Best Practices for Asphalt Emulsion Particle Size Analyses Using a Coulter Counter

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Best Practices for Asphalt Emulsion Particle Size Analyses Using a Coulter Counter

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

by

Logan P. Kiihnl
University of Arkansas
Bachelor of Science in Civil Engineering, 2018

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This thesis is approved for recommendation to the Graduate Council.

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ABSTRACT

As asphalt pavements develop distresses, pavement preservation, maintenance, and rehabilitation treatments are used to mitigate distresses and extend the life of the pavement. Many of these treatments utilize asphalt emulsion. Previous research has linked particle size to material properties including viscosity and storage stability. General statements have also been made about particle size influencing emulsion performance while other researchers have identified a trend between particle size and prime coat penetration. Even though literature discusses the importance of particle size, there is little guidance on the best practices of asphalt emulsion particle size analyses, specifically with a Coulter counter.

Data collected from eight emulsions was analyzed, and a recommended procedure for testing and analyzing particle size results using a Coulter counter was produced in the form of a draft ASTM specification. RStudio was used to identify correlations between particle size parameters and the additional tests.

It is recommended to create three samples for each emulsion being tested and to test each sample three times. Each test should count at least 5,000 particles and a cumulative particle volume of at least 70,000 μm³. To provide values representative of the emulsion, the runs should be averaged together to represent the samples, and the samples should be averaged together to represent the emulsion. The ensure the runs are representative of the samples, the coefficient of variation of the mean particle size in the number basis should be less than 5%. The same is recommended for combining samples to represent the emulsion.

Particle size graphs should be shown as volume % versus particle size and utilize a smoothing technique by averaging up to 7 data points together to create a less cluttered graph.
Finally, the analysis using RStudio identified moderate correlations between the viscosity test and the mean, \(d_{10}, d_{50}, d_{90}\), span and standard deviation of -0.548, -0.565, -0.543, -0.574, 0.427, and -0.474 respectively. These correlations along with guidelines from a particle size analyzer manufacturer led to the recommendation of reporting the mean, \(d_{50}\), and span, in the volume basis, as final results to describe a particle size distribution.

These recommendations and guidelines serve as a steppingstone to further research about the best practices of conducting particle size analyses on asphalt emulsions. The results should be validated and refined with a formal experimental matrix.
ACKNOWLEDGEMENTS

First, I thank God for giving me the desire to become a civil engineer. It is my hope that I will always be a Christian before I am an engineer. Second, I want to thank my wife, Logan, for standing by my side, encouraging me when I wanted to throw in the towel, and for letting me stay up late to work on homework. Without your continued love and support, I could not have accomplished this. To my parents, Gerald and Vanessa, and my sisters, Dana and Kari, thank you for your constant love, and for putting up with my boring explanations about my research.

Thank you, Dr. Andrew Braham, for seeking me out my senior year. Without your pursuing, I would not be presenting this work today. Thank you for your guidance over the past two years and for showing me how to care for your team.

Thank you to my committee members, Dr. Kevin Hall and Dr. Cameron Murray, for your advice, and general conversations about life. Thank you to all of my professors and instructors at the University of Arkansas for taking time to share your knowledge during my undergraduate and graduate studies at the university.

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A huge thank you to our Undergraduate Research Assistants, David Olatunji, Pedro Diaz Romero, Ian Mugabo, and Andy Williams. I could not have done any of this without your help. Thank you for being willing to be at work at 7:00 a.m. and sharing in my frustration when things were not going as planned. I enjoyed getting to learn about each of you while having the opportunity to work with you.
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INTRODUCTION

Every day roads are utilized to transport people and goods safely and efficiently from one location to another. These trips range from short to long, and the loads carried on each trip range from light to heavy. Roadway types can be separated into three discrete types, flexible, rigid, and unbound pavements. Traditional flexible pavements, also known as asphalt pavements, are composed of aggregate and asphalt binder, while rigid pavements utilize aggregate, portland cement, and water. Unbound pavements lack a binding agent like asphalt binder or portland cement. Instead, these pavements rely on aggregate interlock as their sole means of structural capacity.

Approximately 94% of the nation’s paved roadways utilize asphalt pavement surfaces (National Asphalt Pavement Association, 2020). The sheer fact that nearly all of our nation’s paved roadways use asphalt technology demands that research be conducted in order to provide the highest quality pavement surfaces and structures for the public who uses them.

Various surface distresses appear on flexible pavements after exposure to the environment and after traffic has been allowed to utilize the road. These surface distresses are not structural deficiencies, but they affect the ride quality for the user. These surface distresses can include oxidation, raveling, and bleeding. Oxidation of the asphalt occurs due to oxygen interacting with the pavement. Raveling occurs due to stripping of the asphalt binder. If water enters the finished surface, the moisture can strip the asphalt binder off the aggregate. Without the cohesion provided by the asphalt binder, fines begin to wear away followed by coarse aggregate being worn off the surface. This leads to a rough pitted surface. If an asphalt mixture has too much asphalt binder in it, bleeding can occur. The excess asphalt binder rises to the
surface of the pavement. This is dangerous because it can cause a loss of texture in the pavement leading to cars losing traction with the pavement (Mallick & El-Korchi, 2018).

As repeated traffic loads are applied to asphalt pavements, various distresses begin to appear. Two of the most common distresses in flexible pavements are cracking and rutting. Fatigue cracking develops after a pavement has been loaded repeatedly over a period of time to the point where the pavement fails through cracking. Thermal cracking can also occur due to temperature changes. Rutting occurs due to either localized subgrade failures or inadequate mix design. Either way, rutting is a safety issue due to the potential for ponding of water on the roadway leading to the possibility of vehicles hydroplaning. If these distresses continue to exist without any mitigation, the pavement will deteriorate at an accelerated pace.

Pavements are commonly given a rating called a pavement condition index (PCI). The rating can range from 0-100, and it is based on the amount and severity of distresses present in a section of pavement. The number rating is then assigned a letter grade based on a predetermined range for each letter grade. The letter grades are the same as grades given in a typical class setting, A, B, C, D, and F. As stated before, if a pavement with distresses remains untreated, the pavement will continue to deteriorate, but the speed at which it does will increase drastically as time moves forward. This is shown in Figure 1.

In order to prolong the service life of a pavement, pavement preservation and rehabilitation treatments are employed. Often times, these treatments utilize asphalt emulsions in place of the typical asphalt binder or cutback asphalts.
Asphalt emulsions can be used for a number of different pavement preservation and rehabilitation treatments. These treatments can be split into 2 major categories, spray and mix applications. Mix applications can be divided further into non-structural and structural applications. Spray applications use spray trucks to add the emulsion to the surface being treated, and for some applications, aggregate is added to the surface. Mix applications involves an asphalt emulsion being mixed with an aggregate source. Table 1 summarizes the link between different pavement preservation and rehabilitation treatments and the application of the asphalt emulsion used for the treatment (Braham, 2017). More information about each treatment and the cost savings of utilizing these treatments is found in Kiihnl and Braham (2019).
Table 1. Asphalt Emulsions Pavement and Rehabilitation Treatments and their Application Type (Braham, 2017)

<table>
<thead>
<tr>
<th>Application</th>
<th>Treatments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray</td>
<td>• Fog seal</td>
</tr>
<tr>
<td></td>
<td>• Chip seal</td>
</tr>
<tr>
<td></td>
<td>• Crack seal</td>
</tr>
<tr>
<td>Mix (non-structural)</td>
<td>• Slurry seal</td>
</tr>
<tr>
<td></td>
<td>• Microsurfacing</td>
</tr>
<tr>
<td>Mix (Structural)</td>
<td>• Cold In-Place Recycling (CIR)</td>
</tr>
<tr>
<td></td>
<td>• Full Depth Reclamation (FDR)</td>
</tr>
</tbody>
</table>

One of the mix applications, CIR, is typically used to address aged and distressed pavement presenting structural distresses like cracks and ruts. It is important, however, that the aggregate base and subgrade layers are structurally sound at the time of treatment (Yeung, 2017). Performing the treatment on top of a failed aggregate base or subgrade would result in a premature failure of the CIR layer due to a lack in support.

Cationic medium-set and cationic slow-set emulsions are often used in cold in-place recycling (CIR) treatments. CIR is a structural mix treatment that utilizes reclaimed asphalt pavement (RAP) mixed with portland cement, water, and asphalt emulsion to create a new stabilized pavement layer. The RAP is typically provided by millings from the top 3-4 inches of an existing asphalt pavement (Yeung, 2017).

LITERATURE REVIEW

Asphalt Emulsions

A dispersion is a system of at least two phases that are not homogeneous when mixed together. An emulsion is a specific type of dispersion where all of the phases in the system are liquid (Goodarzi & Zendehboudi, 2019). Emulsions can fall into three categories, oil-in-water
(O/W), water-in-oil (W/O), and water-in-oil-in-water (W/O/W). Asphalt emulsions typically fall into the first category, oil-in-water. An asphalt emulsion contains asphalt binder, the oil phase, dispersed into a soap solution, the water or aqueous phase. Soap solutions are a combination of water, a chemical emulsifier, and sometimes an acid or alkali (Braham, 2017). A representation of the final asphalt emulsion product is shown in Figure 2.

Figure 2. Asphalt Emulsion Diagram (Braham, 2017)

Grading of Asphalt Emulsions

Asphalt emulsions are classified using a complex abbreviation system. The first letter represents the ionic charge on the emulsion droplets. Droplets either have a positive, cationic charge, a negative, anionic charge, or a neutral, nonionic charge. For a cationic emulsion, the designation of “C” is given, but for an anionic or nonionic emulsion, there is simply an absence of a letter designating the charge.

The next designation is whether the emulsion is considered high float (HF) or not. A high float emulsion contains chemicals that cause the residue to act like a gel after the water has
evaporated out of the system. This results in a thicker asphalt film on the aggregate (Asphalt Institute, 2008).

The final component to the core of the emulsion grading system is the setting speed. The setting speed represents how fast the emulsion will break or set. The setting speed required changes based on the application of the emulsion. There are four major setting categories, rapid-setting (RS), medium-setting (MS), slow-setting (SS), and quick-setting (QS).

In addition to the three main components of the grading system, various designations are also added to further describe the emulsion. Regarding viscosity, a “1” is listed to indicate lower viscosity, and a “2” is listed for higher viscosities. For binder properties, an “h” is listed if a harder asphalt binder base is used, and an “s” is listed if a softer asphalt binder base is used. Finally, polymers and additives are added to asphalt emulsions to achieve certain qualities in the final product. These are identified by listing “P” if a polymer is added and “L” if latex is added (Asphalt Institute, 2008).

An example of this grading system in action is a CHFRS-2P emulsion grade. The “C” identifies the emulsion as cationic, “HF” denotes it is high float, and “RS” recognizes the emulsion is rapid-setting. In addition to the first three terms, the “2” indicates it has a high viscosity, and “P” means it is polymer modified.

Asphalt Emulsion Formulation

Asphalt emulsions are prepared in two major steps. First, the soap solution is prepared, then the soap solution and asphalt binder are combined to make the asphalt emulsion. To determine the formulation of the soap solution, a manufacturer refers to a formulation sheet provided by an emulsifier supplier. The formulation sheet recommends ranges for the emulsifier
dosage and pH of the soap solution. From the recommended ranges, an emulsifier dosage and target pH are selected. Following selection of emulsifier, emulsifier dosage, and target pH, batch calculations are performed.

The manufacturer first decides how much asphalt emulsion they want. The total amount is based on the type of test(s) conducted, number of replications, or simply based on the amount needed for a specific application. Second, the percent residue is determined. The percent residue is the percent of asphalt emulsion that is asphalt binder. The minimum percent residue required for each specific grade of emulsion is given in AASHTO M 208 (2018) for cationic emulsions, AASHTO M 140 (2018) for anionic emulsions, and AASHTO M 316 (2018) for polymer modified emulsions. Once the percent residue has been finalized, the remaining calculations can take place.

Assuming the user wants 5,000 g of asphalt emulsion with a percent residue of 65%, 3,250 g will be asphalt binder while the remaining 1,750 g of emulsion will come from the soap solution. For the soap solution, the dosage of emulsifier needs to be determined. Assuming the user wants an emulsifier dosage of 1.25%, the amount of emulsifier needed is 21.9 g. The dosage of 1.25% is by weight of the soap solution not by weight of the final emulsion product. Finally, the amount of water is determined. This is calculated by simply subtracting the weight of the emulsifier from the total soap solution weight. Thus, the amount of water needed would be 1,728 g.

To create the soap preparation using the procedure at the University of Arkansas, first, the preparation area is set up. The set up consists of a beaker on a hot plate with a magnetic
stirrer. Also attached are a pH probe and a thermometer. During this setup process, the pH probe is also calibrated to ensure accurate and consistent readings.

To begin with the manufacturing process, two-thirds of the total water amount is added into the beaker. Warm water is used to assist the soaponification process when the emulsifier is added. Then the magnetic stirrer is turned on to approximately 400-500 revolutions per minute (rpm). The pH of the water is then adjusted to the predetermined level using either an acid or alkali. This depends on the charge of the emulsifier that is being used. Once the desired pH is reached, the emulsifier can be added. The pH is adjusted again to return the solution to the desired pH before adding the remaining water. Finally, the pH is adjusted for the final time to the desired pH. The solution mixes for at least 15 minutes, and the soap temperature is adjusted to approximately 55°C (130°F).

