



TRC9111

Detection of Antistrip Additives (Phase 1)

Richard Ulrich, Peggy Carroll

Final Report

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TRC-9111*

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Detection of Antistrip Additives (Phase 1)

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In cooperation with

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| 16. Abstract The purpose of this program is to develop quantitative analytical test methods to determine the amount of amine-based or lime-based antistrip additive in asphalt/or mixes both as-received from the plant or as-sampled from the highway. The goal Phase I (TRC-9111) was to develop a test for amines in asphalt mixtures as-received from the plant. This goal was accomplished through the development of a basicity titration method now called the Single Vessel Titration test (SVT test). Each of the amine-based additives from the AHTD list of approved additives was tested by this method and it was found that the level of additives in asphalt/additives blends could be determined to within a few percent error in levels down to less than 1% by weight. A sample of blank asphalt (no additive) and a sample of the additive in question is required for the test, but it is not necessary to construct calibration curves for each additive/asphalt combination. The test can be performed by virtually anyone after just a few hours of training; the procedure does not require an understanding of the chemical principles involved and the test interpretation is unambiguous. Any technician with laboratory experience should be able to perform the test after a couple of hours training. The cost for lab equipment for the test is a couple of hundred dollars and the materials cost per test is under \$10. At this time, the SVT test is currently qualified for asphalt/additive mixtures only but it may also be applicable to aggregate mixes with some modifications. | | | |
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TRC-9111
Detection of Antistrip Additives - Phase I

Final Report

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PREFACE

This report was prepared was prepared in cooperation with the U.S. Department of Transportation, Federal Highway Administration. The contents of this report reflect the views of the authors who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Arkansas State Highway and Transportation Department or the Federal Highway Administration. This report does not constitute a standard, specification, or regulation. The results of this study are accurate to the best of the knowledge of the authors at the time of publication.

An implementation report is included as a stand-alone document within this report. This implementation report also serves as an executive summary of the overall report.

The authors wish to thank the Arkansas State Highway and Transportation Department for the opportunity to perform this work.

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TRC-9111 IMPLEMENTATION REPORT

The goal of TRC-9111 was to develop a quantitative analytical test that can detect and measure amine-based antistripping additives in asphalt/additive blends. We met this goal through the development of what is now known as the Single-Vessel Titration test (SVT test). The SVT test can accurately detect and measure amine-based additives in amounts less than 1% by weight. It has not been qualified for mixes containing aggregate, but should be applicable to asphalt/additive blends as received from the manufacturer as a quality-control measure. The SVT test will also provide the basis for future testing methods that will be applicable to pavement samples containing aggregate and pavements that have been on the roadway for extended periods of time.

The Single Vessel Titration Test

The SVT test is a wet-chemistry titration analysis that can be performed by virtually anyone after just a few hours of training; the procedure does not require an understanding of the chemical principles involved and the test interpretation is unambiguous. Any technician with laboratory experience should be able to perform the test after a couple of hours training. The cost for lab equipment for the test is a couple of hundred dollars and the materials cost per test is under \$10. At this time the SVT test is currently qualified for asphalt/additive mixtures only but it may also be applicable to aggregate mixes with some modifications. The current incarnation of the SVT test, described below, is effective and practical for its intended application, but there are always room for improvements. Modifications that upgrade the accuracy, ease of use, or range of application will almost certainly be found in Phase II of this program (TRC-9408). One improvement to be considered in Phase II is automation of the test, which will reduce both the time required and the resulting error.

The SVT test requires several repetitions of the same analytical procedure: a titration for basicity. The basicity of a sample of asphalt, additive, or asphalt/additive blend is exactly what it says: how basic (or alkaline) the sample is. A basic chemical has a pH higher than the neutral point, $\text{pH} = 7$. Amine antistripping additives are alkaline compounds and, we have found, detectable by the amount of basicity they add to a given asphalt. The procedure is to measure the basicity of the blank asphalt (containing no additive), measure the basicity of the additive alone, and then measure the basicity of the asphalt/additive blend in question. From the known basicities of the asphalt and the additive alone, the weight fraction of additive in the blend can be determined.

What the SVT Test Can Do at This Time

- Measure the amount of a known amine-based additive in an asphalt/additive blend.

What the SVT Test Cannot Do at This Time

- Measure the amount of a known amine-based additive in a pavement sample containing aggregate.

Non-Consumables Required to Conduct the Test

1. A magnetic-stirrer plate (about \$130, heater is not necessary)
2. Five 250 ml beakers (will be cleaned and reused)
3. pH meter and probe (about \$275)
4. One Titration buret, 10 ml

Consumables Required to Conduct the Test

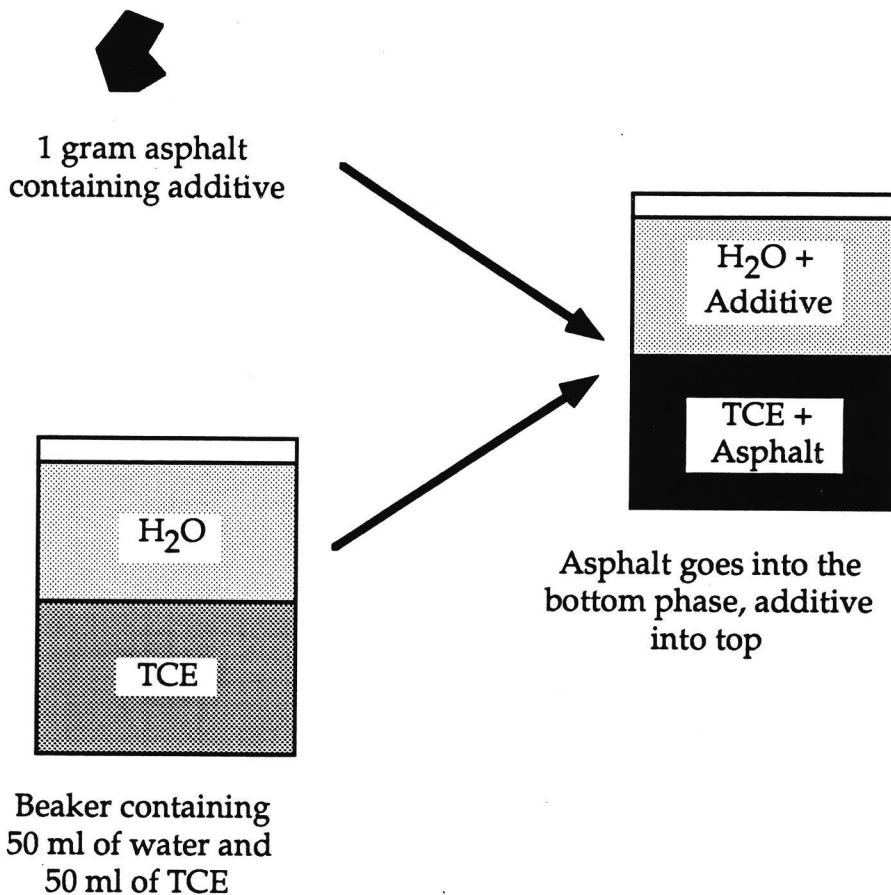
1. 0.5 grams of the antistrip additive in question.
2. 5 grams of the asphalt in question that does not contain additives.
3. 5 grams of the asphalt/additive blend to be analyzed.
4. 250 ml of trichloroethylene (TCE) and 250 ml of deionized water
5. 20 ml of 0.01 N HCl

Titration to Determine the Basicity of a Sample

titration for basicity is repeated five times each on samples of the asphalt alone, the additive alone, and the asphalt/additive blend. The procedure for this titration is the same regardless of the sample composition, so this procedure will be explained first. Again, the basicity of a sample of asphalt, additive, or asphalt/additive blend is exactly what it says: how basic (or alkaline) the sample is. A basic chemical has a pH higher than the neutral point, $\text{pH} = 7$. A titration for basicity provides a quantitative measurement of the basicity of any sample by determining how much of an acid must be added to one gram of sample before the pH falls to 7. This is analogous to adding water to a partially-full barrel until it begins to overflow in order to determine how much empty space was inside. The result from this titration is the basicity of the sample in units of moles basicity per gram of sample.

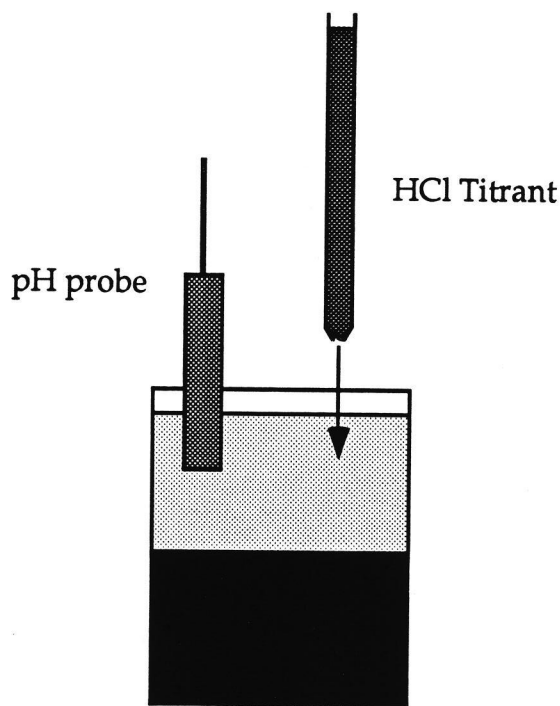
The procedure for the basicity titration is as follows:

1. Dissolve 1 gram of sample in 50 ml of trichloroethylene (TCE) and then 50 ml of water in a 250 ml beaker. Agitate for 1 minute on the stir plate at a high enough speed to mix the two phases together.



Mixing the asphalt-additive and the analysis reagents.

2. Turn down the agitation until two phases form (water on top, TCE and asphalt on bottom). Leave this low level of agitation on throughout the rest of the titration.
3. Place a pH electrode in the water phase (the top phase).
4. Titrate with 0.01 N HCl until pH of the water phase drops to 7.00. Take out pH electrode and stir vigorously, measure pH again, and continue to titrate until the pH remains at 7.00.



Performing the titration.

5. Calculate the basicity from this equation:

$$\begin{aligned} \text{Basicity of Sample (moles basicity/gram of sample)} &= \frac{(\text{ml of acid titrant})(0.01 \text{ N})}{(1000 \text{ ml/liter})(\text{grams of sample})} \\ &= \frac{(\text{ml of acid titrant})}{(100,000)(\text{grams of sample})} \end{aligned}$$

Procedure for the Single Vessel Titration Test

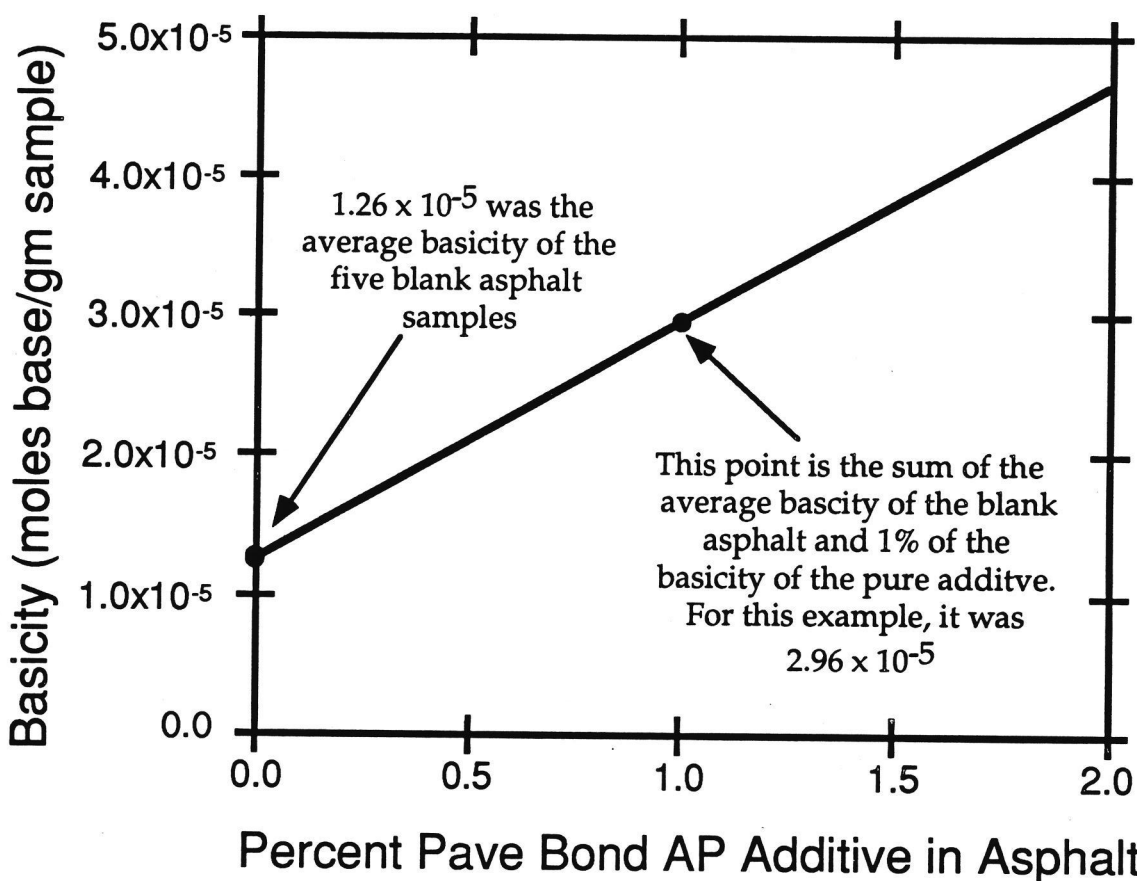
The first step is to make a calibration curve for this particular asphalt/additive blend. This curve will take the form of a graph having sample basicity on the y-axis and weight percent additive on the x-axis. The calibration curve need only be prepared one time for each asphalt/additive blend; it is then applicable to any combination of these two particular compounds no matter how many samples are analyzed in subsequent testing as long as the same asphalt and additive is present in the samples.

The procedure for making a calibration curve is as follows:

1. Measure the basicity of five independent one gram samples of the blank asphalt (containing no additive) and of five independent one gram samples of the pure additive by the titration method described above. Average the basicities of both groups of five. As an example, here are the results using Pave Bond AP:

Blank asphalt was analyzed at 1.26×10^{-5} moles base/gm
Pave Bond AP was analyzed at 1.70×10^{-3} moles base/gm

2. Make a graph with basicity on the y-axis and weight percent additive on the x-axis. Place the average for the blank asphalt as a single point positioned at weight percent additive equals zero (all the way over on the left side). Add the basicity of the blank asphalt to 1% of the basicity of the additive alone and plot that point at 1% on the x-axis. Draw a line between these two point and the result is a calibration curve.



Calibration curve for Pave Bond AP.

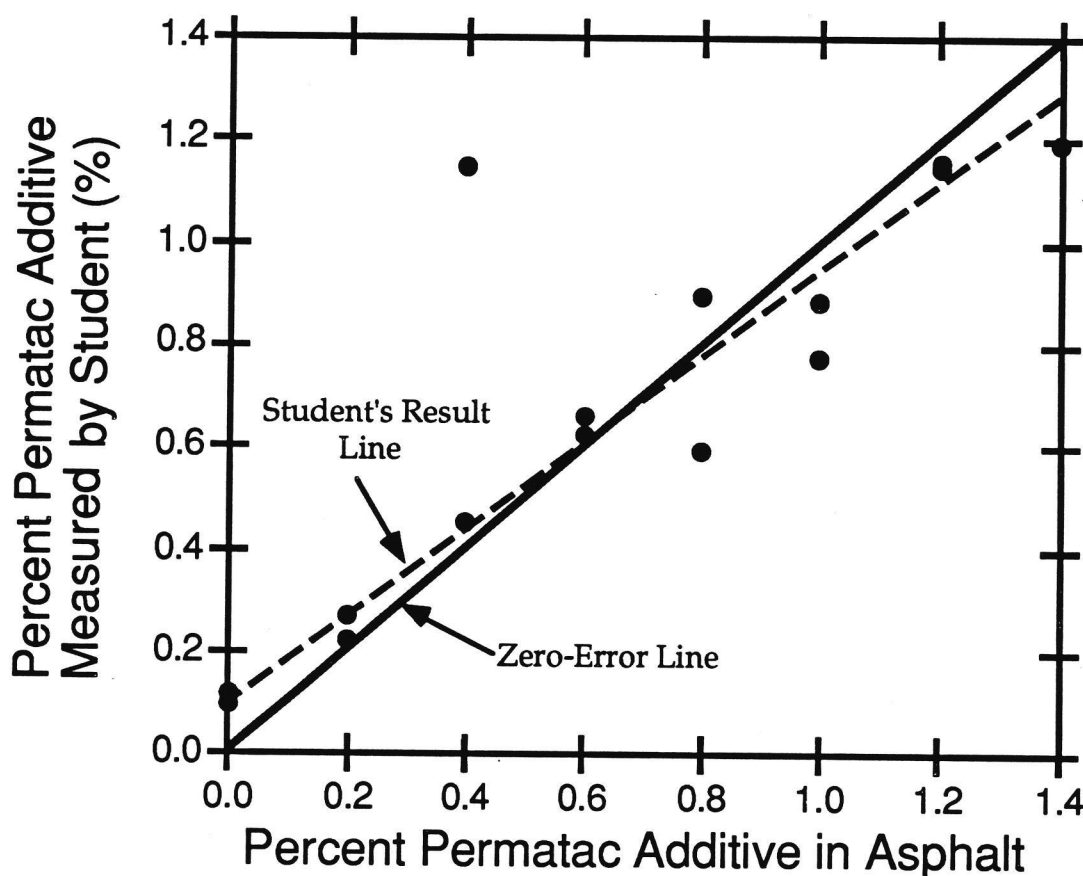
Now that the calibration curve is complete, the unknown samples can be analyzed. The basicity of the five identical one-gram samples of asphalt/additive blend are determined by basicity titration and the percent additive in the samples can simply be read directly off the calibration curve.

Sample preparation for the five titrations can be performed simultaneously and, once the calibration curve is made, it need not be done again as long as the asphalt and the additive do not change properties appreciably. The total time needed to prepare a calibration curve is estimated to be 15 minutes and the time required for the five titrations of the unknowns would be about one day.

Blind Test of the SVT Method

In order to provide an unbiased evaluation of the SVT test, sixteen asphalt/additive samples were made up and tested by an individual that did not know what their composition was. The additive was Permatac and the individual was an undergraduate chemical engineering student. The sixteen samples consisted of two each of 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4% additive. The samples were shuffled before being given to the student.

The figure below shows that, aside from one point, his results fell very close to the actual composition and that there were no systematic errors.



The results of the blind test when the asphalt-additive samples were analyzed by someone who did not know their amounts prior to analyzing the samples.

Basicities of Approved Amine-Based Antistrip Additives

We measured the basicities of all amine-based additives on the approved list. Although it would be best to measure the basicity of a given additive for the purpose of making a calibration curve, these would serve as at least approximate values. The results are listed below in order of the amount of basicity in each. Keep in mind that more basicity is not necessarily better.

| Additive | Manufacturer | Basicity (moles/gm) |
|----------------------|----------------|------------------------|
| Ad-here HP+ | Arr-Maz | 10.3e-3 |
| Kling Beta 2550 (HM) | Scan Road | 7.26e-3 |
| Indulin AS Special | Westvaco | 6.60e-3 |
| Permatac 99 | Scan Road | 6.28e-3 |
| Ad-here LA-2 | Arr-Maz | 5.84e-3 |
| Carstab BA 2000 | Morton Thiokol | 4.95e-3 |
| Kling Beta LV (HM) | Scan Road | 4.72e-3 |
| Permatac Plus | Scan Road | 3.86e-3 |
| Indulin AS-1 | Westvaco | 3.54e-3 |
| Pave Bond AP Special | Morton Thiokol | 3.35e-3 |
| Permatac | Scan Road | 3.32e-3 |
| Acra 500 | Exxon | 2.28e-3 |
| Pave Bond LP | Morton Thiokol | 2.10e-3 |
| Pave Bond AP | Morton Thiokol | 1.70e-3 |
| Kling Beta Lv | Scan Road | 0.462e-3 |

Basicity values for liquid amine antistrip additives on the AHTD qualified products list.

Phase II Improvements to the SVT Test

The following tasks will be performed in order to extend the usefulness and applicability of this testing methodology.

Investigate alternative and improved solvents and titrants for the SVTT - Perchloric acid will be substituted for hydrochloric acid in the test. The stronger acid should give a more definite pH endpoint by more efficiently hydrolyzing the basic amine groups. Other solvents will be investigated for use in the test in order to assure maximum compatibility with those currently used by the AHTD. We will also try out a direct organic phase titration method adapted from techniques used in petroleum analysis. This may enable us to omit the aqueous phase extraction step used in the SVTT and to analyze the mix dissolved directly in a suitable organic solvent.

Extend the SVTT to mixes containing aggregate and mineral filler - Siliceous and limestone-based aggregate will be included in the mix with the ultimate goal of being able to analyze any mix of asphalt/additive/aggregate for the additive, preferably without having to have base asphalt comparison standards.

Include the new low-odor additives - New amine-based additives are coming on the market that have a narrow but high molecular weight distribution resulting in significantly reduced odor during addition to asphalt and application of the mix to the road surface. These additives will rapidly become very important to the technology and may become mandated in some states. Therefore, special attention will be given to analyzing for these compounds in anticipation of their increased usage.

