Bio-Solvents in the Production of Emulsified Prime Coat Systems

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ABSTRACT

Petroleum-based solvents are widely used in the production of Emulsified Asphalt Primer (EAP). These solvents have the capability of lowering the viscosity of asphalt and enabling the emulsified asphalt primer to penetrate through the tightly knitted surface of compacted granular base course. For environmental reasons, this practice is being challenged as it leads to evaporation of Volatile Organic Compounds (VOCs). Consequently, the practice of priming has been declining and alternative solvent-free EAPs have not provided consistent results.

Bio-solvents have been developed following "Green Principles" protocols with the specific objective of reducing or eliminating VOCs. The capacity of bio-solvents to reduce binder viscosity is comparable to petroleum-based solvents. Emulsified asphalt primers produced with bio-solvent have proven to provide binder penetration of granular base course comparable to traditional EAP.

This paper provides information on prime coat systems, their purpose, how they work and the various products currently used. The penetration of prime coat systems in compacted granular base course is influenced by a multitude of factors including mineralogy, gradation and density. The robustness of any EAP relates to its aptitude to penetrate granular base course regardless of field conditions. This study presents an overview of how bio-solvent EAPs were developed to optimize robustness.

RÉSUMÉ

L'utilisation de solvant à base d'hydrocarbures est très courante dans la production des émulsions utilisées comme liant d'imprégnation (EAP). Ces solvants ont la capacité de réduire la viscosité du bitume permettant à l'émulsion de bien pénétrer dans la couche granulaire compactée utilisée comme base dans la chaussée. Pour des raisons environnementales, cette pratique est remise en doute à cause de l'évaporation des composés organiques volatils (COV) qui y sont rattachés. Par conséquent, l'utilisation de liant d'imprégnation est en baisse et les solvants sans hydrocarbures n'ont pas donné des résultats convaincants.

Des bio-solvants ont été développés en suivant un protocole "vert" avec comme objectif spécifique de diminuer ou éliminer les COV. La capacité des bio-solvants de diminuer la viscosité des bitumes est comparable à celle des solvants à base d'hydrocarbures. Les liants d'imprégnation fait avec des bio-solvants ont prouvé qu'ils ont une pénétration dans la base granulaire comparable aux EAP traditionnels.

Cet article donne de l'information sur les liants d'imprégnation, leur utilités, comment ils fonctionnent et sur les différents produits actuellement disponibles. La pénétration de ces liants dans la base granulaire dépend d'une multitude de facteurs, incluant la minéralogie, la granulométrie et la densité. La robustesse d'un EAP est basé sur sa capacité à pénétrer la base granulaire peu importe les conditions sur le chantier. Cette étude présente comment les EAP avec bio-solvants ont été développés pour optimiser leurs robustesses.

1.0   INTRODUCTION

Petroleum-based solvents are widely used in the production of bituminous products. Historically, penetrating prime cutbacks and emulsions are produced with high amounts of petroleum-based solvents because they have the capability of lowering the viscosity of asphalt, thereby enabling the asphalt primer to penetrate deeply through the tightly knitted surface of compacted granular base course. For environmental reasons, this practice is being challenged as it leads to evaporation of Volatile Organic Compounds (VOCs) and regulations are being introduced to minimize and/or eliminate VOC emissions [1].

Bio-solvents can be used to dramatically minimize VOC emissions in roadway applications. Bio-solvents have been developed following "Green Chemistry" principles and work exceptionally well in producing bituminous products that do not emit VOCs. Like petroleum-based solvents, they reduce the viscosity of bitumen sufficiently to facilitate pumping, mixing and handling; however, the method by which these bio-cutbacks "cure" is significantly different. Bituminous products produced with petroleum-based solvents achieve cohesion at least partially through the evaporation of the solvent portion into the atmosphere. Alternately, engineered bio-solvents achieve cohesion by undergoing a "polymerization" reaction. They have the capability of lowering the viscosity of bitumen in order to facilitate its industrial processing at lower temperatures and subsequently increase the viscosity by means of a chemical reaction to provide the bitumen its end-use cohesion/adhesion characteristics.

Emulsified Asphalt Primes (EAPs) provide an alternative to the usage of traditional cutbacks in prime applications. These products typically contain far less solvent, and as a result can be less robust. This has led to a decline in the practice of priming granular base course. This paper presents a detailed study on the formulation of effective emulsified primes using bio-solvents. The paper reviews the various characteristics analyzed when evaluating products used in prime coat systems. It also compares emulsions produced with different chemistries, particle size, solvent type, and amount of solvent in order to determine the optimal formulation.

2.0   PRIME COATS – AN OVERVIEW

2.1   Background

The application of a prime coat involves applying a bituminous binder onto an untreated granular surface. The practice of using prime coat in road construction first appeared in the United States [2]. In the past, the vast majority of prime coating applications used cutback bitumen which contains very high amounts of petroleum-based solvents. Because of the environmental and health impacts of releasing such a high amount of VOCs into the atmosphere and the lack of suitable replacement products, the application of prime coat is often skipped during construction.

