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ABSTRACT

Four normal propyl bromide solvents were evaluated for use as chlorinated solvent replacements in typical hot mix asphalt (HMA) extraction and recovery processes. The experimental design included one method of extraction (centrifuge), one method of recovery (Rotavapor), five solvents (TCE and four nPB products), and six combinations of asphalts and aggregates (PG 46-34, PG 64-22, PG 76-22 (polymer modified); limestone, granite aggregates). Superpave binder properties were determined for the original as well as the recovered binders. A full experimental replicate was conducted so that a statistical comparison of means could be used to evaluate the effect of solvents on recovered binder properties.

Results show that when recovered binder properties were compared, there were few instances of statistically different values. When recovered binder properties were compared to the original binder properties, the TCE solvent combined with the extraction and recovery processes occasionally produced higher (i.e., stiffer) recovered binders. One nPB product appeared to be incompatible with the polymer modified PG 76-22. This was seen as a distinct stringy, rubber-like residue in the extractor.

Data indicate that nPB solvents can be used as direct replacements for the chlorinated solvents historically used for HMA extraction and binder recovery. There are limited differences in binder properties due to the different nPB solvent products. Neither the testing time nor solvent quantity changed significantly when compared to the TCE solvent. Because there may be some nPB product-specific problems with polymer modified asphalts, initial comparisons of results for both a standard chlorinated solvent and a specific nPB product should be made before accepting an nPB product as a chlorinated solvent replacement.

Key Words: nPB, TCE, HMA extractions, binder recovery

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INTRODUCTION

While the need for using solvent extraction methods for determining asphalt content has declined significantly with the growing acceptance of the ignition oven, there are times when solvent extractions are still desirable. Solvent extractions are needed to determine asphalt content of hot mix asphalt (HMA) for quality control and quality acceptance (QC/QA) testing when aggregates degrade substantially during ignition oven testing. Extractions in combination with one of two recovery processes are also needed to evaluate the binder properties of an existing HMA such as an existing pavement or in a reclaimed asphalt pavement (RAP) stockpile. The most commonly used solvents for extractions have been 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE). However, the terms of the Montreal Protocols and US Clean Air Act require that both CFC and HCFC-based chemical solvents are phased out of use for environmental reasons.

The impact of this Act on the HMA industry is that the chlorinated solvents specified in both the American Association of State Highway and Transportation Officials (AASHTO) and the American Society for Testing and Materials (ASTM) HMA extraction and recovery test methods need to be replaced. Several companies have started to market various *normal* propyl bromide (nPB) solvents as direct substitutes for both TCA and TCE. Since these halogenated solvents are new to the HMA industry, there is only limited information as to their effect on HMA test results. This research program was designed to evaluate the potential for using this category of solvent in HMA extractions and recoveries.

BACKGROUND

Extraction and Recovery Methods

Previous researchers found that both the extraction and recovery processes as well as chlorinated solvents can age (i.e., harden) the asphalt cement (1, 2). Research during the Strategic Highway Research (SHRP) program evaluated the effects of solvent hardening. Findings from this work indicated that hardening occurred at about the same level for most solvents.

A number of researchers have shown in the past that the asphalt is never completely removed from the aggregate, regardless of the solvent used. This incomplete extraction results in underestimating the asphalt content from between 0.1 to 0.5 percent asphalt (3). The retained asphalt represents selectively absorbed asphalt fractions by the aggregates which can result in significant changes in the recovered asphalt properties, depending upon whether high or low viscosity fractions are retained on the aggregate (4). When the aggregates that had a high water absorption capacity of greater than 2.5 percent were supplied to the AASHTO Materials Reference Laboratory (AMRL) for inclusion in one set of proficiency samples (1992, samples 17 and 18), the average asphalt content retained by the aggregate was 0.75 percent (4). The recovered binder viscosity of about 4,000 Poise from previous years increased to about 8,500 Poise as a result of the asphalt retained by the aggregate (4).

The ASTM D2172 Standard Test Method for Quantitative Extraction of Bitumen from Bituminous Paving Mixtures includes five methods for extracting binder. The two most commonly used methods are the centrifuge (Method A) and the reflux (Method B). Centrifuge extraction is a cold solvent process and is preferable to the hot solvent reflux method when recovering the binder because it minimizes heat hardening of the asphalts. The statistics for the 1992 AMRL samples showed that the precision for determining the extracted asphalt content

was not statistically different due to aggregate properties when reflux extraction was used (standard deviation of about 0.20 for with-in laboratory). While the centrifuge extraction precision is not statistically different when low water absorption capacity aggregates were used, the standard deviation increased to 0.30 when the high water absorption capacity aggregate mixtures were tested (4).

There are also two methods for recovering the binder from the extraction solvent. The first method used for recovery in the HMA industry was the Abson process. However, subsequent research showed the Abson recovery method (ASTM D1856) left enough residual solvent in the binder so that there was a significant reduction in binder stiffness (5, 3). The Rotavapor method of recovery (ASTM D5404), increasingly used since the 1970s, is the method of choice because of fewer problems with residual solvent and the lower heat needed for recovery (3).

SHRP research also resulted in a new extraction procedure (AASHTO TP2, 1999) which is combined with the Rotavapor recovery method. This method is designed to minimize solvent hardening of the binder, provide a more complete removal of the solvent, and more completely extract the asphalt from the aggregate. Extraction is accomplished by using a rotating cylinder, placed horizontally, with interior flights to facilitate mixing of the HMA and solvent. A vacuum line with an in-line filter at the bottom of the cylinder is used to remove the effluent. Any fines in the solution are removed with a centrifuge prior to Rotavapor recovery of the binder.

Peterson et al (3) modified the SHRP method by altering the filtering methods and equipment. Research was conducted with three solvents (TCE, toluene/ethanol, and EnSolv), two sources of reclaimed asphalt pavement (RAP), and three combinations of extraction and recovery (centrifuge-Abson, centrifuge-Rotavapor, SHRP-Rotavapor). Results confirmed previous researchers' work stating that there was little difference due to solvent or methods in the determination of the asphalt cement content. There was also no significant difference due to solvent type when using the SHRP-Rotavapor method. The within-laboratory coefficient of variation for the $G^*/\sin \delta$ Superpave binder property ranged from 12 to 26 percent.