Include the detection and measurement of hydrated lime additives - The SVTT will be tried on hydrated lime in asphalt to determine if it will work without modification as an analytical method for that class of additive or to ascertain what modifications to the SVTT are necessary to make it applicable.

Investigate the basic mechanisms of antistrip additives - During Phase II we will be spending a lot of time looking into the chemical reactions of these additives for the purpose of determining analytical methodology. We will take that opportunity to learn whatever we can about how the chemical reactions of additives in general result in antistripping activity between asphalt and aggregate phases. As such, this is a nebulous goal, but we plan to take the opportunity to learn about the mechanisms as we perform the tasks listed above. If interesting and pertinent phenomena are noticed during this work, further experiments might be included to try to elucidate the mechanisms of asphalt/aggregate adhesion.

1. INTRODUCTION

.1 STRIPPING OF PAVEMENTS

For bituminous pavements to be durable the asphalt must be able to adhere to the aggregate. If the bond between asphalt and aggregate is broken, the asphalt will strip from the aggregate and the asphalt pavement will deteriorate. This loss of adhesion between asphalt and aggregate and the resultant separation due to the action of water is called stripping. Substances that are added to the asphalt to prevent this displacement due to water are called antistrip additives.

1.1.1 Theories of Adhesion

Antistrip additives work by promoting adhesion between asphalt and aggregate. Adhesion is thought to be by two general mechanisms: mechanical adhesion and chemical adhesion. According to the mechanical adhesion mechanism, various physical properties of the aggregate determine the amount of adhesion between aggregate and asphalt. Some of these properties include the surface area of the aggregate, particle size of the aggregate, surface coatings on the aggregate, surface texture, and porosity [1,2]. Since adhesion takes place at the interface of the aggregate and asphalt, it would only stand to reason that surface characteristics of the aggregate would affect that adhesion. In general, the surface area and particle size refer to the same consideration. The smaller the particles that make up the aggregate, the greater the surface area and consequently the more asphalt that is needed to adequately coat the aggregate. Thus, an asphalt-aggregate mix with an excessive number of fine particles will either tend to strip because of an excessive number of uncoated aggregate particles or the mix will be unstable because of the excessive amount of asphalt needed to ensure a thorough coating.

Porosity refers to the volume of the void space as a percentage of the total volume of the aggregate. In general, it is believed that aggregates with rougher surface texture and a greater porosity will maintain a greater adhesion with asphalt than an aggregate with a smoother texture. The common explanation for this fact is that the asphalt fills the pores and irregularities of the aggregate surface to form a stronger interlock. The absorption features of the aggregate plays a role as well. Some components of the asphalt (mainly the oily components) enter the pores or capillaries of the aggregate where they are preferentially absorbed. As a result, the asphalt on the surface becomes harder due to depletion of these oily components. It is suggested that the interlock of the asphalt with the aggregate pores should make the asphalt adhere more strongly to the aggregate.

Adhesion is also affected by various materials that may be coating the aggregate before the asphalt is applied. If dust or moisture are coating the aggregate an intimate contact between the asphalt and aggregate is prevented. Furthermore, dust is thought to cause an increase in the viscosity of the asphalt. However, some findings indicate that aggregate surface characteristics plays little or no role in

adhesion [3], and some characteristics such as surface roughness and porosity, may actually work against it [2]. Rough surfaces may prevent a complete or thorough coating of the aggregate. A rough textured aggregate would not have as thick or uniform coating of asphalt on the edges. Thus a characteristic that aids adhesion for one reason may inhibit it for another.

According to the chemical adhesion mechanism, interactions between asphalt, aggregate, and antistrip additive determine the amount of adhesion between aggregate and asphalt. After the aggregate has been wetted by the asphalt and absorption occurs, the acidic components in the asphalt react with the basic components of the aggregate [2]. This is a saponification reaction which forms a salt at the asphalt-aggregate interface in which part of the molecule is water insoluble. This theory is supported primarily by several findings which note that stripping is more serious in mixes that have an acidic aggregate than in mixes with a basic aggregate. It has also been found, however, that there is good adhesion between siliceous aggregates which are acidic and some asphalts.

The chemical adhesion mechanism also includes the fact that a liquid will wet a solid better and spreads out more uniformly if the surface tension between the liquid and solid is lowered, that is, if the molecules of the liquid become less strongly attracted to themselves so that they become more strongly attracted to the solid. Antistrip additives fulfill this function of lowering the surface tension of asphalt, which enables the asphalt to better coat aggregate particles.

1.2 Mechanisms Of Stripping

It is generally agreed that stripping occurs because water breaks the bond between asphalt and aggregate and mechanisms for this have been proposed. Two broad categories are delamination and incomplete coating. Delamination is the condition where the asphalt coats the aggregate particles and is later separated by various actions which include such theories as detachment and hydraulic scouring. Detachment occurs when the asphalt is separated from the aggregate surface by a thin film of water as if being peeled [1]. This occurs because the aggregate becomes coated by the asphalt but is sheared away by the action of water. Detachment is considered to be a primary mechanism of stripping. Hydraulic scouring is a mechanism that involves traffic. According to this theory, given by Stevens [4], the bituminous mix has a series of interconnected pores which are partially filled with air and water. When traffic runs on a saturated pavement (as in after a rain) the action of the tire presses water into the pavement in front of the tire and is brought back out as the tire leaves the spot. Dust may become mixed with the water and help in separating the asphalt and aggregate [1].

Incomplete coating is the condition where the asphalt did not completely coat the aggregate in the first place, as opposed to coating them and later detaching. Incomplete coating can promote stripping in the asphalt-aggregate mixture. The film rupture theory is based on the idea that the asphalt does not adhere evenly over the entire surface of the aggregate. As stated earlier, the aggregate consists of

varying sized particles, particles that are various shapes with varying textures, and that have different levels of porosity. As a result, asphalt will coat the aggregate unevenly being thinnest at sharp corners and at the edges of the aggregate. Sufficient amounts of traffic on the thin areas will cause the asphalt film to fracture. The fractured asphalt-aggregate mix will then be more susceptible to stripping.

1.1.3 Factors Influencing Stripping

The study of the stripping of asphalt pavements is complicated by the many factors that influence stripping. Factors that influence stripping fall into the following broad categories: asphalt characteristics, aggregate characteristics, asphalt-aggregate mix design, environmental conditions, traffic, and the effects of antistrip additives [5,6].

Asphalt properties that affect stripping include viscosity, surface tension, and chemical composition and film thickness [2]. In general, asphalts with low viscosities are reported to be more likely to strip than asphalts with high viscosities [2,7]. It is also considered desirable that basic nitrogens and phenols be present in the asphalt because they are fairly adsorptive and, more importantly, they are retained more in the presence of moisture. Carboxylic acids and sulfoxide compounds are more readily adsorbed than nitrogens and phenols but they are also more readily desorbed. It is obvious that a thick asphalt film would be less likely to experience stripping problems than a thin asphalt film.

Although asphalt properties are an important consideration it is generally believed that stripping is primarily an aggregate problem [8,9]. Aggregate properties include aggregate mineralogy, surface chemical composition, surface area, pore size, and condition of the aggregate surface. To promote adhesion between asphalt and aggregate it is important that the aggregate is thoroughly wetted with asphalt, using an asphalt that has the highest viscosity that is practical for a specific application, and to avoid using highly hydrophilic aggregates [1]. Siliceous aggregates (acidic) tend to strip more easily than limestone aggregates (basic). Other desirable aggregate characteristics are an aggregate surface chemical composition which will accept or donate electrons, form hydrogen bonds, form acid and base pairs or insoluble salts [2,7]. In addition, aggregates must be textured, angular, hard, and polish-resistant under wear. It is also desirable to have an aggregate surface that is free of dust and moisture at the time of application.

Three factors of the asphalt-aggregate mix design that influence stripping are air void content, gradation and asphalt content. Asphalt specifications which are established by AASHTO allow for an air void content of 2.5 - 5% of the mix. Air void contents that are too low may cause bleeding after compaction. On the other hand, air void contents that are too high allow water to travel through the mix, thus promoting stripping. The gradation of a mix allows for 2 - 8% of fines according to the specifications also established by AASHTO. An excessive number of fines promotes stripping due to incomplete particle coating. Asphalt content is important because a mix with too little asphalt cement will be brittle while a mix with too

much will be plastic, and lacking in mechanical strength. A plastic mix is one which deforms under pressure, unlike an elastic mix which springs back and retains its form and is able to carry the traffic load.

Environmental conditions during construction naturally have an important effect on stripping. If the temperature is cool and moisture is present during construction stripping is much more likely to occur. Not surprisingly, Tunnicliff and Root [7] reported that construction in the late fall was mentioned by numerous reporting agencies to be related to stripping problems. One explanation for this is that poor compaction, as a result of cold and wet weather, will leave a high air void content that allows water to later penetrate the asphalt mixture. Weather conditions after construction affect stripping as well. Wide temperature fluctuation, freezing, and wet-dry cycles all influence stripping. In addition, the heavier the traffic load, the greater the tendency toward stripping [2].

Finally, the use of antistrip additives and their effectiveness should be noted. Tunnicliff and Root [7] note that of 32 agencies reporting the use of antistrip additives 30 give a partly favorable or generally favorable response to their experience with antistrip additives. It should also be noted, however, that Tunnicliff and Root mention inconsistent assessments of the effectiveness of additives; some states on the east coast that use additives report stripping problems while two bordering states do not use additives and report no stripping problems. Despite these inconsistencies, it has been shown through laboratory tests and experience that the use of antistrip additives is effective in the minimizing of pavement failure due to water damage.

1.2 PREVENTION OF STRIPPING

The following sections discuss stripping and its prevention in more detail. The prevention of stripping reduces to three possible actions: (1) preventing water from entering the asphalt-aggregate mix before, during, and after the laying of the pavement. Heating the aggregate prior to mixing it with asphalt attempts to achieve this but there is no sure way to completely and permanently remove moisture, (2) using aggregates that are known to perform well. However, it is not economically feasible to transport aggregate from one location to another. Therefore, whatever aggregate is found in a given area is generally the aggregate that is used, (3) adding antistrip additives that either improves the bonding capability of asphalt to the aggregate or makes the aggregate less inclined to be coated by water. Of these three actions, the use of antistrip additives seems to be the most cost effective and operationally effective. Thus, it becomes all the more important to have a test that can reliably determine if an additive is in fact present in the asphalt.

1.2.1 Prevention of Stripping With Additives

There are two main mechanisms by which antistrip additives work to prevent stripping. In the first way antistrip additives decrease the surface tension of asphalt making the asphalt a better wetting agent which in turn makes it better able to coat

the aggregate particles. The antistrip additive accomplishes this lowering of surface tension in the following way. Asphalt behaves as any other liquid in that its molecules are attracted to each other by secondary forces. However, the molecules on the surface of the asphalt experience a net inward pull. The effect of this tendency to be pulled inward is manifested as the surface tension of the asphalt. Once on the asphalt interface, the antistrip additive increases the outward pull by surrounding the surface asphalt molecules with a nonpolar environment, which decreases the net inward pull. Thus, the surface tension of the asphalt will be reduced, causing the asphalt to spread more, i.e. to become a better wetting agent. Consequently, the asphalt will better coat any surface to which it is applied. Of course, the rougher the aggregate surface the better the asphalt will coat to a certain extent.

In the second mechanism the antistrip additive forms a bond or bridge between the asphalt and aggregate, performing a function similar to that of glue. This mechanism involves both the asphalt and the aggregate and is accomplished in the following way. The antistrip additive has both a polar and nonpolar end while the asphalt is nonpolar and the aggregate is polar. When the antistrip additive reaches the surface of the asphalt, that is, the asphalt-aggregate interface, the nonpolar end of the antistrip additive is attracted and held by the nonpolar asphalt. At the same time, the polar end of the antistrip additive is attracted and held by the polar aggregate. Thus, the polar-nonpolar antistrip additive bonds the asphalt and aggregate through their mutual bonding with the antistrip additive. This is different from the first mechanism in that the first one occurs with or without aggregate present. That is, antistrip additives with asphalt alone will still decrease the surface tension. In this second mechanism aggregate must be present to form the bond as the result of the polar-nonpolar attraction.

For both mechanisms to occur, the antistrip additive must have both polar and nonpolar ends. Either the additive itself (such as in the case of liquid amine-based additives) is a molecule with polar and nonpolar ends that functions directly as an antistrip additive, or the additive (such as in the case of lime) reacts chemically with asphalt to form in-situ a molecule with polar and nonpolar ends that acts as an antistrip agent. In both instances the end result is the same - a polar-nonpolar molecule improves adhesion between asphalt and aggregate.

In the first case, there is a long hydrocarbon chain (nonpolar) with an amine group (polar) attached. When added to asphalt this may react with some component in the asphalt to produce a charged molecule. Since most aggregates are negatively charged it may very well be the case that this positive charged molecule is attracted to the aggregate. Even if the molecule does not take on a hydrogen ion to give it a net charge on one end, the amine-based additive still has a polar and non-polar end. The extent to which this acquisition of charge is important is not clear. In the second case, lime (which is basic) reacts with acidic components in the asphalt (such as carboxylic acids) and then through a saponification reaction creates a molecule with polar and nonpolar ends. See Figure 1.

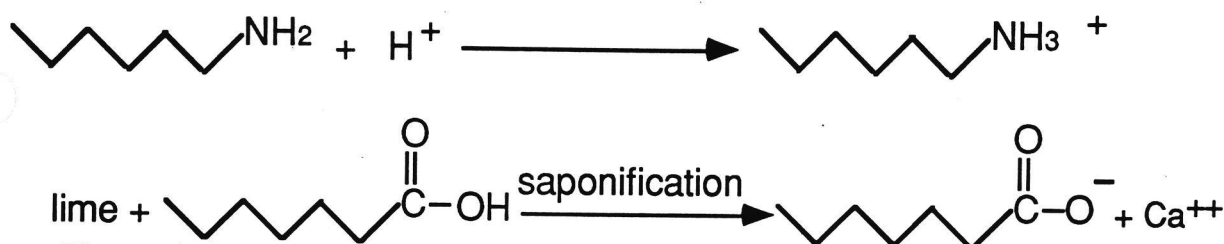


Figure 1. Structures that are representative of liquid amine and lime antistrip additives that show the polar and nonpolar regions that are characteristic of antistrip additives.

1.2.2 Liquid Additives

The most widely used method to prevent stripping is the use of a liquid chemical antistrip additive. There are approximately 27 liquid antistrip manufacturers with 116 approved products [10]. These additives are usually amine based and because of their proprietary nature their exact chemical composition is not obtainable. However, Mathews [11] has shown from his studies that the antistrip molecule performs better if it contains a long-chain alkyl or alkenyl group. Also, a chain length of 16-18 carbon atoms is preferable. He also noted that at least one primary amine group is required for adequate activity.

Not only do liquid antistrip additives work by lowering the surface tension of asphalt and by forming a bond between asphalt and aggregate because of its polar-nonpolar nature, antistrip additives are also believed to improve adhesion through surface charges. Aggregates are mostly negatively charged (except limestone which is positively charged). Cationic antistrip additives are attracted to the negatively charged aggregate surface and they have the ability to displace water from the aggregate surface. Hicks [2] states that the improvement in adhesion between asphalt and aggregate is associated with the fact that antistrip additives give the asphalt cement an electrical charge that is often opposite to that of the aggregate surface.

Liquid antistrip additives are chemically classified as anionic, cationic, or nonionic. The most widely used liquid antistrip additives are cationic surfactants. Cationic surfactants are surfactants carrying a positive charge on the active portion of the molecule. These are the most usable because of their ability to be strongly adsorbed at a negatively charged aggregate surface and are most efficiently used to increase adhesion between acidic aggregates and asphalts. Soaps and other anionic agents are able to reduce the interfacial tension between asphalt and water but only have a small influence on adhesion [11].

Liquid antistrip additives are usually added at a rate of 0.5 to 1.0 percent by weight of the asphalt. Liquid antistrip additives are soluble in asphalt and they migrate to the aggregate surface and become adsorbed, probably selectively [10,12,13]. This results in the aggregate surface becoming hydrophobic or water-repellent and which results in longer adhesion of asphalt to aggregate [11,12]. The extent to which the aggregate surface becomes hydrophobic is proportional to the concentration of the liquid

antistrip additive used, the efficiency of migration, and the strength of the adsorbing bond [12]. According to Dybalski [12], only approximately 30-40 percent of the original concentration of liquid antistrip additive contributes to the promotion of adhesiveness. For liquid antistrip additives to be effective the asphalt must be at a sufficiently low viscosity to permit migration to the asphalt-aggregate interface. For the asphalt to allow this migration it must occur while the asphalt is hot. The problem with this is that it only allows about three hours for migration [12]. Also, studies have shown that storage of liquid antistrip additives at elevated temperatures can reduce their effectiveness [14,15]. Although antistrip additives can be stored at ambient temperatures indefinitely without a loss in effectiveness it has been shown that when stored in hot asphalt at temperatures greater than 100°C the amine can become inactive [14].

Liquid antistrip additives are added to the asphalt while the asphalt is in a heated liquid state and the two are then thoroughly mixed together before the aggregate is added. But, because water can coat the aggregate particles, Dybalski [12] proposes applying the antistrip additive directly to the aggregate so that the water can be displaced before the aggregate is mixed with the asphalt cement. However, blending the antistrip additive with the asphalt is easier, more economical, and is the current practice [9].

Asphalts are normally adhesive to absolutely dry surfaces but in the presence of water they do not adhere or spread on surfaces. While asphalt is hydrophobic, most aggregates are hydrophilic and are therefore more easily wetted by water than by asphalt. It is important that liquid antistrip additives promote adhesion not only during the mixing process of asphalt and aggregate but also during the service life of the bituminous pavement. Asphalt adhesive properties are due to polar or chemical groups such as found in the asphaltene and resin hydrocarbons [16]. However such polar material lacks the necessary surface activity to displace water from wet surfaces. When liquid antistrip additives are used they supply polar material with high spreading activity. Their purpose is to cause asphalts to displace water from wet surfaces before coating it, and to maintain that bond once the asphalt has coated the aggregate surface.

Liquid antistrip additives can change the physical properties of the asphalt cement in various ways. One way the literature indicated is that additives can have a softening effect on the asphalt cement, both before and after aging. Maupin [17] found that penetration values were higher for the asphalt cement containing antistrip additive. A higher penetration value means the asphalt has softened. From tests done by Anderson and Dukatz [18] it was concluded that the abuse of these additives (excessive dosage) may also contribute to tenderness by softening the asphalt or reducing the hardening. Also, some liquid antistrip additives can reduce the viscosity of an asphalt, and possibly the asphalt would not longer meet viscosity specifications. In addition, Dybalski [12] also speculated that surfactants containing amine groups might react with acidic compounds present in asphalt to form amides which are inactive with the aggregate surface when the antistrip agent was mixed with the asphalt.

Concentration of the antistrip additive in the asphalt cement can greatly affect its performance. Liquid antistrip additives are effective if enough of the additive is used, but the majority of antistrip additive added to the asphalt cement never reaches the asphalt-aggregate interface where it should to perform properly [12]. If the concentration of the chemical dissolved in the asphalt is in excess of that needed to satisfy all of the adsorption sites for the aggregate, hydrocarbon to hydrocarbon interfacial orientation can occur creating a mechanically weak, water susceptible, shear plane [12]. Because of this there is a need to determine the concentration of antistrip additive that will be effective for particular asphalt-aggregate mixes. In a study done by Giavarini and Rinaldi [8] they concluded that small amounts of liquid antistrip additives showed better results and that higher contents were not advantageous. Liquid antistrip additives are often preferred to powder (or dry) because of their cost advantage and ease of implementation during construction.

1.2.3 Dry Additives

As previously discussed, hydrated lime produces a decrease in the surface tension between asphalt cement and water. This decrease in surface tension results in improved adhesion between asphalt and aggregate. Another theory suggests that hydrated lime improves adhesion by reacting with acidic components in the asphalt (the carboxylic acids) to form water insoluble compounds that are readily absorbed onto the surface of an aggregate [19]. It has been noted that the mechanism by which hydrated lime improves stripping resistance cannot be completely explained by the reaction of the asphaltic acids with the lime. A third theory states that lime provides calcium ions which can replace hydrogen, sodium, potassium and other cations on the aggregate surface. The calcium-rich aggregate surface reacts with long chain organic acids in the asphalt to form a water-resistant surface [19].

Dry antistrip additives, such as hydrated lime or portland cement, also prevent stripping by acting as mineral fillers (that material passing the No. 200 sieve). Mineral fillers not only serve as mineral aggregate they also fill the voids between larger aggregate particles to strengthen the mix [10]. As the air void content in a given mixture is reduced, the amount of stripping which will occur in the mix will be decreased. Because mineral fillers reduce the air void content of mixes this results not only in less water getting into the mix but also in preventing the moisture that does get in from spreading. Hydrated lime also serves as a neutralizing agent and it has been reported that this neutralizing effect can reduce the rate of aging in pavements [1,10]. All three functions can help prevent the intrusion of water. In addition, powdered additives will stiffen the asphalt cement and therefore increase the viscosity of the pavement.

