

Detection of Amine-Based Antistripping Additives in Asphalt Cement

ARTHUR R. TARRER, HYON H. YOON, BADRU M. KIGGUNDU, FREDDY L. ROBERTS, AND VINAY P. WAGH

This study presents the findings of an effort to develop a test either for detecting the presence of amine-type antistripping (AS) agents in asphalt or, when desired, quantitatively measuring the agent's concentration in asphalt. Four asphalts and two amine-type commercial antistripping agents, each asphalt and agent being from a different source, were used in the study. An ASTM procedure for quantitative measurement of amines in an organic solution was modified to allow direct measurement of the quantity of amine-type antistripping agents in asphalt. As part of the procedure, the additive is titrated directly with an acid, without first having to be extracted from the asphalt. The procedure is simple, requires relatively inexpensive equipment, and, with little further modification, may possibly be used to do field testing.

For a long time, asphalt technologists have been seeking simpler and more reliable techniques for detecting the presence of an antistripping additive in asphalt. Also, for purposes of quality control, they need tests that allow them to determine the exact dosage of additive to be used. And they need to know whether interaction between the additive and the asphalt has occurred to an extent that has reduced additive effectiveness. A number of test methods for additive detection have been proposed, having varying degrees of sophistication (*1*). None of these test methods have been evaluated by determining their repeatability in quantitative terms.²

As part of this work, an ASTM method (D2073) was modified to allow direct measurement of the amount of amine-type additive present in asphalt. The original ASTM method permits the determination of the total, primary, secondary, and tertiary amine values of fatty amines and diamines, and the total amine value of fatty amidoamines. The subject of interest here, however, is only the total amine value, which is assumed to vary directly with the total AS additive concentration. The total amine value is a measure of the sample's basicity and is defined as the number of milligrams of potassium hydroxide (KOH) equivalent to the basicity in 1 g of sample. The original ASTM procedure requires an extraction step to separate the amine-bearing compounds from the sample, and the extracted material is titrated with hydrochloric acid (HCl). To make the procedure simpler and more easily adaptable for field application, a method was developed to allow direct titration of an asphalt sample without having to separate the amine-bearing compounds via extraction.

A blank asphalt sample (with no added additive) is first titrated; then the additive-bearing asphalt samples are titrated. To perform a titration, the sample is first dissolved in isopropyl alcohol and chloroform. It is assumed that the basicity of the blank asphalt and that of the additive are linearly superimposed; that is, there is no interaction between the basic amine groups in the additive and those in asphalt. The amount of additive, or the amine value due to the additive, is assumed to be directly related to the difference between the amount of titrant (HCl) required to attain the desired end point for the blank asphalt and that required for additive-bearing asphalt. The results presented in this report suggest that repeatability within 10 percent is possible using this procedure. (Refer to the Appendix for an ASTM formatted description of the procedure.) Two AS additives, each from different commercial sources, and asphalt from four different manufacturers were used in evaluating the procedure.

Some difficult questions remain to be addressed and are yet to be resolved. For example, what are the performance implications of the results of the test? The test does provide a means of quantitatively determining the presence and dosage of an AS amine-type additive in asphalt. The test further offers the potential to trace the life of the AS additive from the time of induction to some finite future time. The test, most of all, is simple and potentially implementable either in the field or in central laboratories. Also, it uses relatively inexpensive equipment.

The emphasis of this study is on the proposed detection method and not on requirements for an AS additive, such as heat stability and handling considerations. For purposes of verification, the report includes results from an independent evaluation of the procedure by Petroleum Sciences, Inc.

BACKGROUND

Many commercial antistripping additives are known to be amines or chemical compounds containing amines (*2,3*). Like ammonia, amines act as weak Lewis bases. For instance, a solution of ammonia in water does reach the following equilibrium:



Lewis bases react readily with strong acids. Therefore, the basicity of an asphalt depends on the amount of additive

added to the asphalt. The basicity of an asphalt can be determined by titrating the asphalt with an acid such as HCl. If the additive does not interact with the asphalt, the concentration of the additive in the asphalt can be determined from the difference between the basicity of the blank asphalt and that of the asphalt containing the additive.

TEST DEVELOPMENT

Materials

Asphalts: Four AC-20 asphalts from different sources were used in this study. The asphalts were labeled AC-1, AC-2, AC-3, and AC-4.

Antistripping Additives: Two different polyamine-type antistripping additives were used in this study. These additives were produced by different manufacturers; they were labeled Additives 1 and 2.

Procedure

Samples with two or three concentration levels of each additive for each asphalt were prepared, including a blank, or control sample. Each sample was prepared by first placing the desired weight of additive in a glass beaker and then pouring melted asphalt at 275°F into the beaker. The resulting mixture was stirred vigorously for about 30 sec, heated in an oven at 275°F for 5 min, and stirred again for about 1 min. Each sample combination was then tested.

Procedure verification measurements by Petroleum Sciences, Inc., were conducted at 1.0 weight percent additive concentration in triplicate, using two additives and four asphalts. The solvents used by Petroleum Science, Inc., were obtained locally.

Test Method

The specimen of asphalt-additive mixture was dissolved in chloroform and isopropyl alcohol solution containing 5 percent distilled water. The sample solution was then titrated potentiometrically with hydrochloric acid solution (4). The detailed procedure is described in the Appendix.

Stripping Test

Additive effectiveness was evaluated using a boiling water test. The boiling water test used is a modification of the Texas Boil Test (5). To have a high degree of sensitivity, a large mesh-size ($\frac{3}{8}$ in. to 4 mesh), granite aggregate was used. The aggregate was supplied by the Georgia Highway Department. The procedure for the boiling water test used in this study is described next.

