

The use Anionic Bitumen Emulsions in Pavements - A state of the art review

Simon Ignatavicius¹, Alan Kavanagh², David Colleran³, Michael Brennan⁴, Shane Newell⁵

¹Colas & Galway-Mayo Institute of Technology, Dept. of Building & Civil Engineering, ²Technical Manager, Colas Ireland, ³Technical Manager, Chemoran, ⁴Lecturer, NUI Galway (retired), ⁵Lecturer and Chartered Engineer, Galway-Mayo Institute of Technology, Dept. of Building & Civil Engineering

Abstract

Bitumen emulsions can be either cationic with a pH of the order 2 or anionic with a pH of the order 10. The vast majority of emulsions used in the pavement construction and maintenance industry in Europe are cationic. Consequently, knowledge on their use is very limited with very little information available in the current literature. Anionic bitumen emulsions are widely used throughout North America and Africa for a range of road maintenance techniques, including pavement sealing, gravel seals, tack coating and in situ pavement recycling. The objectives of the study described in this paper were (a) to perform a literature review of the state of the art worldwide, (b) to explore the potential for the development of new emulsifiers or bitumen additives to improve the performance of anionic emulsions and (c) to explore the development of their use in Europe.

1 INTRODUCTION

An emulsion is a mixture of two or more liquids that are normally immiscible, for example, water and oil. Water and oil are immiscible because water is polar, i.e. its molecules have an electrostatic charge, while oil is non-polar. In a bitumen emulsion, 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 in suspension in the water phase by electrostatic charges imparted to them by chemical compounds called emulsifiers.

Emulsifiers can be derived from natural materials, such as vegetable oils, or manufactured in industrial chemical plants. The latter are often referred to as “amines”. Emulsifier molecules are usually composed of a head and tail, as shown in Figure 1. The head of the emulsifier is polar and is hydrophilic (i.e. water-loving), while the tail is non-polar and is lipophilic (i.e. oil-loving). It is this characteristic that enables emulsifiers to act at the interphase of the oil (or bitumen) and the water and is why they are often also termed “surface active agents” or “surfactants”.

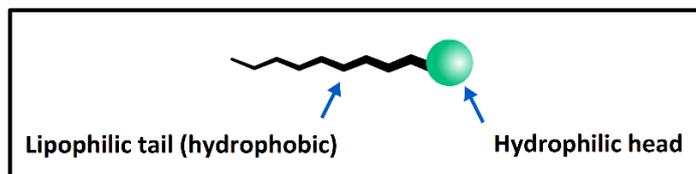


Figure 1: Typical structure of an emulsifier

The first patent describing the utilisation of a bitumen in a water dispersion for the road construction industry was taken out in 1906. 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 paving applications, they were mostly used in spray applications and for dust suppression [1]. By 1960, about 95 % of all bitumen emulsions used in the USA were of the anionic type [2].

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 degree of affinity between the bitumen and most aggregates. They also exhibited a faster “curing time”, i.e. the time required for the residual bitumen to coalesce and achieve its full strength as a binder. Consequently, by the early 1970s, more than 90 % of manufactured emulsions were cationic. By 2005, this figure was nearing 100 % in some countries [3]. However, despite this, anionic emulsions are still used in large quantities in certain countries today, such as the USA, Canada, South Africa and Spain. Their advantages over cationic emulsions are that they can be used with poorer quality aggregates and can be produced using relatively cheap emulsifiers that are by-products from the paper pulping industry. The main objective of this literature review was to establish the state of the art of anionic emulsions and to investigate if their use may be advantageous over cationic emulsions in more widespread applications.

2 EMULSION CHEMISTRY: ANIONIC VERSUS CATIONIC

The main components that are used to manufacture a bitumen emulsion include the bitumen, sometimes a solvent, an emulsifier, an acid or an alkali (depending on the type required, i.e. cationic or anionic) and water. Emulsifiers are commonly supplied in a water-insoluble form so, therefore, they need to be “activated”, so that they dissolve in the water phase and form what is called an aqueous soap. Typically, hydrochloric acid is used to neutralise or “activate” the emulsifier in cationic emulsions, while sodium or potassium hydroxides are commonly used to activate anionic emulsifiers. Cationic emulsions usually have a pH value of 2 to 3, while anionic emulsions have a pH in the range of 10 to 11.