Hydrated lime can be added to the aggregate in many ways: (1) dry hydrated lime (2) hydrated lime slurry (3) dry hydrated lime with moist aggregate (4) hot (quicklime) slurry (CaO). All have been shown to improve stripping resistance. A problem with the application of dry lime is the loss of the lime off of the aggregate before it is coated with asphalt. The main problem with lime slurry application is that the

water must later be removed and that can be expensive. The application of dry hydrated lime with moist aggregate first requires increasing the aggregate water content 3-5% and then adding the lime. The application of quicklime slurry is an exothermic chemical reaction that can cause safety problems. Of these various methods of application it has been shown that slurry applications are the most effective [2,9,10,20]. For the lime to serve as an antistrip additive, moisture has to be present to activate the lime. Both calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂) are reactive with water and therefore can function as antistrip additives. However calcium carbonate (CaCO₃) is not reactive with water and will not produce the desirable effects. Lime is usually added at a rate of 1-2 percent by weight of aggregate. But because finer aggregates have larger surface areas, higher percentages of hydrated lime may be required to sufficiently promote stripping resistance. The resistance to stripping increases with increased amount of hydrated lime.

In an effectiveness survey by Hicks [2] it was shown that pretreatment of aggregate with lime is the most effective. Amine antistrip additives are used by many but their effectiveness was mixed. But other literature indicates that there is greater improvement in coating retention for liquid antistrip additives than for hydrated lime [21]. While both forms have proven to be effective in certain instances, a review of the literature reveals that neither appears to be effective in all aggregate-asphalt systems [6].

1.3 DETECTION OF ANTISTRIP ADDITIVES

Tests for the detection of antistrip additives can be classified as either qualitative or quantitative. A qualitative test determines whether or not an additive is present while a quantitative test determines the amount of additive present. However, neither can determine the dosage required for optimum performance nor can they determine the effectiveness of an additive once it has been applied. These tests do not indicate how much of the antistrip additive is at the asphalt-aggregate interface.

One broad category of qualitative tests are indicator tests. These tests rely on visual estimation and are therefore considered subjective. Indicator tests are not always reliable and are rarely used. One indicator test, the bottle test, uses Ottawa sand and asphalt cement that is cutback with naphtha or some other diluent. The sand and asphalt cement are placed in a container filled with distilled water and after 20-30 seconds of vigorous shaking, the material is poured out and examined [14,22]. If the asphalt completely coats the sand then it is determined that the asphalt contained an additive. But, in one case, the bottle test indicated the presence of an additive when none was used [17]. There are no standardized quantities for the bottle test and various quantities have been experimented with.

Other indicator tests are classified as color indicator tests. One such test uses one gram of asphalt cement in 40 ml of isopropyl alcohol [23]. In another beaker 40 ml of isopropyl alcohol is used as a control sample without the asphalt cement. Both are then heated until small bubbles appear and the sample containing the asphalt shows slight discoloration. The discolored solution is then transferred to a clean beaker

and drops of bromophenol blue indicator at a concentration of 0.2% in isopropyl alcohol are added. The drops are also added to the control and when the control turns yellow the test is complete. The other solution will turn green or dark blue if an amine-based antistrip additive is present. The color indicator test has been modified using various other color indicators. A diazo dye formation method developed by Carstab Corporation [24] is a color indicator test that determines the amount of polyamine additives in asphalt. This is done visually by comparing samples of unknown concentration to known standards. The colored solution can be analyzed with spectrophotometric methods to reduce the subjectivity. Another color indicator test is based on ASTM D-2074 and is a quantitative test that can determine the percentage of amines in the asphalt [25]. This test heats (160 -180°F) 20 grams of asphalt cement in isopropyl alcohol and then is filtered at room temperature to remove the insoluble material. It is then titrated at 150°F with 0.2 N hydrochloric acid with 0.2% bromophenol blue indicator. After titrating the solution is blue to yellow in color. The volume of the solution after titration times the normality of the hydrochloric acid times the combining weight of the additive divided by the weight of the asphalt cement determines the percentage of amines in the asphalt cement. The combining weight is obtained from the manufacturer and is the weight of the amine portion of an additive to the weight of hydrochloric acid. A calibration is determined by using known dosages of additive.

High-performance gel permeation chromatography (HP-GPC) can be used to determine the effect of antistrip additives (both amine additives and lime) on the molecular size distribution of asphalt [26,27]. This test method can be used to determine whether or not antistrip additives are present or it may be useful in indicating if an asphalt and antistrip additive are compatible or not. For example, when lime is used as an antistrip additive the HP-GPC method showed an increase in the large molecular size percentage by 2-5% [26]. This would need to be taken into consideration because large molecular size material above a certain amount is associated with pavement failures. But this method is costly and slow.

2. SCOPE

The purpose of this project was to develop test methods that could quantitatively determine the amount of unknown antistrip additives present in an asphalt sample. The reason for this project is to determine whether or not antistrip additives are being added in the amount claimed. Two test methods were tried for this purpose: titration for basicity and surface tension measurements. This project will use laboratory tests to make this determination but the final goal is to modify these methods so that they are usable as field tests.

3. EXPERIMENTAL

3.1 TITRATION METHOD

This titration method is a basicity analysis that counts the number of basic groups present in the asphalt-additive mixture. This measured basicity is assumed to vary proportionally with the amount of antistrip additive in a mixture.

3.1.1 Development of Titration Method

A single-vessel titration procedure was developed for measuring the amount of amine-based antistrip additive in an asphalt sample. The evolution of this technique is summarized below.

The first test method was a single solvent method to test for total acidity based on ASTM D 974. After being dissolved in a solvent of toluene, isopropyl alcohol, and water the asphalt sample was titrated to a color change endpoint enabling the moles of basicity per gram of asphalt to be calculated. The main problem with this method was difficulty in determining the endpoint by the color change due to the high opacity of the solution. The endpoint was not certain even with a lamp used to shine in from underneath. A pH meter was also used to help determine the endpoint, but the interactions of the non-aqueous solvent resulted in an uncertain endpoint.

To overcome these problems the single-solvent method was modified into an organic - aqueous extraction method. The asphalt sample was first completely dissolved in trichloroethylene and then agitated with water in a separatory funnel. The top layer, the aqueous phase, was separated from the organic layer, filtered, and then titrated to a pH of 7. A second water extraction was done to ensure complete extraction. This was an improvement over the single-solvent method since a definite endpoint could be reached, but the results were too scattered to be satisfactory.

Next, it was thought that the organic - aqueous extract-and-separate method would be more consistent if the two phases were left in contact with one another. This would result in a continuous extraction of antistrip additive as the titration was performed. This method is referred to as the single-vessel method. The asphalt sample was first completely dissolved in trichloroethylene and then agitated with water in the same container in the same manner as the previous method. Two phases would result with the aqueous phase on top. However, the phases were left in contact throughout the analytical procedure. A pH electrode was placed in the water phase and then titrated to a pH of 7. The moles of basicity per gram of asphalt sample was then calculated.

Consistent, repeatable results were obtained with this method. The single-vessel titration test (SVT) is also the simplest of the various techniques tried, requiring only simple laboratory glassware, reagents, and a pH meter. See figures 2 and 3. The single-vessel titration test is known to be accurate provided the following conditions are met:

1. Asphalt/antistrip additive samples are less than 2-3 weeks old.
2. Samples of the base asphalt without antistrip additive are available for comparison.
3. Samples of the antistrip additives are available.

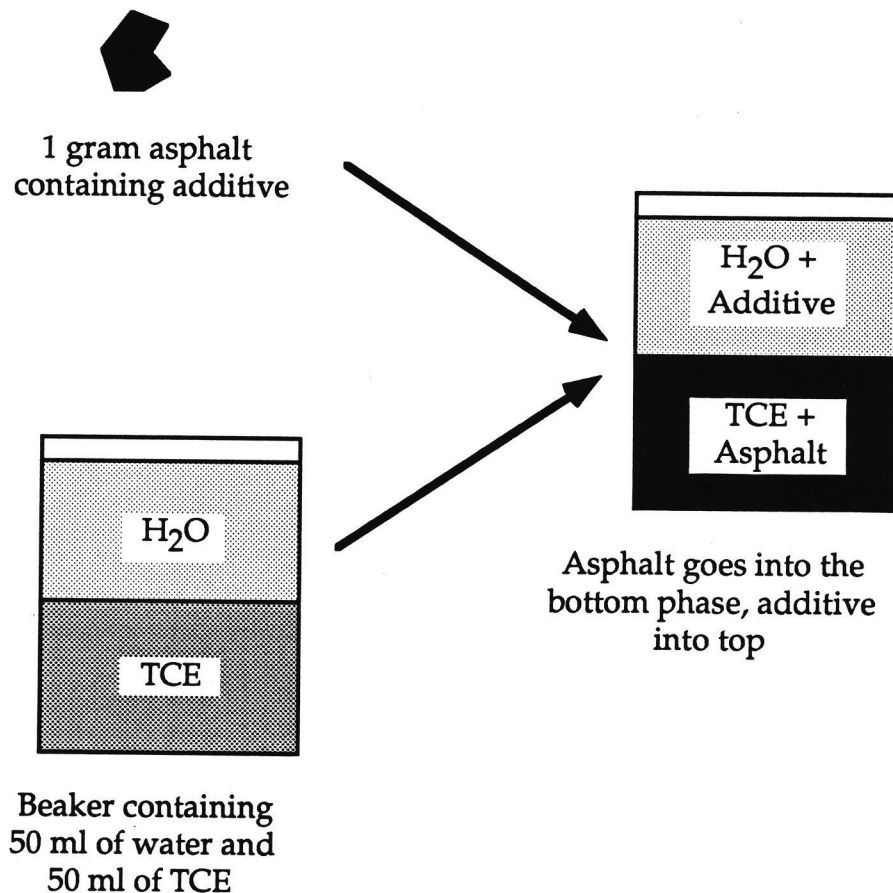


Figure 2. Mixing the asphalt-additive and the analysis reagents.

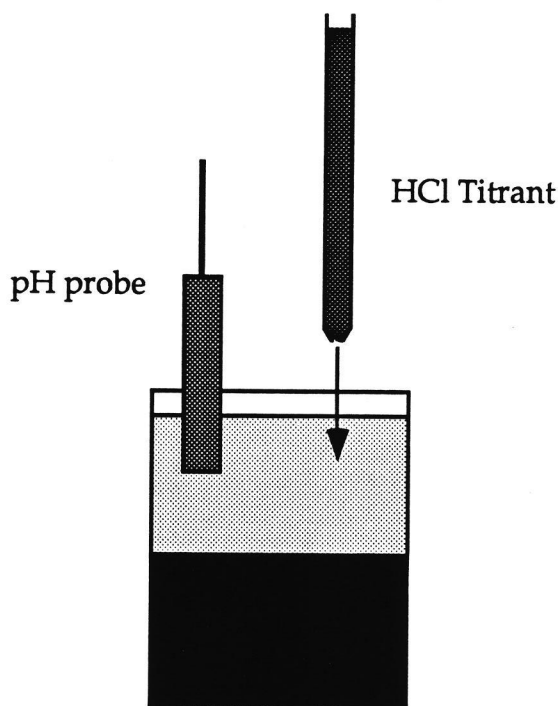


Figure 3. Performing the titration.

3.1.2 Preparation of Asphalt-Additive Samples

All asphalt used in this project is AC-30. All of the siliceous aggregate used in this project is Razorrock crushed gravel (churt) that passes the 3/8 inch sieve and is retained on the #4 sieve. All of the limestone aggregate used in this project is Westfork limestone that passes the 3/8 inch sieve and is retained on the #4 sieve. Asphalt-additive mixtures were prepared by three different methods and analyzed. One method was to weigh out the desired amount of asphalt into a beaker and then weigh out the desired amount of antistrip additive (Exxon Acra 500) into the same beaker. The two would then be mixed together by dissolving in trichloroethylene; this is referred to as "TCE mixed". For example, 1 gram sample of asphalt weighed into beaker and then 0.01 g sample of additive weighed into the same beaker. Another method of preparation was to melt a large sample of asphalt and mix in the desired percentage of additive. For analysis, one gram sample of the asphalt-additive was taken and dissolved in trichloroethylene. This is referred to as "Melt mixed". For example, 100 grams of asphalt was melted and 1 g of additive was stirred in. The third method of preparation is a variation of the second method. A large sample of melted asphalt was poured on top of a previously weighed out amount of additive and mixed together. A one gram sample would be weighed out to be analyzed and then dissolved in trichloroethylene; this method is referred to as "Additive first - melt mixed". For example, 1 g of additive weighed into container and then 100 g of melted asphalt added to it and stirred. See figure 4.

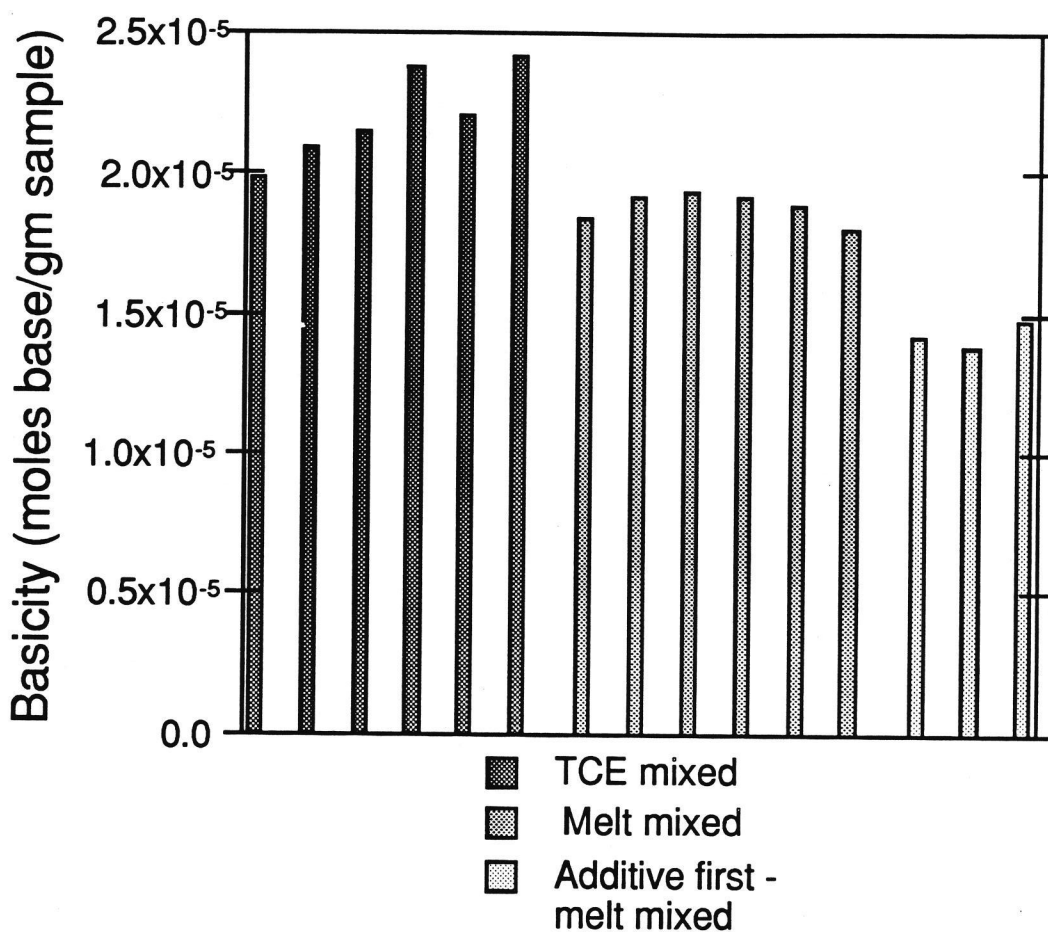


Figure 4. The effect of different methods of preparation on basicity measurements in asphalt-additive mixtures.

The "melt mixed" method is the method that most closely resembles actual practice. This method of preparation enables a large sample of asphalt-additive mixture to be analyzed over a period of time, but it also has the disadvantage in that there is difficulty in properly preparing the mix. Often one gram of antistrip additive would be added to 100 g asphalt and when analyzed the resultant basicity would not be 1%. The error might be the result of operator error in preparing the mix, but the error might also be explained by the additive vaporizing off when put into contact with the hot asphalt. The lower basicities of the "melt mixed" and "additive first - melt mixed" is thought to be mainly the result of the additive vaporizing when put into contact with the hot asphalt because there were visible signs of this when mixing the antistrip additive into the asphalt. The "TCE mixed" is an easier method of preparation and gave more reliable results than the other two methods. This method of preparation always gave the expected basicity results.

3.1.3 Application of Titration Method on Asphalt Samples

These is the procedure for the single-vessel test for asphalt samples:

1. Dissolve 1 gram of asphalt sample in 50 ml of trichloroethylene and then 50 ml of water. Agitate for 1 minute on a stir plate at a high enough speed to mix the two phases together.
2. Turn down the agitation until two phases form (water on top, TCE and asphalt on bottom). Leave this low level of agitation on throughout the rest of the titration.
3. Place a pH electrode in the water phase.
4. Titrate with 0.01 N HCl until pH of the water phase drops to 7.0. Take out the pH electrode and stir vigorously, measure pH again, and continue to titrate until the pH remains at 7.0.
5. Calculate the basicity from this equation:

$$\text{Basicity of Sample} = \frac{(\text{ml of acid titrant})(0.01 \text{ N})}{(1000 \text{ ml/liter})(\text{grams of sample})} \quad (3.1)$$

6. Look up the amount of additive on a calibration curve.

Figure 5 is a calibration curve for Permatac that was produced by making asphalt-additive samples by the "melt mixed" method and analyzing them by the above procedure over a two week period. This graph can be used to determine the percent additive in asphalt from the basicity of the sample.

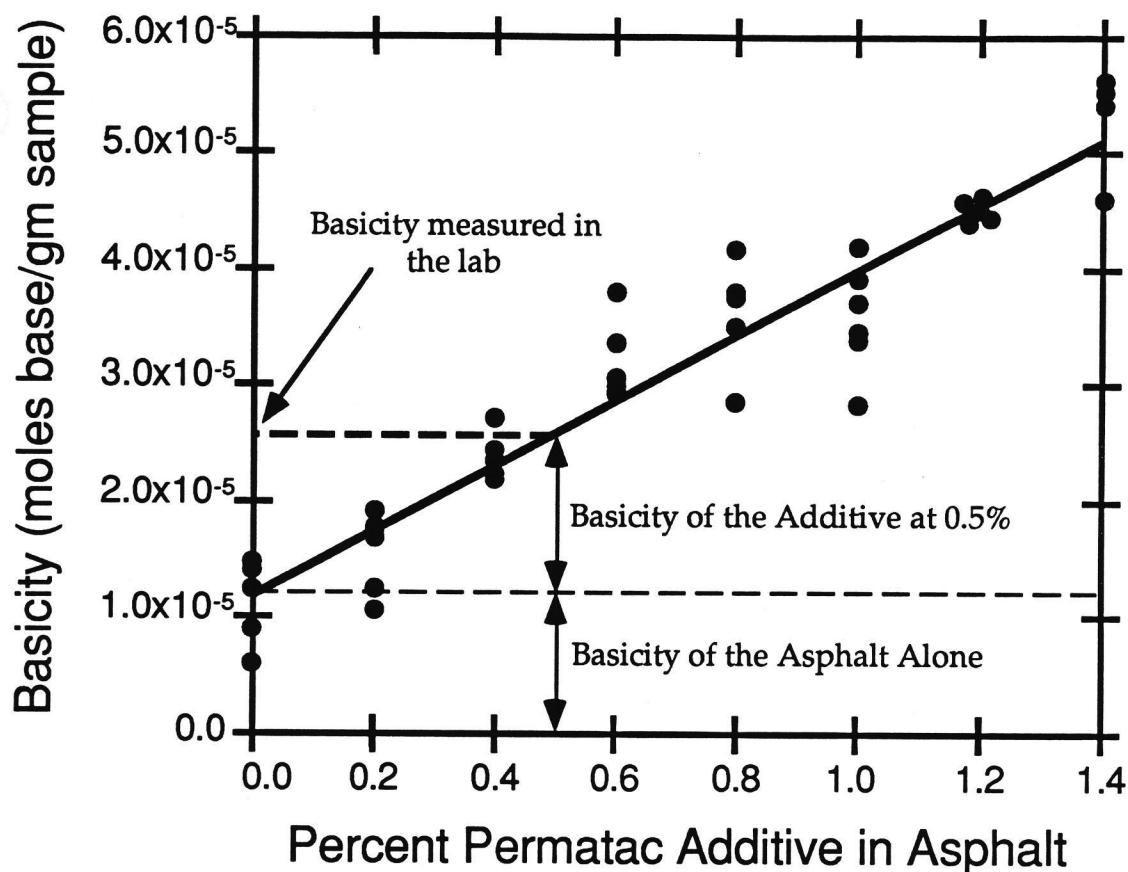


Figure 5. Permatac calibration curve developed from analyzing asphalt-additive mixtures.

At this point it was thought to be necessary that a calibration curve be made up for each additive-asphalt combination. Then, the amount of additive in an unknown sample could be determined by running the procedure used in making the calibration curve and using the measured value of basicity to determine the percent additive in the asphalt. It was then determined that it was not necessary to make the actual asphalt-additive samples to construct the curve, and that all that was needed was an analysis of a blank asphalt sample and of the additive. After being analyzed, the blank asphalt sample gives the y-intercept and the basicity of the additive gives the slope of the line on a calibration curve.

