified Weissenberg rheogoniometer (cone and plate viscometer) to measure viscoelastic properties of unaged and road-aged versions of the same asphalts. The aged asphalts were recovered from 12 roads that are well distributed around the country and have been in service for 11 years. An additional road-aged asphalt was also included from a 3-yr road. Also, another 10 asphalts were made available from a study that aged Marshall samples in the field for 345, 730, and 1,230 days. Asphalts used for the Marshall specimens were also aged in the thin film oven test for various periods to compare the field with the oven hardening. Original asphalts, and asphalts recovered from roads, from Marshall specimens, and those aged in the TFOT were tested for penetration at 77 F viscosity at 140 F and 275 F. Composition was determined by a combined solubility and chromatographic procedure. Glass transition temperatures (Tg) of several asphalts were determined with a modified dilatometer, and the changes in molecular size distribution were measured with a Mochrolabvapor pressure Osmometer. The viscoelastic properties of several asphalts were determined by measurements of stress and strain and their strain relationship at 1, 20, 40, 60, and 80 F and at frequencies from 0.001 to 3 cps. The frequency range was extended by combining the data at different temperatures to a reference temperature of 20 F using the relation between frequency and temperature given by the WLF equation. Changes in the asphalts were defined by the ratio of the complex moduli before and after the TFOT, called the mix ratio (a measure of the hardening produced in producing the road), and by the ratio of the complex moduli of the asphalt in the road to the TFOT asphalt, called the age ratio (a measure of age hardening in the road). Roads from which asphalts were recovered were surveyed for evaluation of the extent of cracking, amount of plastic deformation, and riding quality. Analysis and study of the large data collected in the study lead to the following conclusions: (a) aging produces changes in consistency that appear to be due to the development of a gel structure. Hetro-atoms introduced by aging may form secondary valence bonds that are involved in the gel. Evidence for the gel structure comes from a number of observations: the aged asphalt does not flow back into a crater cut into its surface, the penetration-soften point relation changes, the viscosity increases greatly with a small increase in molecular weight, the WLF constants change, and large changes in viscosity occur without a significant change in glass transition temperature; (h) differences in the complex modulus due to TFOT are small compared to the large differences that may occur in roads; (c) large increases, induced by aging, in the hardness of the asphalt hinder (as measured by the complex modulus) are associated with road cracking; (d) the age hardening of asphalt in the road does not correlate directly with the amount these asphalts harden in TFOT; (e) at traffic stress frequencies, unaged and aged asphalts have essentially the same mechanical properties at low temperatures (0 to 20 F); differences due to aging appear at higher temperatures (60 F and higher) and are more conveniently determined by confining the tests to higher temperatures; (f) aging does not significantly change the glass transition temperature; (g) the time-temperature superposition principle allows the construction of master curves of asphalt viscoelastic properties. At temperatures of 0 to 80 F, the general WLF constants are 28.6 and 292; (h) aging shifts the distribution of relaxation times toward longer times and reduces the ability of asphalt to conform to applied stresses.

Skog, J. (1966). "Durability of Paving Asphalt. Part I. A Study of the Durability and 'Setting' Properties of Paving Grade Asphalts Manufactured in the United States." California State Div. of Highways. Materials and Research Dept. **M/R-633134-1**: 65.

The authors present comprehensive information on the properties of asphalt cements that are associated with essential engineering requirements. Data are included for a series of penetration grades of asphalt cements representing nationwide production in 1954-1955 and a special series of asphalt cements graded by viscosity at 140F also representing nationwide sources. Data are reported to show the rheological properties of the original asphalt and the changes in these properties as a result of weathering by the Shot abrasion test and measurements of viscosity, shear susceptibility and microductility. The authors classify the asphalts into 5 groups, depending upon the changes in the properties induced by weathering.

Skog, J. (1967). "Setting and Durability Studies on Paving Grade Asphalts." Proceedings of the Association of Asphalt Paving Technologists **36**: 34.

