FINAL REPORT

QUANTITATIVE DETERMINATION OF ASPHALT ANTISTRIPPING ADDITIVE

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DISCLAIMER

ABSTRACT

A small device (StripScan) has been developed by InstroTech, Inc., that uses litmus paper and a spectrophotometer to analyze vapors from hot liquid asphalt binders and mixtures to determine the percentage of antistripping additive present. Approximately 60 five-point additive content–color index count regressions were performed on binders and mixtures to determine how well the StripScan device measured additive content. The regressions basically fit the quadratic format that is used by the manufacturer in the recommended calibration process. The regressions were best when the litmus color index count was calculated by subtracting the initial count of the blank strip from the final count after exposure for the mixtures.

Changes to the instrument software and testing temperature were necessary as the investigation progressed to accommodate different grades of binders. After the planned testing was completed, some retesting of the binders was performed using modified equipment and procedures. The changes appeared to improve the consistency of the results; therefore, the author believes that additive content in binders can be determined within ±0.2 percent 95 percent of the time using the modified equipment and procedures. Test results for mixtures were less accurate than for binders; however, if the vapor trap is modified as described, the accuracy for mixtures should be improved substantially. Since the test can be performed quickly, multiple tests on a sample are possible. This would increase the confidence of the test results.

Additional research and development is recommended and necessary before the device can be used for quality assurance testing. An accuracy of ±0.1 percent is a worthy goal.

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INTRODUCTION

Virginia has had problems with moisture damage in asphalt concrete for many years. Moisture entering from the surface or wicking from the bottom layers of asphalt concrete causes the asphalt film to detach from the aggregate surface or soften in an emulsification phenomenon. The weakening resulting from this moisture damage is commonly referred to as *stripping* since the asphalt film is usually stripped from the aggregate particles.

In an effort to combat stripping, the Virginia Department of Transportation (VDOT) requires the use of antistripping additives in all asphalt concrete. Antistripping additives can be either hydrated lime that is applied directly to the aggregate or chemical amine additives that are blended with the asphalt cement. Chemical additives can be blended with the asphalt cement at the terminal before shipping to the asphalt hot-mix plant or added directly to the asphalt cement at the hot-mix plant. It is essential that the asphalt concrete contain the prescribed amount of antistripping additive to minimize pavement failures attributable to moisture damage.

It is difficult to determine the quantity of additive in a liquid binder and even more difficult and nearly impossible to determine how much additive an asphalt concrete mixture contains. At present, liquid binder suppliers certify that the additive is incorporated at the terminal, but no checks are performed. Asphalt plant operators can also incorporate antistripping additive into the liquid asphalt binder before the binder is mixed with aggregate in the asphalt drum during production of asphalt concrete. The incorporation of additive can be stopped and started at the asphalt plant depending whether the asphalt concrete is being supplied to VDOT or private jobs. The presence of additive should be checked at a hot-mix plant where additive may be inadvertently omitted or where additive equipment can malfunction. The bottle test is supposed to check for the presence but not the amount of additive.[1] Additive can be detected by gas chromatography, but this process is so complicated that it is impractical to use.[2] Determining the presence of additive in an asphalt mixture has been a problem because the current chemical extraction process required to separate binder from aggregate tends to destroy additive properties.

Recently, a device (StripScan) was developed by InstroTech, Inc., that the manufacturer claims is simple and requires very little operator involvement. With the device, shown in Figure 1, a sample is heated and placed in an automatic microprocessor-controlled temperature chamber. A litmus test strip sensitive to amines automatically extends over the sample, and vapor from the additive containing primarily amines changes the color of the test strip. The reacted litmus strip retracts within the device, and a spectrophotometer reads the color change.

Figure 1. StripScan Device

The spectrophotometer measures the reflectance spectrum of the litmus in the visible range, specifically the wavelengths between 400 and 520 nm from which a color index is generated. The color index is a direct indication of the concentration of antistripping chemicals in the vapor. The manufacturer claims that the device can be used to measure antistripping additives in liquid binder or an asphalt mixture.

The device would be useful not only for verifying that production material contains antistripping additive but possibly also for providing a forensic tool to check asphalt concrete where problems have developed or where asphalt is suspected to be deficient of additive. Another important usage may be to determine whether additive deteriorates over time as asphalt is stored at high temperatures. The personnel in the binder lab at the Virginia Transportation Research Council have noticed in performing routine binder grading tests that samples containing additive sometimes tend to lose excessive amounts of weight when subjected to high temperatures for extended periods. This raises the question of whether the additive is evaporating or chemical changes are decreasing its effectiveness in storage or during the construction process when a high temperature is necessary.