As an example, here are the results using Pave Bond AP:

Blank asphalt was analyzed at 1.26×10^{-5} moles base/gm

Pave Bond AP was analyzed at 1.70×10^{-3} moles base/gm

These two numbers were used to draw the solid line in figure 6 below. Then, samples of Pave Bond AP and asphalt were mixed up in various percentages by the "melt mixed" method and analyzed within a one week period independently of this line. The analysis points fell directly on the line indicating that the calibration curve can be made up without actually having to make up and analyze asphalt-additive samples.

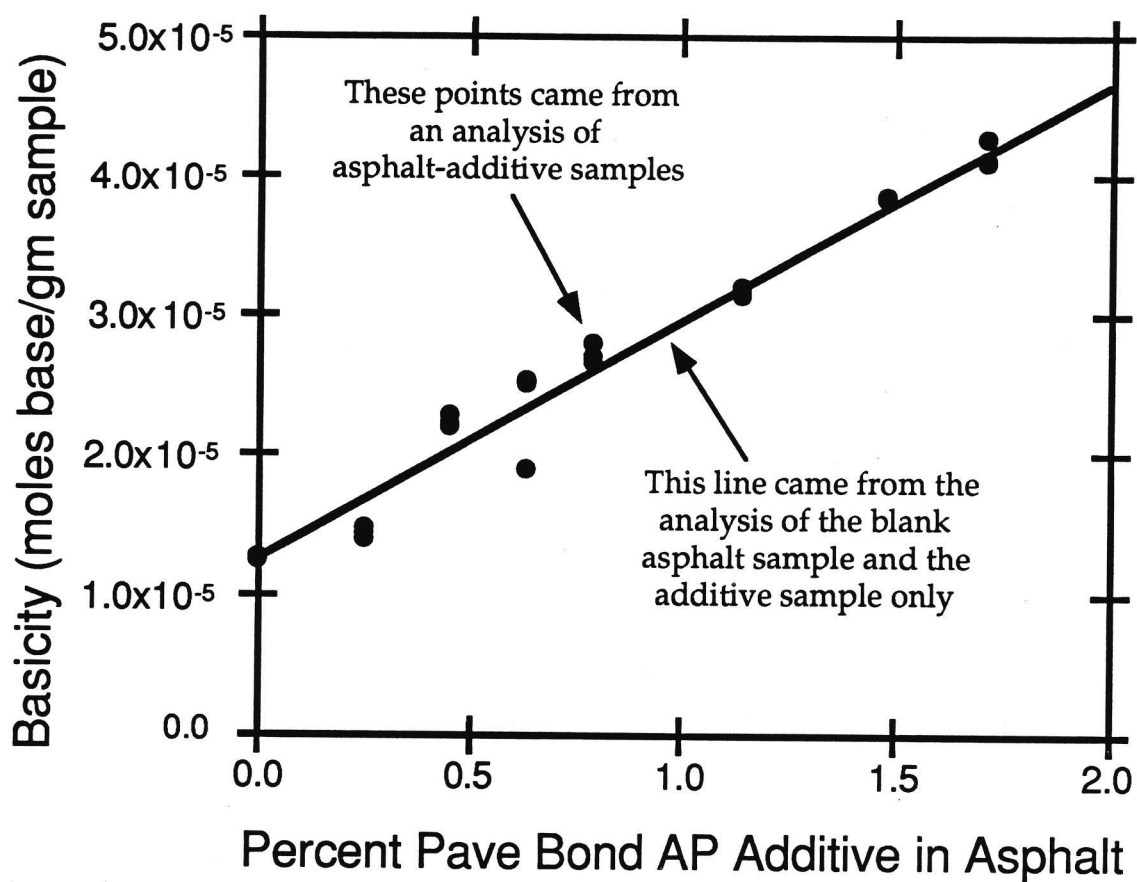


Figure 6. Calibration curve for Pave Bond AP .

Here is the same thing for Acra 500 prepared by the "TCE mixed" method in figure 7. This time, the blank asphalt was slightly acidic, but the calibration line still falls right through the data.

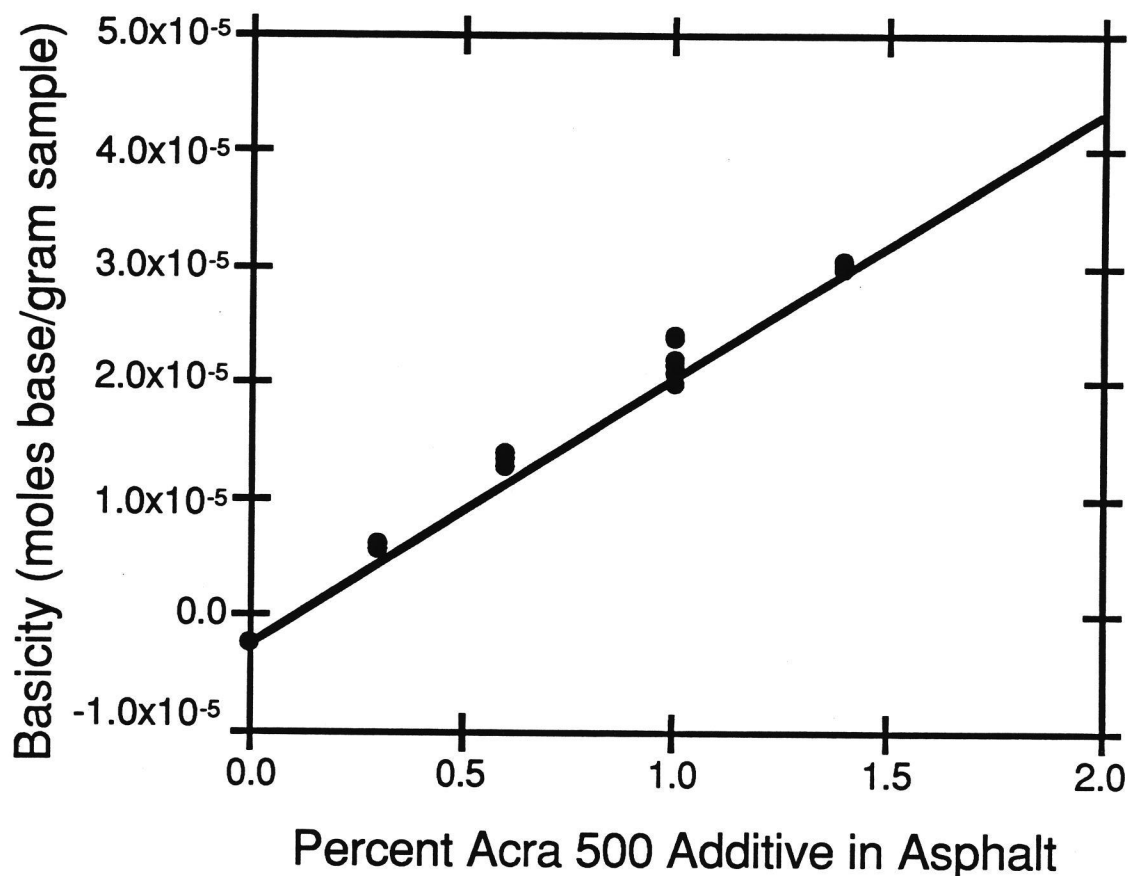


Figure 7. Calibration curve for Acra 500 .

Calibration curves made from asphalt blank and additive only for Permatac and Kling Beta 2550, prepared by the "TCE mixed" method, are shown in figures 8 and 9.

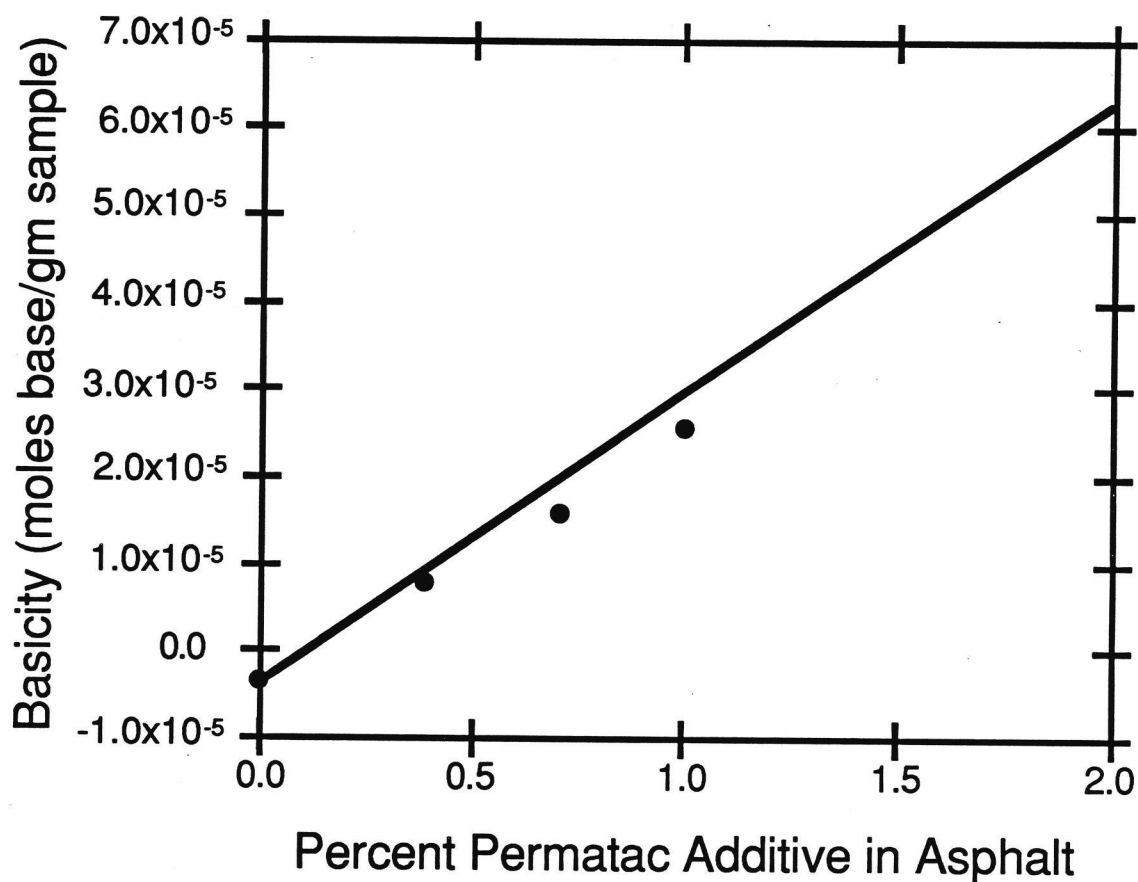
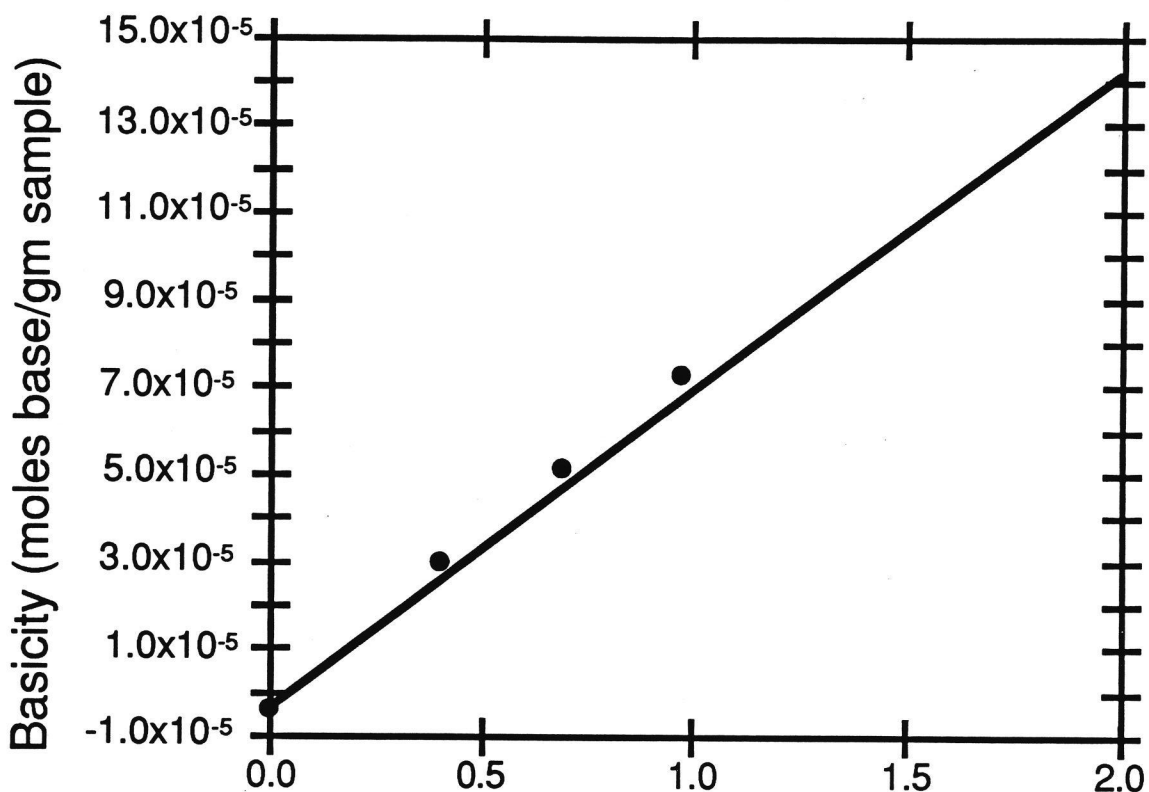


Figure 8. Calibration curve for Permatac .



Percent Kling Beta 2550 Additive in Asphalt

Figure 9. Calibration curve for Kling Beta 2550.

In conclusion, it has been shown that the single-vessel titration method works for Permatac, Pave Bond AP, Acra 500, and Kling Beta 2550 and a simplified way of making up calibration curves was developed.

A blind test was conducted where another student analyzed additive-asphalt samples prepared by the "melt mixed" method without knowing what percentage of additive was in each sample. The results are shown below in figure 10:

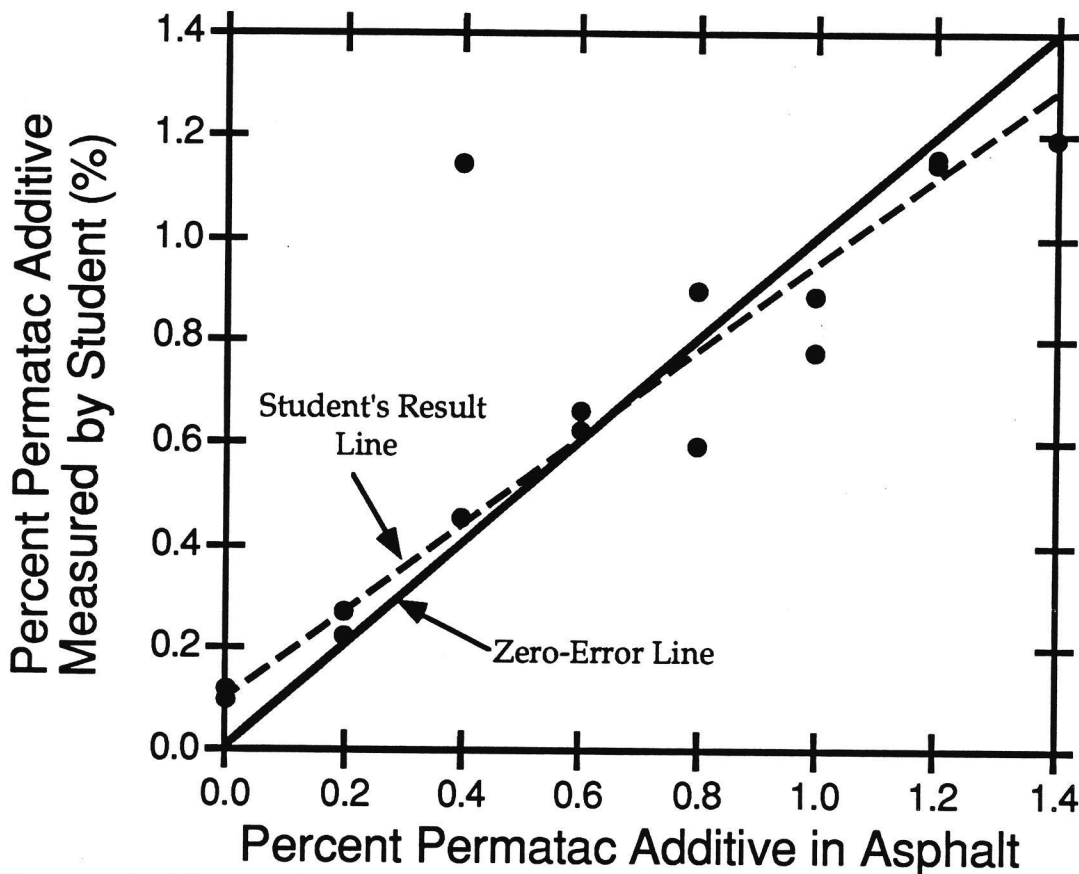


Figure 10. The results of the blind test when the asphalt-additive samples were analyzed by someone who did not know their amounts prior to analyzing the samples.

3.1.4 Chemical Reactions Between Asphalt and Additive

Asphalt samples were analyzed by the single-vessel method to determine what effect melting, aging, and acid-base reactions during mixing had on the asphalt-additive sample.

Changes in Additive Chemistry with Repeated Melting

A large sample of asphalt with Permatac additive was prepared by the "melt mixed" and repeatedly melted and analyzed to determine if melting had an effect on the results of the single-vessel titration method. The figure 11 shows that melting did not cause a change in the results.

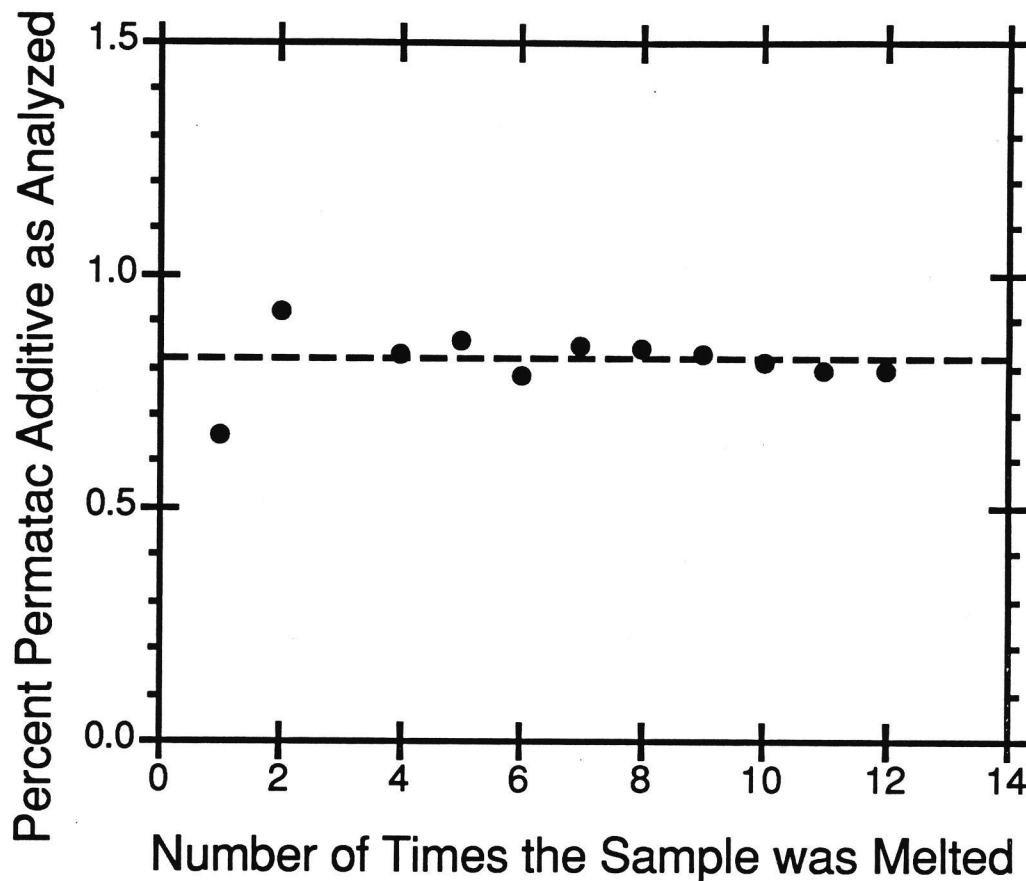


Figure 11. The effect of repeated melting on an asphalt-additive sample.

Changes in Additive Chemistry with Aging in Asphalt

Two large samples of asphalt, one with Indulin AS-1 additive and the other with Pave Bond LP, was prepared and allowed to age over a long period of time and analyzed to determine if aging had an effect on the results of the single-vessel titration method. Figure 12 shows that there is a significant change in the asphalt-additive sample with time.

