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## Experimental investigation of optimum properties and conditions for use of anionic emulsions in road maintenance applications

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**ABSTRACT:** Bitumen emulsions are used for a range of road maintenance applications, including surface dressing, gravel seals, slurry seals, tack coating, cold-mix asphalt and in situ pavement recycling. The emulsions used can be classified as being either cationic (i.e. possessing a positive electrostatic surface charge) or anionic (i.e. carrying a negative electrostatic surface charge). The vast majority of emulsions used for such applications in Europe are cationic, while anionic bitumen emulsions are used widely throughout North America and Africa.

The aims of the experimental study described in this paper were (a) to investigate why one or the other emulsion type is favoured in different global regions, (b) to establish if the aggregates used can be classified as also having a positive or negative electrostatic surface charge and (c) to determine if the surface charge of the aggregate has an effect on the degree of adhesion between the aggregate and bitumen emulsion used. The overall objective of this research project is to study the potential development of new adhesion additives for anionic emulsions used in road applications.

The experimental laboratory work that was performed demonstrated that the electrostatic surface charge of the aggregate plays a significant role in the aggregate–emulsion adhesion mechanism. The laboratory tests results indicated that a higher degree of adhesion was achieved when an aggregate was combined with an emulsion possessing the opposite surface charge. This finding confirms the hypothesis that aggregates possess either an electro-positive or an electro-negative surface charge, depending on their mineralogical composition.

**KEY WORDS:** Anionic, Cationic, Bitumen Emulsion, Electrostatic Surface Charge, Road Maintenance

### 1 INTRODUCTION

#### 1.1 *Anionic bitumen emulsions*

Over 8 million tonnes of bitumen emulsions are used throughout the world annually in road construction and road maintenance techniques. An emulsion is constituted mainly of three components: bitumen, emulsifier and water. The water phase contains a dispersion of minute droplets of bitumen, typically, of the order of 1 to 10 microns in diameter. The bitumen droplets are held apart in suspension in the water phase by electrostatic charges imparted to them by the chemical compounds called emulsifiers [1]. Emulsions can be either anionic or cationic, depending on the chemistry that created the emulsifier. In cationic emulsions, the bitumen droplets possess a positive electrostatic surface charge. In anionic emulsions, the bitumen droplets possess a negative electrostatic surface charge. This fundamental distinction results in significant differences in emulsion behaviour.

The first patent describing the utilisation of bitumen in water dispersion for the road construction industry was taken out in 1906 [2]. The first bitumen-based emulsions to be used commercially were anionic in nature, i.e. the bitumen droplets possessed a negative electrostatic charge. In the 1920s, when bitumen emulsions came into general use for road paving applications, they were mostly used in spray applications and for dust suppression [3]. By the 1960s, about 95 % of all bitumen emulsions used in the USA were of the anionic type [4].

Cationic emulsions, on the other hand, are characterised by positively charged bitumen droplets and were first introduced in 1951. They quickly became popular, as there was a noticeable improvement in the performance levels achieved. They exhibited a significantly faster “curing time”, i.e. the time required for the residual bitumen to coalesce and achieve its full strength as a binder, so allowed for treated pavements to be re-opened to traffic more quickly. Consequently, by the early 1970s, more than 90 % of manufactured emulsions were cationic. By 2005, this figure was nearing 100 % in some countries [5]. However, despite this, anionic emulsions are still used in large quantities in certain countries today, such as the USA, Canada, South Africa and Australia, for a range of road maintenance techniques, including pavement sealing, gravel seals, tack coating, slurry sealing and in situ pavement recycling. Their advantages over cationic emulsions are that their slower break facilitates the use of aggregates with a higher dust content (i.e. lower cost aggregates). For such aggregates, a slow breaking emulsion is more desirable than a more rapid setting (i.e. cationic) emulsion, so that both the coarse and the fine aggregate particles are fully coated and/or bonded to the residual binder. Therefore, anionic emulsions are still more preferable for certain applications (e.g. slurry seals and graded seals) in hot and dry regions where the setting times are accelerated by rapid evaporation of water.

A special type of anionic emulsion called a “high float” emulsion is widely used for graded sealing applications in North America and, particularly, in Canada, where washed

single sized aggregates are not usually available locally. The residual binder of these emulsions possesses a “gel” quality that is more resistant to “flow” or movement during the summer months and is less brittle and more resistant to cracking, during the winter months [6]. Such properties are most desirable in Canada and parts of the USA, where road surface temperatures can vary widely, such as from -50 °C in the winter months up to +80 °C in the summer months. Another advantage of anionic emulsions is that they can be produced using relatively less expensive emulsifiers that are by-products from the paper pulping industry [7], thereby reducing emulsion costs by up to 30 %.