Boiling Water Test

After soaking in distilled water for 24 hr and towel drying, 100 g of saturated aggregate was placed in a stainless steel

bowl and held in an oven maintained at 300°F for 1 hr of preheating time. Next, 5.5 g of asphalt cement (to which, when used, an AS additive had been added) was heated at 275°F for 10 min and then poured onto the preheated aggregate. The asphalt and aggregate were mixed using a hot spatula for 2 min and were placed in an oven maintained at 300°F for 10 min. After the mix was cooled to room temperature, the completely coated aggregate was placed in boiling water (250 ml in a 400-ml beaker) heated by a hot plate. The water was maintained at a slow boil for 10 min; during this time the immersed aggregate was stirred using a glass rod for 10 sec after each period of 4 min and 8 min of boiling. The mixture was then held in the water while it was allowed to cool to room temperature. After cooling to room temperature, the water was drained from the beaker, and the mixture was placed on a paper towel and allowed to dry.

The resultant amount of stripping was determined by visual observation and reported in terms of the observed percentage of asphalt coating retained on the aggregate. A rating board was developed with 10 intervals from 0 to 100 percent of retained coating, in order to standardize the visual evaluation as much as possible.

RESULTS AND DISCUSSION

Titration curves consisting of a plot of sample pH versus amount of acid titrant (HCl) added were determined for two sets of asphalt-additive samples. Each sample set consisted of the blank asphalt, the asphalt containing 1.0 weight percent of additive, and the pure additive. A different commercial additive was used in each of the two sample sets. Figures 1 and 2 show the titration curves for each sample set. Ideally, titration curves are S-shaped, and the inflection point in the curve is the end point or the equivalency point.

It was very difficult to determine the end point of the titration for the blank asphalt samples because there was no clear inflection point (refer to Figure 1, Curve C). There was a

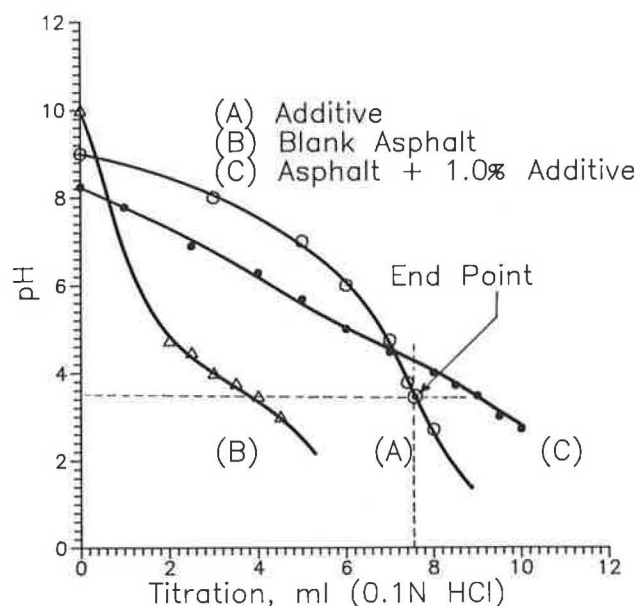


FIGURE 1 Typical titration curves using Additive 1.

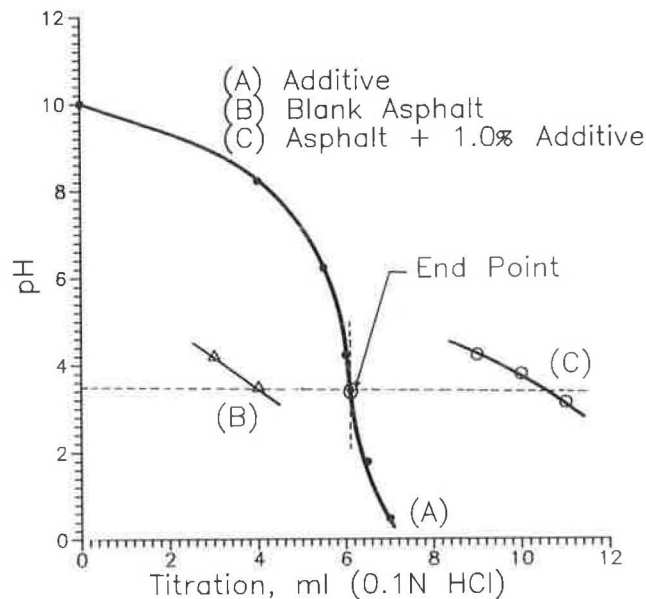


FIGURE 2 Typical titration curves using Additive 2.

clear inflection point for both pure additive samples ($\text{pH} = 3.5$). The end point for the additive-bearing asphalts was taken to be the same as that observed for the pure additives ($\text{pH} = 3.5$).

Titration amounts (milliliters of HCl) required to reach the end point for each of the samples in the four sample sets are listed in Tables 1 and 2. Each sample set consisted of an asphalt to which different specified amounts of one of the two commercial AS additives used were added. A different asphalt was used in each of the four sample sets. Titration amounts are also given for each of the two pure commercial AS additives used. Table 1 consists of the analyses done in the authors' laboratory, and Table 2 consists of those done by PSI, for verification purposes. Triplicate titrations were done for most of the samples; for a few samples, only duplicate titrations or, in some cases, four titrations were done. Mean amounts of titrant required to reduce the sample pH to the end point ($\text{pH} = 3.5$) and standard deviations are shown.

The total number of samples analyzed was relatively small (34 samples, including those done by PSI). Based on this limited sample number, the standard deviation in titrant amount appears to be small for all the samples, including pure additive samples, additive-bearing asphalt samples, and blank asphalt samples. All four of the blank asphalts had an appreciable basicity, implying that a blank determination should be made on the source asphalt containing no additive.