When applied successfully, the usage of prime coat systems has shown to be beneficial to long term performance [3]. Primarily, the application of prime coats provides a hydrophobic surface that waterproofs the granular base. It does this by sealing the surface pores in the granular base and by binding the finer particles of the aggregate. This waterproofing is largely considered the most important function of the prime coat application [4]. Secondly, it provides a bonding layer between the compacted base and the surfacing layers increasing interlayer bond strengths thus preventing slippage between the granular material and the surfacing layers [4, 5].

In order for a prime coat application to be effective and beneficial it must penetrate the surface of the granular base [6]. It is suggested that the minimum penetration depth should be 5 to 10mm [7]. Many factors can influence the penetrative capability of prime coat systems including viscosity of the product applied, viscosity of the residual binder, reactivity and bitumen droplet size. Furthermore, the gradation, density, as well as mineral composition of the granular base can highly influence the penetrative ability of the prime coat system.

Solvents play a critical role in assisting in the capillary movement of bitumen from the surface downward; as a result, cutbacks have proven very robust in prime coat applications. However, the types of cutbacks used in prime applications contain very high amounts of petroleum-based solvent that is generally released into the atmosphere after application. In this study, the penetrative capability of various emulsion formulations are compared against that of a widely used cutback, MC-30, with the intent of determining the optimal formulation that will result in an equally robust product that uses a bio-solvent instead of traditional petroleum-based solvent.

2.2   Types of Prime Coats

Prime coat products can be categorized into four main groups.

- Asphalt cutbacks – are asphalt products produced by blending bitumen with a petroleum-based solvent. The volatility, as well as the quantity of petroleum solvent used, determines the grade. For prime coat materials, the most commonly used cutbacks are MC-30, MC-70, RC-30 and RC-70. Cutbacks are considered to be the most penetrative of prime coat products. However, they release high amounts of VOCs into the atmosphere and can take longer to fully cure than emulsified products.

- Emulsified cutbacks – are inverted emulsions (i.e., water in oil emulsions as oppose to oil in water as typical emulsions). The water content of inverted emulsions is between 10 and 20 percent and, as a result, they typically contain less solvent than cutbacks used in prime applications.

- Emulsions with solvent – contain far less solvent than cutbacks or emulsified cutbacks. Various proprietary products exist in the market and are being used in place of asphalt cutbacks. These products typically cure faster than cutbacks and are generally preferred in that regard. They also release less VOCs, however due to the reduced amounts of solvent, the penetrative ability of these types of emulsions is less robust than that of conventional cutback primes.

- Solvent-less emulsions – contain no solvents and consequently produce no VOCs. Depending on the mineralogy and density of the base course, SS-1 or CSS-1 type emulsions may be used. Several proprietary products are available that use a combination of chemistry and droplet size to maximize penetrative ability. Solvent-less emulsions have not provided consistent results unless it is applied with some sort of in-place mixing.

Generally speaking, prime coat systems can be applied to a granular base in two ways. The first method involves mixing a product into the first few inches of the granular base mechanically followed by compaction. Since the prime coat is being mixed into the material, it is less important that the product be able to penetrate the base, thus eliminating the need for producing a penetrative product. The second method of applying prime is by spraying the product straight onto the compacted granular base. For this method, it becomes critical that most of the applied product penetrates the surface. For the purpose of this

paper, the focus is on the penetrative type of prime coats that are typically sprayed straight onto the compacted granular base.

2.3   Characteristics

In order for a penetrating emulsion prime to be effective and robust, there are four main characteristics that should be assessed:

- Viscosity of the prime coat system – the viscosity must be sufficiently low. This helps increase the flow of the material into the granular base as well as being able to effectively spray the product using a distributor truck (Figure 1).

- Reactivity – the product applied must not react too fast to allow sufficient time for penetration into the base. This is an important characteristic when analyzing different emulsifier chemistries.

- Viscosity of the residual binder – the residual binder in the emulsion is best suited for use in prime coat systems when its inherent viscosity does not prevent it from migrating into the granular base.