The essential engineering properties of paving asphalt are: (1) consistency, (2) rate of curing or setting, (3) durability, and (4) resistance to water action. This report presents the results of tests that appear to provide necessary measurements for the evaluation of mixing and service life durability and "setting" characteristics during and immediately following construction. Two groups of asphalts were used in the test program. The first was composed of forty 85 to 100 grade paving asphalts from the 1954-55 Bureau of Public Roads test series. The second was a group known as the AC series, which were produced to conform to the 1963 tentative grade requirements of the Asphalt Institute. Changes during mixing were studied using the AASHO thin film oven test and the California rolling thin film test. A satisfactory correlation was found for results obtained by both methods in terms of penetration. However, the California rolling test showed a slightly greater hardening when kinematic viscosities at 140 F and 275 F were compared. It was concluded that either method will provide a test for determining change in consistency during mixing. Specification requirements to provide proper "setting" are presented. These requirements were based on controlling grade and the setting property by specifying viscosity ranges in absolute units at 140 F and 275 F on the residue from the California thin film test. These requirements are expected to ensure an asphalt or more uniform consistency in the paving mixture than is now attained by present or other proposed specification. Results showed that a series of asphalts having original viscosity at 140 F within a narrow band had a very wide range in viscosity after the rolling thin film test. The proposed specifications may control such differences. Tests simulating pavement service life were performed on the two groups of asphalts. The forty 85 to 100 grade paving asphalts were subjected to infrared weathering in an oven for 1,000 hours, which was found to be equivalent to at least 5 years of service life, and in a modified thin film oven test for durability requirements in our tentative specification. Measurements of changes in properties during and at the conclusion of these tests were performed by determining abrasion resistance, viscosities at two different shear rates, and ductility. Studies of property changes indicate that the asphalts may be divided into five groups. Some of the asphalts weather very rapidly from volatilization and chemical change while others weather quite slowly as measured by change in consistency, but the shear susceptibility changes very rapidly with a rapid drop in ductile properties. The results indicated that the asphalts weather in different ways and could present different forms of pavement failure. This study indicates that an important problem in asphalt specification requirements is the determination of the maximum amount of shear susceptibility that may develop in a paving grade asphalt prior to pavement failure. A good relation between durability residue shear index and micro-ductility for moderate weathering rate asphalts was found. It seems apparent that the development of a high shear index during weathering may have been the cause of failures previously reported in the literature as concerned with a decrease in ductility values. Both factors, shear index and ductility, related to the internal phase relationship of the asphaltic constituents.

Sparlin, R. F. (1958). "Effect of Ultra-Violet Light on Viscosity of Thin Films of Asphalt Cements." Proceedings, American Society for Testing and Materials **58**.

The hardening of thin exposed films of asphalt in service is partly due to the effect of ultra-violet energy. Asphalt durability studies by others have indicated that ultra-violet energy acts as a catalyst, accelerating oxidation and consequent hardening of the asphalt. The purpose of this investigation 'was to determine whether or not ultra-violet energy is capable of hardening asphalt when oxygen is not present. Thin films of two asphalt cements were exposed to ultra-violet energy while held between glass slides. After exposure the asphalt was sheared in a microviscometer and the viscosity computed. The results were compared by statistical methods to viscosities of control samples. Though the number of tests conducted was quite limited, covering only a few samples of the two paving asphalts, the results indicated that ultra-violet energy is capable of producing measurable increases in the viscosity of asphalt films sealed from the atmosphere.

Stawiarski, A., Jamois-D., et al. (2002). "Project for Developing Performance Related Standards in Europe; Evaluation of Test Methods to Characterize Bituminous Binders." Ninth International Conference on Asphalt Pavements, Copenhagen, Denmark, International Society for Asphalt Pavements.

Presented in this paper are the results of the Eurobitume evaluations of candidate test methods for assessing the following binder properties which are linked to the key asphalt pavement performance requirements: rheological property at elevated service temperatures, in relation to permanent deformation; combined rheological and failure property, in relation to low temperature cracking; short and long term binder aging behavior; binder stiffness modulus in relation to asphalt structural strength; and binder fracture behavior in relation to fatigue cracking. Also provided are recommendations on which tests could be selected for standardization as common European methods and for their possible use in future binder specifications.

Sybilski, D. and T. Mechowski (1996). "Evaluation of Durability of Bituminous Mixtures." Eurasphalt and Eurobitume Congress 1996.

There is an often consideration in Poland that for bituminous pavements of main roads exclusively basalt aggregates should be used. Other aggregates are being applied to a very limited scale, e.g. quartzite or granite. It is caused for fear of pavement's durability which might be decreased by poor adhesion of bitumens to acid mineral aggregate. Adhesion improvers and polymer modified bitumens have become widely accesible and used, however. Research on influence of various aggregates and binders onto bituminous mixture's durability was undertaken in IBDM. Asphalt concrete for wearing and binder course and Stone Mastic Asphalt were tested. Marshall samples were submitted to curing: 7 days in water at 60°C or 25 freeze-thaw cycles at 2% water solution of NaCl salt. Following mechanical properties were tested on samples before and after curing: stiffness modulus at 20°C (ITT-NAT), tensile strength at 5°C (ITT), Marshall

stability at 60°C. Paper presents test methods and some test results with evaluation of bituminous mixture durability. Tests showed that acid aggregates do not decrease mixture's durability when applied with adhesion agents or polymer-bitumens. Application of acid aggregates and polymer-bitumens should be combined with adhesion agents.

Takahashi, M. and K. Nomura (2000). "Examples of the Application of Accelerated Asphalt Aging Method." Road Engineering Association af Asia And Australasia (REAAA) Conference, Tokyo, Japan. 2000. 11p.