PURPOSE AND SCOPE

The primary purpose of this investigation was to determine the accuracy of the StripScan in determining the amount of antistripping additive in liquid binder and asphalt concrete.

The laboratory study tested various combinations of binder, antistripping additive, and aggregates typically used by VDOT.

METHODS

Materials

The binders and additives used in the study are listed in Table 1 and Table 2, respectively. Information for the Superpave mixtures is listed in Table 3. The primary aggregate (50 percent or more) in mixtures 1029, 1030, and 1034 was greenstone (metabasalt), crushed gravel, and diabase, respectively. The primary aggregate in mixtures 1029 and 1034 had a high specific gravity (approximately 2.9) and an absorption of 1 percent or less, whereas aggregate in mixture 1030 had a specific gravity of about 2.65 with a high absorption (approximately 2.0 percent). Mixture 1029 also contained 15 percent RAP (recycled asphalt pavement).

Table 1. Asphalt Binders

Binder Type	Supplier	Source Location
-22	CITGO	Dumfries, Virginia
PG70-22	CITGO	Dumfries, Virginia
PG76-22	CITGO	Dumfries, Virginia
-22	KOCH	Newport News, Virginia
PG70-22	KOCH	Newport News, Virginia
PG76-22	KOCH	Newport News, Virginia

Table 2. Asphalt Additives

Additive	Supplier	Source Location
Kling Beta 2700	AKZO Nobel Chemical	Waco, Texas
Ad-Here HP Plus	Process Chemicals	Winter Haven, Florida
PaveGrip 350	Pre Tech Industries	New Castle, New Hampshire
Morlife 2200	Rohm and Haas Company	North Andover, Massachusetts

Table 3. Asphalt Mixture Design Information

I.D.	Type	% AC	Percent Passing Sieve					
			¾ in	½ in	3/8 in	No. 4	No. 8	No. 200
1029	SM-9.5A	5.8	100	100	93	62	45	5.0
1030	SM-12.5A	6.0	100	96	83		35	5.0
1034	SM-9.5A	5.4	100	100	93	62	43	5.4

Determination of Ability of StripScan to Measure Antistripping Additive

Overview

The first step of the investigation was to determine the ability of the device to detect the presence and to measure the amount of antistripping additive in liquid binder (asphalt cement). If the device did not measure additive in binders, it could not be expected to measure additive in mixtures. The combinations of binder and additive tested are shown in Table 4. The actual

Table 4. Planned Testing for Binder-Additive Combinations

Asphalt Cement Supplier	Asphalt Type	Additive
1,2	64-22	A
		B
		C
		D
	70-22	A
		B
		C
		D
	76-22	A
		B
		C
		D

testing implied by the testing matrix shown in Table 4 was doubled because asphalt from two suppliers was tested. Additives used most often in VDOT work were chosen. A regression analysis was performed for each of the 12 combinations to produce results similar to those shown in Figure 2. Five samples containing five concentrations of additives (0.0, 0.2, 0.4, 0.6, and 0.8 percent) were used to develop each regression plot of color index count versus percent additive. When the device is used in actual practice to determine additive content, a calibration curve similar to that shown in Figure 2 is developed for each asphalt binder and antistripping additive combination. The calibration curve is used with the count obtained on unknown samples to determine the amount of additive present.

A similar type of testing and analysis was done with lab-manufactured asphalt concrete specimens for the combinations of binder, additive, and aggregate indicated in Table 2. Asphalt from only one supplier was used for the mixture tests because after analyzing the results from the tests on two different binders, the author felt that asphalt from different suppliers would not influence the accuracy of the determinations.