Collins-Garcia et al (6) compared the effect of solvent type (TCE, EnSolv) on residual binder properties after reflux-Rotavapor extraction and recovery. A statistical evaluation of solubility, Brookfield viscosities at 60°C, and penetration values indicated there was no significant difference in binder properties due to solvent type. An evaluation of the time needed for recoveries from the EnSolv solvent took slightly less time; whether or not there was a significant reduction in time was dependent upon mix variables. Recovery times ranged from 92 to 103 minutes when using the TCE and from 83 to 89 minutes with the EnSolv.

Solvents

The most commonly used solvents in the past for extractions and recoveries were TCA and TCE. These products were marketed and supplied by two or three large companies with similar manufacturing processes (7). It has been suggested that this resulted in a relatively consistent product, regardless of the solvent source.

In contrast, there may be significant differences between nPB suppliers and brands (7). Properties that may differ include 1) purity, 2) moisture content, and 3) non-volatile residue. Purity is a function of variances in raw materials, manufacturing, and purification processes. These factors in turn produce differences in water content, acidity, non-volatile residue, free bromine, and color. Color is the simplest indicator of purity because relatively small amount of free bromine results in an orange-yellow color.

The ASTM D6368 standard specification for Vapor-Degreasing Grade and General Grade *normal*-Propyl Bromide (8) contains a set of requirement for the base solvent in vapor

degreasing fluids. However, one impurity of potential importance that is not addressed by this standard is a limit on isopropyl bromide (iPB). This component has shown reproducibility toxicity at relatively low levels and is likely to be limited to a maximum of 0.1 percent (1,000 ppm) by the Environmental Protection Agency (EPA) as noted in its Advance Notice of Proposed Rulemaking for nPB.

This impurity is thought by several people in the nPB industry to also have the potential for influencing testing variability and asphalt-solvent interactions. One nPB supplier recommends that iPB be limited in any nPB solvents used in the HMA industry. This supplier considers the suggested EPA limit to be a satisfactory requirement for a minimum level of purity.

Another difference between the nPB products is the type of stabilizer used to maintain an acceptable level of acidity. These additives are usually less than 1.5 to 2 percent of the solvent. The inclusion of a stabilizer is not uncommon; TCE has historically been manufactured with stabilizers for the same reason. In fact, one nPB product uses the same stabilizer formulation as the TCE. There is no information that would indicate whether these additives have the potential for influencing asphalt-solvent interactions.

RESEARCH PROGRAM

Objectives

The objective of this research program was to:

- Evaluate the possibility of recommending n-propyl bromides as a replacement for trichloroethane 1, 1, 1 and trichloroethylene solvents in extraction and recovery HMA test methods.

Scope

The experimental design included one method of extraction (centrifuge), one method of recovery (Rotavapor), five solvents (TCE and four nPB products), and six combinations of asphalts and aggregates (PG 46-34, PG 64-22, PG 76-22 (polymer modified); limestone, granite aggregates).

Three binders that covered a wide range of original binder properties and composition were used. The PG 46-34 was selected as a very low viscosity asphalt. The PG 64-22 is a typical unmodified paving grade binder and the PG 76-22 is an SBS modified asphalt, both of which are commonly used in the Southeastern part of the country. A high absorption Florida limestone and a low absorption Georgia granite were used to prepare one standard aggregate gradation. A Superpave volumetric mix design was used to select the optimum asphalt content for each aggregate source. The optimum asphalt content was then held constant, regardless of the binder grade.

All samples were mixed at appropriate mixing temperatures, cured for 4 hours at 135°C (275°F) then covered and stored for 7 days prior to extraction and recovery of the binder. A single curing time and temperature was selected to minimize the testing variables in the study. The storage time was included to simulate potential time delays that may occur before quality acceptance testing is completed.

Extraction test methods were selected to minimize the heat hardening effect due to the extraction and recovery processes. Based on the literature review, the centrifuge method was selected because it was a cold solvent extraction method that would minimize any heat hardening of the asphalt. While the amount of the binder extracted may be more variable than with the reflux extraction method, it was felt that minimizing the heat hardening of the binder was the primary

consideration. Mineral matter was removed from the extraction effluent with a high-speed centrifuge.

Rotavapor recovery was selected to minimize heat hardening and maximize the solvent reclamation. The TCE solvent was used as the control against which the properties of binders recovered with each of the four nPB products (Lenium, EnSolv, Hypersolv, Leksol) were compared.

The standard Superpave binder tests and test temperatures used to classify the original binders were used to evaluate recovered binder properties. The combined effect of binder hardening due to extraction, recovery, and solvent was evaluated by comparing recovered binder properties to those of the original (i.e., not recovered) binder properties.

MATERIALS

Asphalt Cements

The original binder properties are shown in Table 1. This table also indicates the Superpave binder test temperatures used for each binder grade and test.

Table 1. Binder Test Results and Superpave Test Temperatures

Test	Binders		
	PG 46-34	PG 64-22	PG 76-22
Original G*/sin d, kPa	0.8099	1.783	1.591
Test Temperature, °C	46	64	76
RFTO G*/sin d, kPa	1.628	3.767	3.72
Test Temperature, °C	46	64	76
RTFO + PAV G* sin d, kPa	3377	3838	1291
Test Temperature, °C	10	25	31
BBR Stiffness, MPa	155	292	126
Test Temperature, °C	-24	-12	-12
BBR m-value	0.381	0.314	0.341
Test Temperature, °C	-24	-12	-12

Data average of two test results.

Aggregates

Two aggregates were used: 1) a Georgia granite, and 2) a Florida limestone. Aggregate properties are shown in Table 2. The limestone has a relatively high water absorption capacity. The granite, while having a low absorption capacity, has a history of producing mixtures with low tensile strength ratios after moisture conditioning (TSR typically between 50 and 70 percent). It was expected that these differences in aggregate properties would enhance differences in selective absorption of asphalt components and thus variations in the amount of asphalt that can be extracted (i.e., differences in asphalt content) and recovered binder properties. One gradation was used for both aggregates (Table 2).