This paper reports on an examination of the manufacture of recycled asphalt mixtures. The repeatability of the asphalt aging method applied during the manufacture of asphalt mixtures, and after laying, was also examined. Knowing this, the repeatability of asphalt aging that appears during the manufacturing of aggregate mixtures as well as the quickening of asphalt layer aging were determined. To examine the accelerated asphalt aging method of the aging phenomenon during manufacturing, tests using a hot thin layer rotation device (RTFOT), as well as mixing tests using a laboratory pugmil mixer, were performed. Moreover, to investigate the aging phenomenon observed after laying, the accelerated asphalt aging method was developed under the Strategic Highway Research Program, using a pressure aging vessel, known as PAV, and the observation of asphalt mixtures exposed in pure oxygen gas at a temperature of 60 degrees Celsius (OMT or oxygen aging accelerated test) were performed at the same time. The authors' findings show that the aging phenomenon observed during manufacturing as well as after laying differs in two to three aspects. Next, applying the described accelerated asphalt aging methods led to an examination of the relationship between the rejuvenator and the degree of aging of recycled asphalt. The findings show that the composition of the rejuvenator used in recycled asphalt plays an important role in delaying the aging of recycled asphalt mixtures. (a) For the covering entry of this conference, please see ITRD abstract no. E204151.

Thomas, J. J., W. C. Dixon, et al. (1965). "Additional Study of Asphalt Concrete Mixing Time." NY DOT report: 47.

The investigation was to obtain further information regarding the reduction of specified mixing time requirements for hot bituminous concrete mixtures. The report presents the results of tests on the percentage of coarse particles coated, as determined by the Ross Count Method. Other tests conducted included aggregate gradation and asphalt content to determine mixture uniformity; and penetration or viscosity tests on recovered asphalt to determine the degree of hardening of asphalt during mixing. It was found that (1) batch plants should be evaluated individually to establish minimum mixing times for specific mixtures, (2) for three-ton capacity plants, aggregates in top and binder mixtures were adequately distributed and coated with about 10 seconds dry-mixing and 25 seconds wet-mixing, and for base course mixtures, 10 seconds dry-mixing and 35 seconds wet-mixing; (3) plants of larger capacity may require longer mixing times; and (4) equipment in many batch plants would prevent a reduction in mixing time below that needed for adequate coating and distribution. Asphalt hardening occurred during the first 15 seconds of wet-mixing but no additional hardening could be attributed to continued mixing. The report includes new specification requirements which will permit reductions in mixing time below a minimum of 15 seconds dry-mixing and 45 seconds wet-mixing.

Tia, M., B. E. Ruth, et al. (1994). "Development of Criteria for Durability of Modified Asphalt. Final Report." (FL/DOT/RMC/0516-3532; State Proj 99700-7387-119; WPI 0510516).

A laboratory investigation was conducted to evaluate the effects of a few promising modifiers on the long-term aging characteristics of typical asphalt cements and asphalt concrete mixtures used in Florida. The seven types of modifiers evaluated in this study include (1) gilsonite, (2) carbon black, (3) fine ground tire rubber (GTR-80), (4) coarse ground tire rubber (GTR-40), (5) styrene-butadiene rubber (SBR), (6) ethylene vinyl acetate (EVA), and (7) styrene-ethylene-butylene-styrene (SEBS). These modifiers were blended with an AC-30, AC-20, and AC-5 to produce various modified asphalts for this study. The results of the study indicate that the addition of modifiers generally reduces the rate of aging of the asphalts. AC-30 asphalt appears to be too hard and AC-5 asphalt appears to be too soft for use in modified asphalts in Florida. A more effective grade of asphalt to be used for this purpose appears to be somewhere in between these two grades. The laboratory aging processes of the TFOT, RTFOT, California tilt oven and SHRP PAV appear to simulate the field aging process quite adequately as seen from the similar rheological properties of the aged asphalt binders. The RTFOT is found to be a more severe aging process than the TFOT as seen from the percent penetration retained and absolute viscosity ratio of the aged modified asphalts. The RTFOT is found to be not suitable for use on the coarse ground tire rubber modified asphalts because the modified asphalt binders tend to spill out from the bottle during the RTFOT process. Skin formation tends to occur on the surface of certain modified asphalts during the TFOT process.

Tia, M., O. Sirin, et al. (2000). "Development of a Suitable Procedure for Simulating Aging Effects of Hot-Mixing on Modified Asphalts for Use in Superpave Binder Specifications." (WPI 0510802, Final Rept,; UF Proj 49104504568-12,; State Proj 99700-3369-01).

Prior studies have shown that asphalts modified with coarse crumb rubber and styrene butadiene rubber tended to spill out from the bottles during the Rolling Thin Film Oven Test (RTFOT) process. When the standard Thin Film Oven Test (TFOT) was used, a thin skin tended to form on the surface of some modified asphalt samples, which reduced the homogeneity and the aging of the samples. In this study, the rotavapor apparatus, which was originally used for recovery of asphalt from solution (ASTM D5404), was modified to work as an aging device for asphalt, and evaluated for its suitability as a replacement of the standard RTFOT procedure for simulation of short-term aging of both pure asphalts and modified asphalts. The modified rotavapor aging procedure was found to be a versatile and effective method for aging of pure asphalts and modified asphalts. It has advantages over the standard RTFOT and TFOT procedures in that (1) there was no spillage and skin formation problem, (2) a large sample size can be used, and (3) different levels of aging of the asphalt samples can be achieved. It is recommended that the possible implementation of this aging method for simulation of short-term aging in place of the RTFOT process and long-term aging in place of the RTFOT + PAV process be pursued. This study also resulted in some better understanding of the asphalt extraction process. It was found that the extracted aggregate from the Reflux extraction tended to absorb moisture from the air after it was taken out of the drying oven to cool to room temperature before weighing. This could cause a substantial error in the computation of asphalt content. The problem was solved when the extracted aggregate was left to cool in a desiccator before weighing.