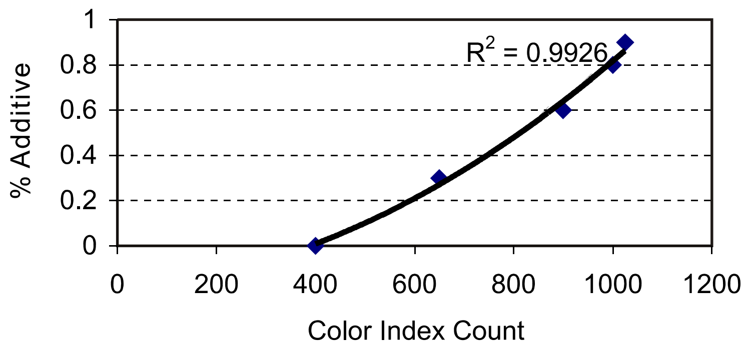

Figure 2. Typical Regression Plot for Liquid Asphalt Binder

Table 5. Planned Testing Program for Asphalt Mixtures

Asphalt Cement	Additive	Aggregate
Citgo 64-22*	A	No. 1
		No. 2
		No. 3
	B	No. 1
		No. 2
		No. 3
	C	No. 1
		No. 2
		No. 3
	D	No. 1
		No. 2
		No. 3

*Matrix repeated for Citgo 70-22 and Citgo 76-22.

Binder Test Procedure

Initial Binder Test Procedure

The following test procedure was initially used: A 100 g sample of asphalt binder was weighed into the 6-in-diameter 5-in-high metal test can, and the appropriate amount of chemical additive ranging from 0 to 0.8 g was added with a disposable pipette. The quantity of asphalt binder was measured to 0.1 g, and the quantity of additive was measured to 0.01 g. Additive concentrations are always expressed as a percentage of the asphalt liquid binder. The sample was then stirred by hand with a metal rod and covered with the top, which contained a hole for the vapor to escape and a small hole for a temperature probe.

The can was then placed in an oven at 280^{o}F for 2 hours. At the end of 2 hours, the sample container was placed on the StripScan hot plate and the test was started. The device automatically monitored the temperature of the binder with a probe and exposed the litmus strip to the sample vapors for 5 minutes when the sample temperature had reached the correct test temperature (originally 205^{o}F). When the litmus strip had been exposed for 5 minutes, it retracted into the device and the color of the strip was automatically recorded. The device automatically retains several tests at various additive contents to develop a calibration file that can be used to measure samples with unknown additive contents. To develop the calibration file, the StripScan software uses a quadratic regression.

Modified Binder Test Procedure

The binder test procedure was modified as the study progressed to make testing easier and improve the accuracy of the results. Since the stiffer grades of binder needed to be handled at higher temperatures, it became necessary to change the testing temperature for different grades. The manufacturer changed the StripScan software to allow the user to adjust the test temperature to match the binder being tested and also change the temperature of the hot plate that heated the sample in the testing device. The aging and test temperatures for the PG64-22, PG70-

22, and PG76-22 binders were 205°F, 250°F, and 250°F, respectively. Attention was directed toward keeping the laboratory process consistent for a specific series of tests to avoid unwanted variability.

Another modification was to change the exposure time from 5 minutes to 30 seconds so that the test strips would not be overexposed for some of the additives. The manufacturer suggested that the exposure be controlled so that the litmus strip color index strip count measured by the device is kept less than 900. After many tests it became evident that the 30-second exposure time was more suitable; therefore, some tests had to be rerun using 30 seconds instead of 5 minutes.

Mixture Test Procedure

The procedure for mixtures was basically the same as that used for asphalt binder. A major difference was that the size of the sample of asphalt mixture was approximately 2100 g. After the sample was prepared, it was aged in an oven for 2 hours initially; however, the time was later shortened to 1 hour upon recommendations by the manufacturer and because the counts were relatively low with the longer aging time. The aging and testing temperature was 285°F, 300°F, and 310°F for mixtures containing PG64-22, PG70-22, and PG76-22, respectively.

RESULTS AND DISCUSSION

Binder Tests

The results of the quadratic regression analyses are shown in Table 6. A plot of these values will yield curves that are similar to those in Figure 2. The results include R-square values and errors of estimate. Examination of the R-square values and errors of estimate gives an idea of the variability that can be expected when the regressions are used to predict additive content. Generally, the values in Table 6 indicate that errors of estimate less than 0.1 produced R-square values of more than 0.9. This magnitude of R-square means that more than 90 percent of the variability in additive content is explained by the color index count. Seven of the 24 regressions contained errors of estimate greater than approximately 0.1. These and their associated R-square values are highlighted in the table. An error of estimate of 0.1 means that 95 percent of the time the estimate of additive content is within ±0.2 percent of the true mean. If the test were to be used for quality control/quality assurance, the error of estimate would have to be decreased by improving the test method or performing multiple tests. A reasonable minimum error of estimate would be 0.05 percent.