- Particle Size – minimizing the particle size of the emulsified bitumen droplets significantly improves the penetrative ability of prime. This is especially important when formulating a very robust product that will provide good penetrative capabilities in even highly densified granular bases.
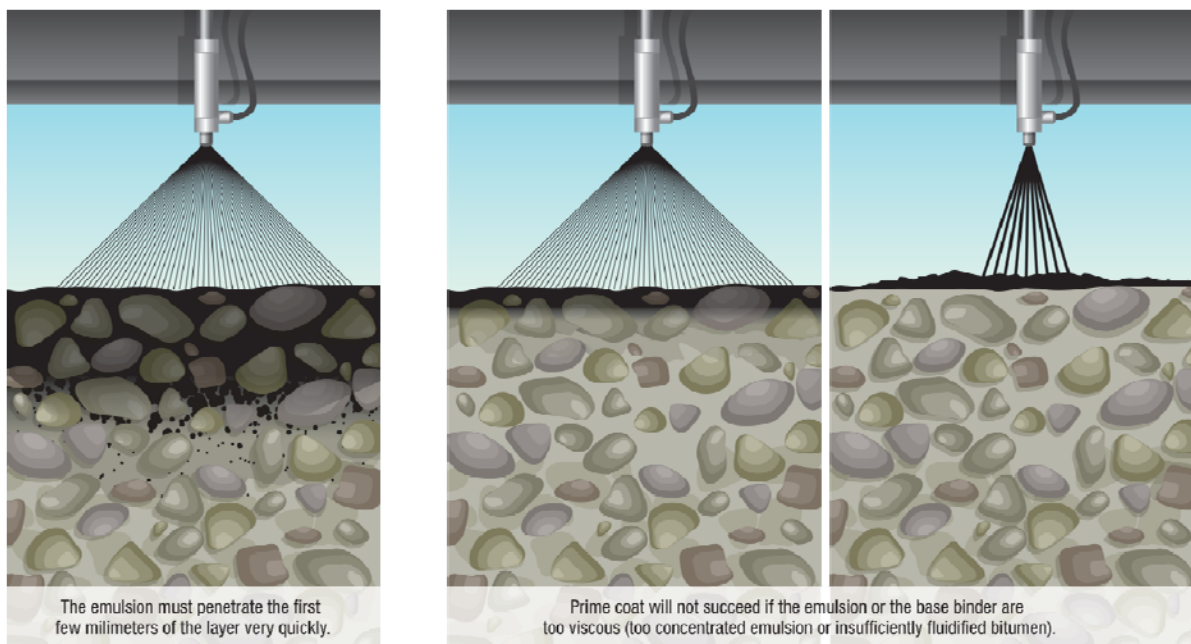

Figure 1. Effective Prime Coat Applications

3.0 VOLATILE ORGANIC COMPOUND EMISSIONS

3.1 Volatile Organic Compounds (VOCs)

The definition of VOCs may be summarized as chemicals containing at least one carbon atom, excluding carbon monoxide and carbon dioxide, which evaporate readily into the atmosphere. These compounds participate in the atmospheric photochemical reactions that contribute to the formation of particulate matter and ozone, which are the two principal components of smog. Smog is an air quality issue that poses serious health and environmental concerns in Canada [8].

Emissions of VOCs originate from both natural and human-made sources. The VOCs that contribute to smog are human-made and tend to be found wherever people live and work. The total human-made VOC emissions in 2007 were evaluated at 1,349,000 tonnes in Canada. Major human-made VOC emissions include: solvents used in various products, transportation sector activities such as the exhaust emissions from vehicles, various industrial processes such as chemical manufacturing, and residential/commercial fuel/wood combustion. Petroleum-based solvents, at 33 percent of the total VOC emissions, are the second largest source of VOC emissions after transportation [8].

In 2010, the amount of VOC emissions originating from the solvents used in cutback bitumen was evaluated at 10,500 tonnes for a total production of approximately 30,000 tonnes of cutback bitumen. The VOC emissions originating from the production and usage of bitumen emulsion are relatively low compared to cutbacks, but not insignificant. The total production of emulsion in Canada is estimated at 350,000 tonnes and the estimated average usage of solvents in emulsion is probably less than 1.0 percent by volume [8].

3.2 Government of Canada Agenda for VOCs Emissions Reduction in the Asphalt Industry

The Government of Canada has initiated an extensive series of actions to control the major sources of VOCs emissions that contribute to the formation of smog [8]. The Federal Ministries of Environment and Health published in 2004 a "Notice of Intent" in the Canada Gazette to control VOC emissions associated with petroleum-based solvents. This document outlined a series of measures that have been implemented between 2004 and 2010 to control and reduce emissions of VOCs from various products.

In March of 2012, Environment Canada released a document regarding possible control measures on VOCs related to cutback and emulsified bitumen. It is estimated that in 2009 up to 60 percent of the total VOC emissions from liquefied bitumen came from cutback bitumen, despite cutback bitumen only representing 15 percent of the total liquefied bitumen usage [1].One of the proposed scenarios from environment Canada is the alignment with the existing California rules. The state of California prohibits the use of cutback bitumen with more than 0.5 percent by weight of petroleum-based solvent boiling at less than 260°C as determined by ASTM D402. It also limits the volatile portion of emulsified bitumen to less than 3 percent at a temperature less than 260°C as determined by ASTM D244 [1]. This proposed strategy would represent a significant VOC reduction of 90 percent in Canada.

The Environment Canada publication recognizes that emulsified prime products may contain 5 to 15 percent VOCs. Environment Canada suggests that "these products would require reformulation by substitution with a diluent that has a narrower upper boiling point range" [1]. Bio-solvents have boiling points that are typically much higher than corresponding petroleum-based solvents. This characteristic makes them ideal replacements for petroleum-based solvents.