Tmmiman, K. A., T. Les, et al. (1962). "Field and Laboratory Studies on the Durability of Road Bitumen." Journal of Applied Chemistry **12, No - 11**: 510.

Study showed only small differences in the road performance by seven asphalts from Middle East, Mexican and Venezuelan crudes used on dolertite or quartzite aggregates, although asphalts from one of the Middle East sources had the best combination of properties. Stripping and binder hardening were the major causes of failure of the quartzite and dolertite road sections, respectively. A broad relationship was observed between hardening and road performance. The original asphalts had different hardening tendencies in the Accelerated Weathering and Thin-Film Oven tests, the results of which correlated well with the relatively great changes in penetration occurring during mixing and laying, and in the early life of the road, After a year or so, penetration differences between the weathered binders become small. The road hardening rates were similar in all cases, and followed a hyperbolic equation.

Traxler, N. (1961). "Relation Between Asphalt Composition and Hardening by Volatilization and Oxidation." Proceedings of the Association of Asphalt Paving Technologists **30**.

Data are reported on six commercial 85-100 penetration asphalts. The Bureau of Public Roads Thin Film Test was run for 5, 10 and 15 hours. A test similar to that proposed by Griffin, Miles and Penther was made on 15 micron films in air at 225 degrees for 2 and 4 hours. Films of the same thickness were also heated for 2 and 4 hours in an atmosphere of nitrogen. Rheological and strain data are given on a number of synthetic asphalts of essentially the same viscosity at 77 degrees F. A correlation was established between the relative viscosity (extent of hardening of the asphalt) and a coefficient of dispersion calculated from asphaltene, resin and oil contents. A high coefficient indicates superior resistance to hardening by oxidation in the dark.

Traxler, R. N. (1961). "Relation Between Asphalt Composition and Hardening by Volatilization and Oxidation." Assoc Asphalt Paving Technol Proc. 1961.

Investigations of the service durability and chemical properties of asphaltic cements are reviewed. Asphalts harden to varying degrees upon aging, and when subjected to heat, oxygen, or actinic light. A consideration variation in susceptibility to hardening exists among commercial asphalts. It is agreed that asphalts are colloidal systems composed of high molecular weight compounds dispersed in an oily medium. Investigation of rheological and colloidal properties have indicated that the amount of dispersed materials (asphaltenes, which are the n-pentane insoluble component of the asphalt) and the chemical composition of the petrolenes (n-pentane soluble component) control the properties of an asphalt. If the petrolenes possess a high content of unsaturated or cyclic compounds the heavy asphaltic bodies are well dispersed. Large amounts of saturated compounds will cause floculation of the heavier bodies and the appearance of internal structure in the asphalt. Studies in the area of cracking of asphalt have proven that its major cause, is the hardening of the asphalt, generally with time. Volatilization and oxidation increase the hardness in the development of insoluble matter in the asphalt. Another cause of the hardening and loss of durability in paving asphalts is the absorption or adsorption of certain components by the aggregate used in building the road.

Traxler, R. N. (1967). "Changes in Asphalt Cements During Preparation, Laying and Service of Bituminous Pavement." Proceedings of Association of Asphalt Paving Technologists **38**: 21.

This paper presents data on the hardening of 85 to 100 penetration asphalt cements (based on viscosity measurements) from the time they entered the hot-mix plant through the laying of

the pavement surfacing and two years of service. Thirteen asphalts (made at nine different refineries), employed by the Texas Highway Department in their maintenance program at 13 locations in the state, were used in the study. Density and permeability of mixes, mineralogical properties of aggregates, and viscosity at 77, 95, 140, and 275 F of the asphalt cements (original and recovered) were measured. Ductilities using the California microductility machine at 77 F were also measured. Susceptibility for hardening of the asphalt cements was tested (15 micron films heated in a dark air oven for 2 hr at 225 F). Asphaltene contents were determined on original and 1- and 2-yr-old asphalts. Recovered petrolenes were tested for viscosity at 77 F. Viscosities at 77 and 95 F were made in the thin film (sliding plate) Hallikanien viscometer at .05 1/sec rate of shear. Penetration at 77 F, 100 grams, 5 sec were determined on each original and recovered asphalt. Results indicated that relatively slow hardening occurs during the preparation of a paving mixture at temperature of 250 to 325 F, laying the surfacing and during the first 2 weeks of service. However, from then up to 2 yr the hardening of asphalts is much more. This hardening varies among the different asphalts combined with different aggregates under various service conditions. Asphaltene content increases during the preparation and laying of the pavement and up to 1 yr of service. Between 1 and 2 yr of service the asphaltene content usually increases, but in a few situations an unexplained decrease is noted. This decrease may be related to absorption and absorption of different asphalt components at the surface of the different aggregates. Viscosities of the petrolens, over the 2-year period increased from 1.05 to 20.1 fold. This increase and the increase in asphaltene content with time do not explain the hardening of the films of asphalt cement during service in every case.