Table 2. Aggregate Properties

Properties	Granite	Limestone
Bulk specific gravity	2.672	2.412
Absorption capacity, %	0.6	4.1
Aggregate gradation		
Cumulative Percent Passing, %	100	
19 mm	99	
12.5 mm	99	
9.5 mm	70	
4.75 mm	44	
2.36 mm	27	
1.18 mm	16	
0.600 mm	10	
0.300 mm	7	
0.150 mm	6	
0.075 mm	2	

Solvents

TCE was used as the control for this study since this solvent is one that has been commonly used in the past. Four nPB products were selected for use in this study: 1) Lenium GS, 2) Leksol, 3) Hypersolv, and 4) EnSolv. This list represents most of the readily available nPB products that could be obtained at the beginning of this study.

TESTING PROGRAM

A 100 N_{design} gyration Superpave mix design was conducted to determine the optimum asphalt content for each aggregate source. Optimum asphalt contents of 6.5 and 8.0 percent were selected for the PG 64-22 asphalt cement mixed with the granite and limestone aggregate sources, respectively. These asphalt contents were held constant for each aggregate source, regardless of the binder grade. Mix temperatures were changed based on standard viscosity-temperature relationships to obtain an equi-viscous condition. These temperatures were 130, 150, and 165°C (266, 300, and 325°F) for the PG 46-34, PG 64-22, and the PG 76-22 binders, respectively.

Individual samples of 4,500 grams were batched, mixed, cured at 135°C (275°F) for 4 hours then covered and stored for seven days prior to each extraction. The storage time was included to allow for further and deeper absorption of the asphalt fractions by the aggregates. It was assumed that this would help maximize any differences between solvents due to mix variables. Centrifuge extraction and correction for fines was conducted according to ASTM D2172. Rotavapor recoveries were conducted per ASTM D5404.

The original (unrecovered) Superpave binder properties were determined for all of the asphalt cements. Recovered binders were tested at the test temperatures used to classify the original asphalts. Both of the dynamic shear rheometers (DSR) used in completing the first round of testing were damaged beyond repair about a third of the way through the replicate testing program as the result of a defective in-house air drying system. A number of tests on binders with known properties

developed with the original DSR equipment was evaluated on the new DSRs. Adjustments were made as needed so that the new equipment produced results statistically similar to those obtained with the original equipment.

Replacement equipment was used for testing the PG 46-34 and PG 64-22 replicate mixtures. Samples for these replicates were prepared, the binder extracted and recovered then stored at cold temperatures in sealed containers until the new equipment could be installed and calibrated. There was about a four month storage time for these binder samples.

Fourier Transform Infrared Analysis

A limited amount of FTIR testing was conducted to determine if there was any indication of the solvent remaining in the asphalt after extraction and recovery. A background spectrometer count of the atmosphere and the cell were initially obtained. The recovered asphalt residue was dissolved in THF and dried on the HATR in a 110°C oven for several minutes. The cell was then placed in the FTIR and the spectrum obtained. The same procedure was used for all of the residual asphalts tested.

RESULTS AND ANALYSIS

An analysis of the individual data (not shown) indicated that the reported asphalt contents were well within single operator precision reported in ASTM D2172. This precision statement indicates a standard deviation of 0.21 percent for centrifuge extractions (aggregate with low water absorption capacity) with an acceptable range in test results of 0.59 percent should be expected. The average asphalt content from two test results is shown in Table 3.

Table 3. Asphalt Cement Contents (Average of Two Tests)

Solvent	Asphalt Cement Content, %					
	PG 46-34		PG 64-22		PG 76-22	
	Granite	Limestone	Granite	Limestone	Granite	Limestone
TCE	6.14%	7.33%	6.02%	7.73%	6.16%	7.26%
Lenium	5.97%	7.55%	6.19%	7.32%	6.34%	7.22%
Leksol	6.27%	7.26%	6.35%	7.27%	6.34%	7.65%
Hypersolv	6.13%	7.43%	6.21%	7.31%	6.18%	7.38%
EnSolv	6.15%	7.23%	6.45%	7.75%	6.44%	7.38%

Granite mixes had a 6.5% optimum asphalt content
 Limestone mixes had an 8.0% optimum asphalt content

The granite aggregate retained (i.e., could not be removed during extraction) between about 0.35 and 0.5 percent asphalt. The limestone retained between 0.25 and 1.0 percent asphalt. These results depended somewhat upon the grade of asphalt mixed with a given aggregate source. For a given combination of asphalt and aggregate, there were no significant differences in the determination of the asphalt content due to the solvent type.

Because of the high cost of solvents, the quantity of solvent needed for each extraction was documented during the testing program. Table 4 shows the quantities of solvents used for the average of two tests. All rows were evaluated for each column of data shown in this table using a Duncan multiple-range comparison test for means (a student’s t-test). This analysis indicated that there were no significant differences in solvent quantities used. A confidence level of 95 percent was used for all comparisons.

Table 4. Quantities of Solvents Used for Extractions (Average of Two Results)

Solvent	Quantities of Solvent Used, Gallons					
	PG 46-34		PG 64-22		PG 76-22	
	Granite	Limestone	Granite	Limestone	Granite	Limestone
TCE	0.750	0.875	1.000	0.750	0.875	0.875
Lenium	0.875	0.875	1.375	1.125	1.500	1.250
Leksol	1.125	1.125	1.250	1.375	1.375	1.250
Hypersolv	1.125	1.250	1.500	1.250	1.500	1.375
EnSolv	0.750	0.750	1.000	0.875	1.125	1.375

The time needed for recovery was also documented (Table 5). The time the binder is exposed to the heating needed to vaporize the solvent is important because it may alter (i.e., harden) the properties. Duncan comparisons were used to determine that, while there may appear to be some differences in times, they were not significant due to the variability in the test results.