4.0   BIO-SOLVENTS

The environmental impact of petroleum-based solvents is a matter that has provided justification for a number of developments over the past few years. Bio-solvents provide characteristics similar to those of petroleum-based solvents but have higher boiling points thus producing far less VOCs. The Colas Group has invested considerable resources and efforts in development and usage of bio-solvent based products for the road industry.

In this study three types of bio-solvents are considered. One is a Colas patented product that is currently marketed under the name Vegeflux® and two other products that are readily available in the market today. All of these products provide properties that differ significantly from other petroleum-based solvents in terms of their VOC emissions. The advantage of using Vegeflux® is that is has been specially engineered to build cohesion after application. As discussed in a paper entitled" Usage of Bio-solvents in the Asphalt Industry to Reduce Emission of Volatile Organic Compounds," the following characteristics apply to bio-solvents [9]:

- Bio-solvents do not evaporate or produce VOCs; the bio-solvent becomes part of the final end-use bituminous binder as it increases in viscosity, thereby permitting some binder savings;

- The quick reactivity of bio-solvents provides rapid build-up of cohesion/adhesion of the end-use bituminous binder; and

- The increased dissolving power of bio-solvents facilitates blending with bituminous binder, thereby allowing some reduction of bio-solvents compared to petroleum-based solvents.

The rapid build-up of cohesion is a characteristic specific to Vegeflux®. It is unclear whether or not the use of Vegeflux® over other bio-solvents is advantageous in terms of penetrative power in prime applications. However, the residual binder of an emulsion produced with Vegeflux® is engineered to harden faster than that produced with a regular bio-solvent.

5.0   DEVELOPMENT OF A BIO-SOLVENT EMULSIFIED PRIME

5.1   Overview

The driving force behind developing an emulsified prime with a bio-solvent was to produce an emulsified prime that performed as well as cutback products and meets the potential new regulations related to VOC emissions for cutback and emulsified bitumen. In order to properly assess the various formulations, the findings were benchmarked against MC-30. This type of cutback is often chosen as a benchmark because of its well documented performance and robustness.

Furthermore, the study also looked at different chemistries and formulations in order to optimize the effectiveness of the prime emulsion. Different aggregates, emulsifiers, and bio-solvents were analysed to be as thorough as possible in the investigation. To assess the penetrative capability of the products, two methods were utilized; a European test method and a Colas in-house method. Both of these methods were slightly modified to incorporate the various aggregates used to assess the various prime coat systems. A particle analyzer was also used to measure the mean particle size and distribution of the bitumen droplet sizes contained in the emulsion. Lastly, all products were analyzed to determine their VOC content.

5.2   Materials

A Canadian asphalt binder was used to produce the different emulsions and the MC-30. The binder originated from eastern Canada and had a performance grade of PG 64-22. This grade was chosen because it was the typical grade of asphalt used in the production of the prime products currently being used in the market place, including MC-30.

The analysis also included a petroleum-based solvent prime emulsion that is currently being used in the market. This emulsion is referred to as E1 (control). Three bio-solvents were evaluated, Bio-solvent A (BSA), Bio-solvent B (BSB) and Vegeflux® (BSV). A total of seven emulsifiers were selected for the study: five cationic and two anionic. All the emulsions produced (E2 through E8) had an equal amount of BSA. The residual AC content, viscosity and particle size of all eight emulsions are shown in Table 1.

Table 1. Test Results of the Various Emulsions Produced

Emulsion	Residue, %	Brookfield Viscosity, 20°C, mPa.s	Mean Particle size, µm	pH value
E1 (control)	54.9	17.6	3.3	9.6
E2	54.9	31.0	9.9	2.7
E3	54.8	35.9	9.9	3.7
E4	54.4	41.4	8.5	2.9
E5	55.6	32.3	9.0	3.2
E6	54.7	27.1	9.1	3.7
E7	55.4	32.9	8.6	10.9
E8	55.3	29.4	7.4	11.7

Six different aggregates from across Canada were used in the study; three from Alberta, one from BC, and two from Quebec. The aggregates were all dried and only the 0-1mm fraction from each was used to evaluate penetrability. Details on the aggregates selected are in Table 2.

Table 2. Sieve Analysis on the Selected Aggregates

Aggregate	Source	Province	Specifications	Passing #63 µm, (%)	Passing #2 mm, (%)	Specific Area, (m²/kg)
AG1	Gravel Pit	Alberta	City of Edmonton GBC 3-20	7.9	41.0	14.34
AG2	N/A	Alberta	City of Edmonton 3-63	5.9	31.0	10.6
AG3	Gravel Pit	Alberta	Designation 2-20	6.6	42.0	12.18
AG4	Gravel Pit	BC	25 WGB	3.3	22.0	6.32
AG5	Granite Quarry	Quebec	MG-20	4.7	37.0	8.81
AG6	Limestone Quarry	Quebec	MG-20	3.2	34.0	6.7

5.3   Penetration Tests

In order to evaluate and compare the penetrative ability of each of the emulsions, two test methods were performed. The first is a European standard test, NF EN 12849, which determines the penetration time and depth of 10g of prime on a reference aggregate mixture (Reference Aggregate) of 50g of fine siliceous and 50g of fine silica sand (see Figure 2).