Tuffour1, Y. A. and I. Ishai (1990). "The Diffusion Model and Asphalt Age-Hardening." Proceedings of the Association of Asphalt Paving Technologists: 72-92.

The interaction of an asphalt cement with its environment is generally considered the main cause of the hardening and deterioration of the material with time. The phenomenon, known as age-hardening, is believed to be primarily due to the oxidation of the material. Oxidative hardening is an irreversible chemical reaction involving the components of an asphalt cement and atmospheric oxygen. The widely-held view regarding the mechanism of the process is that atmospheric oxygen reaches a reactive asphalt component and reacts with it through a process of diffusion. At a given temperature, the oxidation process is controlled by the reactivity of the binder and the rate of diffusion of oxygen into the binder. It is thought that the depletion of those components reactive at the prevailing conditions retards the reaction and the rate of change in consistency properties. The evidence that oxygen reacts with asphalt during aging has been obtained from actual measurements. Indirect evidence has also been obtained in two ways: (1) the increase in the content of carbonyl-type and other oxygen containing compounds in asphalts during aging of the material; (2) the fact that air-blowing, which involves the passing of air (oxygen) into an asphalt stock at an elevated temperature, causes the material to harden.There has been considerable research on characterizing parameters for asphalt durability, but little progress has been made in predicting asphalt property change after some period of service life. Lack of substantial progress in this direction is due, in part, to the vague understanding of asphalt chemistry and its reaction kinetics and, in part, to the complex operative mechanisms of the many environmental variables affecting the process. In spite of such difficulties, some attempts have been made to present empirical models that try to predict the probable level of change in asphalt properties after some period of service life. The present work, using simplifying assumptions, adapts the diffusion model for use in characterizing laboratory aging. Predicted aged viscosities are compared with measured values and found to be in good agreement. Although the model does not purport to predict asphalt aging in the entirety of its aging domain, it represents a good starting point for attempting a quantitative measure of asphalt aging and durability, at least under controlled laboratory-accelerated conditions.

Vallerga, B. A., C. L. Monismith, et al. (1957). "A Study of Some Factors Influencing the Weathering of Paving Asphalts." Proceedings, Association of Asphalt Paving Technologists **26**: 126.

Three asphaltic materials of different weathering resistant characteristics were used to study the influence of variations in weathering conditions on selected asphalt properties. Variations in weathering included: (a) heating in the absence of light, (b) heating with the presence of infrared radiation, and (c) heating with the presence of ultra-violet radiation. For the effect of weathering in the absence of light, the standard BPR thin film oven test and a modification thereof, utilizing a rotating inclined plane principle designed to produce thinner films, were compared. For weathering the infra-red and ultra-violet radiation, the California Division of Highways Infra-Red Weathering Machine was used and also modified to accommodate the inclined rotating plane principle to produce the thinner films of asphalt. The effects of weathering were determined by measuring the changes in penetration, softening point, and ductility of the asphalt residues after various exposure periods. From the results obtained, the following conclusions were drawn: (a) the use of the rotating included (15 degree) shelf principle in which a 5.5-in diameter pan containing 50 ml of asphalt is placed appears to develop film thicknesses more nearly representative of those existing in paving mixtures and to produce more uniform weathering of the asphalt sample with a sufficient amount of asphalt to prepare a specimen for the standard penetration test; (b) weathering in the absence of light at 225 F caused a decrease in penetration and an increase in the softening point temperature of the asphalts with time, the changes being the least for the three weathering conditions used. In this weathering condition, loss in penetration was not generally accompanied by a reduction in ductility. At 325 F, this type of weathering caused substantial reduction in penetration for all three asphalts. At 225 F, however, the reduction was less marked for Samples B and C; (c) weathering in the presence of ultra-violet radiation caused substantial reductions in penetration of asphalts used and increased their softening point temperatures, but caused either an increase or decrease in ductility, depending on the asphalt. The reduction in penetration and the increase in softening point temperature was most marked for this weathering condition; (d) weathering in the presence of infra-red radiation caused a reduction in penetration and an increase in softening point temperatures, the changes being intermediate between those for weathering in the presence of ultra-violet radiation and in the absence of light. Depending on the material, this condition of weathering caused either a decrease or increase in ductility. For Samples B and C, no appreciable loss in ductility resulted; for the longer periods of weathering an increase in ductility was observed.

Vassiliev, N., C. J. Glover, et al. (2001). "Improved HMAC Plant Binder Aging Simulation Report of Preliminary Findings and Intended Project Direction." (FHWA/TX-01/1742-1,; Research Report 1742-1).