Table 5. Time for Rotavapor Recovery of Asphalt Cement (Average of Two Tests)

Solvent	Recovery Time, Minutes					
	PG 46-34		PG 64-22		PG 76-22	
	Granite	Limestone	Granite	Limestone	Granite	Limestone
TCE	65	60	67.5	75	80	82.5
Lenium	75	75	90	60	90	65
Leksol	72.5	80	80	60	62.5	85
Hypersolv	50	60	75	67.5	77.5	65
EnSolv	50	75	57.5	50	105	75

The average Superpave binder properties for all of recovered binders tested in this program are shown on Table 6. Table 7 presents the coefficient of variation (CV) for all tests. The CV for the dynamic shear rheometer (DSR) testing of the PG 76-22 recovered binders was between about 23 and 30 percent; this range agrees with that reported by Peterson et al (3). The increased CVs for the PG 64-22 and PG 46-34 recovered binder properties are most likely a function of replacing the DSR equipment, storage time of the recovered binders and changes in technicians. Since these changes violate the assumption of single operator-same equipment, the CVs for these mixtures should be considered to represent a between—rather than within—laboratory variability.

Table 6. Recovered Binder Properties (Average of Two Test Results)

Test	Solvent Used in Extraction				
	TCE	Lenium	EnSolv	Leksol	Hypersolv
PG 46-34 Granite Aggregate					
Original G*/sin δ, kPa	4.325	2.113	3.521	1.572	1.315
RTFO G*/sin δ, kPa	7.474	3.511	6.775	3.4	2.825
RTFO + PAV G* sin δ, kPa	4535	3607	1462	3992	3086
BBR Stiffness, MPa	176	150	163	128	113
BBR m-value	0.356	0.342	0.337	0.375	0.373
PG 64-22 Granite Aggregate					
Original G*/sin δ, kPa	6.136	5.032	8.546	7.988	3.898
RTFO G*/sin δ, kPa	10.202	8.204	13.701	14.803	8.404
RTFO + PAV G* sin δ, kPa	4051	3963	4839	4528	3447
BBR Stiffness, MPa	214	207	224	208	187
BBR m-value	0.334	0.343	0.34	0.328	0.355
PG 76-22 Granite Aggregate					
Original G*/sin δ, kPa	3.873	2.762	2.826	3.203	5.201
RTFO G*/sin δ, kPa	5.336	4.32	4.042	4.779	11.569
RTFO + PAV G* sin δ, kPa	2186	1373	1488	1901	2407
BBR Stiffness, MPa	211	163	171	177	197
BBR m-value	0.305	0.348	0.329	0.334	0.308
PG 46-34 Limestone Aggregate					
Original G*/sin δ, kPa	2.614	1.973	0.975	1.795	1.837
RTFO G*/sin δ, kPa	5.442	3.346	2.893	2.827	3.485
RTFO + PAV G* sin δ, kPa	2909	2660	2341	2311	1590
BBR Stiffness, MPa	175	148	153	121	129
BBR m-value	0.356	0.367	0.372	0.386	0.38
PG 64-22 Limestone Aggregate					
Original G*/sin δ, kPa	5.74	5.327	4.852	3.913	5.916
RTFO G*/sin δ, kPa	12.441	9.419	8.726	7.215	12.087
RTFO + PAV G* sin δ, kPa	4233	3656	4010	3342	4264
BBR Stiffness, MPa	210	188	201	185	206
BBR m-value	0.33	0.356	0.359	0.368	0.351
PG 76-22 Limestone Aggregate					
Original G*/sin δ, kPa	7.029	4.594	2.702	3.121	6.944
RTFO G*/sin δ, kPa	11.607	6.71	5.18	4.796	16.279
RTFO + PAV G* sin δ, kPa	2359	1614	1416	1379	2086

Table 6. Recovered Binder Properties (Average of Two Test Results)

BBR Stiffness, MPa	196	168	155	160	182
BBR m-value	0.305	0.323	0.344	0.348	0.31

Table 7. Average Coefficient of Variation

Property	Average Coefficient of Variation, %					
	PG 46-34		PG 64-22		PG 76-22	
	Limestone	Granite	Limestone	Granite	Limestone	Granite
Original $G^*/\sin \delta$, kPa	38.5	31.7	64.4	33.4	29.7	23.4
RTFO $G^*/\sin \delta$, kPa	41.8	41.0	61.0	33.7	38.0	18.4
RTFO + PAV $G^*/\sin \delta$, kPa	76.7	40.1	43.7	46.7	18.5	28.4
BBR Stiffness, MPa	17.3	11.3	17.9	33.7	5.6	12.4
BBR m-value	3.6	6.9	7.7	11.6	5.3	7.0

Statistical Evaluation of the Effect of Solvent Type on Superpave Binder Properties

Duncan multiple-range comparisons were used to evaluate statistical differences of a given mean binder property due to solvent type. The Duncan test of means produces a letter ranking, after ordering the means from highest to lowest, that indicates which means are not statistically different. For the following analyses, binder properties with the same letter ranking are not statistically different.

Each combination of binder and aggregate was evaluated individually. All statistical evaluations included the original binder property so that any binder aging could be assessed. Binder aging in this case is due to a combination of factors: selective asphalt absorption by the aggregate, solvent hardening, and hardening due to the recovery process.

DSR $G^/\sin \delta$ (no aging)*--There were no significant differences in binder stiffness, either before or after recovery, due to solvent type for the following combinations of binders and aggregates: PG 46-34 and either the granite or limestone aggregates, PG 64-22 and limestone aggregate, and the PG 76-22 and granite aggregate. That is, the mean recovered binder value was not significantly different from the original (unrecovered) value. No statistically significant aging of the binder occurred for these mixtures.

There were two mixes that did show limited differences in binder stiffness due to extraction and recoveries. These were the PG 64-22 with granite and the PG 76-22 with limestone mixtures. Table 8 shows that none of the recovered asphalts had a statistically different DSR $G^*/\sin \delta$ (A ranking). The TCE, Lenium, and Hypersolv solvents produced recovered binders with DSR $G^*/\sin \delta$ values that were not statistically different from the original binder values for the PG 64-22 with limestone mix (B ranking).

