Proposal

EVALUATION OF REJUVENATING AND SEALING AGENTS: CORRELATION OF CHEMICAL PROPERTIES WITH OBSERVED FIELD PERFORMANCE

INTRODUCTION

This proposal is in response to a request from Mr. Larry Scofield, P.E., Research Engineer and Principal Investigator, Arizona Department of Transportation, Phoenix, Arizona. The work plan, which is described in detail in the following sections, is designed to determine four critical chemical properties of rejuvenating agents and/or sealants. Correlations of these chemical properties with observed field performance will be performed. A data evaluation report will be submitted.

OBJECTIVE

The principal objective of this proposed study is to determine whether there is (are) good correlation(s) between readily measured chemical properties and the observed roadway performance of the rejuvenating and sealing agents. It is the understanding at Western Research Institute that these rejuvenating agents and sealants will be studied in about 30 projects spread across several states. We have, therefore, costed this study on a per sample basis so that any number of sites (all samples or a statistical sampling) can be studied.

PROJECT DIRECTION

Western Research Institute proposes to determine (1) the chemical compatibility of each rejuvenator/sealant with the roadway asphalt where the agent is applied (this will be done with an Automated Flocculation Titrimeter to acquire Heithaus parameters), (2) whether surface-active components (scrubbing agents) are formed in or by these agents during aging, (3) the oxidation and aging propensity of each agent, and mixtures of each agent with the asphalt where it is used, and (4) the compositional similarity (by spectroscopic and wet chemical analysis) of each given rejuvenator and sealant supplied under one commercial brand name, but supplied from different locations. The composition of any given agent may vary from one supply location to another, even though it is marketed under one brand name.

PROPOSED WORK PLAN DETAILS

Core Preparation

Most samples being used in this study will be core samples obtained from the test sections either with or without treatment. The only samples that will not be core samples are the samples of each surface treatment material alone. The core samples used in the study need to be extracted quantitatively to remove all of the binder/surface treatment material in a manner that is not detrimental to either the chemical or physical properties of the material. Western Research Institute will use a cold extraction procedure using toluene-ethanol-water to remove the asphaltic materials from the cores. One extraction will be performed on each sample/core in sufficient quantity to produce enough material for all of the testing proposed by Western Research Institute. The amount of extracted material required for all analyses will be about 25 grams. It is planned to extract only the top one-half inch of each core, therefore, it may be necessary to have two cores from each section. The cost of extraction is estimated to be $400 for each different material.

1. DETERMINATION OF CHEMICAL COMPATIBILITY

Introduction

Historically, asphalt and heavy oil residua have been modeled as colloidal systems in which a polar, associated asphaltene phase (the dispersed phase) is suspended in a maltene solvent phase (the dispersing medium). The extent to which these two phases remain in a given state of peptization is a measure of the compatibility of the system. Compatibility influences important physical properties of these materials, including rheological properties, (e.g., phase angle, viscosity, and aging propensity) of asphalts. Compatibility is such a general property that it even influences coke formation in the refining of heavy oil residua. The term describes the colloidal state of an asphalt. Highly compatible asphalts differ in fundamental properties from incompatible asphalts, but binders of either type are used regularly, depending on their environment and the aggregate with which they are mixed. However, asphalts that are or become highly incompatible often fail quickly. Asphalts range widely over a spectrum of compatibility values. Most asphalts become less compatible as they oxidatively age harden during service.

Compatibility of asphalts has been measured using a variety of methods. The best known of these methods is the classical Heithaus test. This test measures the overall compatibility of an asphalt by determining a parameter referred to as the state of peptization, P. The value of P commonly varies between 2.5 and 10 for unmodified or neat asphalts. Materials calculated to have low values of P are designated as incompatible, whereas materials calculated to have high P values are designated as compatible. Values of P may be calculated as a function of two other parameters that relate to the peptizability of the asphaltene phase (the asphaltene peptizability parameter, p_a) and the solvent power of the maltene phase (the maltene peptizing power parameter, p_o). Values of p_a and p_o are calculated from experimental data. These data are obtained by dissolving a given quantity of an asphalt in several different (three or four) volumes of a solvent, almost always toluene. Each of these solutions of different asphalt concentration then is titrated with a hydrocarbon such as n-heptane, which precipitates asphaltenes. The volume of n-heptane required to just induce flocculation is recorded for each of the solutions. These values are plotted, and a straight line is drawn connecting them. The line is extrapolated to each intercept, and the Heithaus parameters discussed above are calculated from the intercept values.

The classical Heithaus method is largely manual and highly operator dependent. Consequently, Western Research Institute has developed an automated flocculation titrimeter to acquire accurate and reproducible Heithaus values. The new method reduces operator variability, and also reduces test time. The onset of asphaltene precipitation (flocculation) is determined spectrophotometrically and thus is not operator dependent. The hydrocarbon isooctane (2,2,4 trimethyl pentane) replaces n-heptane as the hydrocarbon precipitant (titrant), enabling more waxy asphalts to be analyzed. After preparation of the asphaltene solutions, the entire procedure is performed in a constant temperature apparatus designated as an Automated Flocculation Titrimeter (AFT).