The second test method is a Colas developed method referred to as the MFI test. The MFI test determines the penetrative power of a prime on sikaisol fine material (Reference Aggregate) by measuring the impregnated mass of filler after 24 hours (see Figures 3 and 4).
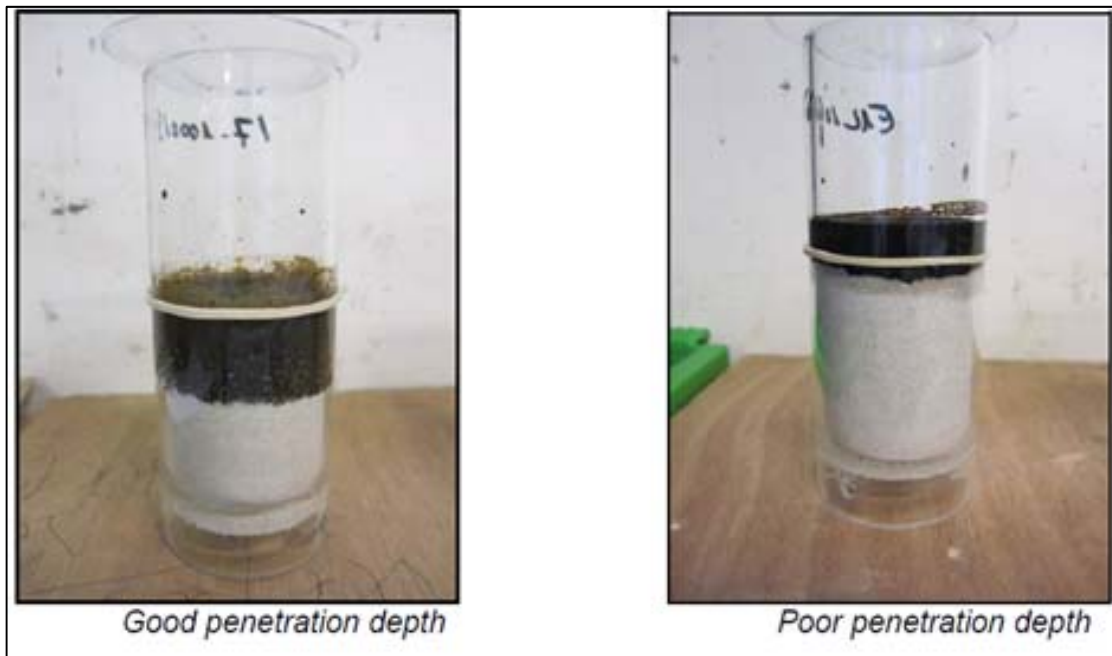

Good penetration depth   Poor penetration depth

Figure 2. European Standard Test NF EN 12849

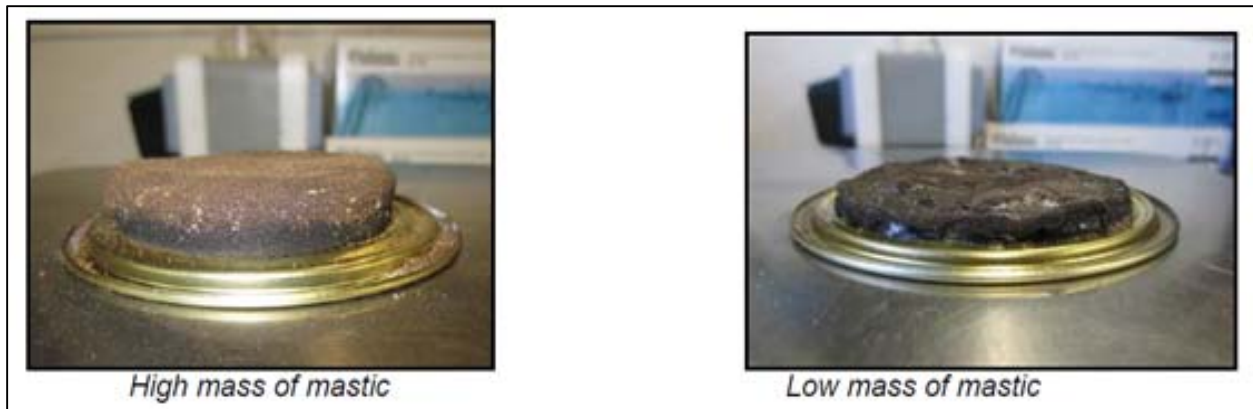**Figure 3. MFI Test – From Start to Finish**

Figure 4. Examples from MFI Test

5.4   Results and Discussion

5.4.1 Overview of Testing Approach

In order to properly screen the various prime coat systems, penetration tests were conducted on a number of different variations. The first step was to test the original formulations using the standard methods described in Section 5.3 and using the sands and fines specified in the original test methods.