### 1.2 Aggregate-Emulsion interaction

For all emulsion-based road construction and maintenance applications, the degree of compatibility between the aggregate and the emulsion has a critical impact on the performance of the technique. In terms of the degree of adhesion or bond between the two, it has been reported in the literature that for a given emulsion, the degree of adhesion achieved will depend on the mineralogy of the aggregate used. Some studies have shown that aggregates can carry different distributions of electro-positive to electro-negative surface charges, depending on their mineralogy [8] [9]. The classification system is based on the silica versus alkaline or alkaline earth oxide contents of the aggregate. A summary of their classification is shown in Figure 1.

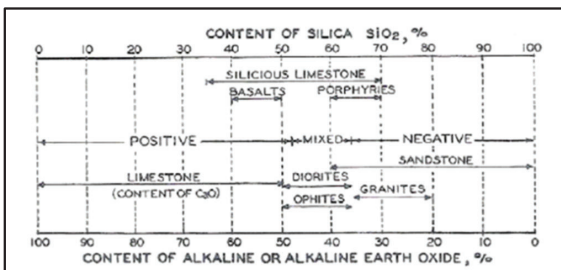


Figure 1. Classification of aggregates by silica content and surface charge [8] [9]

For example, limestone is generally constituted of calcium carbonate and, under this classification, is categorised as possessing an electro-positive surface charge. Siliceous aggregates like sandstone, quartzite or granite are suggested to have an electro-negative charge. In order to obtain the desired maximum degree of adhesion, it would seem rational to select an emulsion with an electrical surface charge opposite to that of the aggregate, as there is an attraction between two oppositely charged materials. Consequently, negatively charged anionic emulsions would be preferred for the electro-positively charged surface aggregates, whereas positively charged cationic emulsions would be preferred for the electro-negatively charged surface aggregates. Conversely, a lower degree of adhesion is expected when an aggregate and an emulsion with the same surface charge are combined. Despite this aggregate versus emulsion compatibility logic, some studies have disputed this aggregate classification [10] [11]. It has been claimed that, when wetted with water, aggregates like

limestone containing calcareous minerals become negatively charged. Therefore, it would appear in the literature that there is no consensus on the aggregate surface charge that is relevant when using bitumen emulsions.

This paper presents the results of an experimental investigation that was carried out to investigate if aggregates can indeed be classified as having either a positive or negative electrostatic surface charge and to determine if the polarity of nominally electro-positive surface charge calcareous aggregates can change if they are wetted.

The overall objective of this research project is to study the potential development of new adhesion additives for anionic emulsions used in road applications.

## 2 EXPERIMENTAL STUDY: SUMMARY

In order to accomplish the above objectives, an experimental study was carried out in the Chemoran laboratory. The objective of the laboratory study was to examine the following two hypotheses:

H1: aggregate can be classified as having either a positive or a negative electric surface charge, depending on its mineralogy as shown in Figure 1;

H2: this electric charge will always be negative when the aggregate is in a damp condition, regardless of its mineralogy.

In order to perform the analyses, both Anionic RS-2 [12] and Cationic C69B 3 [13] rapid set emulsions were manufactured using a laboratory mill. These types of emulsions are usually used in spray-grade applications, more specifically for surface dressing (or “chip sealing”, as it is called in North America). By testing a selection of different aggregates with both emulsion types (to produce one set of results for each aggregate), it would be easy to compare the degree of adhesion achieved with both emulsions and, furthermore, determine which emulsion gave the highest degree of adhesion for each aggregate.

The test aggregate specimens (three from Ireland and one from France) comprised two types of limestone (Limestone A and B), one sandstone and one quartzite. Based on XRF (X-ray fluorescence) test results (Table 1), CaO (calcium oxide) was found to be the major element present in both types of limestone, while SiO<sub>2</sub> (silicon dioxide or silica) was predominant in the sandstone and quartzite. Other alkali earth oxides such as barium oxide (BaO), magnesium oxide (MgO), and strontium oxide (SrO) were also found, to much lesser degrees, in all four aggregate types.

Table 1. Chemical composition of aggregates from the XRF testing

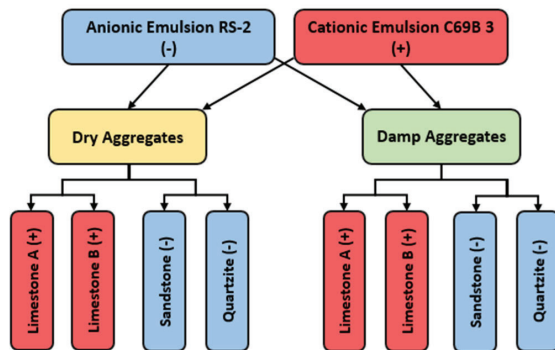
Aggregate Type	Alkaline Earth Oxides				Silica
	BaO	CaO	MgO	SrO	SiO <sub>2</sub>
	%	%	%	%	%
Limestone A	0.02	52.4	1.71	0.08	1.16
Limestone B	0.02	52.3	1.72	0.02	0.4
Sandstone	0.03	4.6	3.7	0.01	59.02
Quartzite	<0.01	0.1	0.07	<0.01	94.46

According to the classification shown in Figure 1 and the results obtained for silica (SiO<sub>2</sub>) content shown in Table 1, both limestone aggregates fall into the “positive” category. The sandstone aggregate just about falls into the negative category while the quartzite aggregate is very much at the negative side of the chart.