While the soap solution is warming, the recirculating mill is warmed up by circulating water in the mill until the water temperature reaches approximately 60°C (140°F). Once the mill has been warmed and the soap solution is finished mixing, the soap is split into smaller beakers, one for each individual batch. For each batch, a final emulsion weight is determined, and the required amount of binder and soap needed to achieve a 65% residue is also recorded. Then the specified amount of soap is added to the mill. The mill is turned on, and the asphalt binder that was warmed to 132°C (270°F) is added at a steady stream, about the width of a #2 pencil, until the required weight is added. All binder is typically added within one minute. The mill runs for a specified amount of time then the emulsion is emptied into a high-density polyethylene (HDPE) container, and the next batch is created.
Formulation Influences on Asphalt Emulsion

Manufacturers have the ability to adjust various formulation parameters in order to change the final emulsion product. They can change the emulsifier, emulsifier dosage, pH, water characteristics, manufacturing temperatures, mill motor speed, residence time in the mill, and mill head gap among other variables. However, the manufacturer needs to understand how altering the formulation of the asphalt emulsion influences its material properties and performance. Multiple studies have been conducted to understand how altering the formulation parameters on an asphalt emulsion influences its performance and material properties.

The type of emulsifier used in an emulsion has a strong influence on the charge and setting speed of an emulsion. Emulsifier chemicals are typically formed from natural fats, oils, and wood. They contain a hydrophilic head group and a lipophilic tail. Different combinations of different tails and heads results in various charges and characteristics for the final emulsion product (James, 1998). Having a strong chemistry background is helpful when trying to understand the influence of emulsifier composition and type on the characteristics of an emulsion.

The amount of emulsifier used in a soap solution also affects the properties and performance of emulsions. Pang et al. (2015) studied the influence of emulsifier dosage on the rheological properties of emulsion residues. They discovered that increasing the emulsifier content also increases the viscosity of the emulsion and the modulus at a given temperature and frequency. It was also determined that having a higher emulsifier content led to an enhanced resistance to emulsified asphalt mixture deformation.
Ouyang et al. (2020) also investigated emulsifier dosage along with other formulation parameters. They also discussed the influence of emulsifier dosage on viscosity and ultimately the ability of an emulsion to penetrate an aggregate base for a prime coat application. They concluded that a high emulsifier content was preferred for emulsions used in prime coats because of its ability to penetrate effectively into the aggregate base.

The pH of the aqueous phase has also been a major source of research. Xiao and Jiang (2013) evaluated the influence of pH values on the resulting emulsion’s physical properties including sieve amount, viscosity, residue ductility, residue penetration, and residue softening point, as well as the emulsion’s storage stability. While each emulsifier has a different optimum pH value, they concluded adjusting the aqueous phase pH would have significant influences on the emulsion’s residual amount on the sieve, viscosity, storage stability, and the residue’s ductility. It was concluded that the pH directly influences the emulsifier’s ability to disperse. This in turn affected the ability for the asphalt binder to emulsify and remain stable.

Cui and Pang (2017) agreed with Xiao and Jiang’s conclusion that achieving an optimal pH value in the soap solution leads to good emulsion stability and performance. However, they attributed the pH influence to interfacial tension. They concluded that a high pH value led to lower interfacial tension which makes emulsification of the asphalt binder easier to accomplish.

Continuing with chemical factors, Baumgardner (2006) discussed the presence of mineral impurities in water when used in the asphalt emulsion. To lower mineral impurities, an ion exchange needs to take place by adding sodium to replace the magnesium and calcium ions commonly found in the water. Neglecting this can lead to the emulsifier losing its emulsifying properties due to unwanted chemical reactions with the magnesium and calcium.
The manufacturing process can also affect the emulsion’s properties. The purpose of the mill is to introduce physical shearing energy to split the asphalt binder into small droplets. There must be enough energy to achieve proper particle size and distribution. Factors that affect the resulting emulsion include manufacturing temperatures, mill speed, residence time in the mill, and the gap between the rotor and stator (Baumgardner, 2006).

Table 2. Summary of Conclusions from Studies on Asphalt Emulsion Formulation Influencers

<table>
<thead>
<tr>
<th>Study</th>
<th>Parameter Investigated</th>
<th>Main Takeaway</th>
</tr>
</thead>
<tbody>
<tr>
<td>James, 1998</td>
<td>Emulsifier type</td>
<td>Emulsifier type changes charge and characteristics of emulsion</td>
</tr>
<tr>
<td>Pang et al., 2015</td>
<td>Emulsifier dosage</td>
<td>Higher emulsifier dosage increases emulsion viscosity</td>
</tr>
<tr>
<td>Ouyang et al., 2020</td>
<td>Emulsifier dosage</td>
<td>For prime coats, more emulsifier allowed for better penetration into the aggregate base</td>
</tr>
<tr>
<td>Xiao and Jiang, 2013</td>
<td>pH of soap solution</td>
<td>Each emulsifier has an optimum pH that controls the sieve, viscosity, residue properties, and storage stability</td>
</tr>
<tr>
<td>Cui and Pang, 2017</td>
<td>pH of soap solution</td>
<td>High pH led to lower interfacial tension</td>
</tr>
<tr>
<td>Baumgardner, 2006</td>
<td>Water chemistry</td>
<td>Ion exchange must happen to prevent the emulsion from losing its properties</td>
</tr>
<tr>
<td>Baumgardner, 2006</td>
<td>Mill properties</td>
<td>Manufacturing temperatures, mill speed, residence time, and mill gap can significantly alter asphalt emulsion properties</td>
</tr>
</tbody>
</table>
Particle Size Analysis (PSA)

There are two broad categories of emulsions: macro-emulsions and micro-emulsions. Macro-emulsions are characterized by droplet sizes of microns while micro-emulsions contain droplet sizes of the nanometer scale. The reason behind this distinction is stability. Macro-emulsions are thermodynamically unstable while micro-emulsions are considered thermodynamically stable (Goodarzi & Zendehboudi, 2019). Asphalt emulsions tend to be macro-emulsions.

For many years, researchers have discussed the importance of asphalt emulsion particle size. In general, knowing the particle size of emulsions can assist in predicting the stability of an emulsion. Typically, the smaller the droplet size in an emulsion, the more stable the emulsion is. According to James (2006), the typical size of asphalt emulsion particles is 0.1-20 μm. Not only can droplet size influence stability, but it can also modify rheological properties of the emulsion (Goodarzi & Zendehboudi, 2019).

Particle Size in Other Areas

Particle size analysis has become a popular tool to characterize various materials in both civil engineering and other industries. One analyzer that has been used is a Coulter Multisizer, a specific model of a Coulter Counter that utilizes the Coulter method. In 1993, Ghosal et al. used a Coulter Multisizer to characterize fly ash size distributions. Their work used a wet-sieving procedure to separate different size particles then used multiple apertures in a Coulter counter to generate counts for each set of particles. They then combined the data from the different apertures to create a particle size distribution describing the entire range of sizes.
Members at the University of Arkansas have also conducted extensive research utilizing a Coulter counter. Zhang et al. (2013) used it to quantify biomass cell and polymer distribution in biofilms. Walden (2017) utilized the apparatus to count microbial culture cells, and Ghebremedhin (2019) used a Coulter counter to measure cell concentrations in a study concentrating on disinfection byproduct mixtures.

Influencers of Asphalt Emulsion Particle Size

Previous research has also explored the influence of formulation parameters on the particle size of asphalt emulsions. According to Baumgardner (2006), particle size of asphalt emulsions can be altered by formulation, raw materials, and equipment used to manufacture the emulsion.

Emulsifiers play a large role in the success of an emulsion. The emulsifier’s duty is to reduce the interfacial tension to help the asphalt binder disperse within the water. Changing the emulsifier employed for the emulsion changes the surface activity in the emulsion. Liu et al. (2013) determined that emulsifiers with higher surface activity, led to emulsions with smaller average particle size diameters. They also concluded that increasing the dosage of the emulsifier reduced the average particle size diameter. Ouyang et al. (2020) arrived at the same conclusion that a higher emulsifier content reduces particle size.

Baumgardner (2006) pointed out that particle size is mainly influenced by the mill and mill residence time. Gingras et al. (2005) studied the influence of process parameters on asphalt emulsions, and they discovered that the average particle size decreases as the mill rotor speed increases and as the emulsification temperatures decreases. This conclusion was supported by the work of Gutierrez et al. (2002).
Gingras et al. (2005) also focused on the asphalt concentration and its effect on particle size. They observed a decrease in droplet size as the asphalt concentration decreased. They attributed this interaction to the increased collision frequency of particles when the asphalt concentration is higher. However, Gutierrez et al. (2002) observed the opposite. They tested higher asphalt concentration amounts than Gingras, but still, their correlations did not match. More research could lead to better explanation, but it is clear the asphalt concentration has an impact on the particle size of the resulting emulsion.

Table 3. Summary of Conclusions from Research on Formulation Influence on Particle Size

<table>
<thead>
<tr>
<th>Study</th>
<th>Parameter Investigated</th>
<th>Main Takeaway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baumgardner, 2006</td>
<td>General formulation</td>
<td>Altered by formulation, raw materials, and manufacturing equipment</td>
</tr>
<tr>
<td>Liu et al., 2013</td>
<td>Emulsifier dosage</td>
<td>Increased emulsified dosage yielded smaller emulsion particle size</td>
</tr>
<tr>
<td>Ouyang et al., 2020</td>
<td>Emulsifier dosage</td>
<td>Increased emulsifier dosage led to smaller particle size</td>
</tr>
<tr>
<td>Gingras et al., 2005</td>
<td>Mill properties</td>
<td>Particle size decreased when mill speed increased</td>
</tr>
<tr>
<td></td>
<td>Asphalt residue</td>
<td>Particle size decreased as residue decreased</td>
</tr>
<tr>
<td>Gutierrez et al., 2002</td>
<td>Mill properties</td>
<td>Particle size decreased when mill speed increased</td>
</tr>
<tr>
<td></td>
<td>Asphalt residue</td>
<td>Particle size increased as residue decreased</td>
</tr>
</tbody>
</table>

*Table 3. Summary of Conclusions from Research on Formulation Influence on Particle Size*

*Influence of Asphalt Emulsion Particle Size on Emulsion Properties*

As mentioned earlier, a general rule of thumb for asphalt emulsion particle size is $0.1 - 20 \, \mu m$ (James, 2006). An example of a particle size distribution is shown in Figure 3.
Particle size has been linked to important physical parameters including viscosity, stability, coating, break rate, and cure rate (Baumgardner, 2006; James, 2006).

![Particle Size Distribution of Asphalt Emulsion](image)

**Figure 3. Example of a Particle Size Distribution of Asphalt Emulsion**

Meeting the specification limits for viscosity of an emulsion is important. An emulsion presenting a viscosity that is too low can result in runoff while the emulsion is being sprayed for an application like a chip seal. Use of an emulsion with too high viscosity can lead to pumping issues during the application process resulting in damaged equipment.

The link between particle size and viscosity has been studied extensively. In the early 2000s, a correlation was discovered between the asphalt emulsion particle size and the emulsion’s viscosity. As the mean droplet diameter increases, the viscosity decreases (Nuñez, et al., 2000; Gutierrez, Silva, Chirinos, Leiva, & Rivas, 2002). Buss et al. (2018) also noted that a wider distribution in particle size was likely the cause for an emulsion having a lower viscosity than another.
Not only can particle size influence physical properties, but it also can change the performance of the emulsion (James, 2006). In the case of Ouyang et al. (2020), smaller particle size led to better penetrative ability of asphalt emulsions for prime coat use. Hou et al. (2018) observed a correlation between the storage stability of an emulsion with its squared particle size.

**Table 4. Summary of Conclusions from Research on Particle Size Influence**

<table>
<thead>
<tr>
<th>Study</th>
<th>Parameter Investigated</th>
<th>Main Takeaway</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuñez et al., 2000</td>
<td>Viscosity</td>
<td>Smaller particle diameter, lower viscosity</td>
</tr>
<tr>
<td>Gutierrez et al., 2002</td>
<td>Viscosity</td>
<td>Smaller particle diameter, lower viscosity</td>
</tr>
<tr>
<td>Buss et al., 2018</td>
<td>Viscosity</td>
<td>Wider particle size distribution led to lower viscosities</td>
</tr>
<tr>
<td>Ouyang et al., 2020</td>
<td>Prime coat performance</td>
<td>Smaller particle size led to better penetration</td>
</tr>
<tr>
<td>Hou et al., 2018</td>
<td>Storage stability</td>
<td>Correlation between squared particle size and storage stability</td>
</tr>
</tbody>
</table>

**Emulsion Stability**

Emulsion stability is an important parameter to consider and monitor when producing an asphalt emulsion. The stability of an emulsion relates to the emulsion’s ability to remain dispersed. Over time, droplets begin to approach one another, however, a layer of emulsifier remains between the two droplets preventing the droplets from contacting. This is called flocculation. Flocculation is reversible by mechanical agitation. If steps are not taken to reverse flocculation, coalescence can occur. With coalescence, the emulsifier dividing layer between the
droplets is compromised allowing the droplets to contact one another. During this process, water can become trapped within the new, larger droplet. Since there no longer remains a physical barrier between the emulsion droplets, the droplets cannot be separated (Braham, 2017). This progression is shown in Figure 4.

Figure 4. Flocculation and Coalescence Process. Left: Stable Emulsion. Middle: Flocculation. Right: Coalescence.