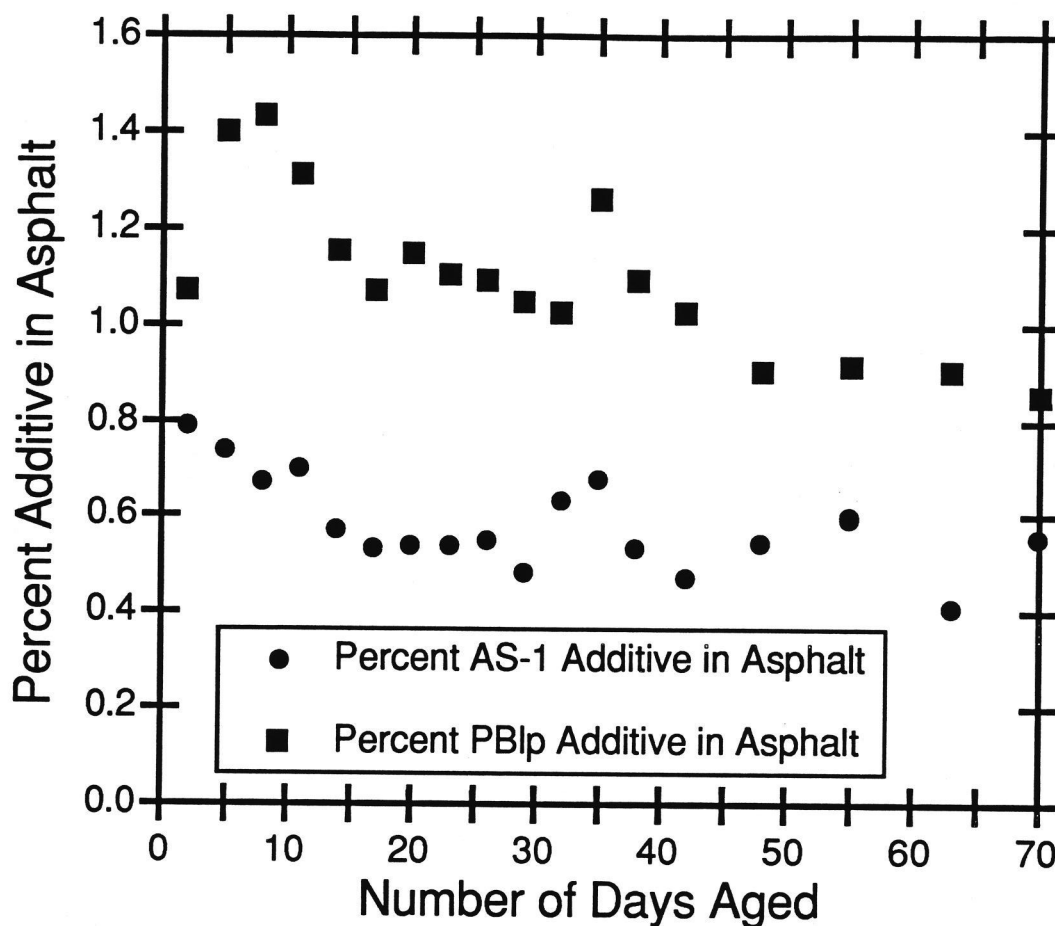


Figure 12. The results of aging asphalt samples with Indulin AS-1 and Pave Bond LP additives.

Asphalt-additive mixtures were allowed to age in different environments in an effort to archive asphalt-additive samples so that they could be analyzed months or possibly years later. One environment had the mixture of asphalt and additive dissolved in trichloroethylene. Another was a mixture of asphalt-additive prepared by the "melt mixed" method and allowed to age. The third environment was a mixture of asphalt-additive prepared by the "melt mixed" method that was kept refrigerated while it aged. As stated previously, "melt mixed" are mixtures that were prepared by melting a large sample of asphalt and mixing in the desired amount of additive. Figure 13 shows the results of this analysis.

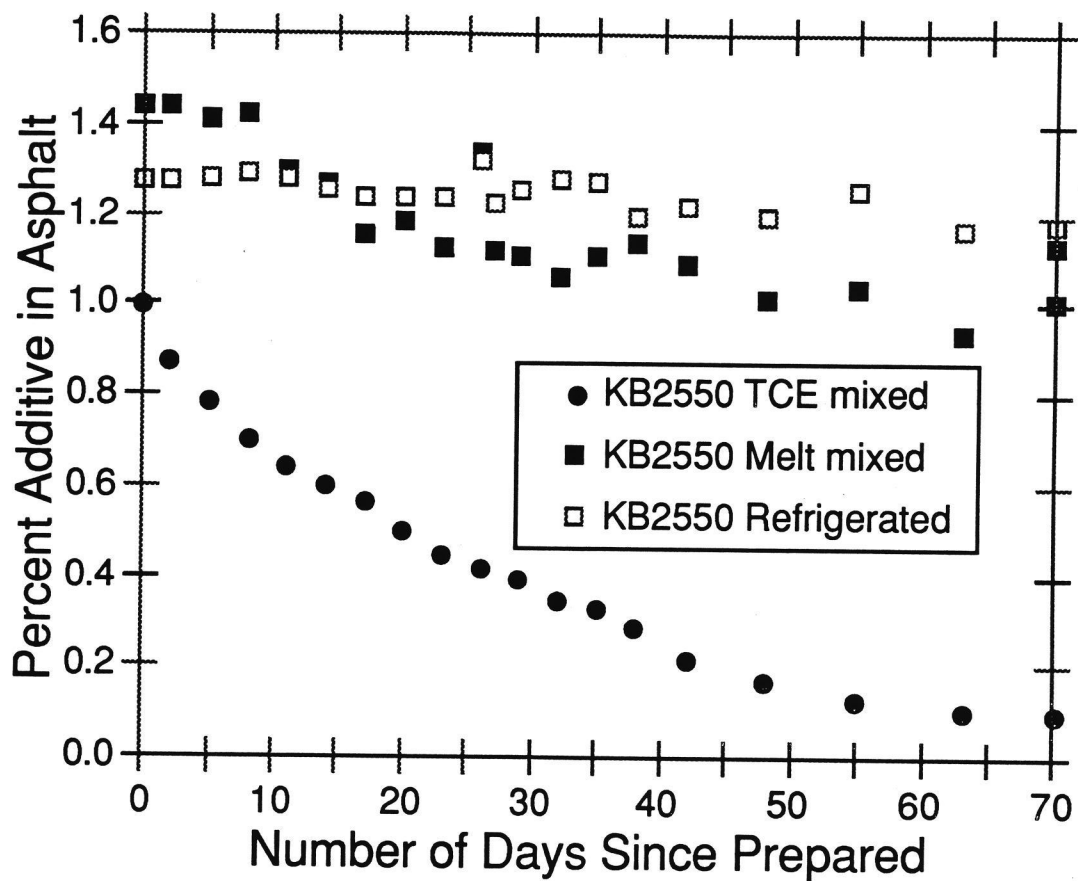


Figure 13. The effect on asphalt samples with Kling Beta 2550 additive when allowed to age in different environments.

From this it can be concluded that asphalt-additive samples can be refrigerated and analyzed more than two months later and still obtain reliable results.

Acid-Base Reactions During Mixing

Asphalt alone and additive alone (Permatac) were analyzed along with the same amounts of asphalt-additive mixtures prepared by the "melt mixed" method. This produced the following bar graph (figure 14) which shows that accounting for base is complete. The results from asphalt and additive alone correspond to the results of when asphalt and additive were mixed together. This is significant because it shows that no acid-base reaction is occurring between the asphalt and additive in the mixture on a time scale shorter than hours. This means that the adhesion mechanism apparently does not employ a saponification of long-chain acid species in the asphalt as some researchers have hypothesized for this method of preparation.

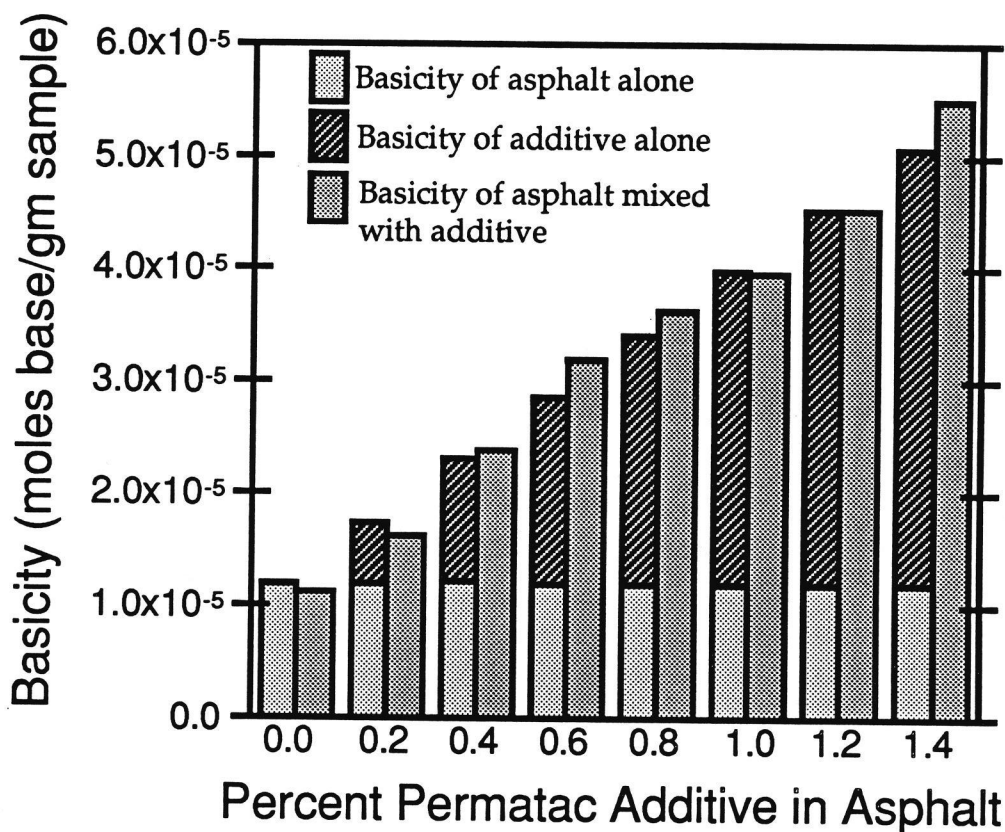


Figure 14. The basicity of asphalt only and additive only compared to when the two are in a mixture.

3.1.5 Application of Titration Method on Asphalt-Aggregate Samples

The following is the procedure for preparing the asphalt-aggregate samples:

1. Melt 100 grams of asphalt and mix in the appropriate amount of additive to obtain a desired percentage. (Adding in 1 g of additive would give a 1% sample).
- Thoroughly wash aggregate with water and heat in oven at 160°F until dry.

3. Weigh out a 1 g sample of asphalt with or without additive and heat until melted at 160°F. Weigh out 20 g aggregate and heat at 160°F. The asphalt amount is 5% by weight of the aggregate. Twenty grams aggregate was arbitrarily chosen and therefore one gram sample of asphalt weighed out to be analyzed.
4. Mix the hot aggregate with the liquid asphalt-additive mixture, thoroughly coating all the aggregate particles.

The following is the procedure for the single-vessel test with asphalt-aggregate mixtures:

1. Dissolve asphalt-aggregate mixture (that has been allowed to cool) with 50 ml trichloroethylene.
2. Filter and then add 50 ml water to the asphalt-trichloroethylene phase. Agitate for 1 minute on a stir plate at a high enough speed to mix the two phases together.
3. Turn down the agitation until two phases form (water on top, TCE and asphalt on bottom). Leave at this low level of agitation on throughout the rest of the titration.
4. Place a pH electrode in the water phase.
5. Titrate with 0.01 N HCl until pH of the water phase drops to 7.0. For blank asphalt samples which may be acidic, titrate with 0.001 N NaOH. Take out pH electrode and stir vigorously, measure pH again, and continue to titrate until the pH remains at 7.0.
6. Calculate the basicity from this equation:

$$\text{Basicity of Sample} = \frac{(\text{ml of acid titrant})(0.01 \text{ N})}{(1000 \text{ ml/liter})(\text{grams of asphalt-additive sample})} \quad (3.2)$$

7. Look up the amount of additive on a calibration curve.

Figures 15 and 16 are plots of just aggregate (both siliceous and limestone) in water only and in trichloroethylene and water - no asphalt or additive present. Once the endpoint of a pH of 7 was reached, the change in pH was recorded. The pH continually climbed because of interactions with the aggregate. Because of this it is necessary to filter off the aggregate before testing asphalt-aggregate mixtures.

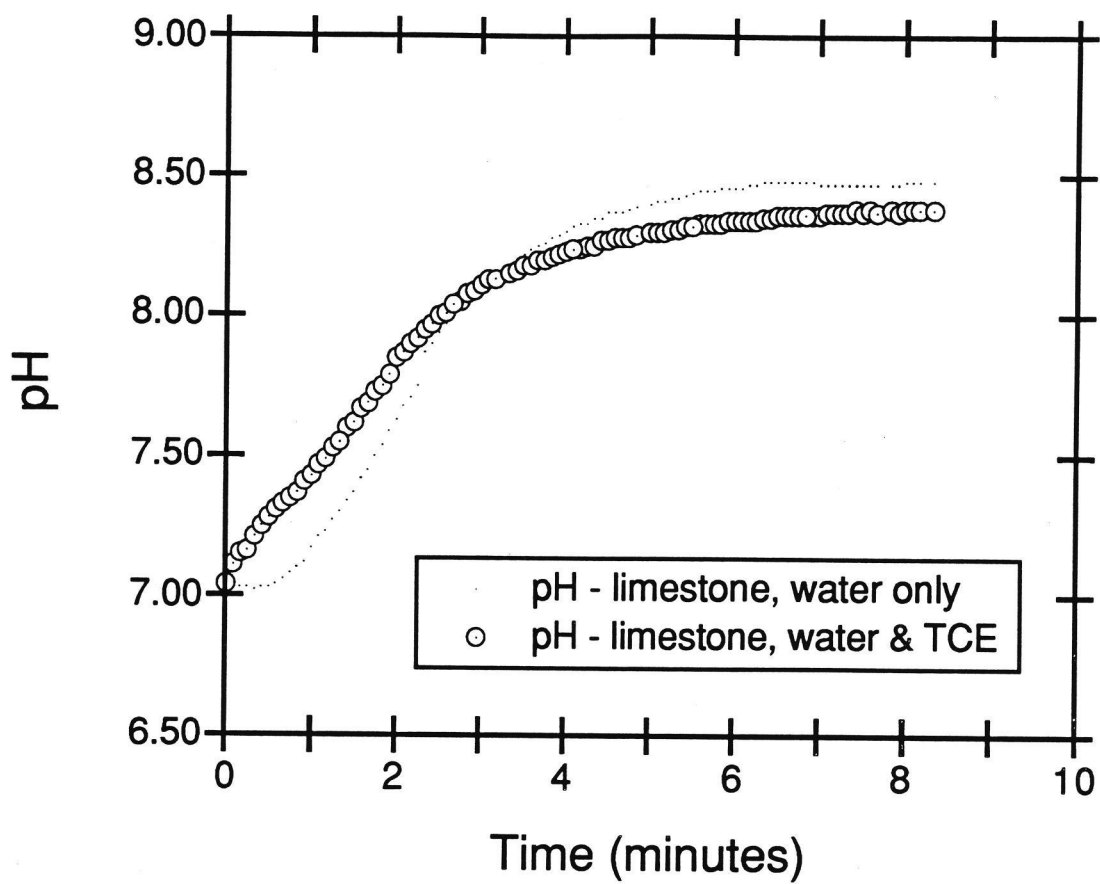


Figure 15. The measurement of pH using limestone aggregate after reaching an endpoint of pH=7.

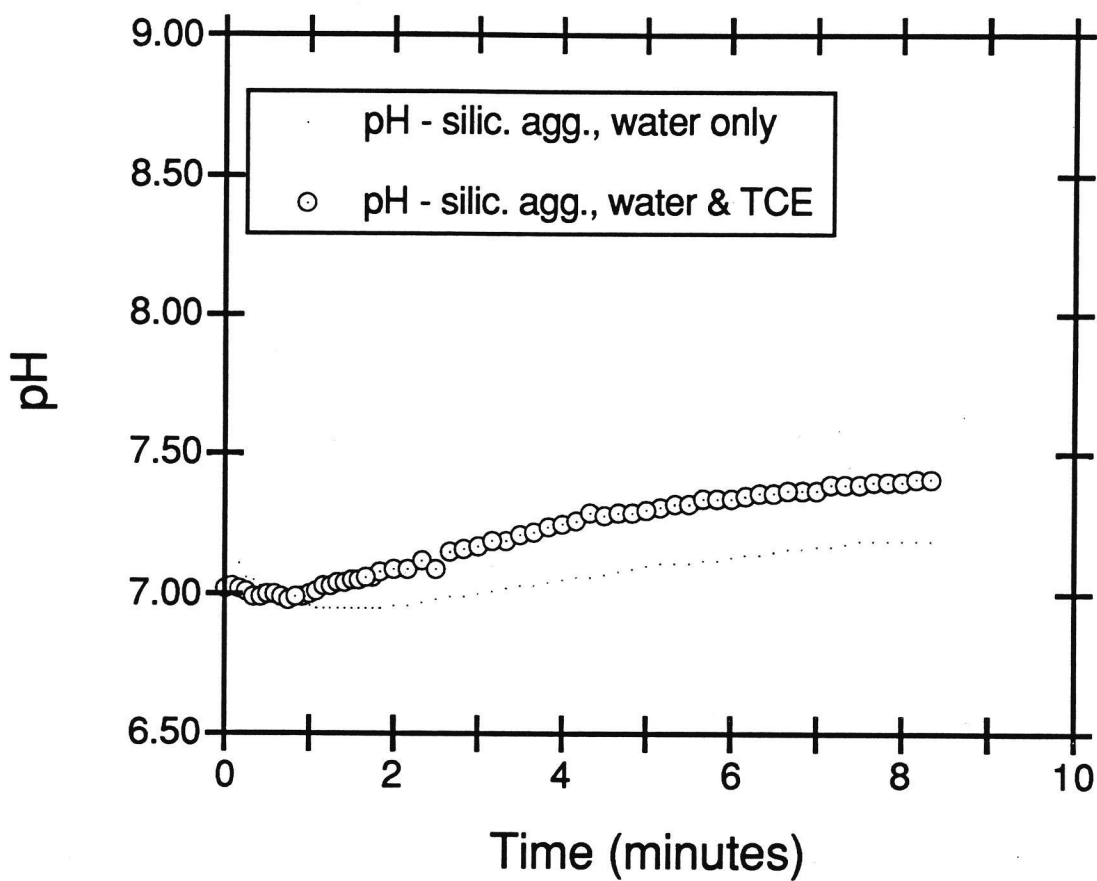


Figure 16. The measurement of pH using siliceous aggregate after reaching an endpoint of pH=7.

Asphalt and asphalt with additive samples, both with and without aggregate, were analyzed to test the reproducibility of the method. These results are plotted in Figures 17 - 26. It was determined that more consistent, repeatable results are obtained when the aggregate has been washed and dried before mixing it with the asphalt. This is due to decreasing or minimizing the amount of dirt or fines that are present with the aggregate.

Figure 17 is the analysis of asphalt alone (no additive or aggregate present). The average of all the samples is denoted by solid line. Plus and minus one standard deviation from the average is shown by the dotted lines.

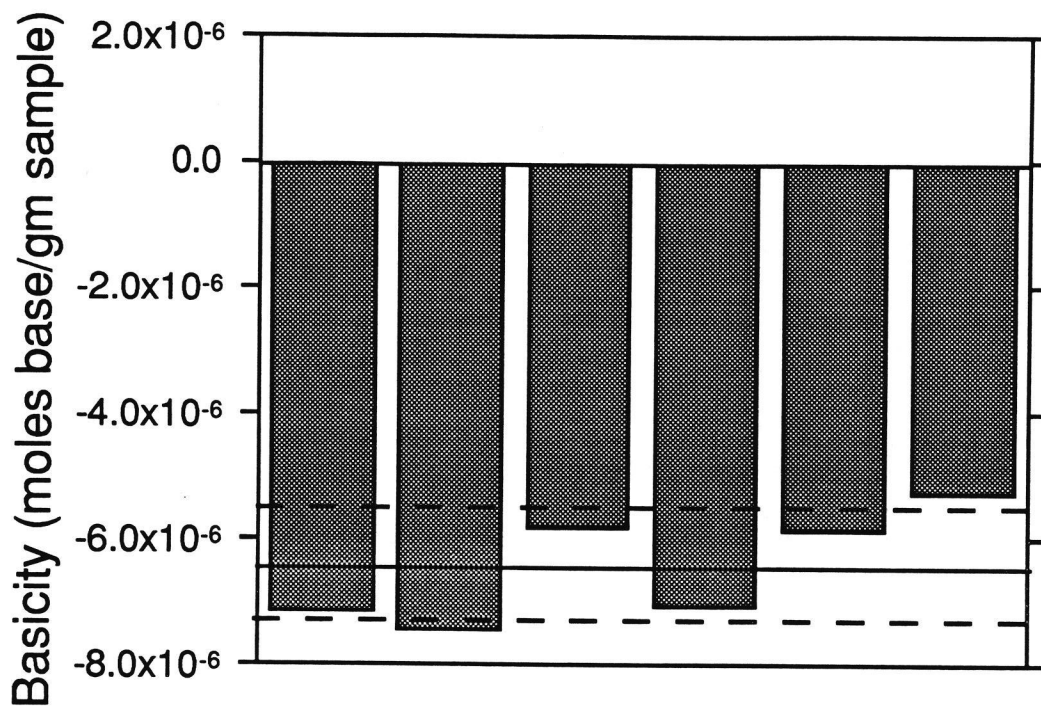


Figure 17. Reproducibility of blank asphalt, without antistrip additive or aggregate.