Throughout the laboratory study, single-sized clean coarse aggregates (chips) were used. Depending on the test method, the chipping size differed to satisfy the specified test requirements. A range of adhesivity tests was performed with the aggregates in both dry and damp state. The following test methods were used:

- I. I.S. EN 13614 Determination of adhesivity of bituminous emulsions by water immersion test [14];
  - a. Immediate adhesivity;
- II. I.S. EN 13614 Determination of adhesivity of bituminous emulsions by water immersion test [14];
  - b. Water effect on binder adhesion;
- III. I.S. EN 12697-11 Determination of the affinity between aggregate and bitumen - Rolling Bottle Method [15];
- IV. I.S. EN 12272-3 Determination of binder aggregate adhesivity by the Vialit plate shock test method [16];
- V. ASTM D3625 / D3625M Standard Practice for Effect of Water on Bituminous-Coated Aggregate Using Boiling Water [17];
- VI. AS 1141.50 Resistance to stripping of cover aggregates from binders [18].

The flowchart of the emulsion-aggregate combinations that were tested is shown in Figure 2.



\*Note: Surface charges shown for the aggregates are based on the classification proposed by Bellanger and Duriez [8]

Figure 2. Flowchart of emulsion/aggregate combinations tested

In order to avoid any subjectivity factor in the interpretation of the test results for test methods I to III, V and VI, the level of adhesion between a given aggregate and the residual binder from the bitumen emulsion used was calculated as a mean of five independent observations. Each individual observation was performed by a member of the laboratory staff. The observers had to visually assess the level of adhesion by quantifying the percentage of the aggregate that was coated by the binder, at the end of the test. The percentage of the aggregate surface covered with a film of the binder was assessed and graded to the nearest 5 %. A high percentage of

coating by the bitumen indicates a high degree of aggregate emulsion compatibility. The result of the “Vialit Plate Shock test” (test method IV) was determined from three adhesivity measurement values, as per standard procedure, and, therefore, did not require five independent observations. In contrast to the other tests, the result for the Australian test, *Resistance to stripping of cover aggregates from binders* test (often referred to as the “Plate test”) described in AS 1141.50 [18] (test method VI) is recorded as the percentage of stripping of the aggregate from the bituminous binder. However, to match the expression of the results for the other test methods, the outcome values of this test were converted to give the percentage of bitumen coverage on the aggregates. All of the obtained aggregate emulsion adhesion test results, except for the Vialit Plate Shock test (test method IV) [16], were expressed as a minimum, maximum and average values of the five individual observations recorded.

### 3 TEST RESULTS AND DISCUSSION

#### 3.1 Emulsion adhesivity with dry aggregates

The first part of this experimental study consisted of assessing the degree of aggregate-emulsion adhesivity, when the aggregates were in their dry state. The objective of this stage of the study was to investigate the first hypothesis (i.e. H1); that aggregates can be classified as having either an electro-positive or electro-negative surface charge when they are dry. For the assessment of the aggregates in their dry state, the chippings were washed to remove adhering dust and then dried to a constant mass in an oven at a temperature in the range 105-110 °C.

The results of the adhesion tests performed with both emulsions on the four aggregate specimens, while in a dry state, are shown in Figures 3 to 8. The classification of the aggregate as being positive (+) or negative (-), in accordance with Figure 1, is shown in brackets, along the horizontal axis of each chart. The electrostatic charge of the emulsions is likewise indicated. The results obtained in all six test methods are summarised in Figure 9, indicating where there is agreement with H1 (✓) or contradiction (X).