Secondly, the bitumen droplet size of the same emulsions was reduced in order to assess the effect of droplet size on the penetrative ability of prime coat systems.

Third, the fine particles in each test method were replaced with the 0-1 mm fractions from each of the aggregates in order to assess the robustness of each formulation with different aggregates.

After this the amount of emulsifier used to produce the emulsion was varied, and lastly, the amount and type of bio-solvent was also varied.

5.4.2 Test Results from Standard Tests

All of the prime coat systems were tested using both methods and with the sands and fines specified by each method. The results are summarized in Table 3.

None of the emulsions were able to completely impregnate the sikaisol sand after 24 hours using the MFI test. The MC-30 produced the best result, and was the only product able to completely impregnate the sikaisol sand after 24 hours. Of all the emulsions tested, E1 showed the best performance according to the NF EN 12849 test method and E2 showed the best performance according to the MFI test.

Table 3. Test Results from the NF EN 12849 and MFI Tests

Emulsion	NF EN 12849 Test			MFI Test	
	Penetration time, (min)	Penetration at 20 min, (mm)	Penetration at 24hrs, (mm)	Mass of Mastic after 24hrs, (g)	Complete impregnation after 24hrs
E1 (control)	>20	15.0	15.0	9.5	No
E2	>20	5.0	6.0	20.0	No
E3	>20	3.0	3.0	10.0	No
E4	>20	3.0	4.0	8.0	No
E5	>20	2.0	2.0	9.0	No
E6	>20	3.0	3.0	8.0	No
E7	>20	2.0	3.0	7.0	No
E8	>20	4.0	4.0	7.0	No
MC-30	>20	11.0	22.0	46.0	Yes

5.4.3 Effect of Particle Size

In order to evaluate the effect of particle size on penetration, the emulsions were produced with a smaller mean particle size (the emulsions with a reduced particle are denoted with "–R"). The same two test methods were performed on the new emulsions and the results are presented in Table 4. Note that all the cationic recipes (E2-R through E6-R) fully impregnated the mastic after 24 hours, which indicates that the reduction in particle size significantly improved the ability of the emulsions to penetrate the sikaisol fines. Emulsions E3-R and E8-R were the only emulsions that did not penetrate within 20 minutes in the NF test. The reduction in particle size greatly improved the results when comparing the penetration time and depth of penetration to that of the MC-30 and E1.

When analyzing the results from the anionic recipes, we quickly note that neither E7-R nor E8-R fully impregnated the mastic after 24 hours. One possible explanation is that the reference sand and fines in the MFI test are more acidic which may influence the reactivity of the anionic emulsion thereby speeding up the break time and reducing the penetrative ability of the anionic emulsion.

Table 4. Test Results after Reducing the Emulsion Particle Size

Emulsion	NF EN 12849 Test			MFI Test	
	Penetration time, (min)	Penetration at 20 min, (mm)	Penetration at 24hrs, (mm)	Mass of Mastic after 24hrs, (g)	Complete impregnation after 24hrs
E1 (control)	>20	15.0	15.0	9.5	No
E2-R	7'55"	25.0	25.0	43.0	Yes
E3-R	>20	11.0	23.0	29.0	Yes
E4-R	6'16"	21.0	23.0	42.0	Yes
E5-R	5'16"	16.0	17.0	38.0	Yes
E6-R	5'20"	20.0	20.0	39.0	Yes
E7-R	10'53"	28.0	28.0	10.0	No
E8-R	>20	17.0	17.0	19.0	No
MC-30	>20	11.0	22.0	46.0	Yes

5.4.4 Penetration Tests using 0-1mm Fractions

To confirm this hypothesis, as well as to better understand which of the formulations is more robust, the emulsions with a reduced particle size were taken and tested using 0-1mm fractions of the six different Canadian aggregates. The aggregate samples were dried to extract the 0-1mm fraction. Each of the fractions was then used in modified versions of the NF and MFI tests. In each of the tests, the fines were replaced with the 0-1mm fraction from each of the aggregates sources. A summary of the results are presented in Table 5. The results from these modified tests were used to rate each of the emulsions in terms of their ability to penetrate a range of aggregates.

As shown, it may be noted that despite the MC-30 penetrating the surface slightly better on average than the emulsions, it does so very slowly. E2-R completely penetrated the highest number of granular materials in less than 20 minutes and has the highest value for impregnation depth after 20 minutes than any other product. This is significant when considering the importance of saving time and not having to wait an extended period for prime application to fully impregnate the granular base. Furthermore, Emulsion B fully impregnated all six of the granular materials after 24 hours compared to only five granular materials fully impregnated by the MC-30.