Table 8. Duncan Comparison of Means (Recovered (no aging) DSR $G^*/\sin \delta$)

PG 64-22 Granite			PG 76-22 Limestone		
$G^*/\sin \delta$ kPa	Solvent	Rank	$G^*/\sin \delta$ kPa	Solvent	Rank
8.546	EnSolv	A	7.029	TCE	A
7.988	Leksol	A	6.945	Hypersolv	A
6.136	TCE	A B	4.591	Lenium	A B
5.033	Lenium	A B	3.121	Leksol	A B
3.498	Hypersolv	A B	2.702	EnSolv	A B
1.783	Original	B	1.591	Original	B

For the PG 76-22, the Lenium, Leksol, and EnSolv were not statistically different from the original binder (B ranking). Laboratory journal notes indicated that the effluent from the Hypersolv extractions with the PG 76-22 was described as “stringy,” “sticky” and having a “lumpy” appearance. These observations suggest that the polymer and the asphalt were separating during extraction with this solvent. None of the other solvents produced these observations.

When just the effect of solvent on the test results is considered, there were no statistical differences due to solvent types (all solvents have an A ranking).

DSR $G^/\sin \delta$ (After Rolling Thin Film Oven Aging)*—Similar results were seen for this property. That is, there were no significant differences in binder properties, either before or after recovery, due to solvent type for the PG 46-34 and either the granite or limestone aggregates, PG 64-22 and limestone aggregate, and the PG 76-22 and granite aggregate combinations of aggregates. The two combinations that showed statistical differences in the original properties also showed statistical differences in the aged properties.

Table 9 shows that there were no differences between the recovered binders. The A ranking indicates that there is no difference due to solvent type. However, the Leksol solvent with the PG 64-22 and granite mixtures produced a recovered binder with significant aging (no B ranking).

Table 9. Duncan Comparison of Means (Recovered (RTFO aging) DSR $G^*/\sin \delta$)

PG 64-22 Granite			PG 76-22 Limestone		
$G^*/\sin \delta$ kPa	Solvent	Rank	$G^*/\sin \delta$ kPa	Solvent	Rank
14.803	Leksol	A	16.278	Hypersolv	A
13.701	EnSolv	A B	11.607	TCE	A B
10.203	TCE	A B	4.796	Leksol	B
8.404	Hypersolv	A B	4.594	Lenium	B
8.204	Lenium	A B	3.720	Original	B
3.767	Original	B	2.702	EnSolv	B

In the case of the PG 76-22 and limestone mixture (Table 9), the Hypersolv solvent produced recovered binders with a higher stiffness than either the original binder or any of the other recovered binders except the TCE (A B ranking).

DSR G sin δ (After Rolling Thin Film Oven and Pressure Aging Vessel Aging)*—The only combinations that showed any statistical differences were the PG 46-34 with granite and the PG 76-22 with limestone (Table 10). While there was no statistical evidence of binder aging for the PG 46-34 with granite aggregate mix for this test, the TCE and EnSolv recovered binder properties were statistically different. The TCE recovered binders had the highest stiffness while the EnSolv value was the lowest. For the PG 76-22 with limestone mix, the TCE solvent resulted in significant aging of the original binder (no B ranking).

Table 10. Duncan Comparison of Means (Recovered (RTFO + PAV aging) DSR G* sin δ)

PG 64-22 Granite			PG 76-22 Limestone		
G* sin δ kPa	Solvent	Rank	G* sin δ kPa	Solvent	Rank
4535	TCE	A	2358	TCE	A
3992	Leksol	A B	2086	Hypersolv	A B
3617	Lenium	A B	1614	Lenium	A B
3377	Original	A B	1416	EnSolv	B
3086	Hypersolv	A B	1318	Leksol	B
1462	EnSolv	B	1291	Original	B

Bending Beam Rheometer (BBR) Values (BBR Stiffness, BBR m-Value)—Table 11 shows that while there were statistical differences in the BBR stiffness for four out of the six asphalt-aggregate combinations, there were no consistent trends in the differences. For the PG 46-34 and granite mix, none of the solvents produced significant aging when compared to the original binder stiffness. Both the TCE and EnSolv produced a significantly higher stiffness than the Hypersolv.

Table 11. Duncan Comparison of Means (Recovered (RTFO + PAV aging) Bending Beam Stiffness)

PG 46-34 Granite			PG 64-22 Limestone			PG 76-22 Granite			PG 76-22 Limestone		
Stiff. MPa	Solvent	Rank	Stiff. MPa	Solvent	Rank	Stiff. MPa	Solvent	Rank	Stiff. MPa	Solvent	Rank
176	TCE	A	292	Original	A	211	TCE	A	196	TCE	A
163	EnSolv	A	210	TCE	A B	197	Hypersolv	A	185	Hypersolv	A B
155	Original	A B	206	Hypersolv	A B	177	Leksol	A B	168	Lenium	A B
150	Lenium	A B	201	EnSolv	B	171	EnSolv	A B	160	Leksol	B
128	Leksol	A B	188	Lenium	B	163	Lenium	A B	155	EnSolv	C B
113	Hypersolv	B	185	Leksol	B	126	Original	B	126	Original	C

TCE and Hypersolv solvent recovered binders and the original PG 64-22 BBR stiffness results were not different. EnSolv, Lenium and Leksol solvents produced lower BBR stiffness values when compared to the original binder. The B ranking indicates that when only the recovered binders are

considered, the type of solvent did not produce a statistically significant difference in the BBR stiffness.

TCE and Hypersolv solvent recovered binders had a statistically higher BBR stiffness than the original PG 76-22 polymer modified asphalt for the granite aggregate mix. The A ranking indicates that none of the recovered binder BBR values were statistically different.

All solvents except the EnSolv produced significantly higher BBR stiffness values than the original binders for the PG76-22 and limestone mix.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Recovered Binders

A limited FTIR study was conducted to determine if the solvent was completely removed from the asphalt. The same amount of PG 64-22 as used in preparing the limestone mixes was dissolved in 1 gallon of a particular solvent, allowed to stand overnight to ensure complete dissolution, then recovered as if the solvent had been obtained from a mix extraction.