Two procedures to simulate hot mix asphalt concrete (HMAC) plant aging are currently used. These are the rolling thin film oven test (RTFOT) and the thin film oven test (TFOT). When used for unmodified asphalts these methods are essentially identical in simulating asphalt short-term aging. However, when applied to modified binders, practitioners have encountered a number of problems with both RTFOT and TFOT procedures. Modified asphalts tend to form surface films that reduce oxygen diffusion and cause uneven aging. Many modified materials are too viscous to form good films in RTFOT bottles and are also difficult to remove after the test is completed. The objective of this research is to develop an improved test procedure and a new apparatus to address the shortcomings of the existing aging techniques. The procedure should meet the following requirements: non-prohibitive cost, similar testing time and aging effect to the RTFOT, capable of producing up to 200 g of aged material per test, no prolonged handling of hot equipment or materials, and simplified cleanup. Preliminary results show that an air blowing technique in an agitated vessel allows duplication of the RTFOT aging effect and therefore can serve as a procedure to simulate HMAC aging. Constant agitation of material by the mixer prevents film formation and enhances air diffusion through the bulk of the asphalt. The time required to achieve the same aging is the same or even shorter than specified by the RTFOT. In addition to these advantages, the ability to control sample temperature, to collect volatile compounds and to use a single, easy to clean reusable container, as well as potentially lower equipment costs and decreased handling of hot equipment should be noted.

Vassiliev, N. Y., R. R. Davison, et al. (2002). "Development of a Stirred Airflow Test Procedure for Short-Term Aging of Asphaltic Materials." Transportation Research Record(1810).

Short-term aging procedures, either the thin-film oven test or the rolling thin-film oven test (RTFOT), are used to approximate the aging that occurs by asphalt binders during the hot-mix process. For unmodified binders, both of these procedures do a reasonable job of duplicating this aging not only with respect to physical property changes in the binder but also with respect to oxidation, as measured by changes in the infrared absorption spectrum. For modified binders, however, significant difficulties exist, among them surface skin formation and poor flow in the bottles. A new apparatus specifically designed to age modified binders as well as unmodified binders has been developed. This apparatus consists of a temperature-controlled vessel, a tube for introducing either nitrogen or air, a dispersing impeller for mixing the air and binder, and a condenser for collecting volatiles. Besides temperature, gas flow rate and mixing speed are controlled to desired values. The collection of volatiles allows a direct, rather than indirect, measure of volatiles loss. The required aging time of 30 min is less than the RTFOT's 85 min. Tests of the process with unmodified binders achieved excellent comparisons with RTFOT aging in both physical properties (dynamic shear rheometer) and oxidative aging (Fourier-transform infrared analysis). Trials with modified binders achieved uniform aging with no complications caused by the rheology of these materials. Modified binders studied included polymer-modified styrene butadiene diblock copolymer and styrene butadiene triblock copolymer materials.

Vassiliev, N. Y., R. R. Davison, et al. (2001). "Air Blowing of Supercritical Asphalt Fractions."

Air blowing of asphalt at higher temperature does not greatly impact such parameters as the softening point-penetration relationship. With new Superpave specification, very good grade asphalts can be produced by air blowing, and the blowing temperature does not seriously impact the grade span. It is shown, however, that the subsequent 88 °C hardening and oxidation rates are higher for materials blown at higher temperature, and this is not detected by Superpave specifications. Blowing fluxes with high saturate content may result in higher grade but can cause subsequent susceptibility to oxidative hardening. The mechanism by which air blowing can affect the 88 °C hardening rate is related to oxidation kinetics and the tendency of oxidation products to form asphaltenes, causing hardening. For some materials air blown at higher temperature, the subsequent accelerated hardening rate results from an increase in the oxidation rate, while the hardening susceptibility may actually decrease.

Verhasselt, A. (1996). "Kinetic Approach to the Ageing of Bituminous Binders." Eurasphalt and Eurobitume Congress 1996.

During the life of a bituminous mix, the bituminous binder is successively subjected to two types of ageing : rapid ageing during the construction (manufacturing - laying - cooling) and slow ageing in service, in the climatic environment of the surfacing. In both cases, the observed modifications are the result of oxidation reactions. Standard tests such as RTFOT or RFT adequately and satisfactorily simulate construction ageing. However, as they are conducted at too high temperatures, they are unsuitable for simulating the ageing in service. Furthermore, they do not bring to light the very important kinetic aspect of the reactions involved. This situation led the development of a new test device for accelerated ageing (temperature between 70 and maximum 100 °C) and of a theoretical kinetic approach to ageing. Based on the latter, the development of some characteristics of the binder can be described in a linear way by the following equation :

$$St = So + K^{1/2} x t^{1/2}$$

Where So and St represent the reaction indicator S at time t = 0 and t = t, K the global reaction constant and t the reaction time. The asphaltenes content, the ring and ball temperature and the reciprocal of penetration can serve as reaction indicators. This equation is valid as far as the test temperature is lower than 100 °C and as So is an initial value and not a value resulting from a preliminary ageing, whether known or not. In such case, it must be proceeded to a generalization of the proposed theoretical approach. Generally speaking, the equipment developed appeared to be appropriate for accelerated simulations of ageing in service. Furthermore, the kinetic approach developed proved to be a very valuable interpretation tool to assess certain laws governing the ageing process. Various aspects, examples of which are given in this paper, have been explored and among others : - ageing susceptibility of various binders, - activation energy of the reactions involved and its impact on ageing in situ, account being taken of the variable temperature of the surfacing, - "laboratory/in situ" link and inversely, - influence of various additives on the ageing of the prepared binder.