It was observed that Additive 1 in each asphalt tested was detected in smaller amounts than the amounts known initially to have been added, as shown in Figures 3 and 4 and in Table 1. Observation suggests that some interaction occurred between the additive and the asphalt components. On the other hand, the amount of Additive 2 in each asphalt tested was detected to be the same as that initially added. This observed difference in behavior between the two additives used implies that some additives may be more reactive with asphalt components than others.

The effectiveness of each additive was directly related to the apparent reactivity of the additives with the asphalts (as shown in Figures 5 and 6): Additive 1 was more effective per

unit amount than was Additive 2; and, as was already shown, Additive 1 appeared to react with the asphalt, and Additive 2 did not appear to react. The detection method appears to be reliable in that the effectiveness of both additives in each asphalt, as measured by the percent retained asphalt coating after boiling, increased as the dosage of the additives was increased.

A comparison of analyses of four sample sets performed by Auburn with those by PSI is given in Table 3. Each sample set consisted of a different asphalt mixed with 1 weight percent of one of the two different commercial AS additives used. The agreement between the amounts of AS additive detected by the two laboratories is acceptable. To assess this agreement quantitatively, an analysis of variance for the detected values was performed. Three basic parameters—the laboratory, the additive type, and the asphalt type—along with the three possible interactions among these parameters were combined linearly to formulate the model for the analysis of variance performed.

The results of the analysis of variance are given in Table 4. The F values for the six different model parameters, the three basic parameters and the three parameters of interaction, are listed. The F value represents the ratio of explained variance to unexplained variance; the unexplained variance is what cannot be explained by the model: the higher the F value, the more significant the model parameter. An overall F value for the model is also given in Table 4. In addition to F values, the probability associated with having an F value greater than that determined for the parameter is also reported. The extent to which the observed variance in detected values is due to a particular model parameter is equal to 1 minus the reported probability for being greater than the F value (as is shown in Figure 7).

The order of significance of the model parameters is as follows: (a) additive type, (b) interaction: additive and laboratory, (c) interaction: additive and asphalt, (d) interaction: laboratory and asphalt, (e) laboratory, and (f) asphalt type. The overall F value and associated probability are 1.54 and 0.402, respectively, indicating that the model is statistically significant.

The statistical significance of the additive type and that of the interaction between additive type and laboratory have a definite implication. It is felt that the statistical importance of these parameters has to do with the need for a standard reference time for the detection method. The degree of interaction between an asphalt and an additive is strongly dependent on the additive type; as was shown earlier, Additive 1 exhibited more interaction than did Additive 2.

Furthermore, as shown in Figures 8 through 13, the degree of interaction between an additive and an asphalt appears to depend not only on additive type but also on mixing and storage temperature and asphalt type. Here, the analytical method used to trace the change in detectable additive concentration with high-temperature storage was a modification of that proposed by Carstab and is described in detail in a separate work (6). This technique involved an extraction step using HCl. The results given in Figures 8 through 13 show that a decrease occurred in additive concentration and effectiveness with increased high-temperature ($>300^\circ\text{F}$) storage time. This was felt to reinforce the need for a standard reference time in performing an additive analysis in order to minimize additive-type dependency and, possibly, asphalt-type dependency.

TABLE 1 ANALYSES OF FOUR SETS OF ASPHALT-AS-ADDITIVE SAMPLES PERFORMED AT AUBURN UNIVERSITY

Sample	Titrant Amount (ml HC)				Average	Standard	Antistrip to	Wt. Percent
	1	2	3	4	Value	Deviation	Titrant Equivalency	Antistrip
					(ml HCl)	(%)	Factor (mg/ml)	Detected
I. <u>Pure Additives:</u>								
Additive #1, 100 mg	7.6	8.1	7.3	7.3	7.6	4.99	13.2	-
Additive #2, 100 mg	6.2	6.0	6.2	6.4	6.2	2.63	16.1	-
II. <u>Asphalt-Additive Mixtures:</u>								
a. <u>Chevron AC20 (AC-1)</u>								
(Blank)	3.8	4.0	4.2	4.2	4.1	4.7	-	-
0.2% AS #1	5.4	5.6	5.4	-	5.5	2.1	-	0.18
0.5% AS #1	6.5	6.3	6.5	-	6.4	1.8	-	0.31
1.0% AS #1	9.0	9.4	9.4	9.3	9.3	2.0	-	0.69
0.2% AS #2	5.2	5.2	5.0	-	5.1	2.3	-	0.17
0.5% AS #2	7.1	7.2	7.1	-	7.1	0.8	-	0.50
1.0% AS #2	10.5	10.5	10.3	-	10.4	1.2	-	1.03
b. <u>Amoco AC20 (AC-2)</u>								
(Blank)	4.1	4.0	4.5	-	4.2	6.3	-	-
0.2% AS #1	5.4	5.5	-	-	5.5	-	-	0.15
1.0% AS #1	10.1	10.2	10.6	-	10.3	2.6	-	0.80
0.2% AS #2	5.3	5.4	-	-	5.4	-	-	0.18
1.0% AS #2	10.7	10.4	10.7	-	10.6	1.6	-	1.03
c. <u>Douglas AR-4000 (AC-3)</u>								
(Blank)	4.7	4.4	5.1	-	4.7	7.4	-	-
0.2% AS #1	6.1	6.2	-	-	6.3	-	-	0.19
1.0% AS #1	10.4	10.3	11.0	-	10.6	3.6	-	0.77
0.2% AS #2	5.9	6.3	-	-	6.1	-	-	0.22
1.0% AS #2	11.6	11.9	11.9	-	11.8	1.5	-	1.14
d. <u>Idaho Asphalt AC10 (AC-4)</u>								
(Blank)	3.2	3.6	3.5	-	3.4	7.5	-	-
0.2% AS #1	4.5	4.8	-	-	4.6	-	-	0.16
1.0% AS #1	9.1	9.2	9.4	-	9.2	1.7	-	0.77
0.2% AS #2	4.4	4.9	-	-	4.7	-	-	0.20
1.0% AS #2	10.4	11.2	10.9	-	10.8	3.7	-	1.19