Statistics of Analysis:

Average = -6.408×10^{-6} , Standard Deviation = 0.887×10^{-6} , Std. Dev./Average = 0.139

The following figure (figure 18) is the analysis of Permatac additive alone, without asphalt or aggregate present.

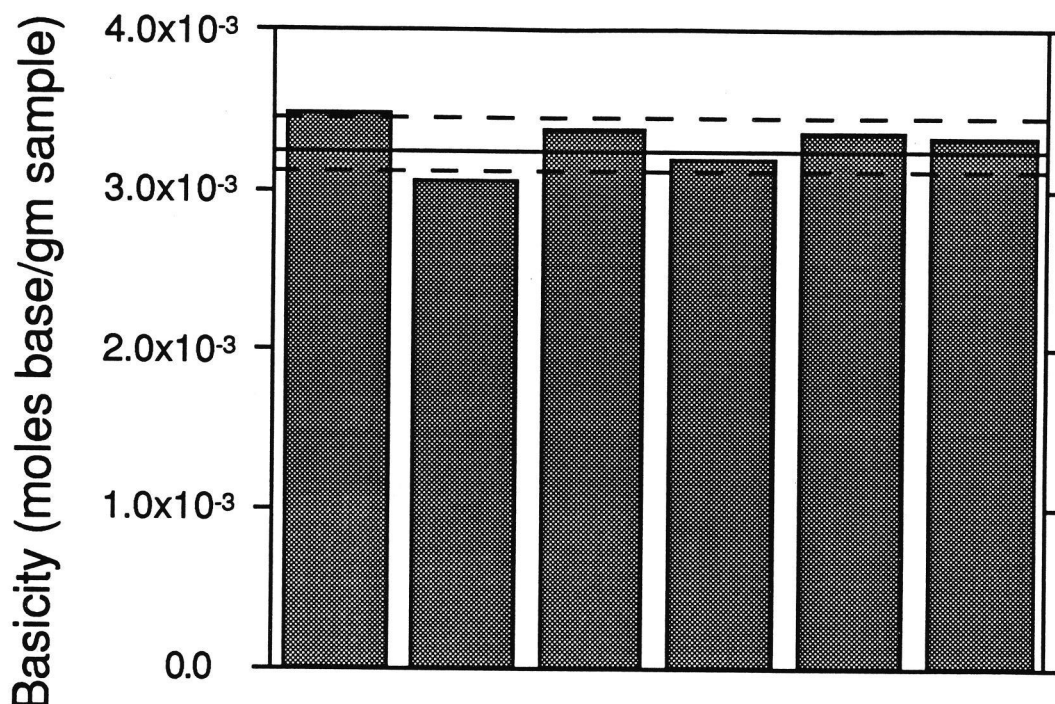


Figure 18. Reproducibility of Permatac antistrip additive, without asphalt or aggregate.

Statistics of Analysis:

average = 3.29×10^{-3} , Standard Deviation = 0.123×10^{-3} , Std. Dev./Average = 0.0374

Figure 19 is the analysis of 1% Permatac additive in asphalt with no aggregate. The average of the blank asphalt results (figure 17) and the average of the Permatac additive only results (figure 18) were used in the calculation to determine the measured amount Permatac additive at 1.06%. The percentage was determined by the following equation:

$$\text{measured basicity of asphalt/additive sample} = \frac{\text{blank asphalt basicity}}{\text{additive only basicity}} \times (\%) (\text{additive only basicity}) \quad (3.3)$$

Rearranging to solve for the percentage of additive in the mixture:

$$\% = \frac{\text{measured basicity of asphalt/additive sample} - \text{blank asphalt basicity}}{\text{additive only basicity}} \times 100 \quad (3.4)$$

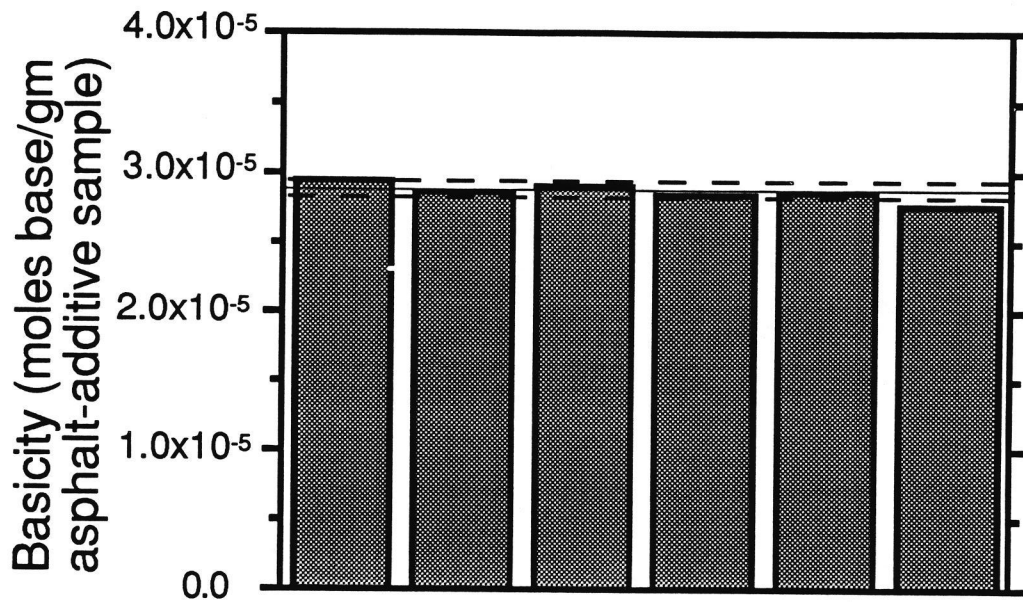


Figure 19. Reproducibility of Permatac antistripping additive in asphalt, without aggregate.

Statistics of Analysis:

Average = 2.86×10^{-5} , Standard Deviation = 0.0602×10^{-5} , Std. Dev./Average = 0.0210

The rest of the repeatability analysis involves aggregate. First siliceous aggregate that had not been washed with water was mixed with asphalt and analyzed, no additive was used. See figure 20.

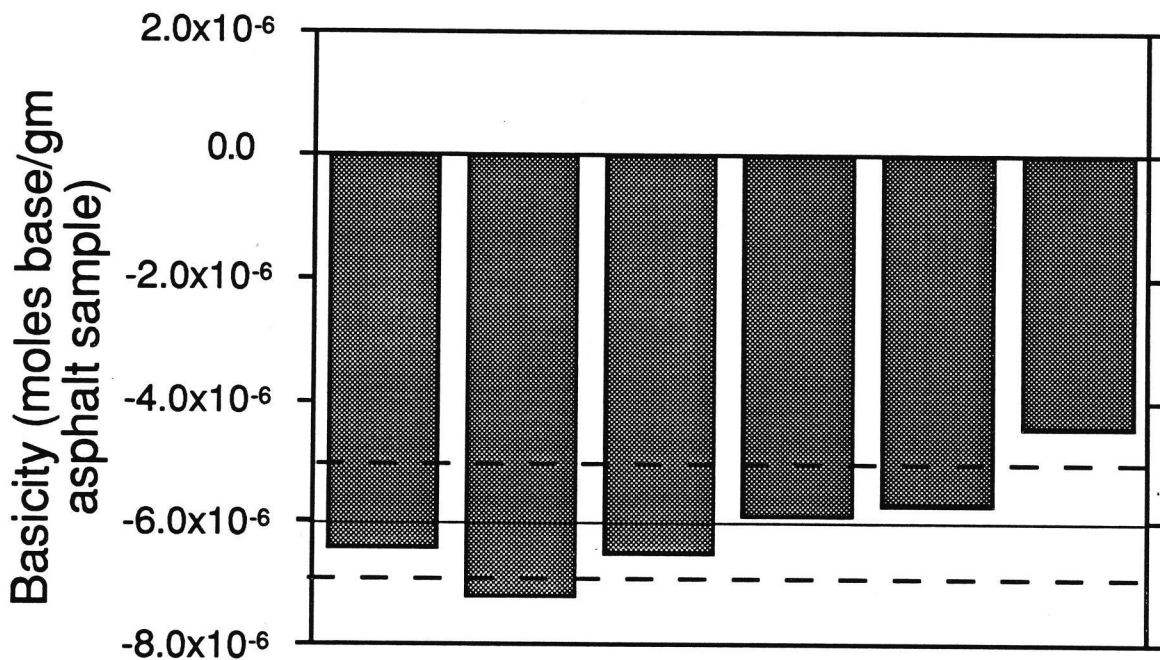


Figure 20. Reproducibility of blank asphalt with unwashed siliceous aggregate, without additive.

Statistics of Analysis:

Average = -6.013×10^{-6} , Standard Deviation = 0.939×10^{-6} , Std. Dev / Average = 0.156

The previous analysis was redone but this time the siliceous aggregate was washed before using it in the asphalt mixture, and again no additive present. See figure 21.

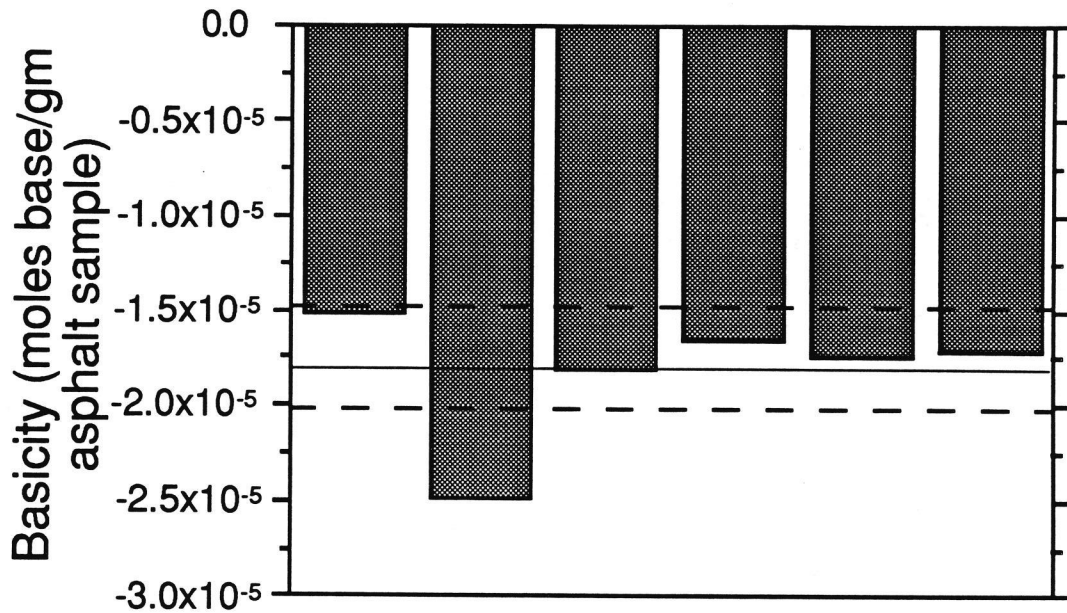


Figure 21. Reproducibility of blank asphalt with washed siliceous aggregate, without additive.

Statistics of Analysis:

Average = -1.82×10^{-5} , Standard Deviation = 0.340×10^{-5} , Std. Dev./Average = 0.187

Figure 22 is the analysis of 1% Permatac additive in asphalt with unwashed siliceous aggregate.

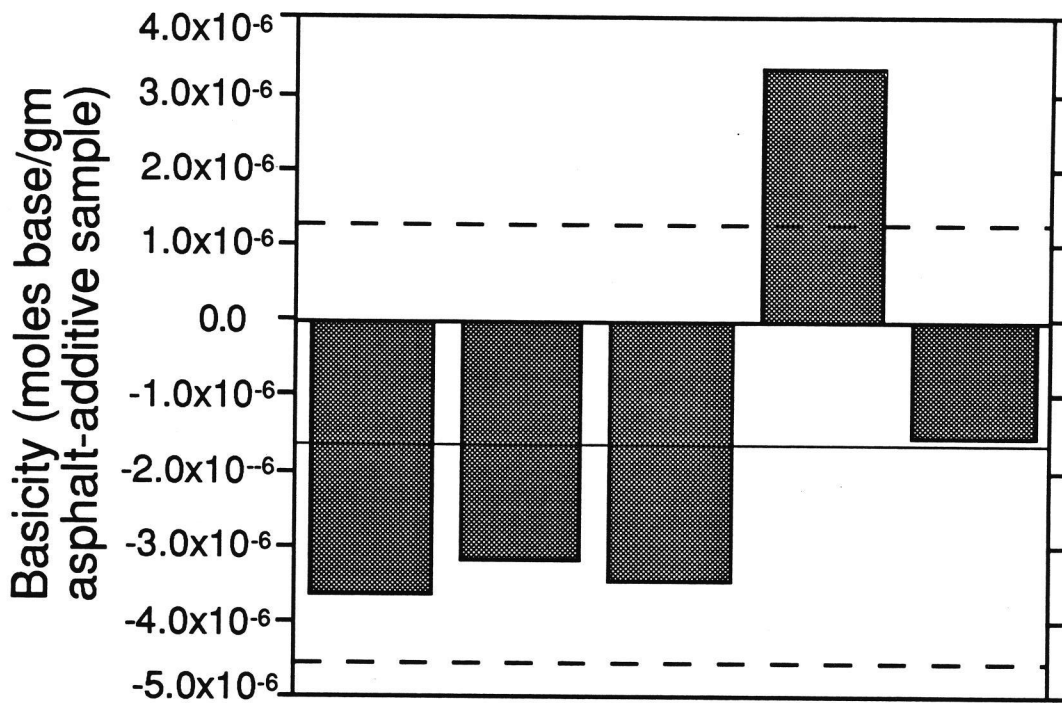


Figure 22. Reproducibility of asphalt/additive sample with unwashed siliceous aggregate.

Statistics of Analysis:

Average = -1.69e-6, Standard deviation = 2.93e-6, Std. Dev/Average = 1.74

his graph (figure 23) shows the analysis for 1% Permatac additive in asphalt when the aggregate was washed. When analyzed the measured percentage of additive present was determined to be 0.7%. The 0.7% was calculated using the average of the blank asphalt samples with washed siliceous aggregate (figure 21) and the average of the Permatac additive only results (figure 18) in equation 3.4.

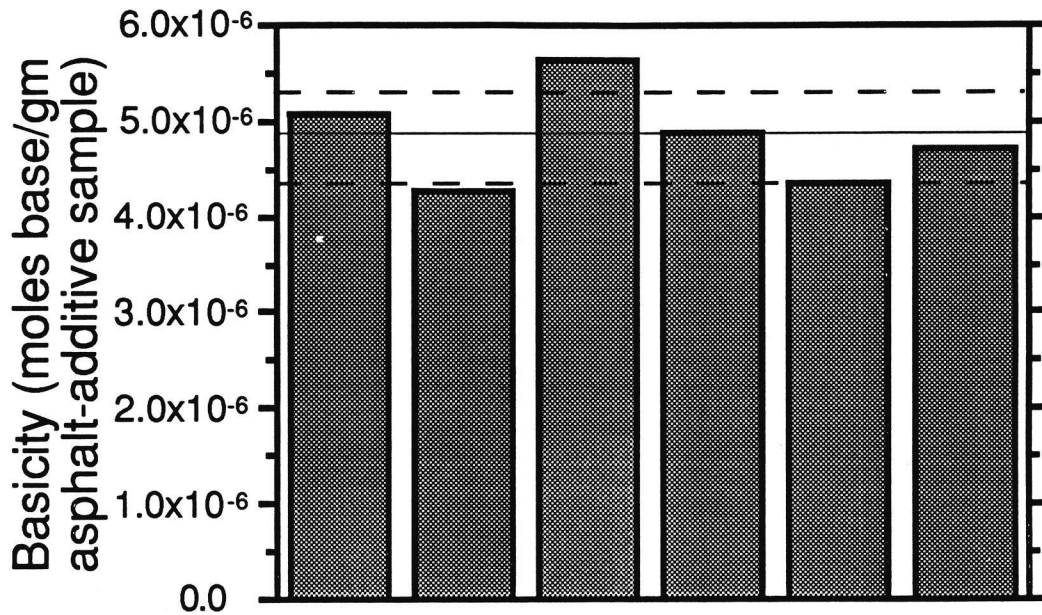


Figure 23. Reproducibility of asphalt/additive sample with washed siliceous aggregate.

Statistics of Analysis:

Average = 4.825e-6, Standard Deviation = 0.506e-6, Std. Dev./Average = 0.105

This figure (figure24) shows the results when limestone aggregate that had not been washed with water was mixed with blank asphalt, no additive present.

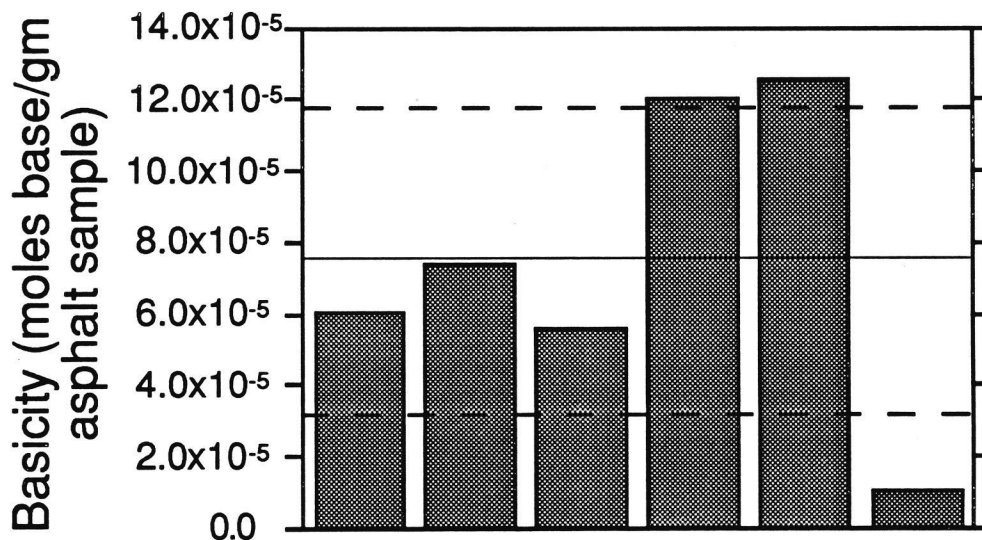


Figure 24. Reproducibility of blank asphalt with unwashed limestone aggregate, without additive.

Statistics of Analysis:

Average = 7.49×10^{-5} , Standard Deviation = 4.32×10^{-5} , Std. Dev./Average = 0.58

This figure (figure 25) is again blank asphalt with limestone aggregate but this time the limestone aggregate was washed with water before preparing the mixture.

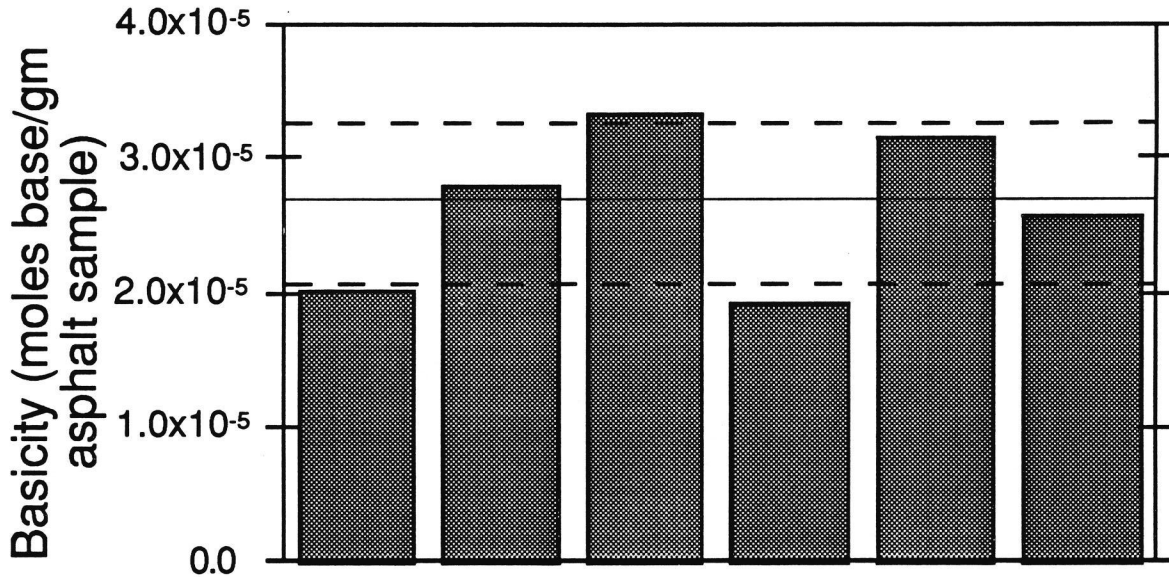


Figure 25. Reproducibility of blank asphalt with washed limestone aggregate, without additive.

Statistics of Analysis:

Average = 2.635×10^{-5} , Standard Deviation = 0.576×10^{-5} , Std. Dev./Average = 0.219

The following figure (figure 26) is of 1% Permatac additive in asphalt with washed limestone aggregate. When analyzed the amount of additive measured in the mixture was -0.3%. This was calculated by using the average of the blank asphalt with washed limestone aggregate results (figure 25) and the average of the Permatac additive only results (figure 18) in equation 3.4.