When a cationic emulsifier is activated, the head of the emulsifier will adopt a positive charge, while the chlorine (Cl) from the hydrochloric acid will take the form of a negatively charged “counter-ion” that is weakly bonded to the polar head. Figure 2 illustrates the activation of an ammonium based cationic emulsifier. The chemical formula for the hydrocarbon tail, which consists of 12 to 18 carbon atoms, is conventionally labelled “R” in such diagrams [5].

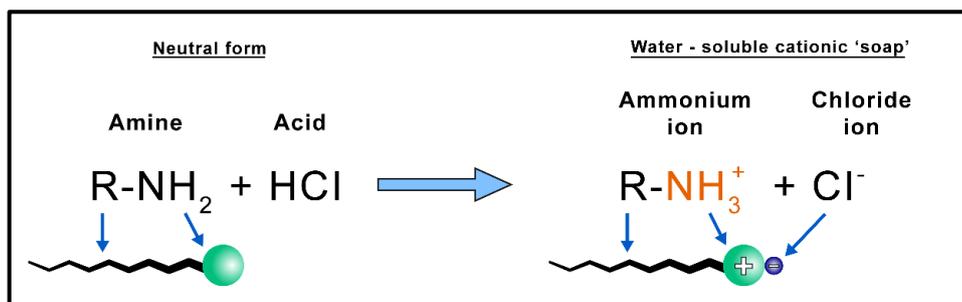


Figure 2: The activation of a cationic amine emulsifier (modified from [4])

Conversely, when an anionic emulsifier is activated, the head of the emulsifier will adopt a negative charge, while the sodium (Na) from the sodium hydroxide alkali will take the form of a positively charged “counter-ion” that is weakly bonded to the polar head. This is illustrated in Figure 3.

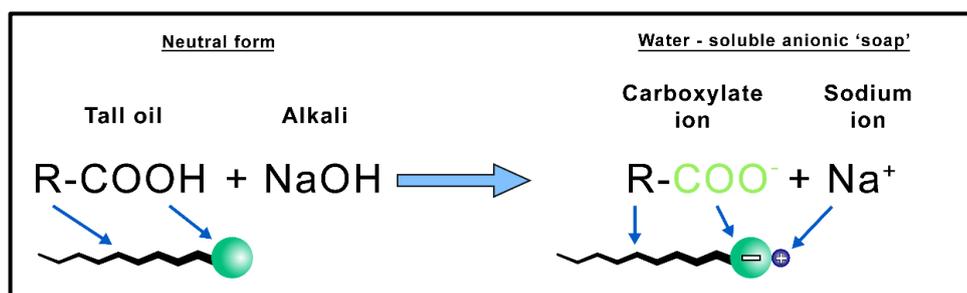


Figure 3: The activation of a tall oil anionic emulsifier (modified from [4])

In a bitumen emulsion, the hydrophilic head of the emulsifier molecule and its associated counter-ion orientates towards the water phase, while the hydrocarbon tail orientates towards the bitumen phase, as illustrated in Figure 4. This distinctive characteristic gives the molecule its emulsifying ability. Because each droplet is similarly charged, they will repel each other while in suspension in the soap/water-phase and, thereby, form a stable emulsion. It is only when an outside agent is introduced to this system, for example an aggregate, that the emulsion will become destabilised and “break”, i.e. separate out into its two original liquid components.