TABLE 2 ANALYSES OF FOUR SETS OF ASPHALT-AS-ADDITIVE SAMPLES PERFORMED BY PSI*

Sample	Titrant Amount			Average	Standard	Antistrip to	Wt. Percent
	(ml HCl)			Value	Deviation	Titrant Equivalency	Antistrip
	1	2	3	(ml HCl)	(%)	Factor (mg/ml)	Detected
Antistrip #1, 100 mg	8.8	8.8	9.0	8.9	1.3	11.2	-
Antistrip #2, 100 mg	7.9	8.3	8.3	8.2	2.8	12.2	-
<u>Chevron AC 20 (AC-1)</u>							
(Blank)	2.7	3.2	2.7	2.9	10.0	-	-
1% AS #1	11.3	12.1	11.7	11.7	3.4	-	1.01
1% AS #2	10.2	10.5	10.7	10.5	2.4	-	0.92
<u>Amoco AC 20 (AC-2)</u>							
(Blank)	3.7	4.25	3.5	3.8	10.0	-	-
1% AS #1	12.7	12.9	13.5	13.0	3.2	-	1.03
1% AS #2	9.7	11.7	12.2	11.2	12.0	-	1.02
<u>Douglas AR-4000 (SM)¹ (AC-3)</u>							
(Blank)	2.6	3.6	4.0	3.4	21.0	-	-
1% AS #1	12.8	13.2	13.5	13.0	2.7	-	1.09
1% AS #2	8.8	9.8	10.5	9.7	8.8	-	0.77
<u>Idaho Asphalt AC 10 (AC-4)</u>							
(Blank)	2.5	2.5	4.3	3.1	34.0	-	-
1% AS #1	8.8	10.0	10.0	9.6	7.2	-	0.69
1% AS #2	10.8	12.2	13.8	12.3	12.0	-	1.07
<u>Viscosity of Asphalts @140°F, p</u>							
Douglas AR-4000				1100			
Idaho Asphalt AC10				1190			

* PSI = Petroleum Sciences, Inc.

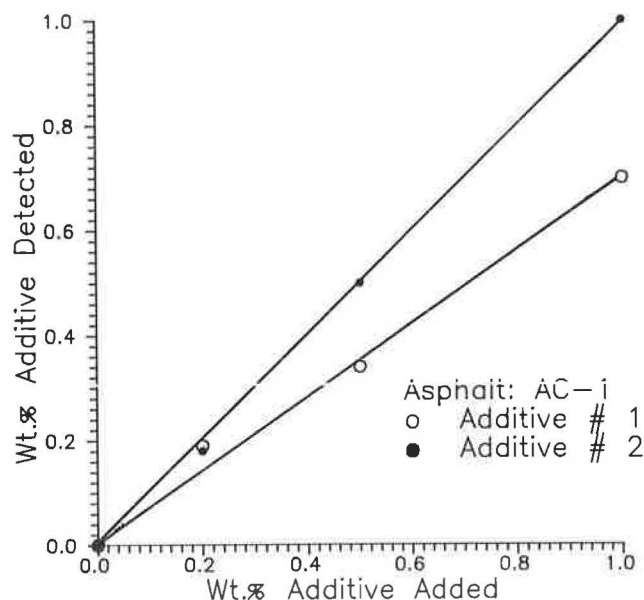


FIGURE 3 Comparison of expectation curves.

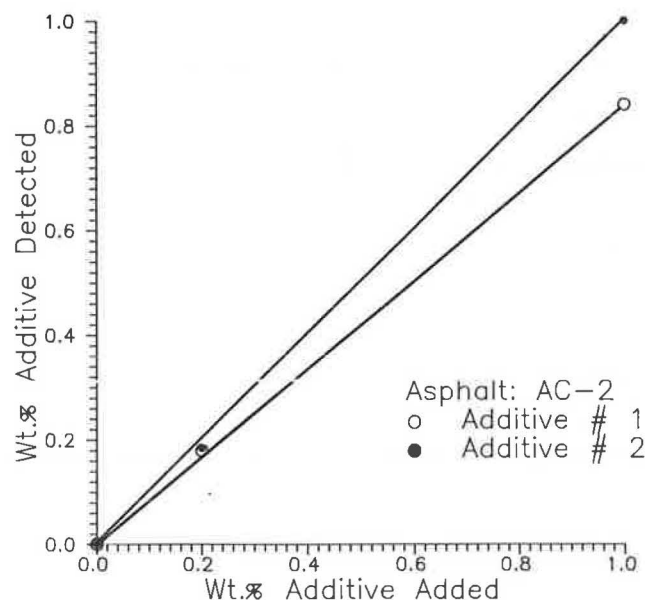


FIGURE 4 Comparison of expectation curves.