Verhasselt, A. (2002). "Long-Term Ageing - Simulation by RCAT Ageing Tests." Conference Title: Ninth International Conference on Asphalt Pavements, Copenhagen, Denmark, Sponsored by: International Society for Asphalt Pavements.

The aging of bituminous binders in service is an important factor in the long term performance of bituminous materials. Relevant simulation by accelerated aging can be achieved if the test is conducted at a temperature below 100 deg. C. Comparison between the RCAT (rotating cylinder aging test) and the PAV (pressure aging vessel) test recommended by SHRP has shown that the reactions involved in these two aging techniques are very similar. This paper examines seven bituminous binders and results obtained for IR spectra, technological characteristics and rheological properties are considered.

Verhasselt, A. (2003). Short- and Long-Term Ageing of Bituminous Binders - Simulation with the RCAT Method. Performance Testing And Evaluation of Bituminous Materials PTEBM'03. Proceedings of the 6th International RILEM Symposium Held Zurich, Switzerland, 14-16 April 2003. 2003.

Both the short-term ageing ("in construction") and long-term ageing ("in service") of the bituminous binder are important factors in the performance of bituminous materials. Short-term ageing can be adequately simulated with the RTFOT method, which has been standardized at the European level. For long-term ageing, BRRC has developed - as an alternative to the less well accepted PAV test - the RCAT (Rotating Cylinder Ageing Test) method, which has aroused much interest over the past few years. In the marketed version of the RCAT apparatus, provision has been made to simulate the two types of ageing. To establish equivalence between ageing times, a systematic comparison between RTFOT and RCAT tests both conducted at 163 degrees C was made with several bituminous binders. The measurements of penetration and ring-and-ball temperature as well as the infrared spectra of the binders have shown that 210-240 min of RCAT ageing approximately correspond to 75 min of RTFOT ageing. As a result, the RCAT apparatus appears to be a very practical device with many possibilities for short- and/or long-term ageing tests on normal or modified binders or even on mastics. For the covering abstract see ITRD E117423.

Verhasselt, A. and A. Vanelstraet (2000). Long-Term Ageing - Comparison between PAV and Rcat Ageing Tests. 2nd Eurasphalt & Eurobitume Congress, Barcelona.

The ageing of bituminous binders in service is an important factor in the long-term performance of bituminous materials. Relevant simulation by accelerated ageing can be achieved if the test is conducted at a temperature below 100 °C. Two techniques are currently in use: the PAV (Pressure Ageing Vessel) test recommended by SHRP, which is, however, subject to some reservation in Europe; and the RCAT (Rotating Cylinder Ageing Test) developed by BRRC, which has some advantages over the PAV test. PAV is a static test (duration: 20 h) performed at 100 °C under a pressure of 2 MPa, whereas RCAT is a dynamic test performed at 85 °C on a sample of 500 g, under a flow of oxygen. The two simulation tests were tried with variable times of exposure on seven bituminous binders (two bitumens and five polymer-modified bitumens), after prior RTFOT ageing or not. A comparison of how the IR spectra, the technological characteristics and the rheological properties (DSR and BBR) develop with exposure time shows that the changes observed and the reaction mechanisms involved are quite similar for the two techniques, unlike the findings that are made at a higher temperature (163 °C in RTFOT). Looking at the aggregate set of characteristics investigated, it can be established that the equivalence between the two techniques is such that 20 h of PAV ageing approximately correspond to 178 ± 20 h of RCAT ageing. Two polymer-modified bitumens stand out with an equivalence of 102 and 230 h, respectively. As a result, the RCAT simulation technique, which has the additional advantage of allowing a kinetic approach to the ageing process, appears to be a well advised alternative to the PAV test at the European level.

Vind, H. P. (1967). "Oxidative Degradation of Asphalt." NCEL Report **NCEL-TN-929**: 20.

Knowledge that the deterioration of asphalt is primarily an oxidative process leads to three general approaches for preventing the deterioration of asphaltic construction mixtures: (1) Agents might be added or other measures might be employed to lower the intrinsic reactivity of asphalt with oxygen, even when the availability of oxygen is not limited; (2) Sacrifical oxygenconsuming agents might be added to the construction mixtures to limit the amount of oxygen available for reacting with the asphalt; (3) Impermeable surface coatings might be applied or fine particles might be added to clog or seal the pores, thereby retarding the diffusion of oxygen through the asphaltic mixtures. The three proposed approaches are applicable irrespective of the involvement of bacteria in the degradation of the asphaltic construction mixtures. Other measures for prolonging the service life of special asphaltic compositions might be the application of heat reflective white coatings to prevent solar heating, or the incorporation of water-absorbing additives to prevent penetration by water.

Whiteoak, C. D. (1990). The Shell Bitumen Handbook.