Proposed Work Plan

The changes in chemical compatibility, as measured by Heithaus compatibility parameters using the AFT will be correlated with pavement performance characteristics. Initial studies will focus on determining blend compatibility between asphalt and rejuvenator/sealant. Studies will then focus on monitoring changes in the compatibility of asphalt-rejuvenator/sealant blends as a function of pavement life.

Duplicate samples of the parent asphalts of the materials recovered from pavement cores will be analyzed by the AFT, and Heithaus parameters will be calculated. Neat rejuvenator/sealant materials also will be analyzed using the AFT if they are soluble in toluene. Recovered asphalt material from pavement cores with rejuvenator/sealant present will then be analyzed using the AFT to determine Heithaus compatibility parameters as a function of pavement aging time. Compatibility parameters measured in these studies will be compared and correlated with pavement performance properties that relate to cracking, oxidative age hardening and rutting propensities.

The cost for analysis of one sample in duplicate is estimated to be $75.

2. FORMATION OF SURFACE-ACTIVE AGENTS

Introduction

It is known that highly surface-active materials may be generated in asphalts as a result of oxidative aging. These surface-active materials may be expected to have considerable influence on the properties of oxidatively aged asphalts and their interaction with aggregate surfaces. In particular, the property of moisture susceptibility is very likely to be influenced by the buildup of surface-active materials as asphalts age over time.

The surface-active materials that are formed during the aging of asphalts mostly consist of materials that form oil-in-water emulsions. Some of the products are strong acids, probably sulfonic acids, which are comparable in acidity to mineral acids, and which are water soluble. It is not known whether these strong acids are reactive toward rejuvenating/sealing agents. It also is not known how rejuvenating/sealing agents affect the process of asphalt oxidative aging. They may enhance, retard, or have no effect on the formation of surface-active materials. The proposed work described below is designed to address these questions.

Work Plan for the Study of Surface-Active Agents

It is planned to study surface-active components formed in asphalts mixed with rejuvenators or sealers by the following set of experiments. Three aliquots of materials extracted from cores by organic solvents will be dissolved in measured volumes of toluene. The toluene solutions will be mixed with deionized water in separatory funnels and the mixtures will be shaken vigorously. It is expected that, after agitation, there will be formed in each funnel a bottom layer of emulsified material separated from an upper layer consisting of toluene soluble material. The two layers will be separated. Conventional demulsification procedures will be employed if necessary. The pH of the water in the aqueous bottom layers will be measured to determine whether strong acids have been formed. If so, non-aqueous potentiometric titration (NAPT) analysis will be performed on a small sample of the extracts to quantify the acids. NAPT is priced in Section 4. The toluene-soluble materials will be mixed with fresh portions of deionized water and the extraction will be repeated. The materials in the lower, emulsified layers will be combined with those from the first extraction. The total amount of organic material in the emulsions will be quantified after removal of water from the emulsions. These data will provide measures of the extent to which surface-active materials form in rejuvenator/sealer-treated asphalt during aging.

In the cases for which samples of original asphalts from newly constructed projects are available, identical treatments as described above will be performed. These materials will be aged in the laboratory by the pressure aging vessel (PAV) procedure to simulate aging in the field. This PAV oxidation will be performed as discussed in the next section, Oxidation and Aging Propensity Study. These PAV-aged asphalts will be subjected to the dissolution-extraction procedure described above. Results will be compared with those obtained from core samples of the same asphalt with rejuvenators/sealers. Any marked differences in the amount and type of surface-active materials in the two materials will provide a measure of the influence of the rejuvenator/sealer agents on the production of surface-active materials during asphalt oxidative aging. The cost of the surface-active analysis on a neat material is estimated to be $150 per sample. The cost of the surface-active analysis on materials extracted from cores or PAV-aged materials is estimated to be $470 per sample.

In separate experiments involving selected rejuvenator/sealer agents, the said agents will be combined with an aqueous solution of strong acids formed during oxidative aging of petroleum. The mixtures of the two materials will be stored at controlled temperatures for selected time periods. The pH of the water will be measured from time to time to determine whether or not acid-base reactions occur between the strong acids and the rejuvenating/sealing agents. Any changes in the physical appearance of the rejuvenator/sealer as a result of acid-catalyzed decomposition also will be monitored. The cost of performing this procedure (not including the PAV-aging procedure on an asphalt sample, which is costed in the next section) is estimated to be $250 per sample.

3. OXIDATION AND AGING PROPENSITY STUDY

The oxidation and aging propensity study is divided into two areas, aging prediction and performance assessment. Both of these areas of investigation require samples of asphalt material that have been extracted from a pavement core.