Figures 1 through 5 show the FTIR fingerprints obtained for the neat asphalt (before contact with any solvent), after dissolution in TCE, Lenium, Leksol, and Hypersolv, respectively. The asphalt fingerprints obtained after contact with the TCE, Lenium, and Leksol and Rotavapor recovery are virtually identical. There is a little increase in the concentration in the 500 to 650 cm^{-1} and the 750 to 850 cm^{-1} absorption ranges. This is associated with a small increase in the alkyl halides, R-Br, and R-Cl, respectively, and indicates that there is a trace of halogens contained in the recovered asphalts.

There is a noticeable increase in the 1050 to about 1200 cm^{-1} absorption range as compared to the neat asphalt for the TCE, Lenium, EnSolv, and Leksol solvent extractions. This would be consistent with an increase in either double bonds or carbon-oxygen bonds and is most likely associated with heat-induced aging of asphalts (e.g. oxidative scission). This is expected since the recovery process subjects the asphalt to heating for about 1 hour.

The fingerprint of the Hypersolv-recovered asphalt is different from any of the other recovered asphalts in that there is still some evidence of R-Br bonds but a decrease in the carbon-oxygen bond or double bond regions as compared to the neat asphalt. Not only is there no evidence of aging, but there appears to be a solvent affect on the chemistry of the neat asphalt. This suggests that this particular solvent is interacting in a different manner than any of the other halogenated solvents. While the reason for the differences cannot be determined from this limited testing, one hypothesis is that something in the Hypersolv solvent is acting as an oxygen scavenger. Since this is the only solvent that showed an incompatibility with the polymer modified asphalt, it is possible that this difference in the FTIR fingerprint may indicate an incompatible asphalt-nPB combination. However, further testing is needed before this hypothesis can be evaluated.

Summary

Figure 6 compares the $G^*/\sin \delta$ values for both the original binder and the binders recovered from the granite aggregate mixtures. Only the EnSolv and Leksol solvents produced recovered binders with a value statistically higher than the original binder. When just the recovered binders are compared to each other, there was no difference due to solvent type. Figure 7 shows the same binder property for the original binders and those recovered from the limestone mixtures. Only the TCE and Hypersolv solvents produced recovered binders with values significantly higher than the original asphalts. Again, if only the recovered binder properties are compared, there was no difference in the results due to solvent type.