Table 5. Test Results using the 0-1mm Fractions

Emulsion	# of Gr. M. Penetrated in less than 20 min, *Max. 6*	NF EN 12849 Test				MFI Test		# of Complete impregnations after 24hrs
		Average Penetration at 20 min, (mm)		Average Penetration at 24hrs, (mm)		Average Mass of Mastic after 24hrs, (g)		
		Avg	Max / Min	Avg	Max / Min	Avg	Max / Min	
E1	2	13.3	23.0 / 6.0	14.5	24.0 / 6.0	29.2	49.0 / 7.0	4
E2-R	3	16.3	31.0 / 3.0	19.7	31.0 / 12.0	38.7	44.0 / 28.0	6
E3-R	1	7.2	17.0 / 1.0	13.7	26.0 / 5.0	28.0	41.0 / 9.0	4
E4-R	1	8.3	22.0 / 1.0	13.7	25.0 / 2.0	23.2	34.0 / 11.0	1
E5-R	1	11.3	25.0 / 1.0	11.7	25.0 / 1.0	22.0	44.0 / 10.0	2
E6-R	1	11.0	30.0 / 1.0	12.2	30.0 / 1.0	27.0	44.0 / 13.0	3
E7-R	2	6.6	23.0 / 1.0	6.6	23.0 / 1.0	27.5	45.0 / 12.0	3
E8-R	2	12.5	24.0 / 1.0	12.5	24.0 / 1.0	28.3	47.0 / 8.0	2
MC-30	1	12.5	20.0 / 3.0	21.8	30.0 / 9.0	62.8	80.0 / 42.0	5

Note: Gr. M. is Granular Materials.

The results from the modified NF EN 12849 and the modified MFI tests were then used to rank the emulsifiers by decreasing average mastic mass and the number of soils penetrated within 20 min. The results are presented in Tables 6 and 7.

Table 6. Emulsion Ranking by Average Mastic Mass (MFI Test)

Emulsion	Average mastic mass, (g)	Ranking
E1-R	26.4	2
E2-R	36.1	1
E3-R	25.5	4
E4-R	20.9	7
E5-R	20.2	8
E6-R	24.4	5
E7-R	24.0	6
E8-R	25.7	3

Table 7. Number of Penetrated Soils before 20min (NF EN 12849)

Emulsion	Number of Penetrated Soils	Ranking
E1-R	3/6	1
E2-R	3/6	1
E3-R	1/6	3
E4-R	1/6	3
E5-R	1/6	3
E6-R	1/6	3
E7-R	2/6	2
E8-R	2/6	2

It should be noted that emulsions E1, E2, and E8 rank in the top 3 in both tests. It is also important to point out that E2 was formulated using a cationic emulsifier whereas E8 was formulated using an anionic emulsifier. This confirms that the unmodified MFI test (using sikaisol fines) incorrectly favours cationic systems. The most effective emulsion formulation was E2 which far outperformed all of the other emulsions in the MFI test.

Once it was determined which of the emulsifiers produced the best performing prime emulsions, the top 2 emulsions, excluding the petroleum-based solvent emulsion (E1), were reformulated using different amounts of emulsifying agent and subjected to the same two modified tests. Table 8 summarizes these results and demonstrates conclusively that varying the amount of emulsifier can influence the effectiveness of prime emulsion.

5.4.5 The Effect of Solvent Type and Content

All the emulsions were produced with a constant volume of BSA. Two other rates were tested on the best performing prime, which was E2. Holding all other ingredients constant, two more emulsions were produced, one with 40 percent less BSA (-RL) and one with 100 percent more BSA (-RM). Due to time constraints and lack of material, only 3 aggregates in addition to the reference aggregate were used for this portion of the study. The results were as expected; less solvent resulted in poorer performance in both tests; consequently more solvent resulted in better performance. These results are summarised in Table 9.

Table 8. Test Results – Influence of Emulsifier Rate

Aggregate	Emulsion	NF EN 12849 Test			MFI Test	
		Penetration time, (min)	Penetration at 20 min, (mm)	Penetration at 24hrs, (mm)	Mass of Mastic after 24hrs, (g)	Complete impregnation after 24hrs
AG2	E2-R	>20	17.0	22.0	39.0	Yes
	E2-R'	>20	18.0	18.0	46.0	Yes
	E8-R	>20	2.0	2.0	18.0	No
	E8-R'	>20	1.0	1.0	22.0	No
AG3	E2-R	>20	12.0	18.0	44.0	Yes
	E2-R'	14.5	17.0	18.0	50.0	Yes
	E8-R	>20	12.0	12.0	11.0	No
	E8-R'	>20	4.0	5.0	17.0.	Yes
AG6	E2-R	2.5	20.0	20.0	42.0	Yes
	E2-R'	11.0	38.0	38.0	51.0	Yes
	E8-R	1.7	20.0	20.0	47.0	Yes
	E8-R'	>20	28.0	30.0	53.0	Yes
Reference Aggregate	E2-R	>20	5.0	6.0	20.0	No
	E2-R'	>20	4.0	8.0	24.0	No
	E8-R	>20	4.0	4.0	7.0	No
	E8-R'	>20	7.0	8.0	8.0	No

Note: -R' Represent emulsions made with a different amount of emulsifier and also reduced particle size.