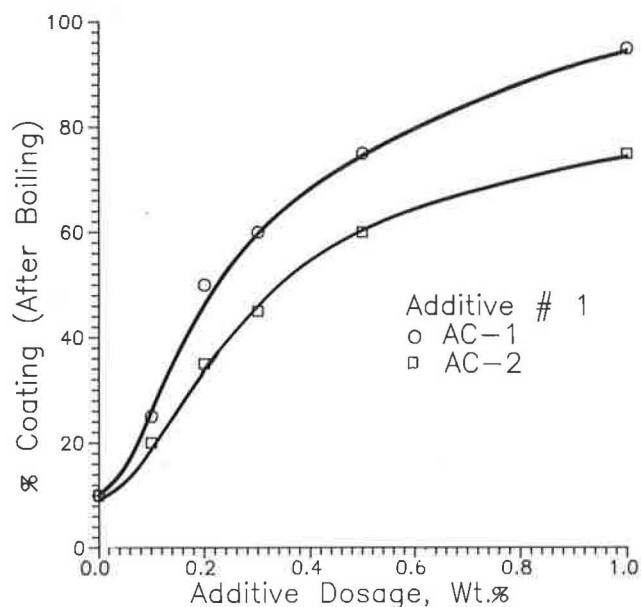


FIGURE 5 Change in additive effectiveness.

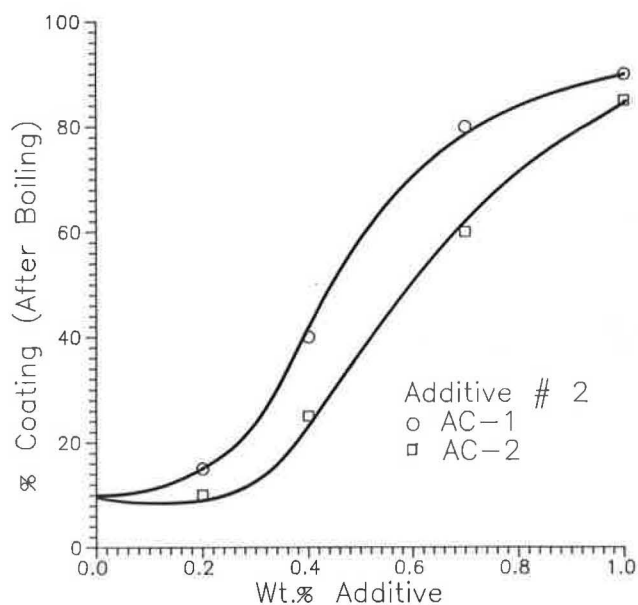


FIGURE 6 Additive effectiveness versus dosage.

TABLE 3 COMPARISON OF ANALYSES PERFORMED BY AUBURN UNIVERSITY WITH THOSE BY PSI

Asphalt Type	Average Titrant Amount (ml HCl)		Standard Deviation (%)		Wt. Percent Antistrip Detected	
	AU	PSI	AU	PSI	AU	PSI
Chevron AC20						
Additive 1	9.3	11.7	2.0	3.4	0.7	1.0
Additive 2	10.4	10.5	1.2	2.4	1.0	0.9
Amoco AC-20						
Additive 1	10.3	13.0	2.6	3.2	0.8	1.0
Additive 2	10.6	11.2	1.6	12.	1.0	1.0
Douglas AR-4000						
Additive 1	10.6	13.2	3.6	2.7	0.8	1.1
Additive 2	11.8	9.7	1.5	8.8	1.1	0.8
Idaho Asphalt AC-10						
Additive 1	9.2	9.6	1.7	7.2	0.8	0.7
Additive 2	10.8	12.3	3.7	12.0	1.2	1.1

TABLE 4 ANALYSIS OF VARIANCE

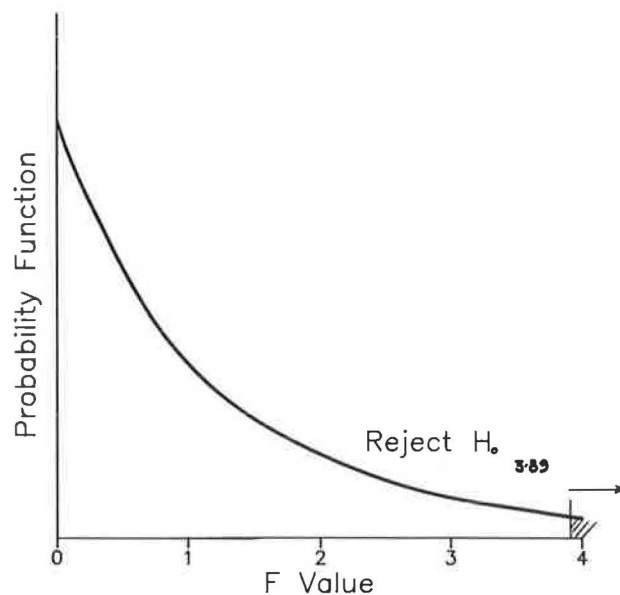
Source of Variation	Degrees of Freedom	Variation; Sum of Squares (10^2)	F Value (explained variance) (unexplained variance)	Probability > than F (Figure 7)
Laboratory	1	0.25	0.15	0.724
Additive Type	1	9.00	5.40	0.103
Asphalt Type	3	0.75	0.15	0.923
Interaction: Additive and Laboratory	1	9.00	5.40	0.103
Interaction: Laboratory and Asphalt	3	2.75	0.55	0.682
Interaction: Additive and Asphalt	3	9.00	1.80	0.321
Model	12	30.8	1.54	0.402
Error	3	5.0		

Overall:

R-Square Value = 0.860

Coefficient of Variance = $\frac{100 (\text{standard deviation})}{\text{Mean}}$ = 13.8

Mean Value of Antistrip Present = 0.94

FIGURE 7 Distribution of F value when H_0 is true.

In summary, then, it was felt that the importance of additive type and interaction between laboratory and additive type had to do with the different laboratories not using a standard reference time. Methodology specifications were thus needed to require minimal hot additive-asphalt mix storage time prior to an analysis.