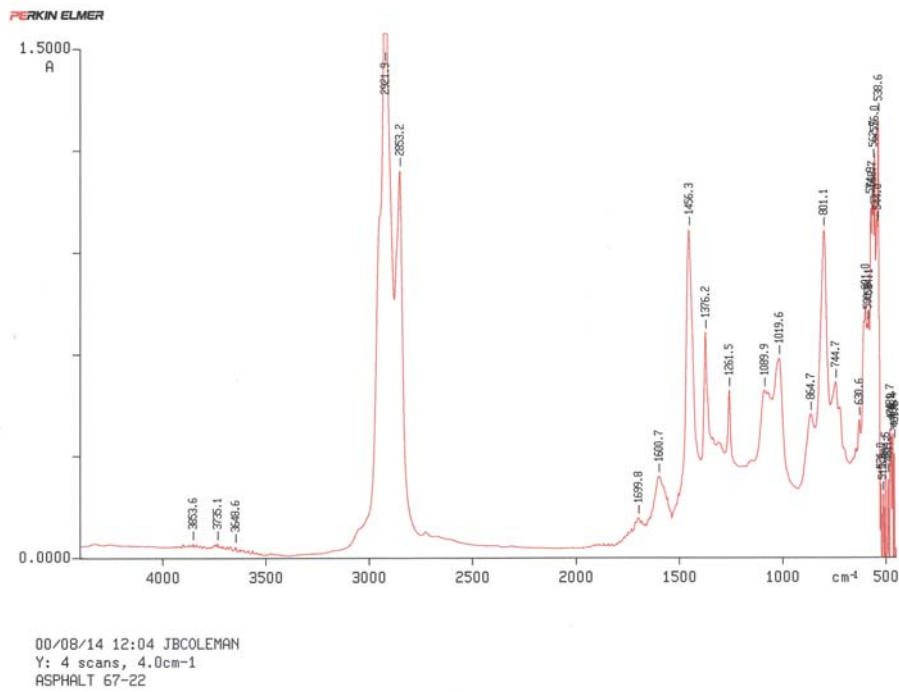


Figure 1. FTIR Results for Neat PG 64-22 Asphalt

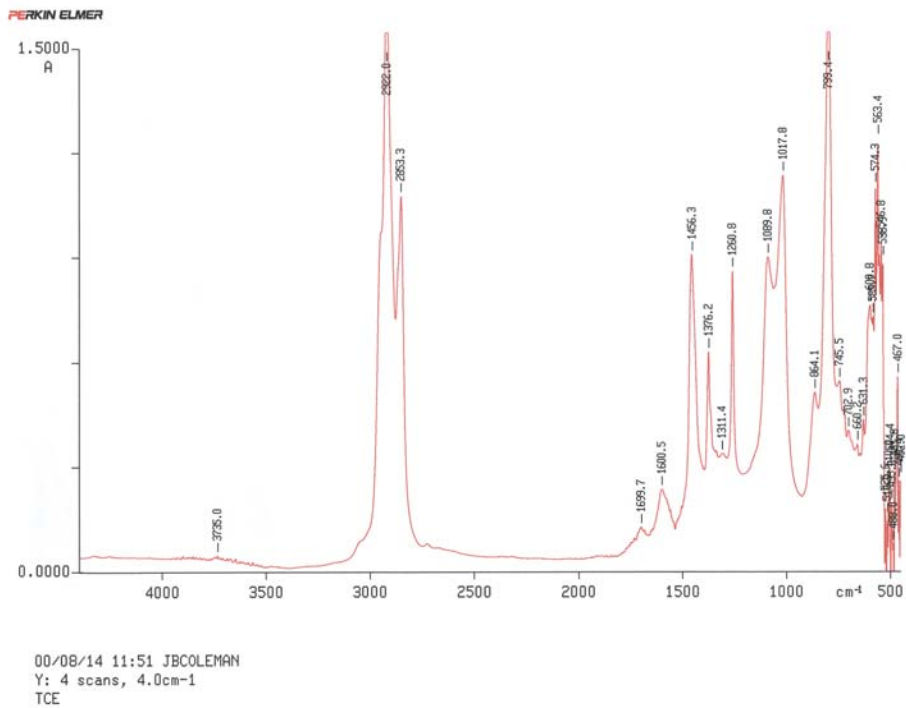


Figure 2. FTIR Results for PG 64-22 Recovered from TCE

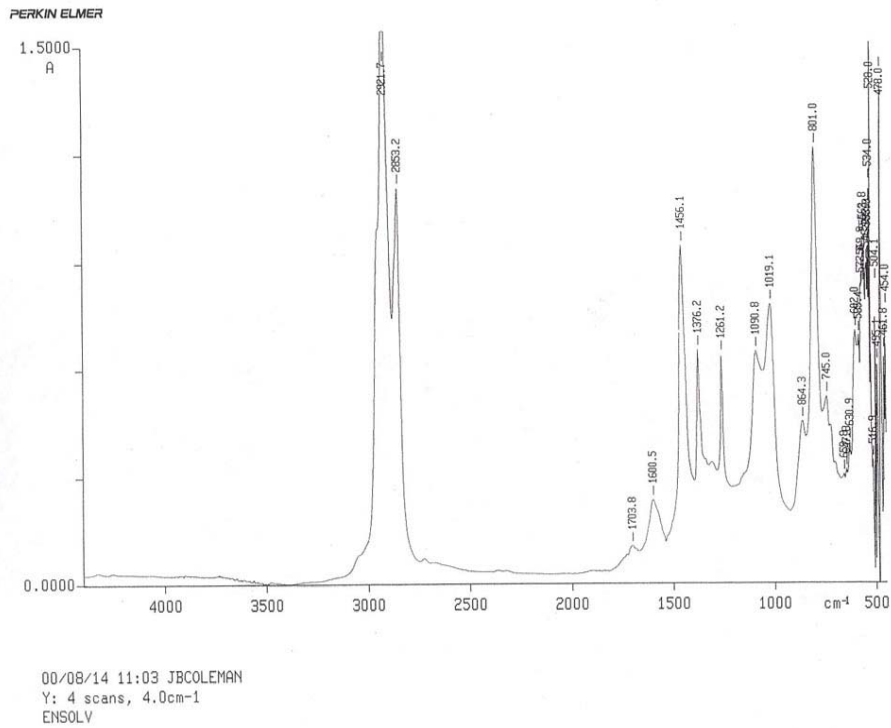


Figure 3. FTIR Results for PG 64-22 Recovered from Lenium

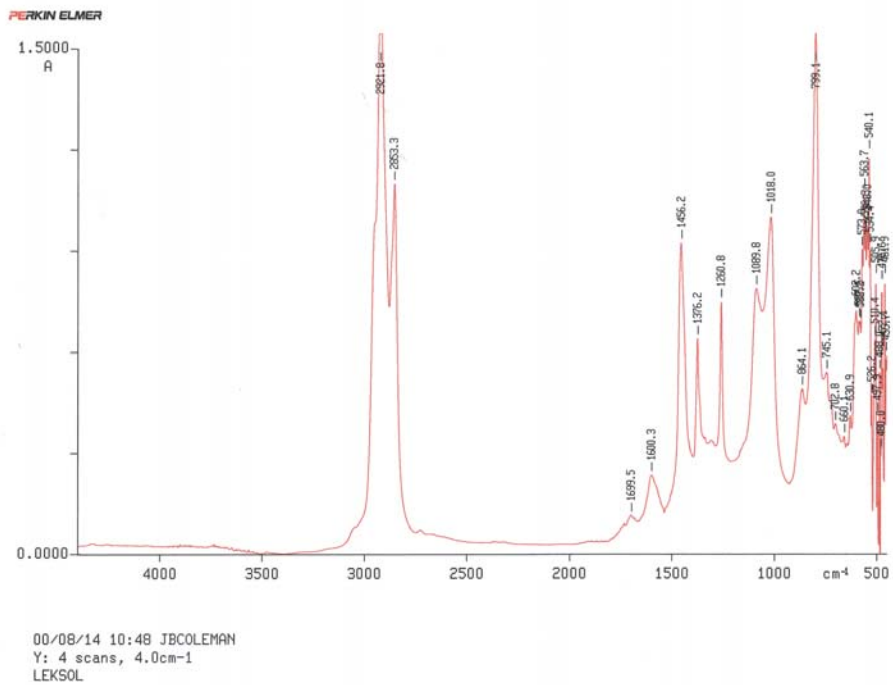


Figure 4. FTIR Results for PG 64-22 Recovered from Leksol

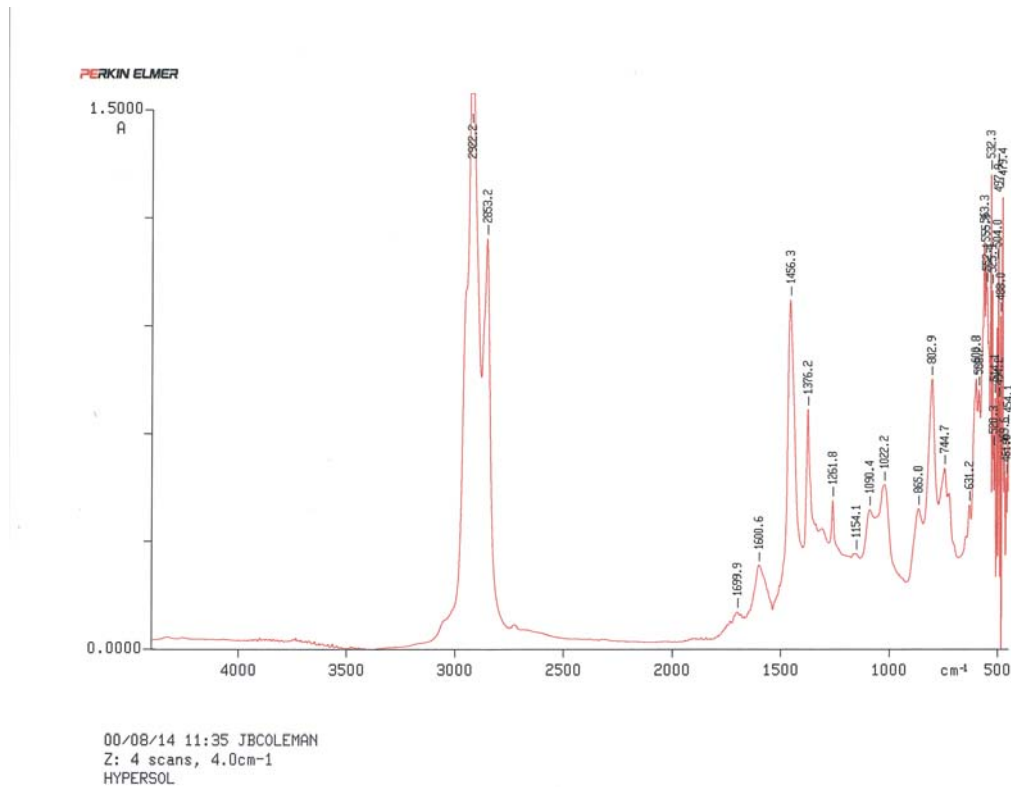


Figure 5. FTIR Results for PG 64-22 Recovered from Hypersolv

While there are some differences seen in the other Superpave binder test results, the above summary of the findings is generally consistently over the range of binder tests.

CONCLUSIONS

The following conclusions can be drawn from this research:

1. There was generally no dependency of the recovered binder Superpave test results on the type of solvent used. However, there did appear to be a potential for solvent-specific binder-solvent interactions when a polymer modified is evaluated. This was limited to only one of the nPB products. It should be noted that this nPB product also yielded a significantly different FTIR fingerprint than any of the other solvents.
2. There appears to be a limited potential for aging of the binder due to extraction, recovery, and solvent, depending on the mix variables. Any apparent aging of the binder will depend on the solvent and specific mix variables.