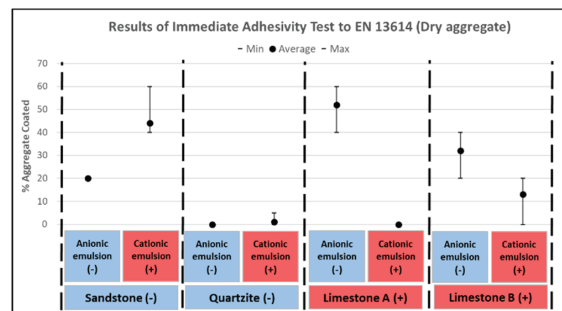


Figure 3. Results of Immediate Adhesivity Test to EN 13614 [14]

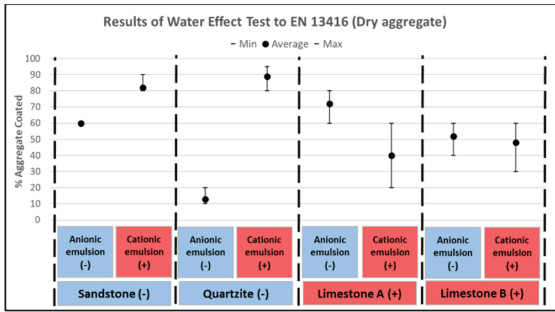


Figure 4. Results of Water Effect Test to EN 13416 [14]

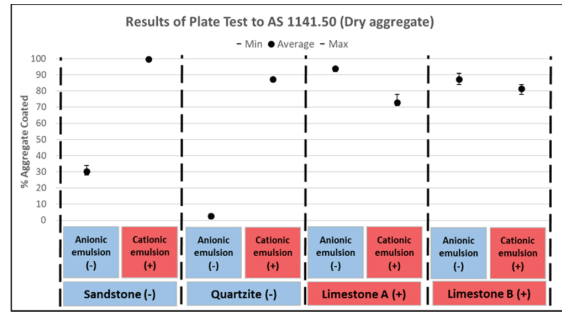


Figure 8. Results of "Plate Test" to AS 1141.50 [18]

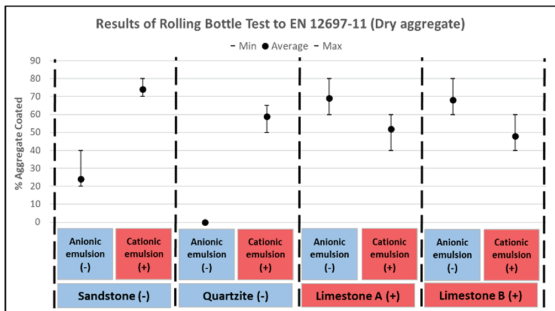


Figure 5. Results of Rolling Bottle Test to EN 12697-11 [15]

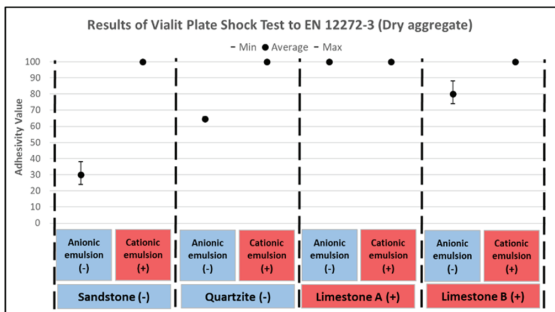


Figure 6. Results of Vialit Plate Shock Test to EN 12272-3 [16]

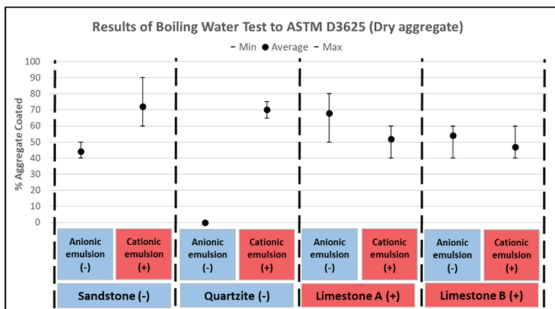


Figure 7. Results of Boiling Water Test to ASTM D3625/D3625M [17]

Test Method	Aggregate Type	Surface Charge Interaction	Emulsion Type	Output	Average Test Result	Hypothesis no. 1 confirmed
I	Sandstone	-	Anionic	% Aggregate Coated	20	✓
		+	Cationic		44	
	Quartzite	-	Anionic		0	✓
		+	Cationic		2	
	Limestone A	-	Anionic		52	✓
		+	Cationic		0	
	Limestone B	-	Anionic		32	✓
		+	Cationic		13	
II	Sandstone	-	Anionic	% Aggregate Coated	60	✓
		+	Cationic		82	
	Quartzite	-	Anionic		13	✓
		+	Cationic		89	
	Limestone A	-	Anionic		72	✓
		+	Cationic		40	
	Limestone B	-	Anionic		52	✓
		+	Cationic		48	
III	Sandstone	-	Anionic	% Aggregate Coated	24	✓
		+	Cationic		74	
	Quartzite	-	Anionic		0	✓
		+	Cationic		59	
	Limestone A	-	Anionic		69	✓
		+	Cationic		52	
	Limestone B	-	Anionic		68	✓
		+	Cationic		48	
IV	Sandstone	-	Anionic	Adhesivity value	30	✓
		+	Cationic		100	
	Quartzite	-	Anionic		65	✓
		+	Cationic		100	
	Limestone A	-	Anionic		100	X
		+	Cationic		100	
	Limestone B	-	Anionic		80	X
		+	Cationic		100	
V	Sandstone	-	Anionic	% Aggregate Coated	44	✓
		+	Cationic		72	
	Quartzite	-	Anionic		0	✓
		+	Cationic		70	
	Limestone A	-	Anionic		68	✓
		+	Cationic		52	
	Limestone B	-	Anionic		54	✓
		+	Cationic		47	
VI	Sandstone	-	Anionic	% Aggregate Coated	30	✓
		+	Cationic		100	
	Quartzite	-	Anionic		3	✓
		+	Cationic		87	
	Limestone A	-	Anionic		94	✓
		+	Cationic		73	
	Limestone B	-	Anionic		87	✓
		+	Cationic		81	