It is important for emulsions to remain stable until they are utilized for a specific application. They need to remain in their homogeneous state until the emulsion contacts the aggregate at which point the emulsion should break. Premature breaking can occur by pumping and transporting the emulsion, or it can stem from the chemical destabilization (Liu & Hou, 2017; Boucard, Schmitt, Farcas, & Gaudefroy, 2015).

There are many factors that influence the stability of an emulsion. The foundation of stability lies within the formulation of the asphalt emulsion. Altering the dosage of the emulsifier, pH level, binder content, and the manufacturing temperatures can all affect the material and chemical properties of the emulsions which in turn affect the stability (Pinto & Buss, 2020).

Measuring Stability

Traditionally the storage stability of asphalt emulsions has been determined using ASTM D6930 Standard Test Method for Settlement and Storage Stability of Emulsified Asphalts.
This method requires the evaluator to place 500 mL of emulsified asphalt in a glass cylinder and allow it to sit for 24 hours. After the 24-hour time period, a representative sample is taken from the top and bottom of the cylinder, and each sample is placed in a beaker. The two beakers are then placed in an oven at a high temperature for 3 hours. Upon completion of the burn off in the oven, the beakers are weighed, and the percent residue is calculated. The allowable difference between the two samples is 1% after the 24-hour settling period (AASHTO M 208-18, 2018).

Destabilization of asphalt emulsions has been observed using particle size. Boucard et al. (2015) observed the changes in particle size distributions after adding a destabilizing electrolytes created from adding different salts to deionized water. The group used static light-scattering utilizing the Mie theory. As a result of adding the electrolyte to the asphalt emulsion, a change in the median particle size and the span of the particle size distribution changed.

Wang et al. (2012) used laser diffraction technology to look at the stability of asphalt emulsions used in cement asphalt (CA) mortar. Their study transferred the stability focus away from a strictly gravitational settling viewpoint to a well-rounded view that also focused on flocculation and coalescence. Not only did they identify the potential of using particle size analysis to quantify stability, but they also identified storage temperature and emulsifier dosage as significant factors that affect stability.

**Particle Size Methods**

There are various particle sizing methods that utilize different theories in order to characterize particle size distributions. These methods vary in the way they determine particle sizes, volumes, and surface areas, and not every method is capable of producing results in every
way. Some of the particle size methods include the electrical sensing zone method (Coulter method), laser diffraction, static image analysis, dynamic image analysis, and dynamic light scattering among others.

A key part to particle size analysis, is how the method determines the size of a particle. It would be ideal but impractical to identify every dimension of a particle to properly characterize its volume and size. In order to simplify the process, an equivalent spherical diameter is determined based on the data captured by the analyzer.

The means used to characterize a particle size distribution can vary depending on the theory used. This paper focuses specifically on the electrical sensing zone method and the laser diffraction method.

*Electrical Sensing Zone Method (Coulter Method)*

The Coulter Method was invented by Wallace H. Coulter in the late 1940s while working under contract with the United States Navy (Lines, 1992). Initially, the method was employed to count blood cells, but over time its use has been applied to other areas including colloidal suspensions, aerosols, and emulsions (Lines, 1992; Beckman Coulter, 2014).

Out of the various particle sizing methods, the electrical sensing zone method is the only one that measures a particle volumetrically. To do this, the material being tested is suspended in an electrolyte solution. The homogenous solution is passed through an aperture, or orifice, in an aperture tube. The aperture tube resembles the appearance of a test tube with the exception of a small opening, the aperture, near the bottom of the tube. Within the tube, there is an electrode. Outside of the aperture tube, but within the sample container, there is another electrode with the opposite charge. A simple schematic of this setup is shown in Figure 5. Between these two
electrodes, an electric current flows setting the baseline current level. As the particles flow through the aperture, a volume of electrolyte is displaced equivalent to the volume of the particle. The analyzer then detects a resistance in the electric current proportional to the volume of the particle. This results in an electrical pulse being recorded for each particle that passes through the aperture. Once the pulses have been recorded, an equivalent spherical diameter for each particle is calculated based on the volume recorded (Lines, 1992).

Figure 5. General Aperture Tube Setup for Coulter Principle

One of the potential downfalls of the Coulter Principle relates to the resistivity of the material being tested. However, this is rarely an issue unless the resistivity of the material is close to the resistivity of the electrolyte solution (Lines, 1992).

Since there are many applications for a Coulter counter, the apparatus must be able to handle a wide range of particle sizes. The Coulter Principle relies on various size apertures to generate accurate results. Currently, apertures can range from 10 μm to 2000 μm, and each
aperture typically sizes particles between 2% and 60% of their aperture opening diameter while some extend to measuring up to 80% of their opening diameter (Beckman Coulter, 2014). Because of these limitations, users must be careful when choosing an aperture for their analyses, or they must use multiple apertures to collect data covering the entire range of their material.

A potential source of error when using the Coulter Principle is rooted in coincident particle passage. If the concentration of a material exceeds 10%, multiple sample particles can pass through the aperture at the same time or too close together resulting in the analyzer recording an inaccurate volume because the volume displaced is more than the volume of a single particle (Lines, 1992; Beckman Coulter, 2014). This error can unintentionally skew the particle size distribution towards the larger particles (Lines, 1992).

**Laser Diffraction**

Laser diffraction is the most used particle size analysis method used for asphalt emulsions. Laser diffraction utilizes a monochromatic light source, typically a laser, and detects particle sizes based on angular distribution and intensity of scattered light. As the light source meets the particle, it is scattered at many different angles. The scattered light then travels to a photo detector, where the numerical value corresponding to the scattered light is recorded. The recorded values are then converted into a particle size distribution. Similar to the Coulter Principle, laser diffraction takes the recorded particle size distribution and converts it to a distribution of equivalent spherical particles that would match the scattering pattern recorded (ISO 13320:2020, 2020).
The most used theory in laser diffraction is the Mie-theory. The Fraunhofer diffraction theory is also used, but due to its lack of ability to give accurate results besides small angle forward scattering, it is less popular (ISO 13320:2020, 2020).

Table 5. Summary of the Electrical Sensing Zone and Laser Diffraction Methods

<table>
<thead>
<tr>
<th>Electrical Sensing Zone Method (Coulter Method)</th>
<th>Laser Diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary: Measures particle volume by detecting a resistance in an electric current</td>
<td>Summary: Determines particle diameter based on the scatter patterns of a light beam</td>
</tr>
<tr>
<td><strong>Pros:</strong></td>
<td><strong>Pros:</strong></td>
</tr>
<tr>
<td>• Measures particles volumetrically</td>
<td>• Popular and accepted in the asphalt emulsion industry</td>
</tr>
<tr>
<td>• Not necessary to know any optical property of the material</td>
<td>• Relatively fast test</td>
</tr>
<tr>
<td><strong>Cons:</strong></td>
<td><strong>Cons:</strong></td>
</tr>
<tr>
<td>• Potential coincident counting</td>
<td>• Must have knowledge of the material’s optical properties</td>
</tr>
<tr>
<td>• Aperture Blockage is possible</td>
<td>• Must choose between Mie model and Fraunhofer model</td>
</tr>
</tbody>
</table>

Other Methods

Other methods for particle size analysis include static image analysis, dynamic image analysis, and dynamic light scattering. Static image analysis is most commonly used for powders. Static image analysis utilizes a microscope and digital camera to gather images of samples on slides. The images are filtered to separate the particles in interest from background particles present on the slide. Once this has taken place, the particles can be analyzed to produce a particle size distribution (Horiba Instruments, 2012).

Dynamic image analysis uses many of the same processes as static light scattering with a few exceptions. First, the sample is moving during the analysis. The sample is dropped in front of two cameras. Second, rather than one camera being used, a basic camera and a zoom camera
are used. The basic camera captures large particles while the zoom camera focuses on fine particles. The images captured from the two cameras are then used to produce a particle size distribution (Horiba Instruments, 2012).

Dynamic light scattering takes a sample suspended in water, and the sample is subjected to random thermal motion. A laser is then passed through the sample, and the scattered light is collected by detectors. The random changes due to the random motion of the particles is converted to particle sizes, and a particle size distribution is created (Horiba Instruments, 2012).

**Interpreting Particle Size Results**

Advanced particle size analysis software produces a multitude of results including mean, median (also written as $d_{50}$), mode, $d_{10}$, $d_{50}$, and $d_{90}$. The results of $d_{10}$, $d_{50}$, and $d_{90}$ refer to the particle size at which 10%, 50%, and 90% are smaller, respectively. These results can be represented in different formats: number, volume, and surface area. While one might be inclined to represent a particle size distribution with only one number like the mean or $d_{50}$, it is advised to not do so (Horiba Instruments, 2012). A better option is to use a single value like the mean or $d_{50}$ and also use either multiple numbers to describe the entire distribution like $d_{10}$, $d_{50}$, and $d_{90}$, or use those numbers to calculate a representative value of the distribution like the span. The span is calculated using the following equation from Horiba (2012):

$$\text{span} = \frac{d_{90} - d_{10}}{d_{50}}$$

(1)

While the span itself is only a single value, it uses three values in its calculation helping describe the entire distribution. This is primarily used to represent the tightness of a particle size distribution (Horiba Instruments, 2012; Mercado & Pumarejo, 2016).
**Number versus Volume**

There are two primary ways of showing particle size data. The data can be shown in the number basis and volume basis. Both have their advantages depending on the application of the distribution data. Typically for asphalt emulsions, the best way to represent the distribution is volume basis.

Horiba (2012) and Beckman Coulter (2014) use the following concept to explain the importance of viewing distributions through the volume lens. Suppose there are nine particles in a particle size distribution. 3 particles are 1 $\mu$m in diameter, 3 particles are 2 $\mu$m in diameter, and 3 particles are 3 $\mu$m in diameter. On a number basis, each particle size represents an equal percentage of the distribution. However, on a volume basis, the 1 $\mu$m particles have a total combined volume of 1.56 $\mu$m$^3$, the 2 $\mu$m particles have a total combined volume of 12.6 $\mu$m$^3$, and the 3 $\mu$m particles have a total combined volume of 43.2 $\mu$m$^3$. Using these values, the 1 $\mu$m particles contribute 2.8% of the total volume, the 2 $\mu$m particles 22% and the 3 $\mu$m particles 75%. Comparing the results based on number and volume, there is a large variation between the percent by number and percent by volume. Therefore, it is important to distinguish which basis is being used to represent a particle size distribution.

**MATERIALS AND METHODS**

Eight emulsions were manufactured for the experiment. Each emulsion formulation was different, and six of the eight emulsions were designed outside of its recommended ranges. The remaining two emulsions, Prop. CSS and Comm. CMS, were created using the average values from the ranges provided in the formulation sheets and a mill time of 30 seconds. Table 6 highlights the information provided on the formulation sheets for the two emulsifiers that were
used. Table 8 is a list of the emulsions that were created, and the key for the sample is provided in Table 7.

**Table 6. Formulation Sheet Information**

<table>
<thead>
<tr>
<th>Emulsifier</th>
<th>Dosage</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commodity CMS</td>
<td>0.25-0.35%</td>
<td>2-4.5</td>
</tr>
<tr>
<td>Proprietary CSS</td>
<td>0.8-1.5%</td>
<td>2-7</td>
</tr>
</tbody>
</table>

**Table 7. Symbol Key for Emulsion Descriptions**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Dosage</td>
</tr>
<tr>
<td>P</td>
<td>pH</td>
</tr>
<tr>
<td>M</td>
<td>Mill Time</td>
</tr>
<tr>
<td>L</td>
<td>Low</td>
</tr>
<tr>
<td>H</td>
<td>High</td>
</tr>
</tbody>
</table>

**Table 8. Emulsion Formulations**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Emulsifier</th>
<th>Dosage (%)</th>
<th>pH</th>
<th>Mill Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSS_DH_PH_MH</td>
<td>Prop. CSS</td>
<td>1.75</td>
<td>No Acid</td>
<td>45</td>
</tr>
<tr>
<td>CMS_DH_PH_ML</td>
<td>Comm. CMS</td>
<td>0.45</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>CSS_DL_PL_MH</td>
<td>Prop. CSS</td>
<td>0.55</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>CMS_DH_PL_MH</td>
<td>Comm. CMS</td>
<td>0.45</td>
<td>1</td>
<td>45</td>
</tr>
<tr>
<td>CSS_DL_PH_ML</td>
<td>Prop. CSS</td>
<td>0.55</td>
<td>No Acid</td>
<td>15</td>
</tr>
<tr>
<td>CSS_DH_PL_ML</td>
<td>Prop. CSS</td>
<td>1.75</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>Prop. CSS</td>
<td>Prop. CSS</td>
<td>1.15</td>
<td>4.5</td>
<td>30</td>
</tr>
<tr>
<td>Comm. CMS</td>
<td>Comm. CMS</td>
<td>0.3</td>
<td>2.75</td>
<td>30</td>
</tr>
</tbody>
</table>

The emulsions were evaluated at four time intervals over a 7-day period by conducting the tests at 2-hours, 1-day, 4-days, and 7-days after manufacture of the emulsion. In addition to conducting particle size analyses on the emulsions, several other tests were performed. The tests conducted at each time interval were as follows:
- Rotational viscosity
- Raveling
- Indirect tensile (IDT) strength

In addition to the tests at the four testing intervals, two quality control tests were conducted immediately following the manufacture of the emulsion. They were the sieve test and residue test.

**Manufacturing Asphalt Emulsion**

The process for manufacturing asphalt emulsion was divided into two large steps. First, the soap solution was prepared, and second, the soap solution and asphalt binder were combined in a mill to produce the asphalt emulsion.