Although an analysis of variance (ANOVA) was not performed, it was obvious from a quick examination of the results that neither the binder type nor the additive type affected R-square values significantly. The R-square values did not appear to differ substantially between binders and between additives.

Table 6. R-Square Values and Errors of Estimate of Regressions for Binder Tests

Asphalt Binder	Additive	R-square	Error of Estimate
Citgo 64-22	Kling Beta 2700	0.631	0.276
	Adhere Plus	0.969	0.081
	PaveGrip 350	0.963	0.097
	Morlife 2200	0.913	0.134
Citgo 70-22	Kling Beta 2700	0.988	0.047
	Adhere Plus	0.995	0.033
	PaveGrip 350	0.952	0.101
	Morlife 2200	0.959	0.090
Citgo 76-22	Kling Beta 2700	0.918	0.126
	Adhere Plus	0.996	0.028
	PaveGrip 350	0.988	0.050
	Morlife 2200	0.950	0.100
Koch 64-22	Kling Beta 2700	0.904	0.152
	Adhere Plus	0.857	0.165
	PaveGrip 350	0.914	0.093
	Morlife 2200	0.978	0.072
Koch 70-22	Kling Beta 2700	0.996	0.029
	Adhere Plus	0.998	0.018
	PaveGrip 350	0.997	0.028
	Morlife 2200	0.886	0.152
Koch 76-22	Kling Beta 2700	0.943	0.107
	Adhere Plus	0.992	0.042
	PaveGrip 350	0.929	0.124
	Morlife 2200	0.999	0.005

The quadratic regressions have the following general form:

$$\text{Additive content} = a(\text{count})^2 + b(\text{count}) + c$$

The *a* term was positive for most of the binder regressions, yielding half-bowl–shaped plots, and each regression was unique. The regression was dependent on the asphalt binder–additive combination and testing variables such as curing time and exposure time. Therefore, it may not be possible to use the same regression calibration to test mulitiple asphalt binder–additive combinations. More work is needed to determine whether the binder source has an influence on the calibration.

Mixture Tests

The R-square values and errors of estimate for the quadratic regression analysis of the mixture tests are shown in Table 7. These values indicate the error that can be expected when the regression equations are used to estimate additive concentrations in a sample of mixture. As for the binder analysis, it was decided that the desirable estimate of the additive content should be within $\pm$0.2 percent of the true mean 95 percent of the time. This means the error of estimate should be 0.1 percent or less. Generally, using this magnitude of error of estimate yielded R-square values of more than 0.95, which means that more than 95 percent of the variability in additive content was explained by the color index count.

Table 7. R-Square Values and Errors of Estimate of Regressions for Mixture Tests

Asphalt Grade	Additive	Mixture	R-square	Error of Estimate
64-22	Kling Beta 2700	1029	0.959	0.093
		1030	0.970	0.078
		1034	0.910	0.136
	Adhere Plus	1029	0.936	0.115
		1030	0.993	0.037
		1034	0.999	0.010
	PaveGrip 350	1029	0.726	0.265
		1030	0.820	0.190
		1034	0.960	0.094
	Morlife	1029	0.993	0.038
		1030	0.890	0.149
		1034	0.931	0.118
70-22	Kling Beta 2700	1029	0.988	0.054
		1030	0.938	0.110
		1034	0.972	0.075
	Adhere Plus	1029	0.910	0.136
		1030	0.962	0.088
		1034	0.996	0.028
	PaveGrip 350	1029	0.904	0.145
		1030	0.964	0.096
		1034	0.924	0.129
	Morlife	1029	0.932	0.115
		1030	0.620	0.276
		1034	0.984	0.055
76-22	Kling Beta 2700	1029	1.000	0.008
		1030	0.984	0.062
		1034	1.000	0.010
	Adhere Plus	1029	0.998	0.019
		1030	0.996	0.029
		1034	0.992	0.041
	PaveGrip 350	1029	0.970	0.078
		1030	0.795	0.227
		1034	0.944	0.112
	Morlife	1029	0.975	0.071
		1030	0.764	0.224
		1034	0.947	0.103

Fourteen of the total 36 regressions yielded R-square values too low to give estimates within $\underline{+}$0.2 percent of the additive content (shaded values in Table 7). It appeared that R-square values were low more frequently for mixture 1030 than for the other two mixtures; however, ANOVA indicated that none of the variables such as asphalt binder grade, additive type, or mixture type had a significant influence on the regressions. It was suspected that mixture 1030 might be more variable than the other mixtures because of the absorptive nature of the aggregate.