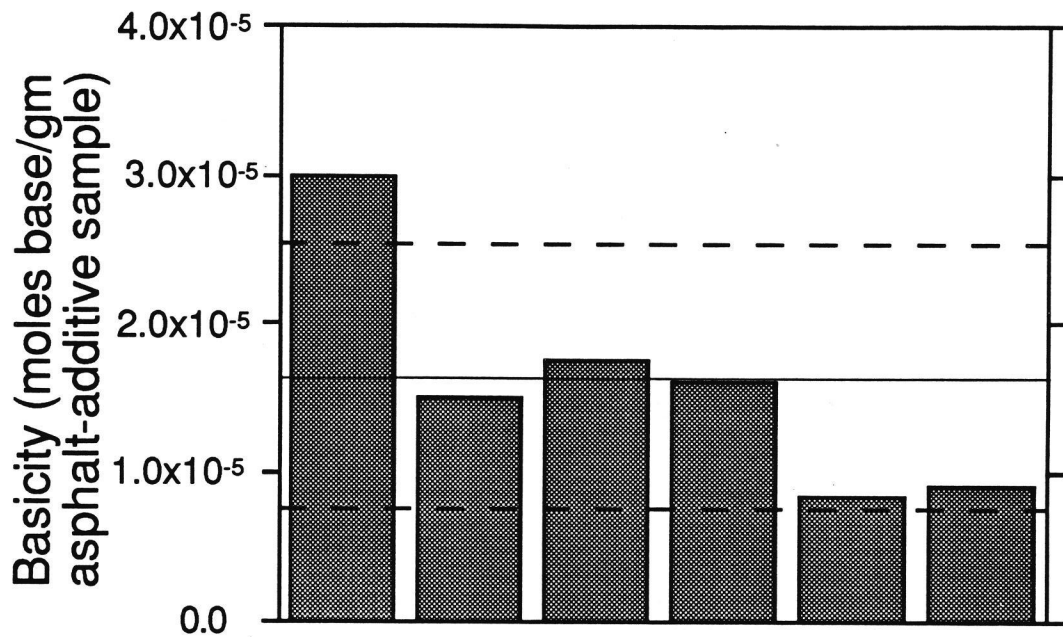


Figure 26. Reproducibility of asphalt/additive sample with washed limestone aggregate.

Statistics of Analysis:

Average = 1.60×10^{-5} , Standard Deviation = 0.782×10^{-5} , Std. Dev./Average = 0.488

The following figure (figure 27) is a summary of all the results of the repeatability analysis (figures 17-26). This figure shows that in samples without aggregate and samples with siliceous aggregate, the blank asphalt is less basic than asphalt with additive, which is to be expected.

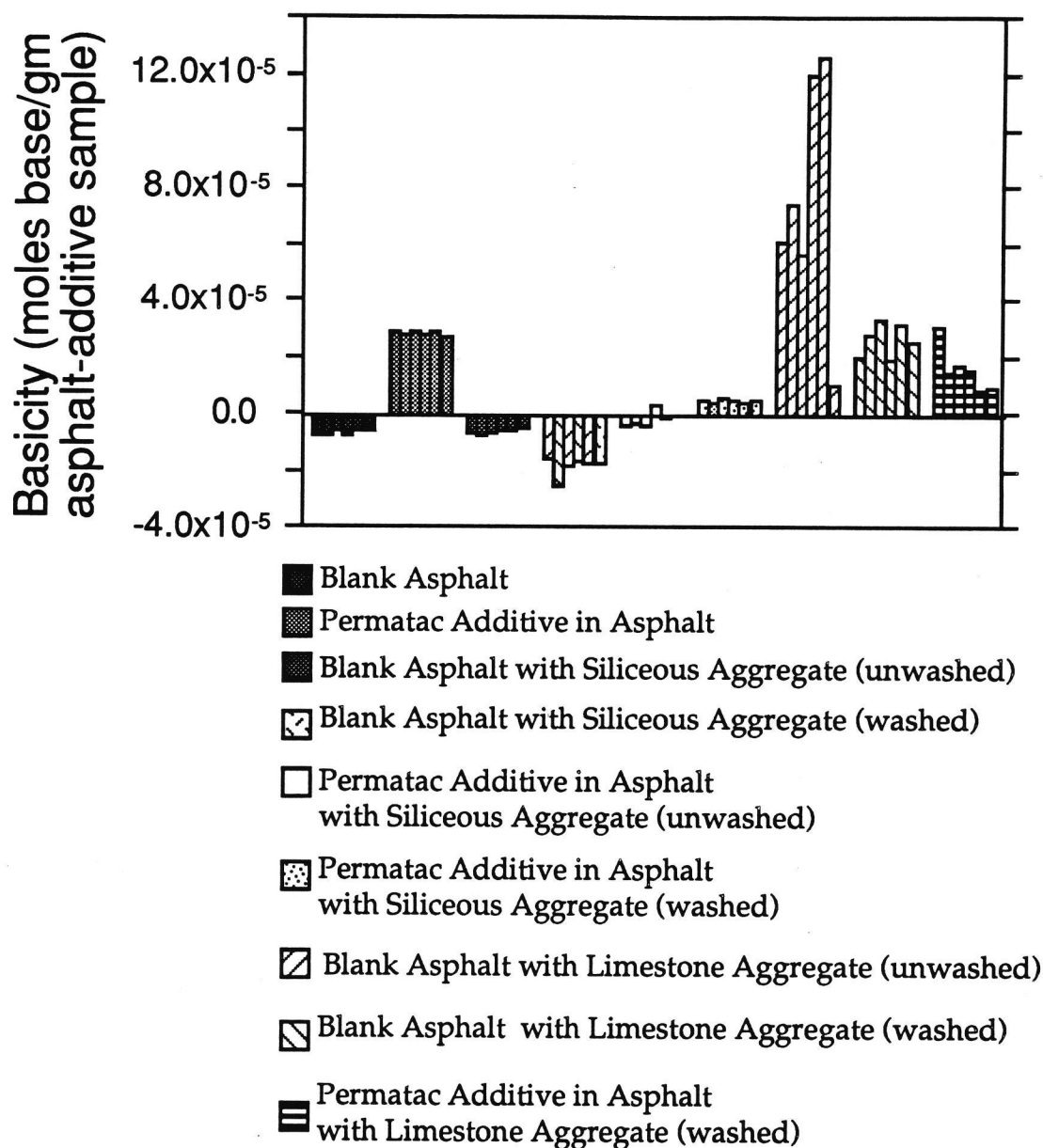


Figure 27. Summary of results of reproducibility analysis.

All of the above experiments have been based on 20 grams aggregate and 1 gram asphalt, or 1.1 grams asphalt with additive.

From the previous results of repeatability analysis, mass balance calculations were done. The results of the asphalt alone and additive alone were plotted together and compared with the result of the sample that was prepared as an asphalt-additive mixture. These calculations were done for all three cases: no aggregate, siliceous aggregate, and limestone aggregate.

Mass balance calculations:

$$\frac{\text{moles basicity}}{\text{gm sample}} = \frac{\text{gmA} \times (\text{mol basA/gmA}) + \text{gmB} \times (\text{mol basB/gmB})}{\text{gmA} + \text{gmB}} \quad (3.5)$$

Using the no aggregate case as an example, a 100 grams of asphalt was heated and 1 gram additive mixed in (a 1% mixture of additive in asphalt). A 1.1 gram sample was analyzed; 1.09 g attributed to the asphalt and 0.01 g attributed to the additive (because it was a 1% mixture).

$$\text{moles basicity/gm sample} = \frac{1.09 \times (-6.408\text{e-}6) + 0.01 \times (3.29\text{e-}3)}{1.09 + 0.01} = 2.36\text{e-}5$$

The result obtained from the equation is what you'd expect to get with the measured basicities. The measured basicity with the samples without aggregate was close to that which was expected from mass balance calculation, but the samples involving aggregate were no where near the expected value, which can be attributed to aggregate interaction.

No Aggregate Case (See figure 28):

The measured results (averages from repeatability analysis) are:

Blank asphalt was analyzed at $-6.408\text{e-}6$ moles base/gm (from figure 17).

Permatac additive only was analyzed at $3.29\text{e-}3$ moles base/gm (from figure 8).

Asphalt with 1% Permatac was analyzed at $2.86\text{e-}5$, with a standard deviation of $0.0602\text{e-}5$ (from figure 19).

Plus or minus one standard deviation from the measured average of asphalt with 1% Permatac is $2.92\text{e-}5$ moles base/gm and $2.80\text{e-}5$ moles base/gm, respectively. The asphalt sample with 1% Permatac was analyzed as 1.06%.

The calculated basicity from equation 3.5 is $2.36\text{e-}5$ moles basicity/gm sample.

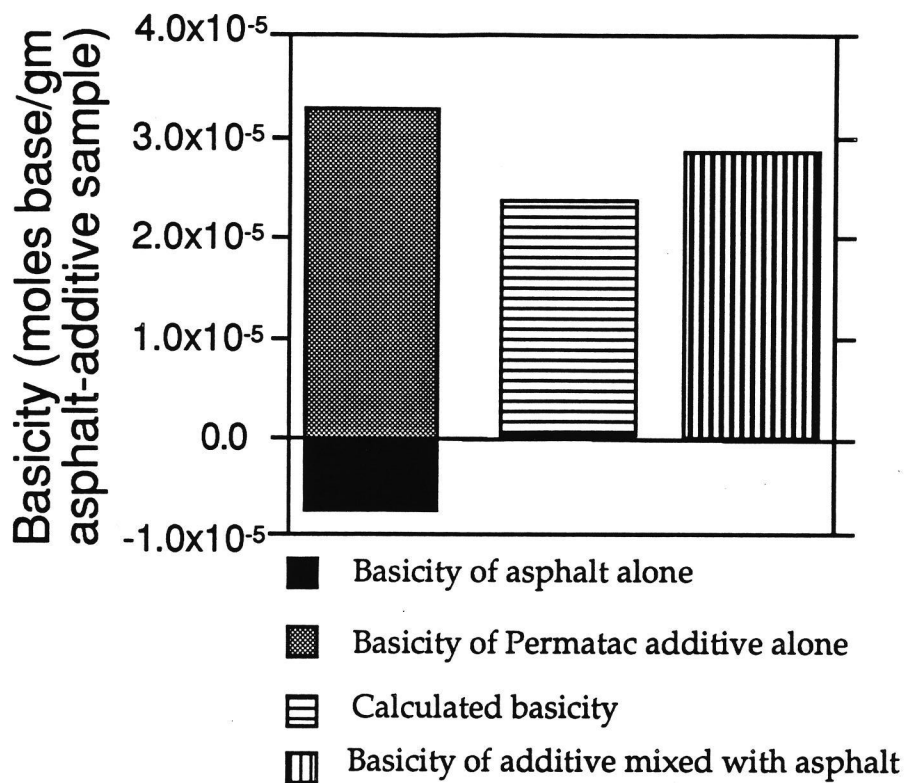


Figure 28. The basicity of asphalt only and additive only compared to when the two are in a mixture, without aggregate.

Referring back to the example calculation, the blank asphalt contribution is $(1.09)(-6.408e-6) = -6.99e-6$ (plotted on the graph as basicity of asphalt alone). The additive only contribution is $(0.01)(3.29e-3) = 3.29e-5$ (plotted on the graph as basicity of Permatac additive alone). Adding these two contributions and dividing by 1.1, the result is $2.36e-5$. The first column in figure 28 shows the individual contributions of the blank asphalt and additive only. The second column is the result of adding each contribution and dividing by the total sample amount (referred to as the calculated basicity). The third column is the measured basicity of an actual asphalt-additive mixture (analyzed as 1.06%).

Siliceous Aggregate Case (See figure 29):

The measured results (averages from repeatability analysis) are:

Blank asphalt was analyzed at $-1.82e-5$ moles base/gm (from figure 21).

Permatac additive only was analyzed at $3.29e-3$ moles base/gm (from figure 18).

Asphalt with 1% Permatac was analyzed at $0.483e-5$, with a standard deviation of $0.0506e-5$ (from figure 23).

Plus or minus one standard deviation from the measured average of asphalt with 1% Permatac is $0.53e-5$ moles base/gm and $0.43e-5$ moles base/gm, respectively. The asphalt sample with 1% Permatac was analyzed as 0.7%.

The calculated basicity from equation 3.5 is 1.19×10^{-5} moles basicity/gm sample.

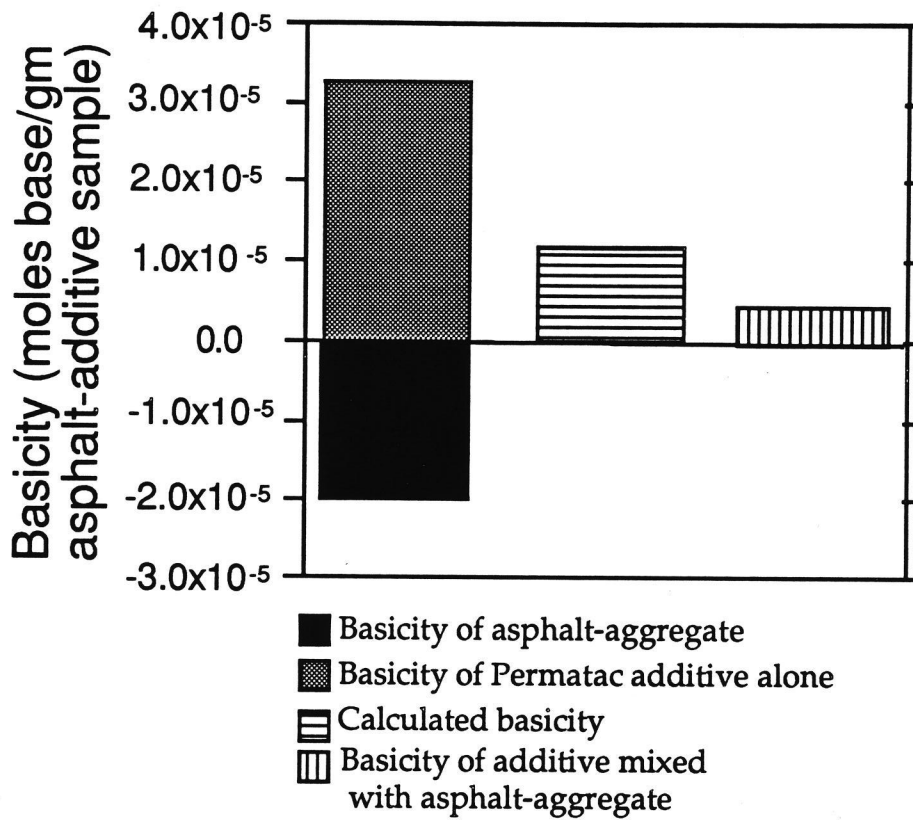


Figure 29. The basicity of asphalt only and additive only compared to when the two are in a mixture, with siliceous aggregate.

Limestone Aggregate Case (See figure 30)

The measured results (averages from repeatability analysis) are:

Blank asphalt was analyzed at 2.635×10^{-5} moles base/gm (from figure 25).

Permatac additive only was analyzed at 3.29×10^{-3} moles base/gm (from figure 18).

Asphalt with 1% Permatac was analyzed at 1.604×10^{-5} , with a standard deviation of 0.782×10^{-5} (from figure 26).

Plus or minus one standard deviation from the measured average of asphalt with 1% Permatac is 2.39×10^{-5} moles base/gm and 0.822×10^{-5} moles base/gm, respectively. The asphalt sample with 1% Permatac was analyzed as -0.3%.

The calculated basicity from equation 3.5 is 5.6×10^{-5} moles basicity/gm sample.

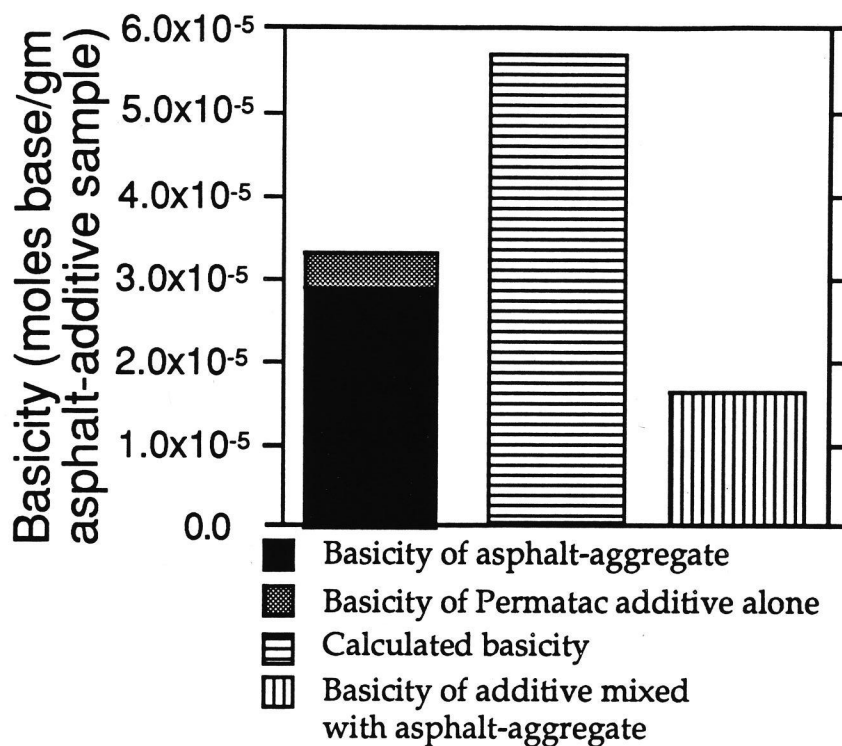


Figure 30. The basicity of asphalt only and additive only compared to when the two are in a mixture, with limestone aggregate.

Figure 31 is the result of analyzing asphalt (with and without additive) with no aggregate, siliceous aggregate, and limestone aggregate. Same procedure in preparing the samples and same procedure in analyzing them by the single-vessel method as previously outlined. As in the asphalt-additive calibration curves without aggregate, the blank asphalt results (without aggregate) gives the y-intercept and the additive only result is the slope of the line.

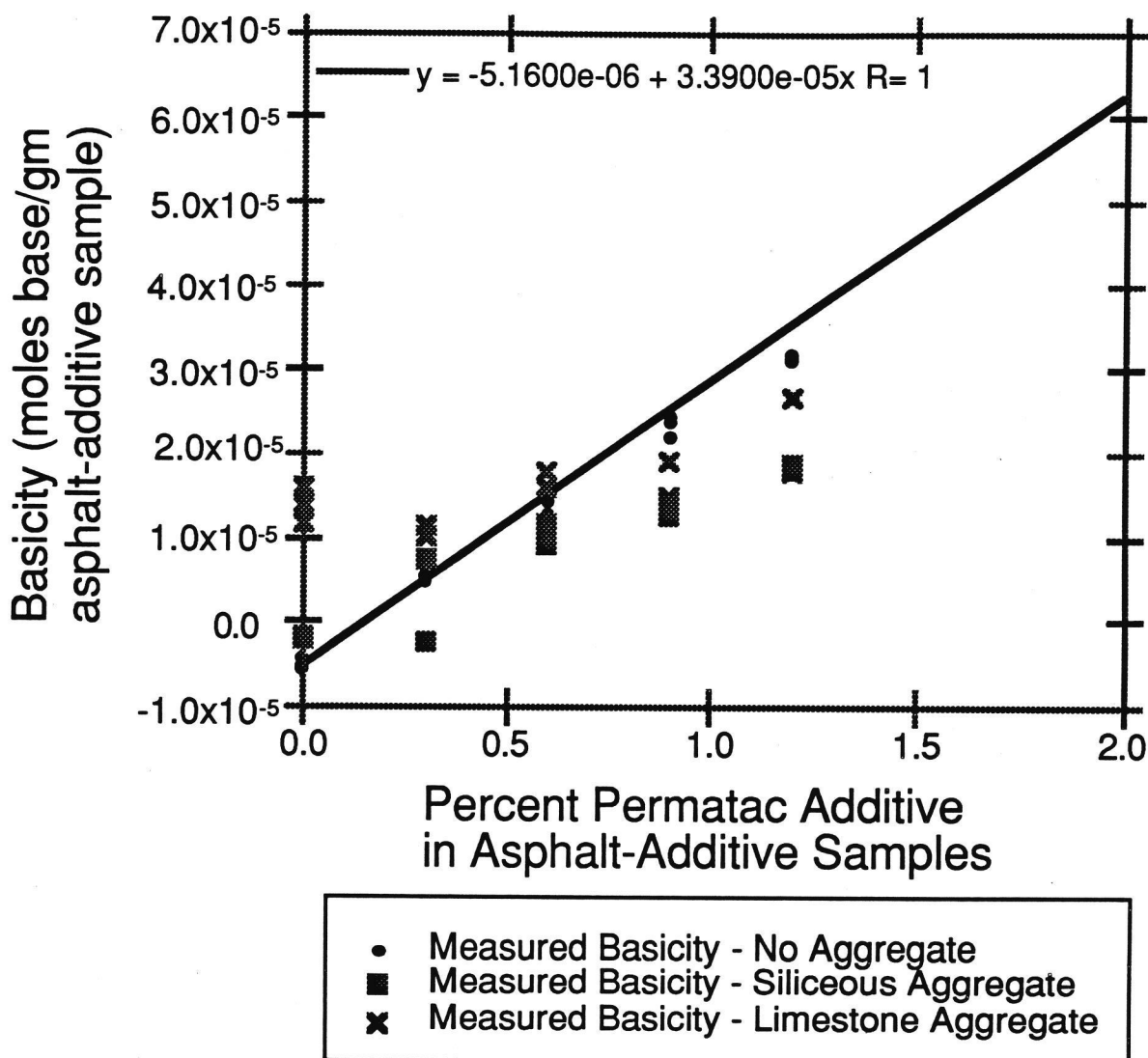


Figure 31. Calibration curve for asphalt/additive samples without aggregate, with siliceous aggregate, and with limestone aggregate.