**Formulation Calculations**

As mentioned before, the majority of the formulation calculations revolve around the percent residue. Guidelines for minimum residue percentages are set forth by AASHTO M 140 (2018) for anionic asphalt emulsions, AASHTO M 208 (2018) for cationic asphalt emulsions, and AASHTO M 316 (2018) for polymer modified asphalt emulsions. According to AASHTO M 208 (2018), the minimum percent residue for a CMS emulsion is 65% while the minimum percent residue for a CSS emulsion is 57%. In order to maintain consistency, a percent residue of 65% was selected for both emulsions. Table 6 provides the information supplied by the formulation sheets that came from the emulsifier supplier.

The following example provides the calculations for creating the emulsion for PB Order 2. According to Table 8, creating the emulsion for PB Order 2 requires the emulsifier for CMS emulsions, a dosage of 0.45%, a soap solution pH of 5, and a mill time of 15 seconds.
The benchtop recirculating mill that was used for manufacturing could produce asphalt emulsion batches of 800-1,000 g. In order to create enough asphalt emulsion to conduct all of the required tests, allow for repeated tests, and account for emulsion sticking to the sample container, five batches of 850 g were created for each emulsion resulting in a total amount of 4,250 grams of emulsion.

Using the final emulsion amount of 4,250 g, the amount of asphalt binder required was calculated using Equation 2.

\[ B = \frac{R}{100} \times F \]  

(2)

where:

\( B \) = Binder mass (g)

\( R \) = Residue (%)

\( F \) = Final emulsion mass (g)

This resulted in 2,763 g of asphalt binder required for the asphalt emulsion.

Next, the amount of soap solution needed was calculated using Equation 3.

\[ S = F - B \]  

(3)

where:

\( S \) = Soap solution mass (g)

\( F \) = Final emulsion mass (g)

\( B \) = Binder mass (g)
The result of Equation 3 was 1,487 g of soap solution required for the asphalt emulsion.

Then the mass of the emulsifier required was calculated using Equation 4.

\[ E = D \times S \]  \hspace{1cm} (4)

where:

\[ E = \text{Emulsifier mass (g)} \]

\[ D = \text{Emulsifier dosage (%)} \]

\[ S = \text{Soap solution mass (g)} \]

Using Equation 4 to calculate the amount of emulsifier needed in the soap solution resulted in 6.7 g of emulsifier.

Finally, the mass of water needed for the soap solution was calculated using Equation 5.

\[ W = S - E \]  \hspace{1cm} (5)

where:

\[ W = \text{Water mass (g)} \]

\[ S = \text{Soap solution mass (g)} \]

\[ E = \text{Emulsifier mass (g)} \]

The amount of water need for the asphalt emulsion was calculated to be 1,480 g by using Equation 5. It is worth noting the acid amount was not accounted for in these calculations because the amount of acid required to adjust the pH level to a given value was not known.
Once all the calculations were completed, batch calculations were performed. The amount of asphalt binder and soap solution needed for each batch was calculated by taking the total amount of asphalt binder and soap solution required and dividing it by the number of batches. Creating 5 batches resulted in 552 g of asphalt binder and 297 g of soap solution. The calculations are summarized in Table 9.

<table>
<thead>
<tr>
<th>Emulsion Mass (g)</th>
<th>Binder Mass (g)</th>
<th>Soap Mass (g)</th>
<th>Emulsifier Mass (g)</th>
<th>Water Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>4,250</td>
<td>2,763</td>
<td>1,487</td>
<td>6.7</td>
</tr>
<tr>
<td>Batch</td>
<td>850</td>
<td>552</td>
<td>297</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Soap Solution Manufacture

Once the calculations were performed, the soap solution manufacturing commenced. To begin, a 4,000 mL beaker with a magnetic stirring bar was placed on a hot plate equipped with a magnetic stirrer. A Fluke contact thermometer and a VWR symphony Meter model SB70P were arranged to take continuous temperature and pH readings of the soap solution. The setup is shown in Figure 6.
The mixing process began by adding 2/3 of the total amount of water needed to the beaker. Warm to hot tap water was used. The hot plate was turned on, and the temperature was set to 50°C. The magnetic stirrer was also turned on and set to approximately 400-500 rpm.

Next, the pH of the water was adjusted to the target pH using hydrochloric acid. For the CSS emulsifier, the hydrochloric acid was diluted to 50% of its original strength with water. This allowed for better control of the pH of the solution. Previous work within the local lab using this emulsifier showed high sensitivity to the original strength of the hydrochloric acid. The dilution was performed by filling a glass jar with water until it was half-full then filling the remaining space in the jar with the HCl. The hydrochloric acid was not adjusted for the CMS emulsion.

At this point, the temperature for the solution was checked to make sure it was above 104°F. Water typically needs to be above this temperature in order for the emulsifier to properly
activate, or saponify (Baumgardner, 2006). Once the water temperature had surpassed the bottom limit, the emulsifier was added.

To wrap up the soap solution manufacturing process, the pH was adjusted again to the target pH level, the remaining water was added, and the pH was adjusted once more to the target pH. The solution mixed for an additional 15 minutes until being split into smaller beakers for each batch for the emulsification process.

**Milling Process**

Unmodified PG64-22 asphalt binder was employed for asphalt emulsion manufacture. Two hours before the planned start time of the emulsification process, the asphalt binder was placed in an oven at 330°F. The asphalt binder was in quart-sized tin coated steel cans to allow for easy handling during the emulsification process.

While the soap solution was mixing for 15 minutes, the recirculating mill was warmed up using water. Warm water was placed into the mill, and the mill was turned on. The water circulated until the water temperature rose to approximately 140°F. The water temperature was measured using a Fluke handheld laser thermometer. Once the water reached the desired temperature, the recirculating valve was turned to direct the water through the exit line of the mill. Once the mill had been drained, the valve was turned back to the recirculating position.
Before placing the soap solution and asphalt binder into the mill for emulsification, the temperatures necessary for each component was calculated. According to Baumgardner (2006), the exit temperature of the emulsion should not exceed 212°F because the emulsion will begin to boil. Therefore, the following equation was used from Baumgardner (2006).

\[
ET = \frac{(AW \times AT \times 0.5) + (SW \times ST \times 1.0)}{(AW \times 0.5) + SW}
\]

where:

\(ET\) = Emulsion temperature (°F)

\(AW\) = Asphalt binder weight (%)

\(AT\) = Asphalt binder temperature (°F)
\[ SW = \text{Soap solution weight (\%)} \]

\[ ST = \text{Soap solution temperature (°F)} \]

After multiple iterations, the final concluding temperatures were 270°F for the asphalt binder and 130°F for the soap solution.

The proper amount of soap solution was then added to the mill at approximately 130°F. The asphalt binder was retrieved from the oven and allowed to cool to 270°F. When the asphalt binder had reached the desired temperature, the mill was started, and the soap solution circulated for 5-10 seconds. Then the asphalt binder was added in a steady stream, about the size of a #2 pencil. The asphalt binder took approximately one minute to add to the mill. While the asphalt binder was being added, the emulsion was stirred with a glass rod to assist in the mixing of the binder and soap solution. Once the proper amount of asphalt binder was added, a timer was started for the mill time. The emulsion circulated in the mill until the mill time was completed. The mill was turned off, the valve was turned to allow the emulsion to go through the exit line into a high-density polyethylene (HDPE) container. The mill was restarted to assist in the emptying process. Once the mill was emptied, the remaining batches were manufactured. All emulsion batches were placed in the same HDPE container for storage. They were stirred with a glass rod to effectively mix all of the emulsion batches together.

The milling process requires at least two people to operate. Operator 1 is responsible for adding the proper amount of soap and asphalt binder to the mill as well as controlling the recirculating valve while Operator 2 is responsible for managing the mill power switch, stirring the emulsion, and keeping the time recorded.
Following the completion of all batches, a cleaning process was conducted on the mill. Warm water with dish soap added was poured into the mill, circulated for one to two minutes, then emptied into a waste container. This process was repeated until it appeared the mill was running smoothly without any asphalt binder clogs. Then warm water was circulated to remove the dish soap from the system followed by emptying into the waste container. This process was repeated until the water appeared clear without dish soap present.

The cleaning process is vital to the success of the next emulsion produced in the mill. If a large amount of asphalt binder is left behind in the mill, the binder will solidify and prevent the mill rotor from spinning freely. Many times, if the mill was not properly cleaned, extensive cleaning had to take place. Extensive cleaning required using a propane fueled torch to externally increase the temperature of the mill head to liquify the asphalt binder inside. If heating with the torch did not work, WD-40 had to be added through the hopper to help free the binder from the mill. This should be avoided as much as possible because residual WD-40 could be left behind after cleaning and become mixed with the asphalt emulsion affecting its properties. Finally, if the first two attempts could not successfully clean the mill, then the mill had to be taken apart and cleaned by hand with WD-40.

**Test Methods**

Following the manufacturing of an asphalt emulsion, tests were conducted to determine properties regarding application and performance. The following sections explain several tests and their significance.
The first two tests conducted were quality control tests to determine the percent residue of the emulsion and the percentage of oversized particles in the emulsion. The remaining tests were used to evaluate the material and performance properties of the emulsions.

*Residue Test*

The residue test (ASTM D6934-08, 2016) is a standard test for determining the amount of asphalt material in an asphalt emulsion. This test verifies that the target residue value was achieved during manufacture. If the test result differs from the planned percent residue, then there is a possibility formulation errors occurred which can lead to emulsion instability (Braham, 2017).

The test has two procedures for determining the percent residue. Procedure A, a faster method, is used when the residue does not require further testing while Procedure B is followed when additional testing of the asphalt residue is required. Since the residue did not require further testing for this research, Procedure A was followed.

To begin, 3 – 1,000 mL beakers were selected, and glass stirring rods were placed in the beakers. The beakers were weighed and recorded as the tare mass (C). The emulsion was stirred with a glass rod to achieve homogeneity. Next, the beakers were filled with 50 ± 0.1 grams of the asphalt emulsion, and a new mass was recorded and listed at the original mass (A). Following filling, the beakers were placed in the oven at 163°C ± 3.0°C for 3 hours total and stirred at each hour. Following the 3-hour process the beakers were removed from the oven, and the mass was recorded as the final mass (B).

According to ASTM D6934 (2016), the percent residue should be calculated using the following equation:
\[ residue,\% = 2(A - B) \quad (7) \]

where:

\( A \) = Original mass (g)

\( B \) = Final mass (g)

However, a more precise equation was used than the equation provided in ASTM D6934 (2016). It is shown in Equation 8.

\[ residue,\% = \frac{(B - C)}{(A - C)} \times 100 \quad (8) \]

where:

\( A \) = Original mass (g)

\( B \) = Final mass (g)

\( C \) = Tare mass (g)

**Sieve Test**

The sieve test (ASTM D6933-18, 2018) is used to determine the percent of oversized particles in an asphalt emulsion. If the particle size of asphalt emulsions is too large, the emulsion can be prevented from passing through spray nozzles and can cause pump stability issues (Kadrmas, 2006).

For this test, approximately 800 grams of emulsion was poured through a #20 sieve. The emulsion remaining on the sieve was washed with distilled water in a squeeze bottle then placed in the oven at 110°C for 2 hours to evaporate the water out of the emulsion. Following the
removal from the oven, the sample was weighed, and the percent residue was calculated using

\[
Oversized\ Partsles,\ % = \left(\frac{B - A}{C - D}\right) \times 100
\] 

(9)

where:

\(A\) = Mass of sieve and pan (g)

\(B\) = Mass of sieve, pan, and residue (g)

\(C\) = Mass of full sample container (g)

\(D\) = Mass of empty sample container (g)

Rotational Viscosity

Viscosity is a main test for asphalt emulsions, and there are two different methods for
measuring the viscosity: Saybolt, and rotational. The rotational viscosity test (ASTM D7226-13,
2017) was used for this research project. Viscosity is important in the application of the
emulsion. In mix applications, the emulsion needs to have a low enough viscosity to coat
aggregate, but it needs to be high enough to form a suitable layer of asphalt emulsion around the
aggregate. In spray applications, the viscosity needs to be low enough to flow through the
spraying apparatus, but high enough to not run off of the road (Kadrmas, 2006).

The test makes use of a rotational paddle viscometer. According to ASTM Standard
D7226 (2017), the emulsion should first be poured through a #20 sieve to ensure there are no
oversized particles present. However, this was not performed in this study due to issues with the
emulsion being too thick to pass through the sieve. Therefore, the emulsion was poured directly
from the sample container into the sample cup until it reached the fill line.
The standard also states that the test should be conducted at the temperature corresponding to the emulsion grade set forth in ASTM Standard D2397 Specification for Cationic Emulsified Asphalt (2019). This means the CSS emulsion should have been tested at 25°C and the CMS emulsion should have been tested at 50°C. However, the rotational paddle viscometer that was available for testing the viscometer does not conduct tests at 25°C. Therefore, both emulsions were tested at 50°C.

**Particle Size Analysis**

There is not a specified ASTM or AASHTO standard specification to follow to conduct a particle size analysis using a Coulter counter for emulsified asphalt. The process is discussed in greater detail in the section titled Detailed Methods for Particle Size Analysis. In general, for this set of tests two asphalt emulsion samples were taken, and three runs for each sample were conducted in the Beckman Coulter Multisizer 4.

**Raveling**

The raveling test (ASTM D7196-18, 2018) is a test used to quantify the curing of compacted CIR samples. The results can be used to determine how different mixtures and curing times affect return to traffic and resistance to weather damage.