Figure 9. Summary of obtained tests results (dry aggregates)

From the above figures, it can be seen that for twenty-two of the twenty-four sets of adhesion tests performed (where a set consists of the same aggregate tested with both emulsions), a higher degree of adhesion was achieved when the test aggregate was combined with an emulsion with the opposite electro-static surface charge, i.e. the result obtained was consistent with the



hypothesis being tested. The exceptions were the two sets of results for the Vialit plate shock test on the two limestones. For one of the limestone sets, the level of adhesion was equal while, for the other set, the result was opposite to what would have been expected. Two broadly equivalent results were achieved on quartzite with the EN 13614 method (a) Immediate Adhesivity test procedure (test method I, Figure 3). The contra-hypothesis test result in the Vialit Plate Shock test (test method VI, Figure 6), provided an adhesivity value of 80 when the Limestone B (+) aggregate was combined with the anionic (-) emulsion, compared to an adhesivity value of 100 when the cationic (+) emulsion was used. However, on reflection having conducted the full suite of tests, it is the opinion of the authors that both of these test methods are possibly not the most suitable for discriminating between the levels of adhesion that can be achieved in practice. For example, in the Immediate Adhesivity test, the aggregates are only in contact with the emulsion for a matter of seconds before the coated specimens are subjected to washing by water. There is an inadequate time duration (i.e. not representative of on-site conditions) for adhesion to develop. On the other hand, with the Vialit Plate Shock test (test method IV), the test result is not merely based on the number of chippings that are bonded to the metal tray but also on the number of the fallen chippings that have remained stained by the bitumen.

Regardless of the two exceptions, to achieve the expected result in 22 of the 24 sets of combinations is a significant level of evidence to support the first hypothesis (H1). For the Water effect test to EN 13614 method (b) (test method II, Figure 4), the Rolling Bottle test method (test method III, Figure 5), the Boiling Water test (test method V, Figure 7) and the Plate test (test method VI, Figure 8), both limestone aggregates (+) showed a higher degree of adhesion to the anionic (-) emulsion. Likewise, when both the sandstone and the quartzite aggregates (-) were tested with these four test methods, a higher degree of adhesion was always achieved with the cationic (+) emulsion.

For illustration, the degree of coating achieved when the quartzite aggregate (-) was coated with the anionic (-) and cationic (+) emulsions, after the Boiling Water test (test method V) are shown in Figures 10 (a) and (b), respectively.

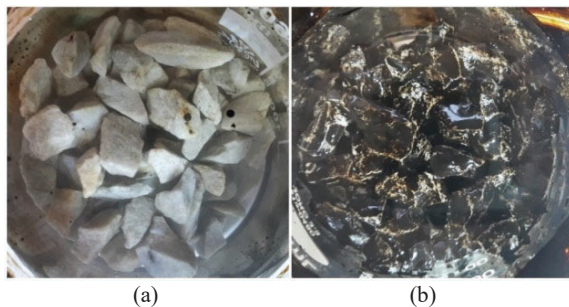


Figure 10. Quartzite coating after Boiling Water test with (a) anionic emulsion (0 % aggregate coated) and (b) cationic emulsion (70 % aggregate coated).

The degree of coating achieved when Limestone A (+) was coated with the anionic (-) and cationic (+) emulsions, after

performing the Immediate Adhesivity test (test method I) are shown in Figures 11 (a) and (b), respectively.

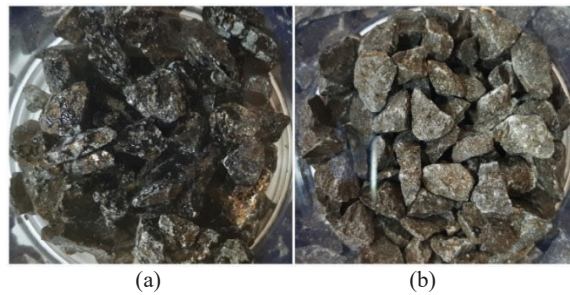


Figure 11. Limestone A coating after Immediate Adhesivity test with (a) anionic emulsion (52 % aggregate coated) and (b) cationic emulsion (0 % aggregate coated).