The *a* term of the quadratic regression was negative for 50 percent of the regressions and positive for 50 percent of the regressions; therefore, there was no consistency for the shape of the additive content–count plots. Each asphalt binder type, additive type, and mixture type combination produced a unique regression. Each mixture would have to be calibrated to determine additive content.

After the regression results were viewed, the original data were reexamined. Regressions were recomputed using the final spectrophotometer count minus the initial count of the unexposed litmus strip. Table 8 shows the comparison of the R-square values using total count after exposure to vapors and the R-square values using total count after exposure minus initial count. The average R-square values were improved from 0.932 to 0.967, and the number of unacceptably high values was reduced approximately 50 percent.

Table 8. Recalculation of R-Square Values Mixtures Using Total Count – Initial Count

Asphalt Grade	Additive	Mixture	R-square Using	
			Litmus Total Count	Litmus (Total Count – Initial Count)
64-22	Kling Beta 2700	1029	0.959	0.998
		1030	0.970	0.994
		1034	0.910	0.884
	Adhere Plus	1029	0.936	0.991
		1030	0.993	0.995
		1034	0.999	0.994
	PaveGrip 350	1029	0.726	0.999
		1030	0.820	0.903
		1034	0.960	0.976
	Morlife	1029	0.993	0.956
		1030	0.890	0.918
		1034	0.931	0.941
70-22	Kling Beta 2700	1029	0.988	0.995
		1030	0.938	0.956
		1034	0.972	0.998
	Adhere Plus	1029	0.910	0.943
		1030	0.962	0.975
		1034	0.996	0.999
	PaveGrip 350	1029	0.904	0.981
		1030	0.964	0.984
		1034	0.924	0.977
	Morlife	1029	0.932	0.974
		1030	0.620	0.880
		1034	0.984	0.978
76-22	Kling Beta 2700	1029	1.000	0.994
		1030	0.984	0.987
		1034	1.000	0.991
	Adhere Plus	1029	0.998	0.923
		1030	0.996	0.998
		1034	0.992	0.996
	PaveGrip 350	1029	0.970	0.985
		1030	0.795	0.985
		1034	0.944	0.959
	Morlife	1029	0.975	0.969
		1030	0.764	0.833
		1034	0.947	0.978
Average			**0.932**	**0.967**

A similar analysis was done for the binder regressions; however, there was no improvement when the initial blank litmus strip values were taken into account. The average of the R-square values when using and when not using the blank values was 0.944 and 0.942, respectively. Since the total counts were generally less for the mixture tests than for the binder tests, the percentage effect would have been more for the mixture tests when the count reading of the blank strip was subtracted.

Since mixture counts were highly sensitive to aging time, reheating samples would affect values obtained when using a calibration based on unaged samples. If the procedure is used to measure additive concentration of production samples, the samples would have to be taken and tested immediately. It appears that forensic testing of pavement samples could possibly determine the presence of antistripping additive, but quantitative estimates would be poor.

Additional Testing

During the testing, two observations were made that indicated changes might be made to reduce the testing variability. Quite often, the litmus strips after testing were not uniform in color. The device had a vapor trap surrounding the litmus strip that allowed vapor to escape from the trap at the hole where the litmus strip entered the trap (see Figure 3). Quite often, the litmus paper was darker on the open end where vapor escaped, indicating more exposure to the asphalt binder additive vapors. The lack of uniformity in the litmus paper color after testing probably produced variable test results that resulted in poor regressions.