The CIR samples are batched, mixed, compacted, and cured. Following curing, the mass of the sample is recorded then abraded with a rubber hose on a Hobart HL120 mixer for 15 minutes in accordance with the standard. Once the test is complete, the mass of the abraded sample is determined again, and the percent mass loss is calculated using the following equation from ASTM D7196-18 (2018):
\[
\% \text{ Mass Loss} = \frac{A - B}{A} \times 100
\]  \hspace{1cm} (10)

where:

\(A\) = Mass of sample before raveling (g)

\(B\) = Mass of sample after raveling (g)

**Indirect Tensile (IDT) Strength**

The IDT Strength test (ASTM D6931-17, 2017) was used to evaluate the tensile strength of laboratory-mixed CIR specimens. This test was chosen in order to gather information about the strength of the mix. While the raveling test could reveal the specimen’s resistance to raveling relative to other samples, it does not give a strength value. Specimens were batched, mixed, compacted, and cured before being tested. The height of the cured sample was then measured at two points approximately 90° apart and the average height was recorded. The specimen was loaded into the IDT strength apparatus and loaded to failure. The file recorded by the connected computer was then analyzed and the maximum load was recorded. The IDT strength was calculated as follows (ASTM D6931-17, 2017):

\[
S_t = \frac{2000 \times P}{\Pi \times t \times D}
\]  \hspace{1cm} (11)

where:

\(S_t\) = IDT strength (kPa)

\(P\) = Maximum load (N)

\(t\) = Specimen height immediately before test (mm)
\[ D = \text{Specimen diameter (mm)} \]

**Creating Cold In-Place Recycling (CIR) Samples**

To begin creating CIR samples, the RAP obtained from Sharp’s quarry in Springdale, Arkansas was dried in a laboratory oven for at least 48 hours at 60°C. Once the RAP had been dried, it had to be split to size for each batch. This was done by following ASTM C702 Standard Method for Reducing Samples of Aggregate to Sample Size (2018). The RAP was split using a mechanical splitter until the sample weight was close to the required weight for the test. Then the weight of the split sample was adjusted with a scoop until the required sample weight was achieved. The samples were then placed into a plastic 6-inch diameter concrete cylinder mold.

Following batching, the samples were hydrated. This was done by first calculating the amount of water needed for each sample. The mix design approved by Paragon Technical Services, Inc. (PTSI) stated an amount of water equal to 6.8% of the dry RAP weight should be added. The amount of water required for each sample mass is provided in Table 10. Samples were hydrated at least 18-hours before being mixed, and the cylinders were sealed using a resealable bag and duct tape. Adding water 18-hours before testing is a step not mentioned in ASTM D7196-18 (2018). When cold in-place recycling is performed, the RAP is not dried before mixing unlike laboratory experiments. Adding water prior to mixing in the laboratory allows the RAP to reach a condition similar to an in-situ condition in the field before the mixing process begins.

**Table 10. Formulation for RAP Samples**

<table>
<thead>
<tr>
<th>Test</th>
<th>RAP (g)</th>
<th>Water (g)</th>
<th>Emulsion (g)</th>
<th>Gyrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raveling</td>
<td>2600</td>
<td>177</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>IDT Strength</td>
<td>2300</td>
<td>156</td>
<td>63</td>
<td>30</td>
</tr>
</tbody>
</table>
According to the mix design, Type I/II portland cement equal to 0.5% of the dry RAP weight along with asphalt emulsion equal to 2.75% of the dry RAP weight should be added to the RAP. However, results from a small experiment evaluating the effect of using cement in CIR mixes led to the decision to not use cement for the experimental matrix to prevent the presence of cement masking the effect of the emulsion formulation on its performance.

To mix the CIR samples, the RAP was placed into a metal bucket on a mixing stand. The mixer was turned on and the emulsion was added in a steady stream. The entire mixing process lasted for one minute. The sample was then transferred to a 6-inch diameter slotted Troxler mold. The sample was leveled with a spatula, and the top plate was placed on top of the sample. The sample was then placed inside the Troxler gyratory compactor, and the sample was compacted to the number of gyrations specified by the test.

Following compaction, the samples were removed from the mold and placed in an environmental chamber at 25°C around 20-25% humidity. The samples cured for 4-hours on porous stones to allow water to efficiently exit the sample. This was a deviation from ASTM D7196-18 (2018). Previous conversations with industry professionals discussing the limited curing of samples on a flat nonporous surface led to the decision to deviate from the specification.

**Detailed Methods for Particle Size Analysis**

The following section details the steps followed to test the particle size using a Beckman Coulter Multisizer 4.
Sample Preparation

One blank sample and two asphalt emulsion samples were created for each testing interval. To prepare the blank sample, 100 μL of the soap solution corresponding to the emulsion being tested was placed in an Accuvette vial. Then the vial was filled to the 10 mL mark with filtered electrolyte solution.

To create the emulsion samples, 10 mL of the soap solution corresponding to the emulsion being tested was placed in a 15 mL plastic centrifuge tube. Then a mechanical pipette with a disposable pipette tip was used to gather a drop of emulsion on the tip, and it was stirred into the soap solution in the centrifuge tube. This sample was further diluted by obtaining 100 μL of the emulsion and soap solution and placing it in an Accuvette vial which was then filled to the 10 mL mark with the filtered electrolyte solution.

Isoton II was the default electrolyte solution, however, there were chemical incompatibility issues when it was added to the soap solution for the commodity CMS emulsion. Attempts were made to disperse the CMS emulsion directly into the Isoton II without the addition of the soap solution, but the emulsion did not disperse well. After consulting Beckman Coulter about the issue, a decision was made to use 0.1M hydrochloric acid (HCl) as the electrolyte for the commodity CMS emulsion.

Another issue arose with the commodity CMS emulsion after switching to using HCl. Number counts were steep in the lower particle diameters, and analysis results were not desirable. After consulting with Beckman Coulter again, the recommendation was made to try not using the soap solution in the dilution process. This approach yielded good results. The revised sample preparation process for the commodity CMS emulsion began with adding 10 mL
of filtered HCl to a 15 mL plastic centrifuge tube. Then a mechanical pipette with a disposable pipette tip was used to gather a drop of emulsion on the tip, and it was stirred into the soap solution in the centrifuge tube. This sample was further diluted by obtaining 100 μL of the emulsion and soap solution and placing it in an Accuvette vial which was then filled to the 10 mL mark with filtered HCl. The blank sample for the commodity CMS emulsion also changed. The blank sample was simply 10 mL of filtered HCl.

The electrolyte solutions used were filtered with a 0.2 μm cellulose acetate filter. This filter was placed in a magnetic filter funnel which was attached to a Type II Class I filter flask that met the specifications of ASTM Specification E1406 (2016). Filtering the electrolyte solutions is important to the testing process because it eliminates noise in the lower particle diameters.

Apparatus Preparation

To begin preparing the Multisizer for testing, it was first turned on to allow time for stabilizing. Before each day of testing, the machine was subjected to a cleaning process in accordance with the User’s Manual (Beckman Coulter, 2008). The cleaning process consisted of four distinct phases. The four phases are cleaning with deionized water, cleaning with a bleach solution, cleaning with deionized water, and filling with filtered electrolyte.

For the cleaning phases, the analyzer was drained then filled with either deionized water or the bleach solution according to the cleaning process. The bleach solution was one-part bleach and three-parts deionized water. The deionized water came from an Elga Purelab Flex portable water system. Each cleaning liquid was filled and drained from the Multisizer three times before moving to the next liquid.
Once the cleaning liquids were passed through the machine, the Multisizer was filled with the filtered electrolyte solution appropriate for the emulsion, and the system was flushed three times.

**Testing Samples**

Once the apparatus was cleaned, the tests could be run. There are four types of control modes: time, volumetric, total count, and modal count. For these tests, the time control mode was used with a testing time of 15 seconds. There are also multiple aperture sizes that can be used ranging from 10 μm to 2000 μm. These tests used the 20 μm aperture. The sample was placed on the sample tray and the platform was raised to the testing position with the aperture opening submerged in the Accuvette cup.

To begin the test, the Preview procedure was selected, and the sample information was entered. As the concentration meter appeared, the sample concentration was checked to make sure the concentration was not rising above 10% per the recommendation of the User’s Manual (Beckman Coulter, 2008). The test was then started. The Multisizer performed the test for 15 seconds. The process was repeated at least two more times, sometimes more in order to produce up to 6 runs total. Initially, only three runs for each sample were conducted, however, 6 runs began to be conducted for each sample due to the ease and quickness of the test.

**RESULTS AND DISCUSSION**

After conducting numerous tests using the Multisizer, questions arose on how runs should be evaluated, what is considered a good run, and how the runs should be presented.
Number versus Volume

As mentioned before, Horiba (2012) detailed the importance of stating the basis of measurement when reporting statistical values of a particle distribution. Data collected during this experiment agreed with those results. Table 11 shows the difference between the statistics reported based on the basis of measurement. Figure 8 and Figure 9 show the visual differences between the number and volume bases of measurement.

Table 11. Number versus Volume Results

<table>
<thead>
<tr>
<th>Basis of Measurement</th>
<th>Number/ Volume (-) / (μm³)</th>
<th>Number%/ Volume % (%)</th>
<th>Mean (μm)</th>
<th>S.D.¹</th>
<th>d10 (μm)</th>
<th>d50 (μm)</th>
<th>d90 (μm)</th>
<th>Span (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number</td>
<td>1069</td>
<td>99.9</td>
<td>2.5</td>
<td>1.93</td>
<td>0.445</td>
<td>2.207</td>
<td>4.972</td>
<td>1.16</td>
</tr>
<tr>
<td>Volume</td>
<td>29921</td>
<td>99.99</td>
<td>6.628</td>
<td>2.65</td>
<td>3.159</td>
<td>6.595</td>
<td>10.31</td>
<td>1.48</td>
</tr>
</tbody>
</table>

¹S.D. – Standard Deviation

Emulsions statistics should be reported on a volume basis for two reasons. First, to maintain consistency with the asphalt emulsion community. In his document giving an overview of asphalt emulsions, Alan James (2006), provided a figure of a particle size distribution graph where the percent of total volume was related to particle diameter. His approach matched other researchers including Nuñez et al. (2000), Gingras et al. (2007), and Boucard et al. (2015). Second, using the reasoning of Horiba (2012), the volume basis provides a better representation of the physical distribution given a specified volume of emulsion. While a number distribution can give valuable information, a volume distribution provides a better visual representation of the distribution if it is thought about as a distribution of a fixed volume. Developing volume based graphs as well as proper utilization of number graphs is discussed further in the following paragraphs.
Graph Smoothing

The Multisizer software has the ability to provide size listings with varying levels of smoothing. Smoothing is accomplished by averaging a number of data points together. Figure 10
shows the original particle size distribution for a given sample without smoothing. The figures below show a progression of the number of data points averaged together to create a smoother graph.

In Figure 10, there appears to be several distinct rays from around 7 μm in diameter to the upper end of the x-axis. This corresponds to the number of particles counted for a given particle size diameter. The data points along the x-axis represent the sizes where 0 particles were counted for the given diameter. The first group above the x-axis corresponds to particle diameters where one particle was counted, and each ray following corresponds to one more particle counted than the last group.

For each group with the same number of particles counted, a positive trend is apparent. This is because a particle with a larger diameter will have a larger volume. A larger volume in turn, accounts for a larger portion of the volume than particles with a smaller diameter. This causes the spike in the upper diameters in Figure 9.

As the number of data points averaged together increases, the data produces a more aesthetically pleasing graph. The Multisizer software allows data smoothing up to 7 points averaged together. It is not clear why Beckman Coulter chose to limit the average to 7 data points, however, there must be a stopping point because a point would be reached where the averaged data is no longer representative of the original data.
Figure 10. Volume versus Particle Diameter with no Smoothing

Figure 11. Volume versus Particle Diameter Averaging Every Three Values
From the figures above, it is easy to see the visual effect of averaging data points together in order to produce a more fluid graph. Failing to employ data smoothing can result in cluttered graphs when overlaid with similar graphs for comparison as seen in Figure 14. While comparing
smoothed graphs may not be the most accurate, it provides figures with less variability to make comparing samples easier as seen in Figure 15.

**Figure 14. Cluttered Overlay Without Data Smoothing**

**Figure 15. Overlay with Averaging Every Seven Values**
Smoothness Due to Number of Particles Counted

Another method to achieve a smoother graph is by increasing the number of particles counted and volume of particles measured. Figure 16 shows three different particle size distributions with varying number of particles counted. As shown in Table 12, the High number count included 18,352 particles, the Medium number count included 5,206 particles, and the Low number count included 569 particles.

Table 12. Low, Medium, and High Number of Particles Counted and Volume of Sample Analyzed

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number Counted</th>
<th>Volume of Sample Analyzed (μm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>569</td>
<td>18,890</td>
</tr>
<tr>
<td>Medium</td>
<td>5,206</td>
<td>72,410</td>
</tr>
<tr>
<td>High</td>
<td>18,352</td>
<td>152,400</td>
</tr>
</tbody>
</table>

Figure 16. Smoothness of Distribution Due to Number of Particle Counted

On the surface, it is easy to see as the number count increases, the graph is smoother. This is most noticeable when the particle diameter is greater than 6 μm. For the Low number
count, the graph abruptly jumps on the y-axis compared to the other two samples. This is due to the power that a single, large diameter particle has compared to the total volume of the sample. In the lower count, a single 12 μm particle with a volume of 905 μm$^3$ in a total volume of 18,890 μm$^3$ accounts for 4.8% of the total volume. In the higher count, a single 12 μm particle with a volume of 905 μm$^3$ in a total volume of 152,400 μm$^3$ accounts for 0.6% of the total volume. Reducing the power a single particle count can have on the distribution is critical to achieving graph smoothness.