### 3.2 Emulsion adhesivity with damp aggregates

The second part of the experimental study included performing the same range of tests on the same aggregates but with the aggregates in a damp state. The objective of this stage of the laboratory study was to investigate the second hypothesis (H2), that the surface charge of a positively charged aggregate will change to negative, after being wetted with water. Therefore, prior to the aggregates being combined with the emulsions, they were soaked in distilled water at room temperature for 24 hours, and then they were allowed to drain for 30 minutes. While the hypothesis is only concerned with the two limestone aggregates (as both the quartzite and sandstone aggregates are already considered to have a negative surface charge under the classification proposed by Bellanger and Duriez [8]), the quartzite and sandstone aggregates were included in the study to examine if wetting these aggregates would have any effect on the degree of adhesion achieved, compared to that achieved when they were dry.

The results of the tests performed are shown in Figures 12 to 17. In order to keep the aggregate classification consistent with section 3.1, the same surface charges are shown (consistent with the classification proposed by Bellanger and Duriez [8]). The results obtained in all six test methods are summarised in Figure 18.

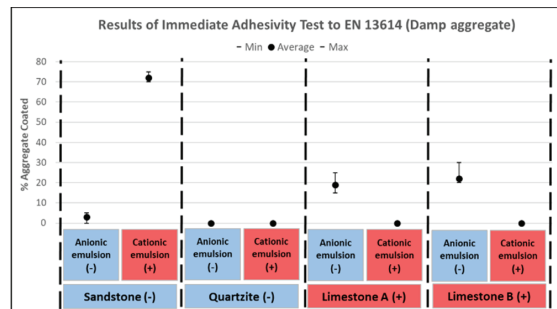


Figure 12. Results of Immediate Adhesivity Test to EN 13614 [14]

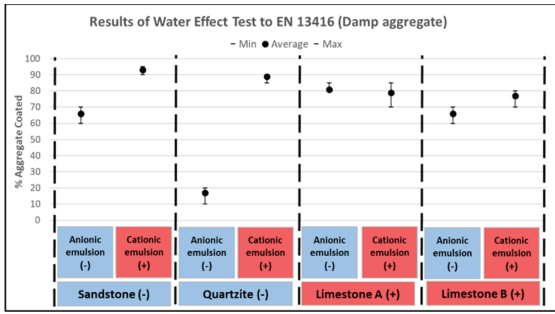


Figure 13. Results of Water Effect Test to EN 13614 [14]

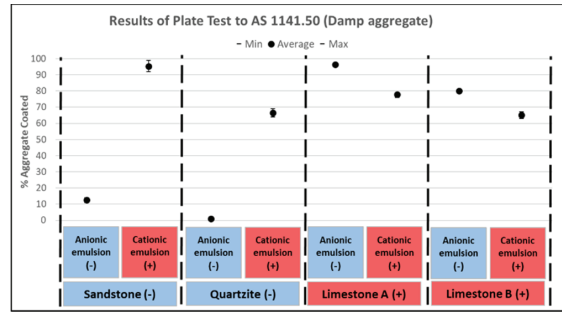


Figure 17. Results of Plate Test to AS 1141.50 [18]

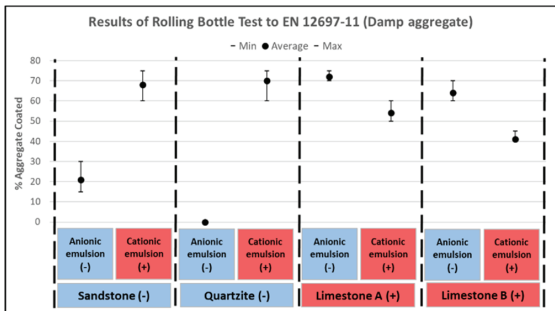


Figure 14. Results of Rolling Bottle Test to EN 12697-11 [15]

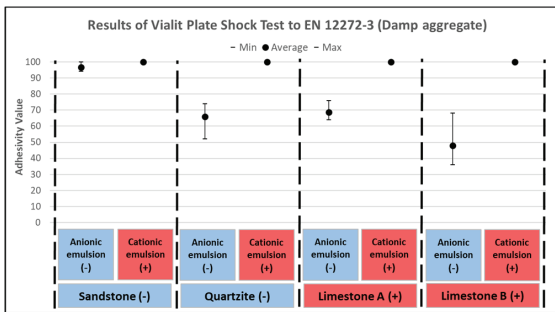


Figure 15. Results of Vialit Plate Shock Test to EN 12272-3 [16]