From this it can be seen that more accurate results were obtained when no aggregate was used in the asphalt/additive mixture than with either siliceous or limestone aggregate in the mixture. This means that an asphalt/additive sample can be accurately analyzed for the percentage of additive present in the sample before the aggregate has been mixed in.

3.1.6 Basicities of Approved Amine-Based Antistrip Additives

The basicities of all amine-based additives on the AHTD approved list were measured, see table 1. Although it would be best to measure the basicity of a given additive for the purpose of making a calibration curve, these would serve as at least approximate values. The results are listed below in order of the amount of basicity in each. It is important to keep in mind that more basicity is not necessarily better.

| Additive | Manufacturer | Basicity (moles/gm) |
|----------------------|----------------|------------------------|
| Ad-here HP+ | Arr-Maz | 10.3e-3 |
| Kling Beta 2550 (HM) | Scan Road | 7.26e-3 |
| Indulin AS Special | Westvaco | 6.60e-3 |
| Permatac 99 | Scan Road | 6.28e-3 |
| Ad-here LA-2 | Arr-Maz | 5.84e-3 |
| Carstab BA 2000 | Morton Thiokol | 4.95e-3 |
| Kling Beta LV (HM) | Scan Road | 4.72e-3 |
| Permatac Plus | Scan Road | 3.86e-3 |
| Indulin AS-1 | Westvaco | 3.54e-3 |
| Pave Bond AP Special | Morton Thiokol | 3.35e-3 |
| Permatac | Scan Road | 3.32e-3 |
| Acra 500 | Exxon | 2.28e-3 |
| Pave Bond LP | Morton Thiokol | 2.10e-3 |
| Pave Bond AP | Morton Thiokol | 1.70e-3 |
| Kling Beta Lv | Scan Road | 0.462e-3 |

Table 1. Basicity values for liquid amine antistrip additives on the AHTD qualified products list.

3.2 TENSOMETRY

This method involves measuring the surface tension of asphalt dissolved in a solvent. Because antistrip additives act as surfactants, it is expected that they will migrate to a solvated asphalt-air or asphalt-water interface and modify the surface tension there in some proportion to their amount. The surface tension will be measured with a tensiometer and the concentration of antistrip additive in the asphalt will be determined from a calibration curve.

3.2.1 Theory

The other test method that was employed involved the use of a tensiometer. The tensiometer that was used employed the ring method to measure surface tension between any two phases. Surface tension is an effect that arises because the molecules in the middle of a liquid experience isotropic forces which means that the molecules are pulled in all directions by the same amount of force. The molecules on any surface experience anisotropic forces which means that the molecules are not being pulled equally in the same direction. These surface molecules are being pulled inward since there are no molecules of that substance providing a countering force on their surface sides. Surface tension arises because of this anisotropic force field. Surface tension then is just the attraction or inward pull of a liquid on its surface molecules. The amount of surface tension for a liquid depends on the strength of the mutual attraction between the substance molecules.

Antistrip additives are surface-active agents that like to go to phase boundaries such as asphalt-aggregate interface where they modify the chemical and physical

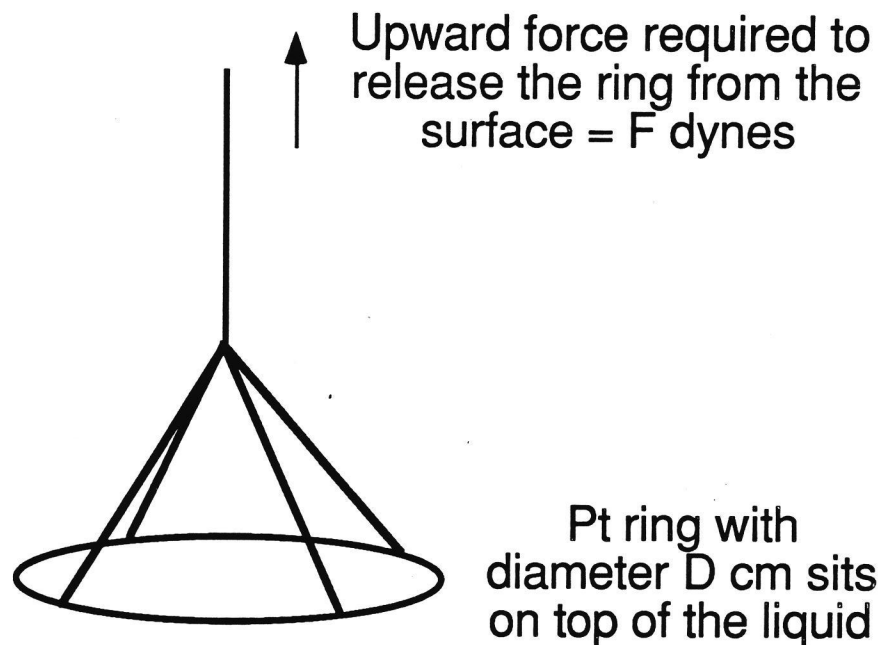
properties. In this test, we will provide an asphalt-air or an asphalt-water interface for these molecules to go to. It is possible to measure the surface tension of these interfaces to a high degree of accuracy using a tensiometer. It is assumed, therefore, that the amount of surface tension modification that will be seen at an asphalt-air or asphalt-water interface is a function of the amount of surface-active antistrip agent present.

A tensiometer measures the surface tension of a liquid through the placing of a metal ring on the surface of the liquid and suspending that ring with a metal wire (See Figure 32). The wire is used to lightly separate the ring from the surface of the liquid on which the ring is suspended. The inward attraction of the liquid molecules provides a resistance to the separation of the ring from the surface of the liquid (or interface of two liquids). In effect, the liquid has an inward pull on the ring in the same manner that it has on its own surface molecules. Thus, in measuring the amount of resistance (or pull) that the liquid has on the ring being withdrawn, this test measures the strength of pull (force) the liquid has on its surface molecules. This force is used to calculate the surface tension of that liquid by the following relationship:

$$\text{surface tension} = \text{force} / (2 \times \text{circumference}). \quad (3.6)$$

The denominator is two times the circumference because the ring has an inside and an outside. The amount of unknown additive in an asphalt sample can be determined with this test by comparing its surface tension to the surface tension measurement of various known amounts of additive in asphalt.

The DuNouy tensiometer that was used employed a fine torsion wire for applying the necessary force required to withdraw a platinum-iridium ring from the surface of an asphalt sample. Measurement values are reproducible to within ± 0.05 dyne/cm. A graduated dial permits direct reading to 0.0083 dyne/cm. Measurements can be made within 15-30 seconds. By using a DuNouy tensiometer the surface tension of asphalt cement with various known amounts of antistrip additive will be determined. The asphalt cement will be dissolved in a trichloroethylene which itself has a surface tension of 31.74 dyne/cm. A plot will be made correlating the surface tension of asphalt to the amount of the additive. The surface tension will be determined using the tensiometer and from the plot the amount of antistrip additive can be determined.



$$\text{Surface Tension} = F/2\pi D \text{ dynes/cm}$$

Figure 32. Ring apparatus for measuring surface tension.

2.2 Application of Tensiometry

Varying amounts of Permatac additive were dissolved in trichloroethylene and the surface tension measured. The figure 33 shows that for different amounts of additive there was no difference in the measured surface tension.

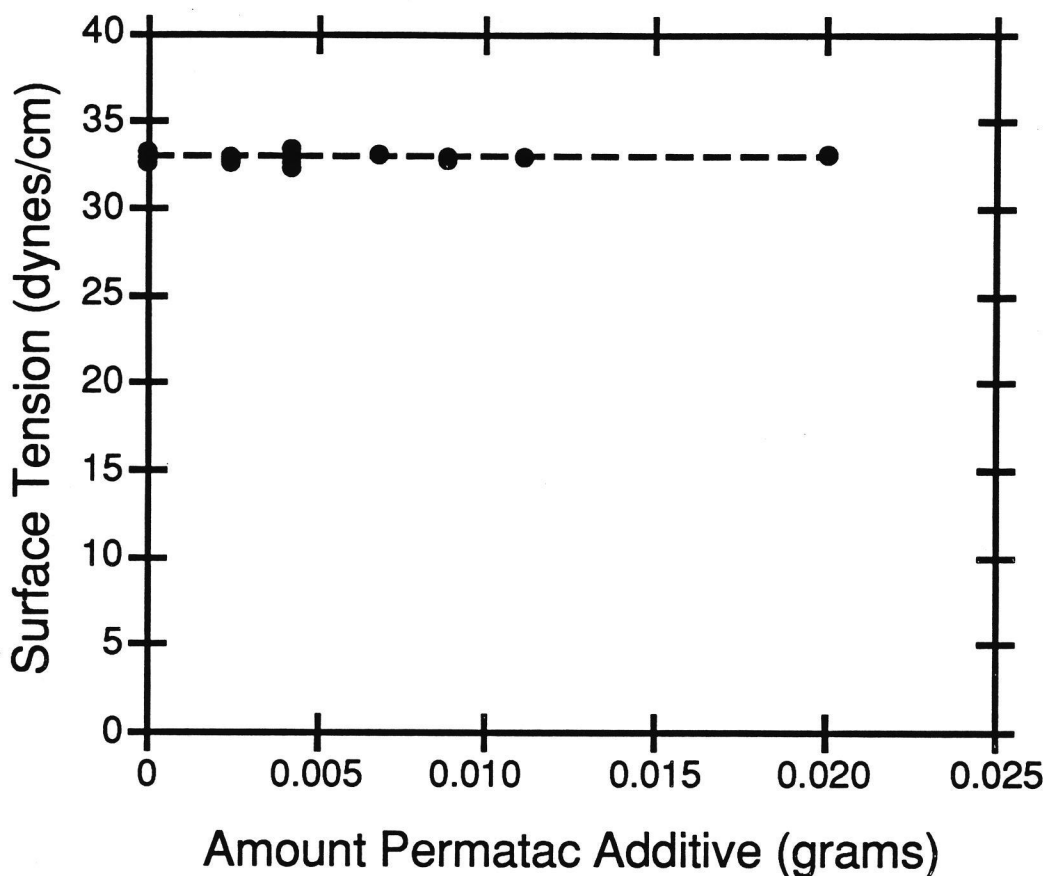


Figure 33. Asphalt-additive analysis after being dissolved in trichloroethylene.

Different amounts of Permatac additive were then dissolved in water and the surface tension measured. The figure 34 shows that there is a difference in surface tension with different amounts of additive when using water as the solvent.

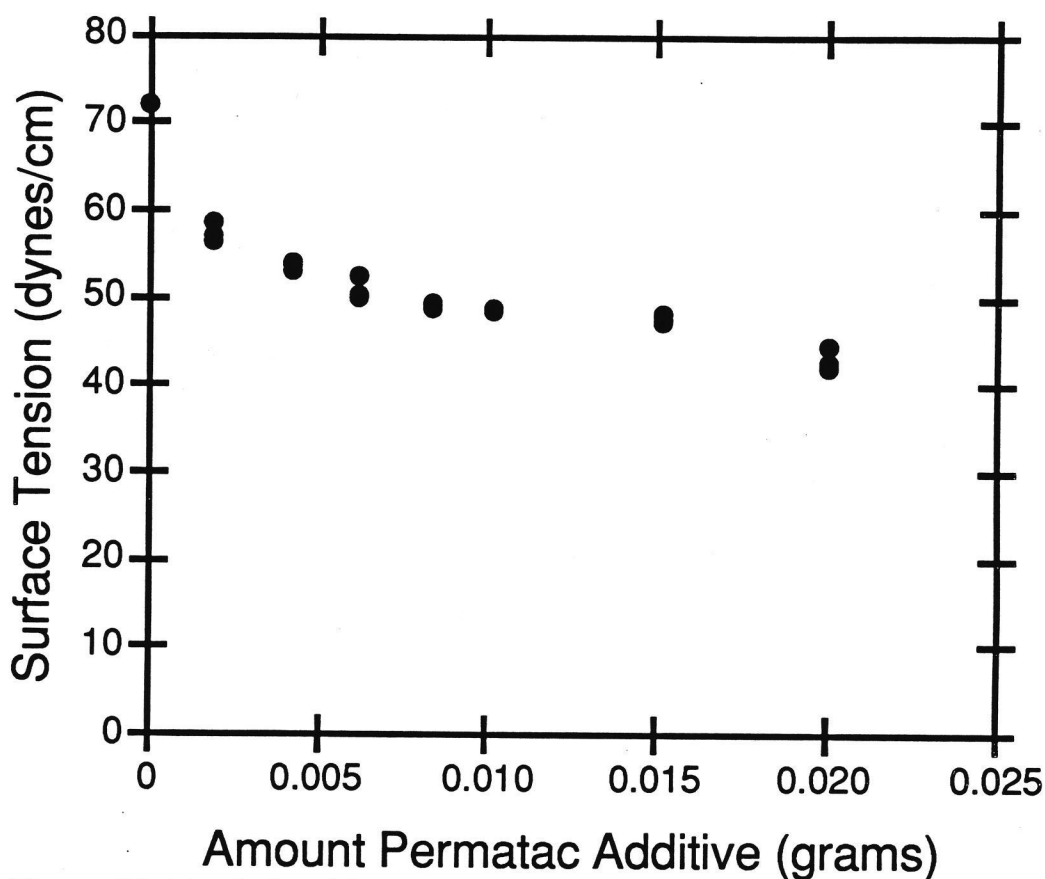


Figure 34. Asphalt-additive analysis after being dissolved in water.

Asphalt-additive mixtures were then made, dissolved in trichloroethylene, and then extracted into a water phase of which the surface tension was measured in the same manner as we use in the single-vessel titration method. After mixing with water the sample had to be filtered before testing because of a "scummy" surface layer that prevented us from achieving consistent results. Although the following graph (figure 35) shows a definite trend, the ranges for surface tension measurements are wide due to this surface contamination from other compounds in the asphalt. By using less water the additive will be more concentrated in the water phase and could possibly get better results.

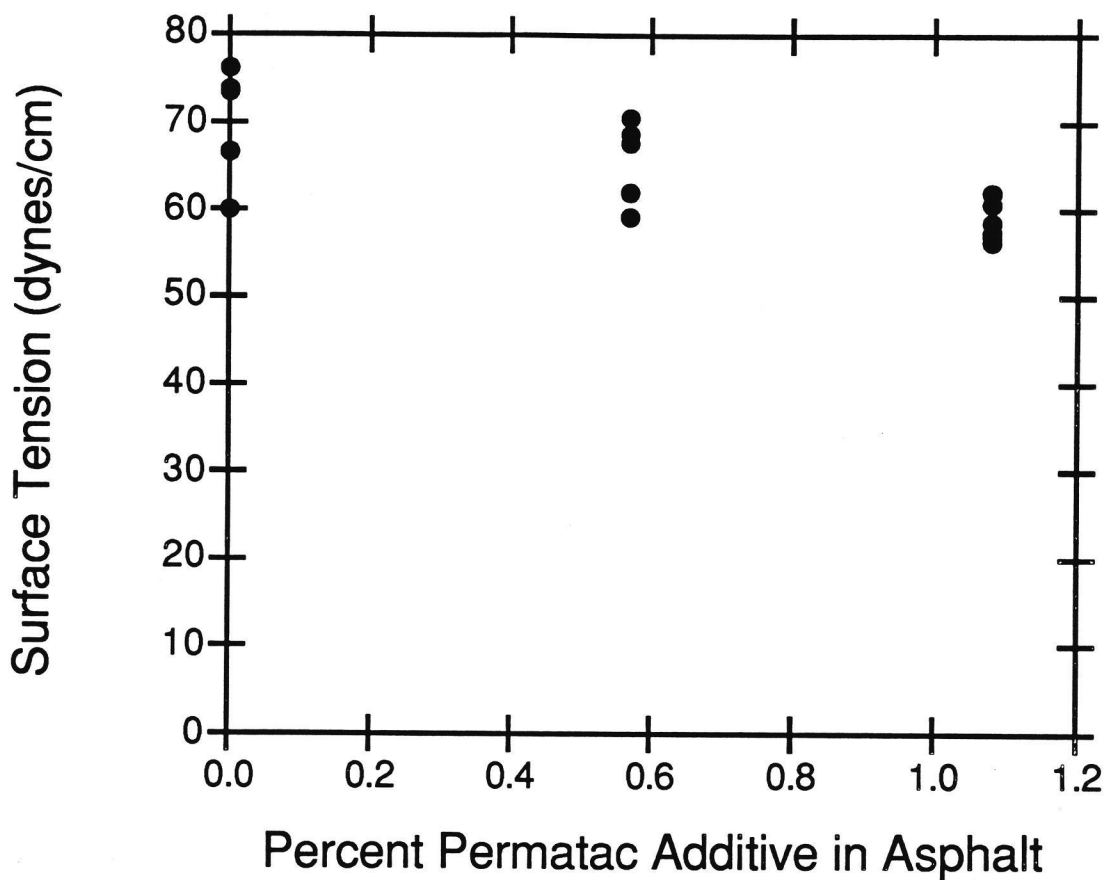


Figure 35. Asphalt-additive analysis after being dissolved in trichloroethylene and extracted into a water phase.

Work on surface tension testing will continue to determine if it has any advantages over the single-vessel titration method.

3.3 EXPERIMENTAL ISSUES

3.1 Spectroscopy

Spectroscopy is another method to possibly quantify the amount of antistrip additive. There are several ways in which this might could be done. One method employs using the spectrophotometer in helping to determine the endpoint. This could be done by having the same amount of asphalt dissolved in solvent in several volumetric flasks, add pH color indicator, and varying amounts of titrant. The spectrophotometer would then be used to determine at what level the color changes. Another way along this same idea is to titrate simultaneously using the spectrophotometer. Spectroscopy could also be used to determine the concentration of additive without determining the endpoint. This could be done by standard additions, which involves taking several asphalt samples that do not have additive and adding varying amounts of additive while leaving one as it is. Each one would be diluted to the same volume and the absorbance measured. From a graph of absorbance versus amount additive added, the concentration of additive could be determined by extrapolating the line backwards to the negative x-axis.

4. DISCUSSIONS AND CONCLUSIONS

From the results of the titration portion of this project, it has been concluded that it is possible to determine the amount of liquid antistrip additive in an asphalt sample when there is no aggregate in the mixture. This is done by the single-vessel titration test (SVT) and it means that the asphalt will have to be tested at the point after the additive has been blended in but before the aggregate has been mixed in. This achieves the goal of being able to know if antistrip additives are being added in the amount claimed, which is useful as a quality control measure.

There are several hypothesis of why the single-vessel test does not work with aggregate present and solutions are recommended with each. One possibility includes such things extraneous to the aggregate, such as dirt, moisture, and fines on the aggregate. Attempted solutions to this included thoroughly washing the aggregate with water and heating until dry before using. Another solution not attempted and left for future researchers is to use a stronger acid as a titrant. It is very possible that not all of the basic components are being extracted and titrating with a stronger acid would extract more into the water phase to be titrated. From the analysis with aggregate it was found that measured results were much lower than expected. This means that not as much acid was used in titrating. For siliceous aggregate this can be attributed to the acid coming from the aggregate and thus less titrant needed to reach the endpoint. This explanation is not possible for the limestone aggregate situation.

Another possibility is the aggregate itself. This includes the fact that there is obviously aggregate-asphalt interactions. An attempted solution was to filter off the aggregate before analyzing. Another concern regarding the aggregate is the possibility of additive residue on the aggregate. The attempted solution was to rinse the aggregate with trichloroethylene during the dissolving part of the procedure. Although there was not visible sign of asphalt-additive present that may not mean that antistrip additive is not there. A solution not attempted and left for future researchers is to analyze asphalt-aggregate samples with a different solvent. A solvent that might be better suited is perchloric acid. Perchloric acid is a stronger acid that should be able to give a more definite pH endpoint by more efficiently hydrolyzing the basic amine groups and result in a greater degree of amine reaction. Another recommended solution is to try a direct organic phase titration method adapted from techniques used in petroleum analysis. This will enable omitting the aqueous extracting step used in the single vessel titration test and to analyzed the mix dissolved directly in a suitable organic solvent.

In regard to tensiometry it is concluded that the method employed in this project is not able to quantitate the amount of antistrip additive present in a asphalt sample. Further research could be conducted in this area exploring other methods of measuring surface tension.

The successful qualification of an analytical technique, such as SVT, for antistripping additive in mixes would enable the AHTD to perform on-site quality checks. This capability covers a wide range of benefits for AHTD including product control, consistency checking, contractor monitoring, and possible advantages in liability cases.

5. BIBLIOGRAPHY

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