Because of this, a minimum number count or a minimum volume count is recommended in order to create smooth graphs representative of their sample. Based on Figure 16, it is recommended that at least 5,000 particles be counted after the blank run is subtracted, and at least 70,000 μm$^3$ of the sample is analyzed for each run.

**Compromised Samples**

A common source of error in this study came from compromised samples. Samples were considered compromised if there was a spike in the lower particle diameters of the number graph after the blank was subtracted. An example of this is shown in Figure 17. On first thought, this seems potentially catastrophic to the analysis. While this could give inaccurate information regarding the number basis, it seems to have little impact on the percent of the total volume in Figure 18.

Even though this impact is potentially minimal on the volume statistics, it would be best practice to only analyze distributions where the blank sample properly eliminates noise in the lower particle diameters. In order to minimize noise in the lower diameters, users should only use filtered electrolyte in the apparatus and the sample cup. Also, users should filter the soap
solution used in an attempt to minimize the particle diameters of the soap solution below the measuring threshold for the apparatus.

**Figure 17. Number versus Particle Diameter Compromised Sample**

**Figure 18. Volume versus Particle Diameter Compromised Sample**
Proposed Analysis Procedure

Given the lessons learned from the plethora of tests conducted, the following is a recommended analysis procedure for asphalt emulsion data using a Beckman Coulter Multisizer 4. Along with this recommended procedure, a draft ASTM specification is also provided as an appendix to this document.

To begin, the runs are opened in the software, the average blank run should be subtracted from each run. It is recommended that users conduct at least three runs with good results. In order to determine if the run is good, the runs should be overlaid with each other and analyzed.

Removing a Bad Run

During testing, blockages can occur in the aperture tube opening. This can be observed visually when runs are overlaid with one another in a number graph like in Figure 19. In Figure 19 four runs were conducted for the CSS design emulsion sample 1. During the 3rd run, it appears the aperture tube experienced a blockage resulting in a high count of small diameter particles. While it may be easy to identify these variances visually, it does not provide a standardized, scientific method to decide when a run should not be considered due to it not being an accurate representation of the sample. In order to try to determine a statistical way to evaluate whether or not to remove a run, the overlay statistics were gathered and analyzed. These are shown in Table 13.
Table 13. Overlay Statistics for the Blocked Run

<table>
<thead>
<tr>
<th>Number Statistics</th>
<th>Mean $\mu m$</th>
<th>S.D.$^1$ $\mu m$</th>
<th>Variance $\mu m^2$</th>
<th>Mode $\mu m$</th>
<th>d10 $\mu m$</th>
<th>d50 $\mu m$</th>
<th>d90 $\mu m$</th>
<th>Span $\mu m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>2.524</td>
<td>1.258</td>
<td>1.582</td>
<td>2.792</td>
<td>1.189</td>
<td>2.319</td>
<td>3.965</td>
<td>1.197</td>
</tr>
<tr>
<td>Run 2</td>
<td>2.526</td>
<td>1.255</td>
<td>1.574</td>
<td>2.521</td>
<td>1.207</td>
<td>2.325</td>
<td>3.968</td>
<td>1.188</td>
</tr>
<tr>
<td>Run 3</td>
<td>1.065</td>
<td>1.196</td>
<td>1.431</td>
<td>0.405</td>
<td>0.41</td>
<td>0.515</td>
<td>2.781</td>
<td>4.604</td>
</tr>
<tr>
<td>Run 4</td>
<td>2.505</td>
<td>1.224</td>
<td>1.499</td>
<td>2.542</td>
<td>1.2</td>
<td>2.303</td>
<td>3.905</td>
<td>1.175</td>
</tr>
<tr>
<td><strong>Avg</strong></td>
<td><strong>2.155</strong></td>
<td><strong>1.233</strong></td>
<td><strong>1.522</strong></td>
<td><strong>2.065</strong></td>
<td><strong>1.002</strong></td>
<td><strong>1.865</strong></td>
<td><strong>3.655</strong></td>
<td><strong>2.041</strong></td>
</tr>
<tr>
<td><strong>C.V.$^2$ (%)</strong></td>
<td><strong>33.70</strong></td>
<td><strong>2.40</strong></td>
<td><strong>4.70</strong></td>
<td><strong>53.90</strong></td>
<td><strong>39.40</strong></td>
<td><strong>48.30</strong></td>
<td><strong>16.00</strong></td>
<td><strong>83.73</strong></td>
</tr>
<tr>
<td><strong>S.D.$^1$</strong></td>
<td><strong>0.727</strong></td>
<td><strong>0.029</strong></td>
<td><strong>0.071</strong></td>
<td><strong>1.113</strong></td>
<td><strong>0.394</strong></td>
<td><strong>0.9</strong></td>
<td><strong>0.583</strong></td>
<td><strong>1.709</strong></td>
</tr>
<tr>
<td><strong>Max</strong></td>
<td><strong>2.526</strong></td>
<td><strong>1.258</strong></td>
<td><strong>1.582</strong></td>
<td><strong>2.792</strong></td>
<td><strong>1.207</strong></td>
<td><strong>2.325</strong></td>
<td><strong>3.968</strong></td>
<td><strong>4.604</strong></td>
</tr>
<tr>
<td><strong>Min</strong></td>
<td><strong>1.065</strong></td>
<td><strong>1.196</strong></td>
<td><strong>1.431</strong></td>
<td><strong>0.405</strong></td>
<td><strong>0.41</strong></td>
<td><strong>0.515</strong></td>
<td><strong>2.781</strong></td>
<td><strong>1.175</strong></td>
</tr>
</tbody>
</table>

$^1$S.D. – Standard deviation  
$^2$C.V. – Coefficient of variation

The statistics are split into two parts. The top section evaluates each run by calculating the mean, standard deviation, variance, mode, d10, d50, d90, and span. The span was manually calculated given the other values and added to the overlay statistics. The bottom section calculates the average, coefficient of variation, standard deviation, maximum, and minimum.
values for each statistic between all the runs. Taking the mean for example, the average mean between the four runs is 2.155 $\mu$m, the coefficient of variation of the four means is 33.70%, the standard deviation of the means was 0.727 $\mu$m, the maximum mean was 2.526 $\mu$m, and the minimum mean was 1.065 $\mu$m.

Upon inspection of the upper section of the table, the mean of Run 3 is 1.4-1.5 $\mu$m smaller than the rest of the runs. This along with the fact that the coefficient of variation for the mean is 33.70% is concerning. In an attempt to understand the impact Run 3 has on the data, it was removed, and the statistics were compared again. This is shown in Table 14.

Table 14. Overlay Statistics Without Run 3

<table>
<thead>
<tr>
<th>Number Statistics</th>
<th>Mean $\mu$m</th>
<th>S.D. $\mu$m</th>
<th>Variance $\mu$m$^2$</th>
<th>Mode $\mu$m</th>
<th>d10 $\mu$m</th>
<th>d50 $\mu$m</th>
<th>d90 $\mu$m</th>
<th>Span $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>2.524</td>
<td>1.258</td>
<td>1.582</td>
<td>2.792</td>
<td>1.189</td>
<td>2.319</td>
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<tr>
<td>Run 2</td>
<td>2.526</td>
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<td>1.574</td>
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<td>2.325</td>
<td>3.968</td>
<td>1.188</td>
</tr>
<tr>
<td>Run 4</td>
<td>2.505</td>
<td>1.224</td>
<td>1.499</td>
<td>2.542</td>
<td>1.2</td>
<td>2.303</td>
<td>3.905</td>
<td>1.175</td>
</tr>
<tr>
<td>Avg</td>
<td>2.518</td>
<td>1.246</td>
<td>1.552</td>
<td>2.618</td>
<td>1.199</td>
<td>2.316</td>
<td>3.946</td>
<td>1.186</td>
</tr>
<tr>
<td>C.V. (%)</td>
<td>0.50</td>
<td>1.50</td>
<td>3.00</td>
<td>5.70</td>
<td>0.80</td>
<td>0.50</td>
<td>0.90</td>
<td>0.95</td>
</tr>
<tr>
<td>S.D.</td>
<td>0.011</td>
<td>0.018</td>
<td>0.046</td>
<td>0.151</td>
<td>0.0092</td>
<td>0.011</td>
<td>0.036</td>
<td>0.011</td>
</tr>
<tr>
<td>Max</td>
<td>2.526</td>
<td>1.258</td>
<td>1.582</td>
<td>2.792</td>
<td>1.207</td>
<td>2.325</td>
<td>3.968</td>
<td>1.197</td>
</tr>
<tr>
<td>Min</td>
<td>2.505</td>
<td>1.224</td>
<td>1.499</td>
<td>2.521</td>
<td>1.189</td>
<td>2.303</td>
<td>3.905</td>
<td>1.175</td>
</tr>
</tbody>
</table>

1S.D. – Standard deviation
2C.V. – Coefficient of variation

The statistics shown in the bottom portion of Table 14 are significantly different than those shown in Table 13. For the mean, the coefficient of variance dropped from 33.70% to 0.50%. This drop in the coefficient of variance is seen across all the statistical values gathered. Seeing these drops leads to the conclusion that the coefficient of variance between runs should be used to identify whether a run is considered accurate enough to be considered in the average. It is recommended that the combination of runs be acceptable if the coefficient of variation of the
mean particle diameter using the number basis is less than 5%. If the coefficient of variation is above 5%, the run causing the high coefficient of variation should be removed, and another test shall be run to replace it.

This is one of the only situations where it is recommended to use the number basis of measurement rather than using the volume basis of measurement. This is because the graphs in this study have shown a large amount of variation in the larger particle diameters of the volume basis. Using the number basis for this analysis will allow decisions to be made regarding the accuracy of a run while capitalizing on the minimal variability in the graphs.

Combining Runs

Once there are at least three good runs for a single sample, the data should be combined. This process can be using the Multisizer software, but it can also be done manually. To produce the average results manually, the size listing for each run is obtained from the software. The total particle counts for each diameter bin from the number basis is added and divided by the number of runs. The same happens for the volume of particles counted for each particle diameter bin. The result is an average number and volume of particles counted for each particle size bin. The result is distributions in either the number, percent of total number, volume, or percent of total volume. At this point, the samples can be compared with the other two samples. It is important to note the average blank run will have to be re-loaded for the new, averaged run.
Combining Samples

A similar process should take place when combining samples. Rather than opening individual run files, the samples should be opened and overlaid. Similar to the runs, the overlay statistics should be analyzed for accurate runs. If the coefficient of variation of the mean particle size in the number basis is greater than 5%, the inaccurate run should be discarded, and a new sample should be created and tested. Once the user has at least three good samples, the samples can be averaged to produce a single sample representative of the asphalt emulsion.

Reporting Results

The Multisizer software can provide a plethora of statistics and meaningful values. However, reporting every value available would only result in clutter and chaos. In order to justify which statistics to report, RStudio was utilized. The ggpairs function from the GGally package was used to identify correlations between the results from the residue, sieve, rotational viscosity, raveling, and IDT strength tests and the particle size data including the mean, \( d_{10} \), and \( d_{50} \).
d$_{90}$, span, and standard deviation. The correlations are shown in Table 15, and the excel file read, input code, and output are shown in Appendix C: RStudio Input and Output. It is important to note, that although statistics are being used to make this recommendation, they should not be taken as definite conclusive values because the data used in this analysis was not a partial or full experimental design. At best, these correlations are general trends seen in the data.

### Table 15. Correlations ($r$) Between Tests and Particle Size Data

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>$d_{10}$</th>
<th>$d_{50}$</th>
<th>$d_{90}$</th>
<th>Span</th>
<th>S.D.$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue</td>
<td>0.417</td>
<td>0.382</td>
<td>0.416</td>
<td>0.466</td>
<td>-0.188</td>
<td>0.434</td>
</tr>
<tr>
<td>Sieve</td>
<td>0.308</td>
<td>0.219</td>
<td>0.296</td>
<td>0.407</td>
<td>-0.0379</td>
<td>0.438</td>
</tr>
<tr>
<td>Viscosity</td>
<td>-0.548</td>
<td>-0.565</td>
<td>-0.543</td>
<td>-0.574</td>
<td>0.427</td>
<td>-0.474</td>
</tr>
<tr>
<td>Raveling</td>
<td>-0.137</td>
<td>-0.137</td>
<td>-0.0996</td>
<td>-0.164</td>
<td>0.124</td>
<td>-0.199</td>
</tr>
<tr>
<td>IDT Strength</td>
<td>-0.144</td>
<td>-0.114</td>
<td>-0.171</td>
<td>-0.196</td>
<td>-0.0395</td>
<td>-0.144</td>
</tr>
</tbody>
</table>

$^1$S.D. – Standard Deviation

Table 16 shows the categories of the correlation strength based on its value. These ranges were based off the notes from Dr. John Tipton’s class STAT 4003: Statistical Methods at the University of Arkansas (2019).