3. There is a large variability associated with determining recovered binder properties. The within-laboratory coefficient of variation is about 23 to 30 percent. The between-laboratory coefficient of variation appears to be around 38 to 45 percent. While this is not desirable, it is consistent with other recovered binder studies.
4. Even when there were no statistical differences in the results, the TCE solvent usually produced recovered binders with the one of the highest (stiffest) values. It is possible that if the test method precision were improved, these values might then be seen as statistically different.

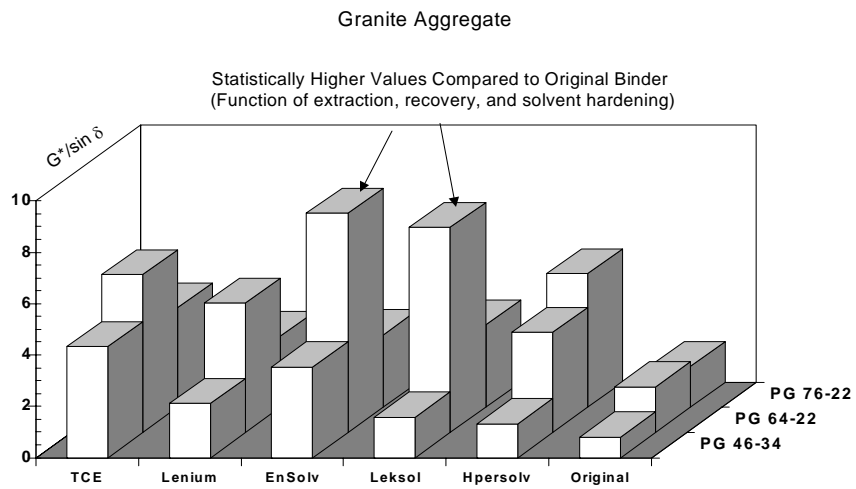


Figure 6. $G^*/\sin \delta$ for Granite Mixtures

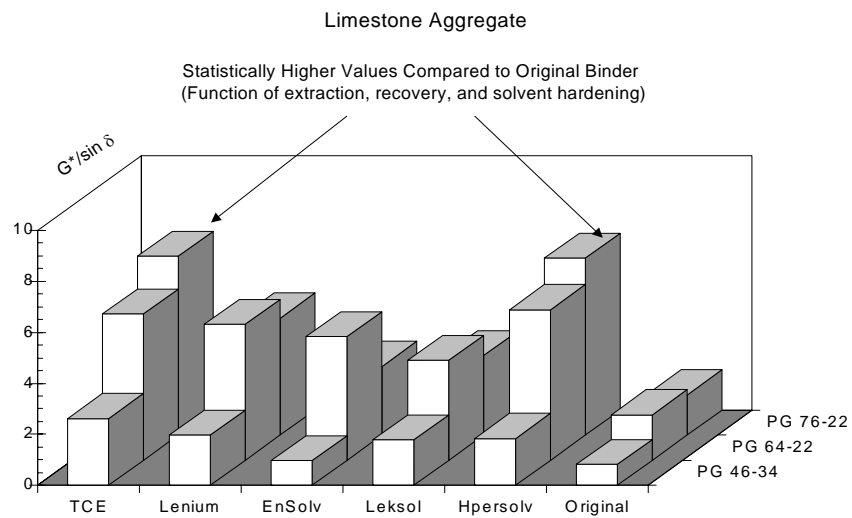


Figure 7. $G^*/\sin \delta$ for Limestone Mixtures

RECOMMENDATIONS

Based on the results of this study, it appears that the nPB solvents can be used as direct replacements for the TCE solvent. There is some indication that a change to the nPB solvents would reduce some of the solvent aging seen during TCE solvent extraction and recovery processes. There appears to be a potential for nPB product-specific incompatibilities with a polymer modified asphalt. These product-specific interactions may be due to differences in the purity of the various nPB products and/or the type(s) of stabilizer additives. Since these factors cannot be readily assessed at this time, any solvent replacement should be evaluated prior to adoption to ensure that test results are similar to those historically obtained by the agency with their traditional solvent(s).

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