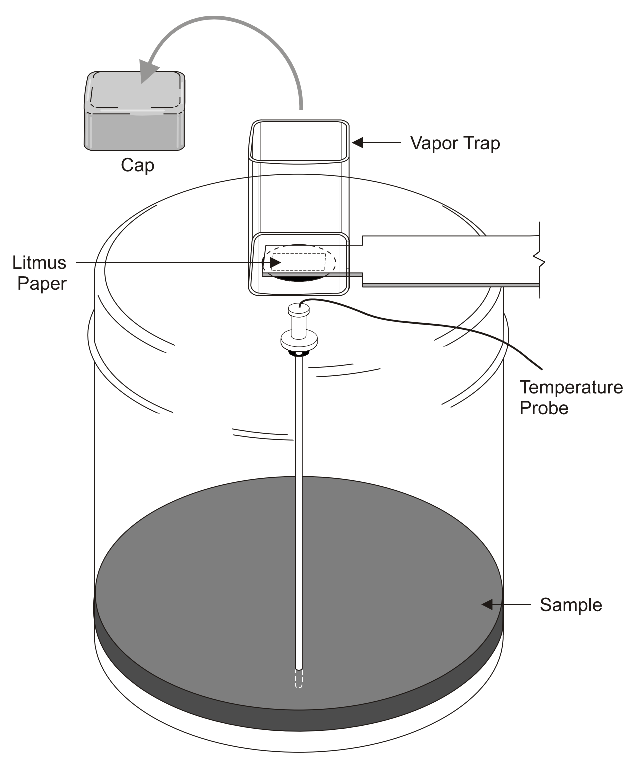

Figure 3. StripScan Binder Sample Being Tested

The technician also noticed that the time for the device hot plate to heat the sample to the required testing temperature after the sample was in an oven at constant temperature varied substantially from sample to sample. Only 100 g of asphalt binder was specified in the original procedure; therefore, the depth of the probe in the binder was only about 0.15 in. Only the tip of the temperature probe that controlled the hot plate heating was submerged in the binder, which could have caused faulty readings and been a source of error. If the temperature of the binder, as indicated by the probe, is not representative of the sample, then the amount of vapor to which the litmus is exposed would not be the true additive content of the sample.

A small number of tests were performed on binder after changes were made in the equipment and testing procedure because of the shortcomings described. The top of the vapor trap was removed to allow the additive vapors to flow upward, creating a uniform flow around the litmus strip rather than flow out near one end of the strip. The other change was to use 200 g of binder instead of 100 g in an attempt to expose more of the temperature probe to the binder (approximately 0.4 in), which increased the accuracy and consistency of the hot plate temperature between tests. The R-square values for the tests before and after changes were made are shown in Table 9.

The results demonstrate an appreciable improvement in six of the eight regressions after the testing changes were made. Although these results represent only one third of the total binder tests, they clearly show that improvement is possible by making several changes; therefore, the majority of the results presented in this report could be improved. Although no further testing was done with the mixtures because of time and budget limitations, the author believes that the accuracy for mixtures would also be improved by at least making the change concerning the vapor trap and possibly using the blank strip count to develop the regression. The suggested change concerning the amount of sample is not applicable for mixtures because the sample size was already large enough to cover a large part of the temperature probe.

Table 9. Comparison of R-Square Values for Binders Before and After Testing Changes

Asphalt	Additive	R-square Before	R-square After
CITGO 64-22	Kling Beta 2700	0.631	0.971
	Adhere Plus	0.969	0.978
	PaveGrip 350	0.963	0.962
	Morlife 2200	0.913	0.994
KOCH 64-22	Kling Beta 2700	0.904	0.998
	Adhere Plus	0.857	0.984
	PaveGrip 350	0.914	0.940
	Morlife 2200	0.978	0.952
Average		**0.891**	**0.972**

CONCLUSIONS

- Approximately two thirds of the binder regressions yielded predictions within ±0.2 percent of the percentage of additive.

- Approximately 60 percent of the mixture regressions yielded predictions within ±0.2 percent of the percentage of additive. The prediction accuracy improved considerably when the blank strip count was used to develop the regressions.

- Limited supplementary testing suggests that additional improvements can be adopted for binder tests by changing the vapor trap and increasing the size of the sample from 100 g to 200 g.

- Although no additional tests were performed on mixtures after the vapor trap was modified, it is likely that the change would also improve the regressions for mixtures because the color of the litmus paper would be more uniform.

RECOMMENDATIONS

1. *VDOT could use the StripScan device to gain additional experience with testing for binders that have additive blended at the terminal.* Additional work will have to be done to reduce variability and establish acceptable statistical limits for quality assurance testing.

2. *Additional tests should be done by the manufacturer to establish the accuracy for mixtures using the modified vapor trap and the new calculation method described in this report.* An accuracy of approximately ±0.1 percent would be a worthy goal in order to consider using the device for quality assurance testing.

3. *Since several asphalt suppliers sometimes furnish asphalt to a hot-mix plant, additional work should be done by the manufacturer to determine the effect of changing asphalt source on calibrations.*

4. *Additional work should be done by the manufacturer to determine if the device would be useful for forensic investigations and to determine whether additives deteriorate over time.*

ACKNOWLEDGMENTS

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