### Table 16. Correlation Strength (Tipton, 2019)

<table>
<thead>
<tr>
<th>Strength</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>$</td>
</tr>
<tr>
<td>Moderate</td>
<td>$0.4 &lt;</td>
</tr>
<tr>
<td>Strong</td>
<td>$</td>
</tr>
</tbody>
</table>

Using the information from Table 15 and Table 16, the correlations were grouped by their strength and organized in Table 17.
Table 17. Correlations Grouped by Strength

<table>
<thead>
<tr>
<th>Weak</th>
<th>Moderate</th>
<th>Strong</th>
</tr>
</thead>
<tbody>
<tr>
<td>[</td>
<td>r</td>
<td>&lt; 0.4]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mean</th>
<th>(d_{50})</th>
<th>Span</th>
<th>Mean</th>
<th>(d_{90})</th>
<th>Span</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Sieve</td>
<td>• Raveling</td>
<td>• IDT Strength</td>
<td>• Residue</td>
<td>• Viscosity</td>
<td>• Viscosity</td>
</tr>
<tr>
<td>• Raveling</td>
<td>• IDT Strength</td>
<td></td>
<td>• Sieve</td>
<td>• Viscosity</td>
<td></td>
</tr>
<tr>
<td>• IDT Strength</td>
<td></td>
<td></td>
<td>• Raveling</td>
<td>• Viscosity</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(d_{10})</th>
<th>S.D.</th>
<th>(d_{90})</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Sieve</td>
<td>• Raveling</td>
<td>• IDT Strength</td>
<td>• Residue</td>
</tr>
<tr>
<td>• Raveling</td>
<td>• IDT Strength</td>
<td></td>
<td>• Residue</td>
</tr>
<tr>
<td>• IDT strength</td>
<td></td>
<td></td>
<td>• Residue</td>
</tr>
</tbody>
</table>

Based on this analysis, there was a moderate correlation between all the particle size parameters recorded and the viscosity results. This seems to support the idea that particle size could potentially be used to predict viscosity performance. Also, the mean, \(d_{50}\), \(d_{90}\), and standard deviation results displayed moderate correlations with the residue test results. This is an odd observation because in theory, the residue results should remain the same among the emulsions regardless of particle size. Lastly, the \(d_{90}\) and standard deviation displayed moderate correlations with the sieve test results. There were not any strong correlations observed in the analysis. However, it is not clear which value or values should be used to characterize the distribution.

As mentioned before, Horiba (2012) suggests using more than one parameter to describe a particle size distribution. This can be done by providing \(d_{10}\), \(d_{50}\), and \(d_{90}\) values, Horiba’s span calculation, or standard deviation among other parameters. It is recommended that the guidance from Horiba is used. While the mean or \(d_{50}\) can provide useful information, it does not yield
information regarding the tightness of the distribution like the span. The span also displayed a moderate correlation with the viscosity test suggesting its potential usefulness.

Based on correlations, the mean and d50 values provided similar correlations. While the mean provided slightly better correlations, it can be more sensitive to outlier values in the distribution than the more robust d50 parameter which is influenced less by extreme observations (Diez, Barr, & Cetinkaya-Rundel, 2015). However, the d50 parameter is used in calculating the span. Because of this, it is not recommended to only report d50. Based on the correlations, information from Diez et al., and the recommendation from Horiba Instruments (2012) to report a value describing the distribution, it is recommended that at a minimum, the mean, d50, and span, all in the volume basis, should be reported in the final results to characterize the particle size distribution.

CONCLUSION

Across the United States, almost all of the paved roadways utilize an asphalt pavement surface. The abundance of asphalt in our country warrants the attention of researchers to make sure the money of taxpayers is being used to its full potential. Over time, flexible pavements will deteriorate, and it is to the economic advantage of the owner to preserve, maintain, and rehabilitate roadways. In order to use some of the treatments, asphalt emulsions must be used.

There are many formulation parameters that influence the material properties of an asphalt emulsion including water quality, emulsifier type, emulsifier dosage, soap solution pH, and mill properties. These formulation parameters in turn influence the viscosity, residue properties, storage stability, and particle size of the asphalt emulsion.
Work has been conducted to evaluate the influence of emulsion particle size on its storage stability, but research lacks in relating the performance of an asphalt emulsion to its particle size. Research also lacks in the procedures for conducting particle size analyses for asphalt emulsions using a coulter counter and analyzing results.

Eight emulsions were made and tested to help develop a recommended procedure for testing and analyzing test results along with a draft ASTM specification was produced. Among these procedures, several key recommendations were made. First, when analyzing an asphalt emulsion, 3 samples should be created, and each sample should be tested three times. Next, after subtracting the average blank from each run, the run should have a number count of at least 5,000 particles and a total volume measured of at least 70,000 μm³.

Next, when combining runs and samples, the coefficient of variation of the particle diameter mean in the number basis should be less than 5%. Also, when showing graphs or comparing data on graphs, it is recommended to show volume % versus particle diameter, and the graphs should be smoothed by averaging up to seven data points together.

Finally, the ggpairs function was used in RStudio to identify potential correlations between particle size and the additional test results. The test identified moderate correlations between the viscosity test and the mean, d₁₀, d₅₀, d₀₀, span and standard deviation of -0.548, -0.565, -0.543, -0.574, 0.427, and -0.474 respectively. These moderate correlations support the idea that particle size could be used to predict viscosity.

Based on the correlations between the original experimental matrix tests and the particle size analysis results, at a minimum, the mean, d₅₀, and span should be reported in the volume basis as final results to describe the particle size distribution. It is also noted that the correlation
analysis utilized data from an incomplete experimental matrix, and it should only be taken as
general trends, not definitive results.

This research exploring the best practices for using a Coulter counter for measuring the
particle distribution of asphalt emulsions has only scratched the surface of the topic.
Recommended topics for future work include:

- Creating a correlation between results using Coulter counters and laser diffraction
  analyzers
- Exploring the use of different control methods to characterize asphalt emulsion
  particle size, and identifying which is best
- Identifying an approved electrolyte solution compatible with most asphalt
  emulsion soap solutions
- Evaluate the influence of changing multiple formulation factors at the same time
  on particle size and other material properties
- Research how particle size distribution affects coating of aggregate and field
  performance
REFERENCES


Horiba Instruments. (2012). *A Guidebook to Particle Size Analysis*.


APPENDICIES

Appendix A: Draft ASTM Specification

The ASTM draft specification begins on the next page.
Standard Test Method for
Particle Size of Emulsified Asphalts Using Electrical Sensing Zone Method

This standard is issued under the fixed designation D XXX; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method utilizes a particle size analyzer that used the electrical sensing zone method to determine key values that describe the particle size distribution of emulsified asphalt.

It is applicable to all emulsifier asphalts described in Specification D977 and D2397.

1.2 A precision and bias statement for this standard has not been developed at this time.

Therefore, this standard should not be used for acceptance or rejection of a material for purchasing purposes.

1.3 Units - The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

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*This test method is under the jurisdiction of ASTM Committee and is the direct responsibility of Subcommittee D04.41.*

Current edition: approved XXX, XX, XXXX. Published XX XXXX. DOI:10.1520/XXXXXX

*This specification was developed using a Beckman Coulter Multisizer 4. Other apparatuses that use the electrical sensing zone method may vary slightly in their processes.*

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2. Referenced Documents

2.1 ASTM Standards:

D140/D140M: Standard Practice for Sampling Asphalt Materials

D977: Standard Specification for Emulsified Asphalt

D2397: Standard Specification for Cationic Emulsified Asphalt

E832: Standard Specification for Laboratory Filter Papers

E1406: Standard Specification for Laboratory Glass Filter Flasks

3. Terminology

3.1 Definitions:

3.1.1 Equivalent spherical diameter – the final particle size reported whose volume is equivalent to the volume of the particle recorded by the apparatus.

3.1.2 Particle size – the equivalent spherical diameter corresponding to the volume of the droplet of emulsified asphalt measured by the apparatus (μm).

3.1.3 Particle size distribution – the range and occurrence frequency of particles of a given material. Typically expressed as a graph of number of particles or volume of particles versus the particle diameter.

3.1.4 Run – one repetition of a test.

3.1.5 Sample – a physical sample used for testing purposes.

4. Summary of Test Method
4.1 An emulsified asphalt sample is created and tested in a particle size analyzer that uses the electrical sensing zone method. The apparatus records pertinent information including the number of particles counted, volume of particles measured, mean, median, d10, d50, and d90.

5. Significance and Use

5.1 Research shows a significant link between the particle size and distribution of emulsified asphalt and its stability. Determining the particle size and characterizing the distribution of a sample can help predict the stability and performance of the emulsified asphalt.

6. Apparatus

6.1 Coulter Counter – The work conducted to produce this specification utilized a Multisizer 4 from Beckman Coulter along with the software supplied with the instrument. Using a different apparatus may require slightly different steps than those detailed in this specification.

6.2 Beckman Accucette ST Vial, 25 mL – These cups will be used to hold the sample suspended in the electrolyte solution, Isoton II.

6.3 Adjustable Volume Mechanical Pipette, 100 μL – An adjustable volume mechanical pipette capable of transferring at least 100 μL of liquid.

6.4 Pipette Tips, 100 μL – A pipette tip that is compatible with the 100 μL pipette selected to aid in the transfer of liquids.

6.5 15 mL Centrifuge Tube – A plastic centrifuge tube capable of holding at least 15 mL of liquid.
6.6 Filter Flask, Type II Class 1 – A Type II Class 1 filter flask in accordance with Specification E1406.

6.7 Magnetic Filter Funnel – a magnetic filter funnel compatible with the filter flask selected.

6.8 Cellulose Acetate Filter – A sterile filter with a pore size opening of 0.2 μm with a diameter compatible with the magnetic filter funnel chosen.

6.9 Sterile Syringe, 10 mL – A sterile syringe capable of holding and transferring at least 10 mL of liquid.

6.10 Sterile Syringe Filter, 0.2 μm opening – A sterile syringe filter compatible with the sterile syringe chosen with a pore opening of 0.2 μm in accordance with Specification E832.

7. Reagents and Materials

7.1 Emulsified Asphalt – emulsified asphalt sampled in accordance with D140/D140M.

7.2 Soap Solution – A soap solution matching the soap used to create the emulsified asphalt. This can be achieved by manufacturing extra soap during the production process.

7.3 Isoton II – A proprietary electrolyte solution produced by Beckman Coulter.

7.4 Purified Lab Water – Water that has been distilled and deionized using equipment similar to the Elga Process Water System Purelab Flex 4.

7.5 Common Bleach – regular bleach used for cleaning purposes.

8. Sampling, Test Specimens, and Test Units

8.1 Sample emulsified asphalt in accordance with ASTM D140/D140M.
8.2 All emulsions with viscosity requirements of 50°C should be heated to 50 ± 3°C in the original sample container in a water bath or oven. The container should be vented to relieve pressure. After the sample reaches 50°C, stir the sample with a glass rod to achieve homogeneity. If the sample temperature is greater or less than 50°C, then it should be conditioned to the required test temperature.

8.3 Emulsified asphalts with a viscosity testing temperature requirement of 25°C should be conditioned at 25 ± 3°C in the original sample container to achieve homogeneity.

8.4 Prepare Three Emulsified Asphalt Samples

8.4.1 Using a 10 mL disposable sterile syringe and a 0.2 µm cellulose acetate sterile syringe filter, put 10mL of filtered soap solution into a 15 mL centrifuge tube. Using the mechanical pipette and 100 µL pipette tip, obtain a drop of emulsified asphalt from the sample container, and add it to the soap solution in the centrifuge tube aiding the mixture by manually stirring of the pipette. Further dilute the sample by obtaining 100 µL of the soap and emulsified asphalt mixture and place in a 25 mL Accuvette vial. Using a squeeze bottle filled with filtered Isoton II, fill Accuvette vial to the 10 mL mark. This is sample number one. Repeat this process for the remaining two samples.

8.4.2 Chemical incompatibility could occur between the soap solution and the Isoton II. This is apparent when the solution becomes cloudy when the Isoton II is added to the soap solution. If this occurs, then the user should attempt to use another approved electrolyte solution. Approved electrolyte solutions can be found in the user manual for the coulter counter.

8.5 Prepare Blank Sample
8.5.1 Using a 10 mL disposable sterile syringe and a 0.2 \( \mu \text{m} \) cellulose acetate sterile syringe filter, put 10mL of filtered soap solution into a clean beaker. Then use the mechanical pipette and 100 \( \mu \text{L} \) pipette tip, and place 100 \( \mu \text{L} \) of filtered soap solution in an empty Accuvette vial. Using a squeeze bottle, fill the Accuvette vial to the 10 mL mark with filtered Isoton II.

9. **Preparation of Apparatus**

9.1 Supplemental information can be found in Beckman Coulter’s User Manual\(^1\).

9.2 *Filtering Isoton II* – Using unfiltered electrolyte solution in the analysis process can add noise to the particle size distribution. This can skew results leading to a particle size distribution that is not representative of the distribution of the emulsified asphalt.

9.2.1 Set up a Type II Class 1 filter flask, a magnetic filter funnel, and a 0.2 \( \mu \text{m} \) pore size cellulose acetate filter and attach a rubber tube from the flask to the vacuum line. Add Isoton II to the filter funnel, and open vacuum valve. Close the valve when all the liquid has been filtered. Ensure electrolyte is draining into beaker and not going through vacuum tube.

9.3 Ensure the correct aperture tube is attached to the machine and change it if necessary. Change the aperture tube by following the steps listed in the Change Aperture Tube Wizard. It is housed under the Run tab.