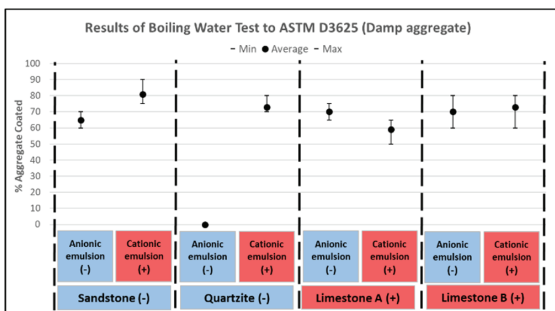


Figure 16. Results of Boiling Water Test to ASTM D3625/D3625M [17]

Test Method	Aggregate Type	Surface Charge Interaction	Emulsion Type	Output	Average Test Result	Hypothesis no. 2 confirmed
I	Sandstone	-	Anionic	% Aggregate Coated	3	-
		+	Cationic		72	-
	Quartzite	-	Anionic		0	-
		+	Cationic		1	-
	Limestone A	-	Anionic		19	X
		+	Cationic		0	X
	Limestone B	-	Anionic		22	X
		+	Cationic		0	X
II	Sandstone	-	Anionic	% Aggregate Coated	66	-
		+	Cationic		93	-
	Quartzite	-	Anionic		17	-
		+	Cationic		89	-
	Limestone A	-	Anionic		81	X
		+	Cationic		79	X
	Limestone B	-	Anionic		66	✓
		+	Cationic		77	✓
III	Sandstone	-	Anionic	% Aggregate Coated	21	-
		+	Cationic		68	-
	Quartzite	-	Anionic		0	-
		+	Cationic		70	-
	Limestone A	-	Anionic		72	X
		+	Cationic		54	X
	Limestone B	-	Anionic		64	X
		+	Cationic		41	X
IV	Sandstone	-	Anionic	Adhesivity value	97	-
		+	Cationic		100	-
	Quartzite	-	Anionic		66	-
		+	Cationic		100	-
	Limestone A	-	Anionic		69	✓
		+	Cationic		100	✓
	Limestone B	-	Anionic		48	✓
		+	Cationic		100	✓
V	Sandstone	-	Anionic	% Aggregate Coated	65	-
		+	Cationic		81	-
	Quartzite	-	Anionic		0	-
		+	Cationic		73	-
	Limestone A	-	Anionic		70	X
		+	Cationic		59	X
	Limestone B	-	Anionic		70	✓
		+	Cationic		73	✓
VI	Sandstone	-	Anionic	% Aggregate Coated	13	-
		+	Cationic		95	-
	Quartzite	-	Anionic		1	-
		+	Cationic		66	-
	Limestone A	-	Anionic		96	X
		+	Cationic		78	X
	Limestone B	-	Anionic		80	X
		+	Cationic		65	X

Figure 18. Summary of obtained tests results (damp aggregates)

From the above figures, it can be seen that only four of the 12 sets of test results for the two limestone aggregates were in agreement with Hypothesis 2 (H2) and that two of these sets were obtained with the Vialit Plate Shock test that has already been described as not being a suitable test for discriminating

between the levels of adhesion that can be achieved in practice. Moreover, one of the sets of test results that agreed with H2 was only marginal with a result of 70 % being achieved when the anionic emulsion was used versus 73 % when the cationic emulsion was used in the ASTM Boiling Water test (test method V) for Limestone B.

On balance, with eight of the twelve sets of results contradicting H2, there is sufficient evidence to reject the second hypothesis, as proposed by Schilling and Schreuders [10] and Peltonen [11].

For illustrative purposes, the degree of coating achieved when Limestone B was coated with the anionic (-) and cationic (+) emulsions, after performing the Rolling bottle test (test method III) are shown in Figures 19 (a) and (b), respectively. This result provides evidence that the surface charge on both limestone aggregates did not change from a positive one to a negative one, as a result of the aggregate being damp. (Results of 68 % and 48 %, respectively, were achieved when Limestone B was tested in dry condition.) Similar results were obtained with methods I and VI.

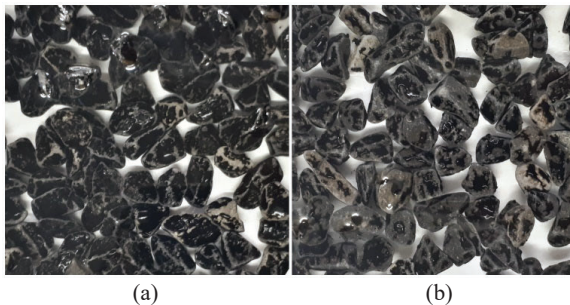


Figure 19. Limestone B coating after Rolling Bottle test with (a) anionic emulsion (64 % aggregate coated) and (b) with cationic emulsion (41 % aggregate coated).