Table 9. Test Results – Adjusting Bio-Solvent Rate

Aggregate	Emulsion	NF EN 12849 Test			MFI Test	
		Penetration time, (min)	Penetration at 20 min, (mm)	Penetration at 24hrs, (mm)	Mass of Mastic after 24hrs, (g)	Complete impregnation after 24hrs
AG2	E2-RL	>20	6.0	10.0	24.0	No
	E2-R	>20	17.0	22.0	39.0	Yes
	E2-RM	>20	16.0	16.0	52.0	Yes
AG3	E2-RL	>20	1.0	3.0	21.0	No
	E2-R	>20	12.0	18.0	44.0	Yes
	E2-RM	9	22.0	24.0	43.0	Yes
AG6	E2-RL	>20	5.0	8.0	41.0	No
	E2-R	2.5	20.0	20.0	42.0	Yes
	E2-RM	10	40.0	40.0	68.0	Yes
Reference Aggregate	E2-RL	>20	1.0	2.0	11.0	No
	E2-R	>20	5.0	6.0	20.0	No
	E2-RM	8	20.0	21.0	35.0	Yes

Note: -RL and -RM Represent emulsions made with less and more solvent respectively.

We also used the best performing emulsions to produce other formulations using different types of bio-solvents holding all other portions of the formulation constant. Bio-solvent B and Vegeflux® were both used in conjunction with the best cationic and the best anionic emulsions. The results concluded that the Vegeflux® penetrated more granular materials within 20 min in the EN test and resulted in higher average mastic mass in the MFI test as shown in Table 10.

Table 10. Bio-Solvent Ranking

Solvent	Average Mastic Mass, g (MFI test)	Number of Penetrated Soils within 20min (NF EN 12849 test)
Vegeflux®	40.0	2/4
Bio-solvent A	36.0	1/4
Bio-solvent B	36.0	0/4

6.0   VOC ANALYSIS

In order to assess the VOC emissions, we looked at the distillation data to determine the amount of solvent present in the distillate at temperatures up to 260°C as measured by ASTM methods D402 and D244. As was expected, the MC-30 was the highest and lost 27.2 percent of its total mass. E1, one of the solvent based emulsions currently used in the market lost 6 percent of its total weight, which is double that of the 3 percent limit suggested by Environment Canada [1]. Lastly, an emulsion produced with Vegeflux® lost only 1 percent of its total weight at 260°C confirming the limited release of volatiles when using bio-solvents.

Another European test (NF EN 13074-2), which is typically used to recover binders from both cutbacks and emulsions, was also used to analyze the mass lost by the MC-30 and each of the bio-solvent produced emulsions over a period of 24 hours and at a temperature of 85°C. The results shown in Table 11 confirm that the bio-solvent produced emulsions all lose a very small portion by total weight compared to MC-30.

Table 11. Mass Loss Results from NF EN 13074-2 Test

Product	Mass loss, % by total weight
MC-30	37.9
Emulsion with Vegeflux®	1.6
Emulsion with Bio-solvent A	1.8
Emulsion with Bio-solvent B	1.7

7.0   CONCLUSIONS

The priming of granular base is a critical step in the construction of pavements. By applying an effective prime coat emulsion, the base is protected from the detrimental effects of weather and traffic, as well as provides a good interface for the subsequent pavement layer.

In following the noted approach for designing a prime coat emulsion, a number of important characteristics are highlighted that should be analyzed when formulating an effective product:

- Bio-solvents can be used to replace petroleum-based solvents in prime applications. The greater the amount of solvent used, the greater the penetrative capabilities of the emulsion. Also, the type of bio-solvent used can influence the penetrative ability of the prime emulsion. Bio-solvents have the advantage of producing low VOC emulsions even when used in high dosage levels and can be considered far superior in terms of safety and environmental friendliness.

- Particle size plays a large role in producing an effective prime coat emulsion. The results showed a clear relationship between particle size, depth of penetration, and mass of mastic after 24 hours. Furthermore, it may be possible that by lowering the particle size the amount of solvent needed to enhance penetrative properties may be reduced.

- The type of emulsifier and dosage levels impact the effectiveness of prime emulsions and should therefore be tested thoroughly before a selection is made. Furthermore, the test used to screen these emulsifiers may favor one type of chemistry over another. Modification of the test method or a range of different test methods may be needed to properly assess the prime emulsion.

- When emulsions are produced with a bio-solvent as opposed to petroleum-based solvent, the bio-solvents do not evaporate into the atmosphere and remain part of the residual binder. This allows the user to potentially lower the application rate since the residual binder obtained from an emulsion produced with a bio-solvent is higher than that of an emulsion produced with a petroleum-based solvent.

- As previously demonstrated [9], the advantage in using Vegeflux® over other bio-solvents is in the hardening properties resulting from the rapid polymerization of the Vegeflux over time. Furthermore, the current study showed greater penetration and robustness when using Vegeflux® than when using the other two types of bio-solvents. This confirms that not all bio-solvents are equally effective in prime applications and testing should be completed in order to better understand the properties of the bio-solvent selected.

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