The degree of variance due to the individual analyst's technique must be addressed because a significant model param-

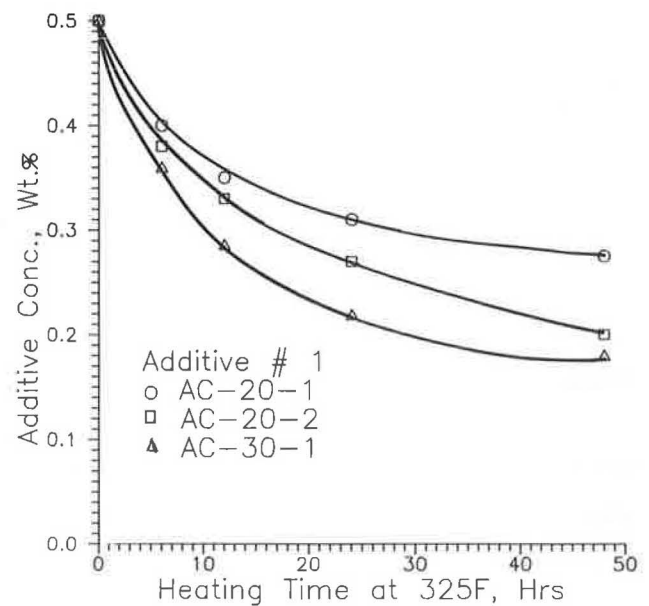


FIGURE 8 Additive concentration versus heating time.

eter was the interaction between the laboratory and additive type. It should be noted, however, that the laboratory, by itself, did not exhibit any statistical significance. When the lower-reactivity additive (Additive 2) was used, the agreement among the laboratories was much better than when the higher-reactivity additive was used. Again, as already emphasized, it was felt that much of the variance associated with analysis technique had to do with additive-asphalt hot storage

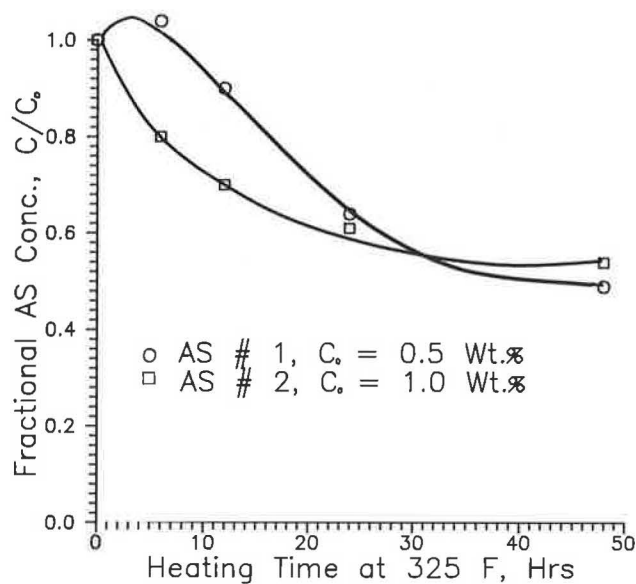


FIGURE 9 Additive concentration versus heating time.

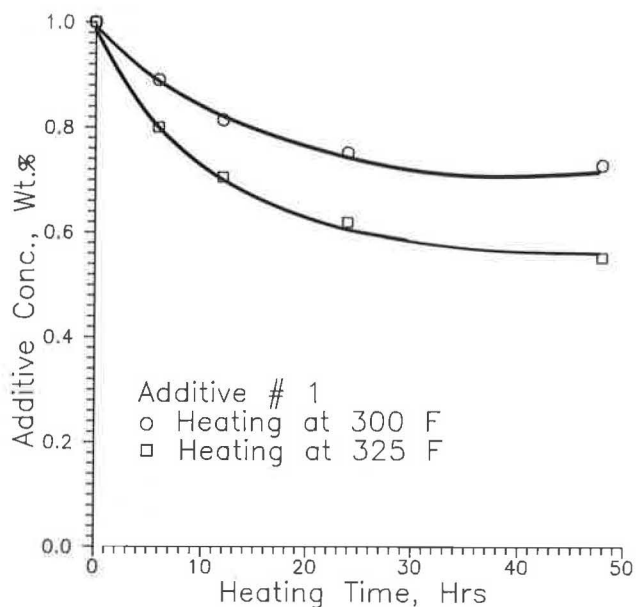


FIGURE 10 Additive concentration versus heating time.

and handling and could possibly be minimized by specifying a standard reference time for hot additive-asphalt mix preparation and storage prior to doing the analysis.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. An amine-type additive concentration in asphalt can be determined by simple acid-base titration.
2. For any amine-based antistripping additive, percent additive present in an asphalt can be estimated most accurately by comparing the additive-asphalt basicity in terms of HCl titration milliliters to that of a known standard asphalt sample containing the additive.

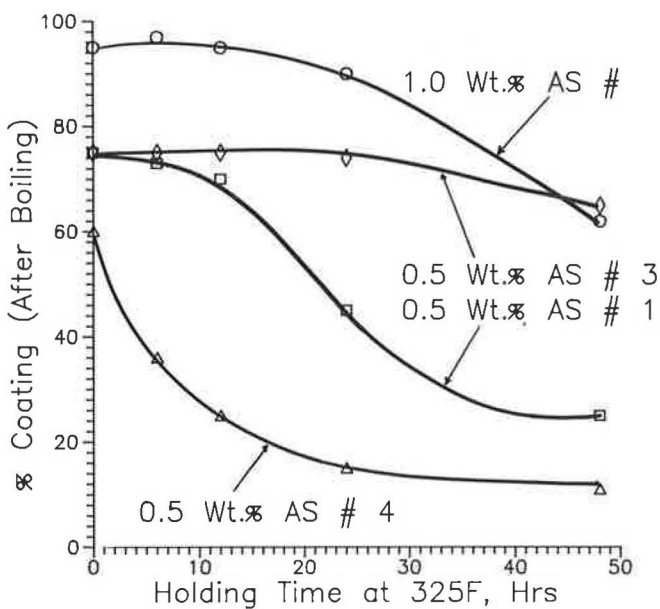


FIGURE 11 Heat stability of AS agents in AC-20-1.