Witt, H. P. (1976). "Determination of the Long Term Effect of Air on a Thin Film of Bitumen Heated at 100 Degrees C (ARRB Durability Test)." Australian Road Research Board, 500 Burwood Road, Vermont South, Victoria 3133, Australia.

This method determines the time of exposure for a thin film of a bitumen heated at 100 degrees C in air, in the absence of light, to reach an apparent viscosity of 5.67 log Pa.s at 45 degrees C and a shear rate of .005 1/sec. Application has so far been restricted to Class 160 bitumens which have been subjected to the Rolling Thin-Film Oven (RTFO) test treatment. When the relatively non-volatile residual bitumens used for paving purposes are tested, the hardening produced by the treatment is mainly due to chemical attack by oxygen. If the procedure is used to evaluate other types of bituminous paving binders, a check should be done to determine whether the observed hardening is caused, in part, by evaporation of volatile constituents. A loss in mass of a binder film greater than two per cent can be detected by weighing a test bottle on an anlytical balance before and after exposure.

Wright, J. R. and P. G. Campbell (1962). "Determination of Oxidation Rates of Airblown-Asphalts by Infra-Red Spectroscopy." Journal of Applied Chemistry: 256.

Oxidation rates for eight airblown asphalts were determined by measuring the change in infra-red absorption at 5.88 v-mu with time of exposure to the radiant energy of a carbon arc. While all the asphalts oxidized at different rates, those from the same geographical areas had similar rates; those from different areas varied considerably. The pattern of oxidation was generally the same for each of the eight asphalts, in that there was an induction period followed by a steady oxidation rate until near the failure point, beyond which time the oxidation rate accelerated until film failure as denoted by asphalt film cracking. An inverse relationship was found between the rate of oxidation and the accelerated weathering durability of each asphalt.

Wright, P. H. and R. J. Paquette (1966). "The Hardening of Asphalt in Hot Bituminous Mixes During the Hauling Process." **A-711; 0605**: 77.

The research reported herein was performed at Georgia Tech under the sponsorship of Georgia Highway Department and the Bureau of Public Roads to determine the significance and seriousness of asphalt hardening during the period of haul. Samples of hot bituminous mix were taken from trucks traveling enroute from the mixing plant to the paving site at times of one, two, and four hours after preparation of the mix. In addition, mix samples were taken immediately after mixing, and after the material had been placed on the roadway. A total of about 100 field samples were taken from ten trucks, including asphalts manufactured from four sources of crude. (Author)

Wurstner, R. G., W. A. Higgins, et al. (1960). "Laboratory Evaluation of Factors Influencing the Performance of Paving Asphalts." Proceedings of the Association of Asphalt Paving Technologists **29**: 253.

Asphalts age-harden at different rates. This can be shown by both the Thin Film Test and the Hveem Abrasion Test. Oxygen plays a principal role in age hardening of paving asphalts. Chemicals which effectively inhibit oxidation in other hydrocarbon systems do not do so in these asphalts. Certain oxygen-resistant polymers improve the abrasion resistance and reduce the age-hardening of asphalts. Consistency, as indicated by absolute viscosity, is not the only factor which determines the effectiveness of an asphalt in binding aggregates. Adhesivity and cohesivity are equally important properties. Asphalts produced by non-conventional experimental methods show promise of having outstanding resistance to age hardening.

Zupanick, M. (1994). "Comparison of the Thin Film Oven Test and the Rolling Thin Film Oven Test." Journal of the Asssociation of Asphalt Paving Technologists **63**: 346-366.

The Thin Film Oven Test (TFOT) and the Rolling Thin Film Oven Test (RTFOT) are two common aging tests for asphalt cement. Both tests are intended to simulate hot-mix plant aging. The TFOT is the primary aging test used throughout most of the United States, while the RTFOT is used in some western states, and has been recommended for use under the proposed SHRP specifications. Most published reports suggest that the TFOT and RTFOT tests are approximately equivalent, and there is a common assumption that the tests can be used interchangeably. The validity of this assumption is particularly important as we begin to implement the SHRP specifications. To test this assumption, we analyzed the AASHTO Materials Reference Laboratory (AMRL) database, which contains comparative data typically representing 5200 repetitions of the TFOT and 1800 repetitions of the RTFOT. The data was analyzed for each of four commonly used aging ratios: viscosity ratio at 140F (60C), viscosity ratio at 275F (135C), percent retained penetration at 77F (25C), and percent weight change. Because of the large number of test repetitions, we were able to make statistically valid conclusions about the relative severity and precision of the two tests. In addition, because this study involved many asphalt testing labs, it is unlikely that the results are biased, a potential problem with smaller studies. The data indicates that the RTFOT is a more severe test than the TFOT for each of the four aging ratios examined. Perhaps more importantly, the tests appear to rank asphalts differently. This difference in ranking appears to be partially related to the initial viscosity of the sample; the data is sufficient to conclude that the TFOT will tend to have a lower relative severity for asphalts that have a high initial viscosity. In addition, skin formation in the TFOT may also affect this ranking difference. Skin formation can occur in the TFOT, but does not occur in the RTFOT.