It is interesting to note that, even though the results obtained with the sandstone and quartzite aggregates also suggest that their surface charge did not change, when the aggregates are damp, a higher degree of adhesion (by at least 5 %) was achieved in 7 of the 24 emulsion/aggregate combinations, when the aggregate was damp, compared to that achieved when they were dry. In contrast, the dry aggregates achieved a higher degree of adhesion (by at least 5 %) in 5 of the 24 emulsion/aggregate combinations, compared to when they were damp.

Of the total 48 sets of test results summarised in Figures 9 and 18, a higher degree of coating (by at least 5 %) was achieved when the aggregate was damp in 15 of the 48 sets (7 out of 24 for the tests performed on the sandstone and quartzite aggregates and 8 out of 24 for the tests performed on the two limestones). Conversely, 13 of the 48 sets showed that a higher degree of adhesion (by at least 5 %) was achieved when the aggregate was dry (6 with the quartzite and sandstone, 7 with the two limestones). A higher degree of coating (by at least 5 %) was achieved with the cationic emulsion in 25 of the 48 sets (12 out of 24 when the aggregate was dry and 13 out of 24 when the aggregate was damp). On the other hand, the anionic emulsion out-performed the cationic emulsion (by at least 5 %)

in 16 of the 48 sets of results (9 of which were when the aggregate was dry and 7 when the aggregate was damp).

The overall average degree of adhesion achieved in the first part of this study (i.e. with the dry aggregates) when the cationic emulsion was used was 64 %, compared to 47 % when the anionic emulsion was used. However, when only considering the degree of adhesion achieved when the emulsion was combined with an aggregate of the opposite surface charge, the average results were 73 % and 69 %, respectively. Of the results achieved when the aggregates were damp, the average degree of adhesion was 76 % with the cationic emulsion and 63 % with the anionic emulsion, when the emulsions were combined with the aggregate of the opposite surface charge in accordance with the classification of Bellanger and Duriez [8].

Overall, it was observed that the EN 13614 Immediate Adhesivity test method (test method I) [13] was not very discerning. The aggregate coatings obtained were difficult to interpret, as it was complicated to differentiate between binder adhesion and aggregate discolouration. The EN 12272-3 Vialit Plate Shock test (test method IV) [16] was also found to be not very indicative of the variation in the performance levels achieved between the anionic and cationic emulsions, in terms of the degree of adhesion with an aggregate. The other test methods used in this study were clearly more discerning. Consequently, in subsequent laboratory testing, it is proposed to omit the Immediate Adhesivity test and the Vialit Plate Shock test.

#### 4 CONCLUSIONS

Cationic emulsions are the emulsions of choice, throughout the world, for most road maintenance applications. They are especially preferred where a high level of performance is required, in terms of early cohesion build-up to allow for quick re-opening of the treated road section to traffic. Over the years, road engineers have also found that high-silica (i.e. non-limestone) aggregates possess a higher resistance to polishing by traffic and give a longer service life under high traffic loadings. The findings of this study confirm that when such aggregates are being used, a higher degree of adhesion is achieved with cationic emulsions. However, the findings of this study also suggest that, if a low-silica content aggregate, such as limestone, is being used (when allowed by a lower performance specification for the road section in question) then a higher degree of adhesion can be achieved by using anionic emulsions. These findings demonstrate that aggregate mineralogy and, in particular, its associated electrostatic surface charge, as proposed by Bellanger and Duriez [8], plays a very significant role in the aggregate-emulsion adhesion mechanism. Overall, the laboratory tests results confirm the hypothesis that aggregates possess either an electro-positive or an electro-negative surface charge. Consequently, as a result of its electrostatic charge, an aggregate will have a preference for either a cationic or anionic emulsion.

The results obtained with both limestone aggregates tested in a damp condition contradict Hypothesis 2 that the polarity of the electro-positive surface charge on limestone aggregates will change to negative if they are wetted. On average, a higher degree of adhesion was still achieved when the limestone aggregates were coated with the emulsion with an electrical



surface charge that was opposite to that of the dry aggregate, i.e. the anionic emulsion.

While the results of the study indicate that it is preferable to combine limestone aggregates with anionic emulsions (for the range of adhesivity test methods used), the results also indicate that the degree of adhesion obtained when using a cationic emulsion, regardless of the aggregate type, was, on average, higher than that of the anionic emulsion (at 64 % versus 47 % coating). This indicates that cationic emulsions are more compatible with a wider range of aggregates, regardless of the aggregate's surface charge, and is possibly a factor that is influencing their dominant position in the market.

The next phase of this research project is to investigate the development and use of adhesion agents to improve the adhesivity properties of anionic bitumen emulsions. The ultimate aim of this research is to develop new anionic emulsions with improved performance for road applications.

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