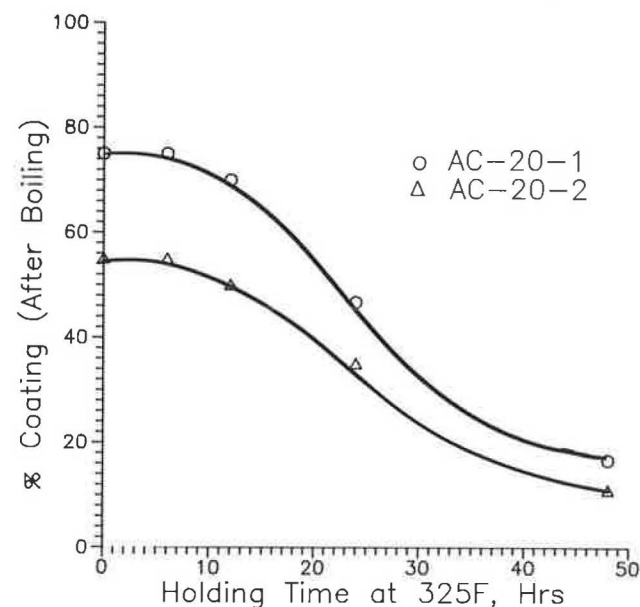


FIGURE 12 Heat stability of AS Agent 1.

3. This test provides a rapid and simple method, possibly suitable for field laboratory use, for detection of amine-based additive dosage in an asphalt.

4. This test provides a means for tracing additive concentration changes with time of hot storage of an additive-asphalt mix and, thereby, provides an indication of additive-asphalt reactivity.
5. A standard reference time for sample handling at high temperatures needs to be used in performing the proposed additive detection method.

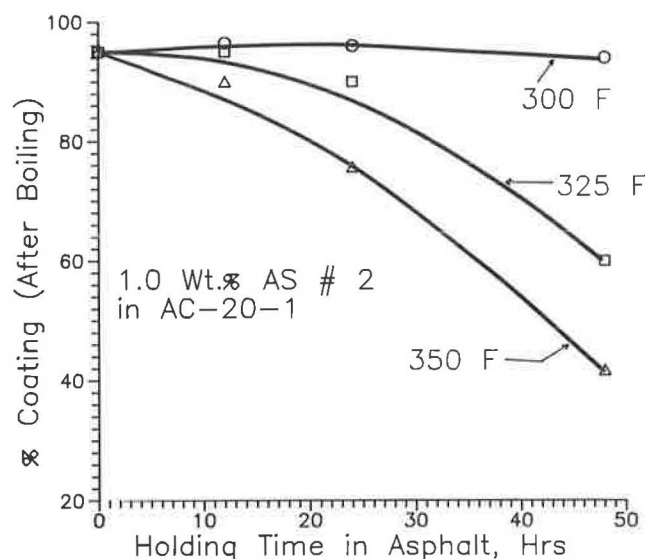


FIGURE 13 Heat stability of AS Agent 2.

6. The results from this test do not define the effectiveness of an additive, and further testing and field performance are needed to determine how such information can best be discerned.

Recommendations

1. This test should be applied to a wide range of amine-based additive-asphalt systems to establish precision.
2. Inferences from the test results to mixture performance should be explored.

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APPENDIX: Detailed Test Procedure Developed for Determination of Amine-Based Antistripping Additives in Asphalt Cement

1. Scope

1.1 This method determines the presence and amount of antistripping additive in an asphalt.

Note 1. This method is applicable only to polyamine-type additives.

2. Applicable Documents

2.1 ASTM Standards:

D2073 Test Methods for Total, Primary, Secondary, and Tertiary Amine Values of Fatty Amines, and Diamines by Referee Potentiometric Method

E70 Test Method for pH of Aqueous Solution with the Glass Electrode

D3665 Practice for Random Sampling of Construction Materials.

3. Summary of Method

3.1 The asphalt sample is dissolved in isopropyl alcohol and chloroform. The sample solution is then titrated potentiometrically with hydrochloric acid. A known standard should be determined for each additive-asphalt combination to obtain quantitative results.

4. Significance and Use

4.1 This test provides a rapid method for detection of the presence and dosage of an antistripping additive in asphalt.

4.2 This test provides a means for determining additive reactivity with an asphalt. Additive-asphalt reactivity is determined by measuring the change in additive dosage and that initially specified for the asphalt-additive mixture tested.

4.3 This test is suitable for both central and field laboratory applications.

5. Apparatus and Reagents

5.1 Glass beaker, 250-ml capacity, or other suitable container.

5.2 Glass electrode pH meter, conforming to the requirements of method E70 or similar potentiometric titration.

5.3 Hot plate, with variable heat control and variable-speed stirring control. The magnetic stirrer should be made of inert plastic.

5.4 Buret, graduated to 0.1 ml and a capacity of 50 ml.

5.5 Purity of Reagents. Reagent-grade chemicals shall be used in all tests.

5.6 Chloroform (CHCl_3).

5.7 Hydrochloric Acid, Standard Solution (0.1N). Add 16.5 ml of concentrated hydrochloric acid (HCl, sp. gr. 1.19) to 1,000 ml of isopropyl alcohol in a 2-l volumetric flask. Dilute to volume and mix.