9.4 *Cleaning the Multisizer*

9.4.1 Begin by emptying the waste jar. Then remove the electrolyte jar and pour electrolyte in a clean beaker. Drain the Multisizer by using the Drain procedure located on the bottom toolbar.
9.4.2 Using deionized water, rinse out the electrolyte jar, and fill the jar with deionized water. Place the electrolyte jar into the Multisizer. Run the Fill and Drain procedures (located on the bottom toolbar) on the Multisizer three times with deionized water. Before commencing the Drain procedure, remove the electrolyte jar then replace it after the Drain procedure has finished. Run the Empty Waste Tank procedure as necessary. Remove electrolyte jar, and empty.

9.4.3 Fill electrolyte jar with a mixture containing one-part bleach and three parts water. Run the Fill and Drain procedures three times with water and bleach solution. Before commencing the drain procedure, remove the electrolyte jar then replace it after the Drain procedure has finished. Run the Empty Waste Tank procedure as necessary. Remove electrolyte jar, and empty.

9.4.4 Using deionized water, rinse out the electrolyte jar, and fill the jar with deionized water. Place the electrolyte jar into the Multisizer. Run the Fill and Drain procedures (located on the bottom toolbar) on the Multisizer three times with deionized water. Before commencing the Drain procedure, remove the electrolyte jar then replace it after the Drain procedure has finished. Run the Empty Waste Tank procedure (located on the bottom toolbar as Empty) as necessary. Remove electrolyte jar, and empty.

9.4.5 Fill electrolyte jar with filtered Isoton II. Run the Fill procedure (located on the bottom toolbar) on the Multisizer. Conduct the Flush procedure (located on the bottom toolbar) three times.

10. Calibration and Standardization

10.1 Calibrate the Multisizer at periodic intervals or when the aperture tube or electrolyte solution in the machine is changed.
10.2 Choose an appropriate particle standard that is 10-20% of the aperture size.

10.3 Fill a 25 mL Accuvette vial with 20 mL of filtered Isoton II. Add a few drops of the calibrator beads to the Accuvette vial. Place the filled Accuvette vial on the platform. Select the Preview procedure, and verify the concentration is as close as possible to 10%. If it is below 10%, slowly add calibrator beads until the 10% concentration is met. If the concentration is above 10%, repeat the step from the beginning using less calibrator beads.

10.4 Select the Aperture Calibration Options menu housed under the Calibration tab. Choose the calibration basis according to the assay sheet provided with the calibrator beads. Input modal size of calibrator beads listed in the assay sheet provided with the calibrator beads. Click Start. Once the apparatus completes the calibration process, click the Accept New Kd button in the dialogue box.

11. Procedure

11.1 Lower the sample tray while spraying aperture tube with filtered Isoton II with a spray bottle. Remove existing Accuvette vial from the machine and dispose of liquid.

11.2 Place the Accuvette vial containing the blank run on the tray and raise the tray to the proper testing position.

11.3 Load the proper Standard Operating Procedure (SOP) file in the software. Input proper sample information under the Edit Sample Info button.

11.4 Click the Preview button (located on the bottom toolbar). Ensure the sample concentration is below 10%. If the sample concentration is above 10%, run the Flush an Unblock procedures (located on the bottom toolbar). If the concentration remains above 10%, recreate
sample starting at 9.2 using less emulsified asphalt. Press the Start button, verify the sample information is correct, and commence test. Once the test is finished, ensure that at least 5,000 particles were counted, and the volume of particles measured is at least 70,000 μm³. Repeat process at least two more times (two more runs). Conduct at least three runs total.

11.5 Repeat process for the three samples containing emulsified asphalt.

12. Calculation or Interpretation of Results

12.1 Open all runs for blank as an overlay. Open overlay statistics while viewing a number basis graph. Ensure the coefficient of variation (C.V.) of the mean particle size is less than 5%. If it is not, remove the run causing the source of variation. Retest samples as necessary to achieve at least three runs. Once three good runs have been conducted and verified, average run together.

12.2 Open runs for sample 1 as an overlay. Open overlay statistics while viewing a number basis graph. Ensure the coefficient of variation (C.V.) of the mean particle size is less than 5%. If it is not, remove the run causing the source of variation. Retest samples as necessary to achieve at least three runs. Once three good runs have been conducted and verified, average run together. Load the average blank run as the blank for the sample. Repeat process for all samples.

12.3 Open all samples as an overlay. Open overlay statistics while viewing a number basis graph. Ensure the coefficient of variation (C.V.) of the mean particle size is less than 5%. If it is not, remove the sample causing the source of variation, create a new sample, and repeat the testing and analysis process for the sample. Once three good samples have been conducted and verified, average samples together. Load the average blank run as the blank for the averaged sample file.
12.4 Change views to the Volume % graph, open the Statistics under the Calculation tab and record the following statistics: mean, median, $d_{10}$, $d_{50}$, $d_{90}$.

12.5 Calculate the span of the particle size distribution

$$S = \frac{(d_{90} - d_{10})}{d_{50}}$$

where:

- $S =$ span, µm
- $d_{90} =$ diameter at which 90% of the particles are smaller
- $d_{10} =$ diameter at which 10% of the particles are smaller
- $d_{50} =$ diameter at which 50% of the particles are smaller

13. Report

13.1 Report the following using the volume basis of measurement: mean, $d_{50}$, and span.

14. Precision and Bias

14.1 Since a precision estimate for this standard has not been developed, this test method is to be used for research or informational purposes only. Therefore, this standard should not be used for acceptance or rejection of a material for purchasing purposes.

15. Keywords

15.1 particle size analysis, emulsified asphalt, Beckman Coulter Multisizer, Coulter method
Appendix B: Additional Results

The following tables show hourly results along with percent changes from the design emulsions. The following figures show various test results over time.
### Table 18. 2-hour CSS Data

<table>
<thead>
<tr>
<th>Viscosity</th>
<th>Raveling</th>
<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prop CSS</td>
<td>262.6</td>
<td>13.8</td>
<td>49.5</td>
<td>4.926</td>
<td>2.391</td>
<td>4.240</td>
<td>8.683</td>
<td>1.484</td>
</tr>
<tr>
<td>CSS_DH_PH_MH</td>
<td>446.3</td>
<td>14.3</td>
<td>66.7</td>
<td>4.794</td>
<td>2.331</td>
<td>4.110</td>
<td>8.490</td>
<td>1.499</td>
</tr>
<tr>
<td>CSS_DL_PL_MH</td>
<td>128.1</td>
<td>14.0</td>
<td>56.5</td>
<td>5.185</td>
<td>2.405</td>
<td>4.608</td>
<td>9.044</td>
<td>1.441</td>
</tr>
<tr>
<td>CSS_DL_PH_ML</td>
<td>55.3</td>
<td>17.0</td>
<td>53.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 19. 2-hour CSS Percent Different

<table>
<thead>
<tr>
<th>Viscosity</th>
<th>Raveling</th>
<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prop CSS</td>
<td>262.6</td>
<td>13.8</td>
<td>49.5</td>
<td>4.926</td>
<td>2.391</td>
<td>4.240</td>
<td>8.683</td>
<td>1.484</td>
</tr>
<tr>
<td>CSS_DH_PH_MH</td>
<td>69.9%</td>
<td>4.0%</td>
<td>34.5%</td>
<td>-2.7%</td>
<td>-2.5%</td>
<td>-3.1%</td>
<td>-2.2%</td>
<td>1.0%</td>
</tr>
<tr>
<td>CSS_DL_PL_MH</td>
<td>-51.2%</td>
<td>1.8%</td>
<td>14.1%</td>
<td>5.3%</td>
<td>0.6%</td>
<td>8.7%</td>
<td>-2.9%</td>
<td>3.3%</td>
</tr>
<tr>
<td>CSS_DL_PH_ML</td>
<td>-79.0%</td>
<td>23.2%</td>
<td>7.2%</td>
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<tr>
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<td>-20.1%</td>
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</table>

### Table 20. 1-Day CSS Data

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<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
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<tr>
<td>Prop CSS</td>
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<td>5.0</td>
<td>63.9</td>
<td>4.756</td>
<td>2.365</td>
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<td>8.183</td>
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<td>755.0</td>
<td>12.8</td>
<td>58.1</td>
<td>4.851</td>
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<td>4.129</td>
<td>8.740</td>
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<td>6.384</td>
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### Table 21. 1-Day CSS Percent Different

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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
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<td>2.0%</td>
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<td>-0.1%</td>
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<td>10.5%</td>
<td>7.8%</td>
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<td>202.5%</td>
<td>-22.1%</td>
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<tr>
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<td>321.1%</td>
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<td>-17.0%</td>
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### Table 22. 4-Day CSS Data

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<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
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<td>67.2</td>
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<td>4.065</td>
<td>8.320</td>
<td>1.476</td>
<td>2.30</td>
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<td>10.040</td>
<td>1.576</td>
<td>2.75</td>
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<td>50.0</td>
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<td>6.166</td>
<td>10.680</td>
<td>1.241</td>
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### Table 23. 4-Day CSS Percent Different

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<th>Raveling</th>
<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSS_DH_PH_MH</td>
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<td>-0.8%</td>
<td>-1.6%</td>
<td>-1.4%</td>
<td>-0.7%</td>
<td>1.0%</td>
<td>-0.9%</td>
</tr>
<tr>
<td>CSS_DL_PL_MH</td>
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<td>-</td>
<td>16.0%</td>
<td>2.5%</td>
<td>17.3%</td>
<td>19.8%</td>
<td>7.9%</td>
<td>18.5%</td>
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</tr>
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<td>CSS_DL_PH_ML</td>
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<td>-25.1%</td>
<td>37.0%</td>
<td>28.4%</td>
<td>49.6%</td>
<td>27.4%</td>
<td>-15.1%</td>
<td>19.4%</td>
</tr>
<tr>
<td>CSS_DH_PL_ML</td>
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<td>950.5%</td>
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<td>-14.8%</td>
<td>-16.7%</td>
<td>-19.7%</td>
<td>-8.9%</td>
<td>17.4%</td>
<td>-1.3%</td>
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</tbody>
</table>
### Table 24. 7-Day CSS Data

<table>
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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
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<tr>
<td>Prop CSS</td>
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<td>4.080</td>
<td>7.393</td>
<td>1.242</td>
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<td>67.1</td>
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### Table 25. 7-Day CSS Percent Different

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<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prop CSS</td>
<td>15.2</td>
<td>53.2</td>
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### Table 26. 2-hour CMS Data

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<th>Mean</th>
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<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
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<td>Comm CMS</td>
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<td>29.9</td>
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<td>29.1</td>
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<td>#DIV/0!</td>
<td>16.48</td>
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Table 27. 2-hour CMS Percent Different

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<th>IDT</th>
<th>Mean</th>
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<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
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Table 28. 1-Day CMS Data

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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comm CMS</td>
<td>69.4</td>
<td>23.4</td>
<td>29.7</td>
<td>7.030</td>
<td>3.222</td>
<td>6.888</td>
<td>11.020</td>
<td>1.132</td>
<td>2.88</td>
</tr>
<tr>
<td>CMS_DH_PH_ML</td>
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<td>22.0</td>
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Table 29. 1-Day CMS Percent Different

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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comm CMS</td>
<td>69.4</td>
<td>23.4</td>
<td>29.7</td>
<td>7.030</td>
<td>3.222</td>
<td>6.888</td>
<td>11.020</td>
<td>1.132</td>
<td>2.88</td>
</tr>
<tr>
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<td>-30.6%</td>
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Table 30. 4-Day CMS Data

<table>
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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comm CMS</td>
<td>189.8</td>
<td>22.1</td>
<td>31.5</td>
<td>6.904</td>
<td>3.333</td>
<td>6.751</td>
<td>10.940</td>
<td>1.127</td>
<td>2.70</td>
</tr>
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### Table 31. 4-Day CMS Percent Different

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<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
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</thead>
<tbody>
<tr>
<td>Prop CSS</td>
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<td>22.1</td>
<td>31.5</td>
<td>6.904</td>
<td>3.333</td>
<td>6.751</td>
<td>10.940</td>
</tr>
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</tr>
<tr>
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<td>-100.0%</td>
<td>-13.8%</td>
<td>-24.8%</td>
<td>-24.6%</td>
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### Table 32. 7-Day CMS Data

<table>
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<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
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### Table 33. 7-Day CMS Percent Different

<table>
<thead>
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<th>Raveling</th>
<th>IDT</th>
<th>Mean</th>
<th>d10</th>
<th>d50</th>
<th>d90</th>
<th>Span</th>
<th>SD</th>
</tr>
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<td>Comm CMS</td>
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<td>752.1</td>
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<td>20.0</td>
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<td>-53.2%</td>
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</table>
Figure 21. Proprietary CSS Viscosity Over Time

Figure 22. Proprietary CSS Raveling Over Time
Figure 23. Proprietary CSS IDT Strength Over Time

Figure 24. Proprietary CSS Mean Particle Size Over Time
Figure 25. Proprietary CSS Span Over Time

Figure 26. Proprietary CSS Sieve Test Results
Figure 27. Commodity CMS Viscosity Over Time

Figure 28. Commodity CMS IDT Strength Over Time
Figure 29. Commodity CMS Raveling Over Time

Figure 30. Commodity CMS Mean Particle Size Over Time
Figure 31. Commodity CMS Span Over Time

Figure 32. Commodity CMS Sieve Results
Appendix C: RStudio Input and Output

The following images show the RStudio input, initial excel table used in the analysis and RStudio output of the ggpairs function.

Figure 33. RStudio Code to Run ggpairs Function
Figure 34. Excel Table Used in `ggpairs` Analysis
Figure 35. RStudio Output from ggpairs Function