Aging Prediction

The aging prediction study will start with asphalt materials from the beginning of each project and will only be conducted once for each different project. Asphalt extracted from a core sample of pavement prior to surface treatment with rejuvenator/sealant and similar samples of extracted materials for each treatment just after surface treatment will be aged using the PAV method at 60°C (140°F) for 144 hours. Asphalt materials from projects in states with hotter climates may be aged in the PAV using slightly higher temperatures such as 70°C (158°F). The choice of the PAV temperature should be correlated with the PAV aging temperature that would be used for binder selection at the project site, (i.e., a site that would use 100°C [212°F] PAV temperature for AASHTO binder grading would use a 60°C [140°F] PAV temperature in this study and a site that would normally use 110°C [230°F] PAV for binder grading would use a 70°C [158°F] PAV temperature in this study). The use of the lower temperature (60°C or 70°C [140°F or 158°F]), longer time PAV procedure is more representative of pavement temperature and is more appropriate for a research project that doesn't have narrow time constraints of specification methods. After PAV aging, each sample will be analyzed by dynamic shear rheology (DSR) at two temperatures to determine the amount of change in rheological properties which has occurred. Further, each sample will be analyzed by infrared spectroscopy to obtain a functional group analysis (IR-FGA). This will be done to measure the concentration of oxygen-containing functional groups. These results will be compared with the rheological and chemical properties of asphalts recovered from each site over the course of the study to determine how well a laboratory-aging procedure predicts field-aging properties. The aging prediction studies can be performed for an estimated cost of $360 per sample.

Performance Assessment

Surface treatment of pavements with rejuvenating or sealing agents is performed to extend the useful life of a pavement by restoring properties of the asphalt to an earlier point in time, protecting it from further degradation by the environment, and/or slowing down the deleterious response of the pavement properties to environmental factors. Some important aspects of using rejuvenator/sealer materials as pavement surface treatments are to determine whether or not the surface treatment materials improve the rheological properties of the surface of the pavement, reduce the further oxidation of the surface, and/or change the sensitivity of the rheological properties to an increase in oxidation products.

The performance assessment study will assess both the chemical and rheological changes that occur in each section compared with an untreated section from each project with time over the course of the study. Western Research Institute will use the infrared functional group analysis (IR-FGA) to measure the increase in oxygen-containing chemical compound types for each section with time. In addition, the changes in physical properties with time will be followed using dynamic shear rheology at two temperatures, such as 25 and 60°C (77 and 140°F).

Correlation of the increase in oxygen-containing compound types with the change in rheological properties produces a measure of the sensitivity of a material to oxidation. Comparison of the amounts of oxidation, changes in rheological properties, and differences in oxidation sensitivities will provide a means of assessing the differences in the effect of each rejuvenator or sealant within a specific project site. The cost for performing the IR-FGA is estimated to be $160 per sample and the cost for the rheological analysis is estimated to be $160 per sample.

4. COMPOSITIONAL SIMILARITY OF AGENTS

Specific rejuvenators and sealants may be sold under the same brand name, however there is no guarantee that they are compositionally the same when manufactured and distributed in different locations. Thus, the goal of this task is to determine several important chemical characteristics of each agent that is used in this project. The chemical characteristics that will be determined will be those that are considered to have a major impact on the future performance of the agent after it has aged in a service environment. Specifically, the characteristics (or properties) that will be determined will include the sulfur content, the acid content, the concentration of specific functional groups, and the aliphatic/aromatic distribution (aromaticity) of the various agents.

Determination of the sulfur content is important because it has been demonstrated that the oxidation of sulfur-containing compounds in asphalts can lead to the production of strongly acidic compounds in the asphalt. These compounds can react not only with other compounds in the asphalt, but, perhaps, more importantly, with the aggregate itself. This may cause a loss of adhesion between the asphalt and the aggregate and result in deterioration of the pavement. The total acid content of the neat rejuvenator/sealer materials will be determined using non-aqueous potentiometric titration (NAPT) . This technique can differentiate between and quantify the strong acids produced by oxidation of the sulfur-containing compounds and the weaker carboxylic acids, most of which are naturally present in asphalts. This analysis will be conducted in duplicate. Infrared (IR) and nuclear magnetic resonance spectroscopy (NMR) will also be used to profile the various agents that will be used in the project. Specifically, they will be used to determine if there are differences in agents produced by different manufacturers or sold by different suppliers that are located in different places in the country. In addition, an estimate of the level of oxidation and the chemical nature of the agents can be determined using these techniques.

Application of these techniques can provide information regarding the uniformity of the production of rejuvenators and sealants by different manufacturers, the uniformity of these agents sold in different locations in the country, the chemical nature of the different agents, and the oxidation of the agents while in service in the field.

Cost estimates for these analyses on a per sample basis are:

Sulfur content	$ 28.00
NAPT analysis	$ 70.00
IR analysis	$ 50.00
NMR analysis	$180.00

DATA EVALUATION REPORT PREPARATION

All of the analytical data collected in this project will be reported to the Principal Investigator, or to his designated person, on a schedule and in a format to be agreed upon between Western Research Institute and the Principal Investigator. This will include reporting all correlations which are developed between measured chemical properties and observed performance of rejuvenators and/or sealants. The cost of report preparation will be determined by the number of samples analyzed, the desired format, and the required frequency of reporting. This cost remains to be negotiated upon clarification of the project size and the reporting complexity.

TRAVEL

It is anticipated that travel will include two trips per year to attend Technical Working Group (TWG) meetings. These will be charged on a cost reimbursement basis. Based upon two trips per year, the estimated cost is $2,000 per year.