5.8 Isopropyl Alcohol Solution. Add 5 ml of distilled water to 95 ml of isopropyl alcohol.

Note 2. Caution: The U.S. Food and Drug Administration has declared that chloroform is injurious to health. Care should be used in handling chloroform as it can be absorbed through the skin.

6. Sample Preparation

6.1 Weigh 10.0 g of the asphalt into a 250-ml beaker. Add 135 ml of chloroform and 15 ml of isopropyl alcohol. Heat to

boil, and hold at boiling for 1 min on a hot plate, maintaining vigorous stirring without any splattering occurring. Remove from the hot plate, and cool to room temperature.

6.2 Weigh the desired amount of AS agent, for example, about 0.100 ± 0.005 g (for 1 percent dosage), in a suitable 250-ml container. Add 10.00 ± 0.05 g of molten asphalt (275°F), and stir the mixture vigorously for 30 sec using a glass rod. Place the contents in an oven at 275°F for 5 min, and stir for 1 min outside the oven. Cover the container with aluminum foil, and cool to ambient temperature. Blends using various dosages are prepared the same way. Then follow the procedure in section 6.1.

6.3 Weigh (± 0.005 g) various amounts of AS agent to be tested, using at most three levels. The following are suggested as corresponding dosages: 0.25 percent, 0.5 percent, and 1 percent. Then dissolve each level of AS agent as discussed in 6.1.

7. Procedure

7.1 Immerse the lower half of each electrode of the pH meter (Note 3) in the sample solution, prepared as described in item 6. Start the stirrer, and adjust the speed so that vigorous stirring is maintained without splattering.

Note 3. Standardize the pH meter at a pH of 4.0 and 7.0 while carefully following the manufacturer's instructions.

7.2 Titrate with 0.1 NHCl standard solution.

Note 4. Record the pH readings every 1 ml of HCl, but in the vicinity of the end point (Note 5) record the pH readings every 0.5 ml of HCl. Plot a titration curve showing the pH's against milliliters required for titration. Occasionally, a long stabilization time (on the order of minutes) for the pH meter reading is required before a reading is taken.

Note 5. The end point is the midpoint of the inflection on the titration curve. Record the milliliters of 0.1 NHCl required to titrate to the end point. In some cases, it is very difficult to determine the end point because there is no clear inflection point in the titration curve. However, the titration curve for an antistripping additive itself has a clear inflection point. To obtain this titration curve, weigh 0.100 g of the antistripping additive to be analyzed into a 250-ml beaker and then follow the procedure described above. Find the end point from the titration curve. Then, the pH at this end point can be used in the titration of the asphalt sample for greater accuracy. In general a pH of 3.5 may be used as an approximate end point of the titration for any antistripping additive.

7.3 Titrate 0.100 g of the AS agent to be tested, dissolved in 135 ml of chloroform and 15 ml isopropyl alcohol solution with the 0.1 NHCl solution (Note 6) as described above.

7.4 Titrate 10.0 g of a blank asphalt with the 0.1 NHCl solution (Note 6), according to the procedure in Steps 6 and 7.

Note 6. Once a bottle of 0.1 N HCl solution has been consumed, a new standardization against the AS agent controls and asphalt blanks must be done.

8. Calculations. Two methods are discussed below with no indication of preference:

8.1 First Method. Calculate the amount of antistripping additive present in the asphalt by comparing the milliliters of HCl required for titration to a known standard.

$$\text{percent antistripping additive} = \frac{U - B}{K - B} \times P$$

where

U = millimeters of HCl required for titration of the unknown asphalt sample that contains an unknown amount of additive dosage;

K = milliliters of HCl required for titration of the known standard sample (which contains a known amount of additive dosage, Note 7);

B = milliliters of HCl required for titration of the blank asphalt (without additive, Note 8);

P = percent additive in the known standard asphalt sample.

Note 7. The known standards should be generated with the specific asphalt and additive used in the construction project. The required amount of the antistripping additive is mixed with the asphalt by first placing the additive in a glass beaker and then pouring heated asphalt at 275°F into the beaker. The mixture is then stirred vigorously with a spatula for 30 sec at ambient condition.

Note 8. A blank determination should be made on the source asphalt containing no antistripping additive.

8.2 Alternate Method. Percent antistripping additive can also be calculated using the following equation:

$$\text{percent antistripping additive} = \frac{V - B}{S} \times F \times 100$$

where

V = milliliters of HCl required for titration of the asphalt-additive sample;

B = milliliters of HCl required for titration of the blank asphalt (without additive);

S = 10.00 g (specimen weight); and

F = A/R (factor: combining weight of additive Note 9).

Note 9. The factor F must be determined for each antistripping additive to be analyzed. See Note 3 for the procedure. The factor may be obtained from the known weight percentage of additive used as recommended by the additive manufacturer. The combining weight is the ratio (A/R) of the weight of the additive, which combines with hydrochloric acid to the volume of hydrochloric acid required to reach a defined end point. Here, the concentration of the HCl solution must be standardized by titrating with Na_2CO_3 or some other standard base where A equals 0.100 g (grams of antistripping additive) and R equals milliliters of HCl required for titration of antistripping additive itself.

9. Report

9.1 The asphalt and additive types and sources.

9.2 Dosage of additive given and detected.

9.3 Description of action of additive on asphalt.

9.4 Any other particular observations.

10. Precision and Bias

10.1 Precision requirements for this test method have not been established.

10.2 Results from limited testing within one laboratory suggest that repeatability (D2S percent) between duplicate runs for percent additive should not exceed 0.14 weight percent.