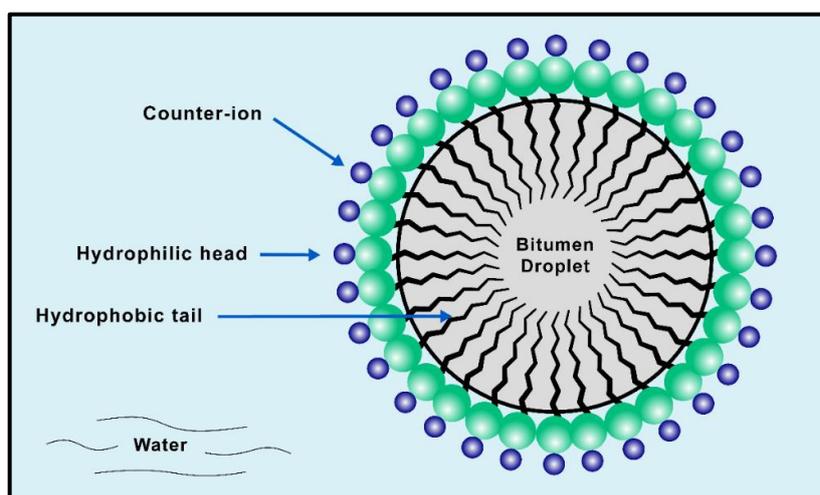


Figure 4: An illustration of an emulsifier stabilised bitumen droplet

In an anionic emulsion, the positively charged sodium counter-ion will dissociate from the emulsifier head in the aqueous solution, thereby, leaving the rest of the emulsifier head negatively charged at the surface of the droplet. For a cationic emulsion, it is the chlorine counter-ions that are lost to the water and leave the remaining emulsifier with a positively charged head at the surface of the bitumen droplet [5, 6]. It is this characteristic that makes it possible to determine if an emulsion is cationic or anionic, by placing them in an electric field between an anode and a cathode. The negatively charged bitumen droplets in an anionic emulsion are drawn to the anode, while the positively charged bitumen droplets in a cationic emulsion are drawn to the cathode.

2.1. Anionic Emulsifiers

Oleic acid, which is a fatty acid that occurs naturally in various animal and vegetable fats and oils, is reported to be the first type of emulsifier that was used for the emulsification of bitumen [7]. Generally, any type of long chain fatty acid or mixture of fatty acids can be used. A fatty acid is a carboxylic acid consisting of a long hydrocarbon chain and a terminal carboxyl group, i.e. the “R” and the “COOH” shown in Figure 3. The chain is termed a hydrocarbon as it consists of hydrogen and carbon atoms, while the carboxyl group contains a particular arrangement of carbon, oxygen and hydrogen atoms. Nowadays, anionic emulsifiers are mainly derivatives of by-products from the paper or “kraft” pulp industry, i.e. tall oil fatty acids (TOFA), tall oil rosins and lignin.

The kraft pulping process involves the separation of cellulose fibres from wood via chemical processing. This is achieved by dissolving the lignin, the material that binds the cellulose fibres together, in a mixture of sodium hydroxide and sodium sulphide. High alkalinity and high temperatures convert the fatty and rosin acids that are present into sodium soaps, forming a black liquor. This black liquor is evaporated in order to recover the pulping chemicals for re-use. During the recovery of the pulping chemicals, tall oil soaps start to float in the storage tank and are then skimmed off and collected. Subsequently, the skimmed soap is acidified with sulfuric acid and converted to crude tall oil (CTO) [8].

The CTO can then be further refined into tall oil fatty acids (TOFA), distilled tall oil (DTO), tall oil rosins and tall oil pitch, as shown in Figure 5 [9]. The main constituents of TOFA are oleic acid, linoleic acid and abietic acid [7].

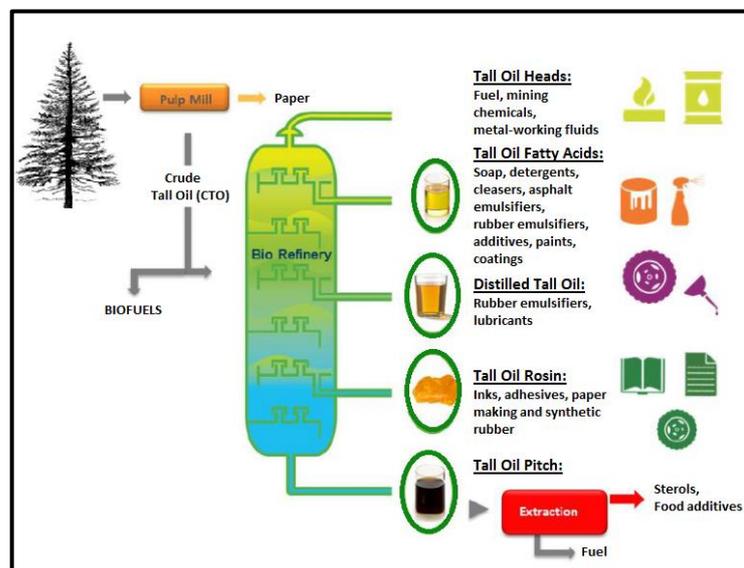


Figure 5: The various derivatives of CTO [modified from 9]

A special type of anionic emulsion called a “high float” emulsion can be manufactured when either CTO or DTO is used at high dosage rates, i.e. of the order 1.5 to 2.0 %. Such emulsions were developed by McConnaughay in Canada in the 1950s [10] and are termed “high-float” emulsions, as they are characterised by a test procedure known as the “float test”, as described in ASTM D 139 [11]. The high emulsifier dosage rates result in a chemical modification of the bitumen in the emulsion, so that after the water evaporates, the residual binder possesses a “gel” quality that is more resistant to flow and less temperature sensitive [12], as shown in Figure 6.

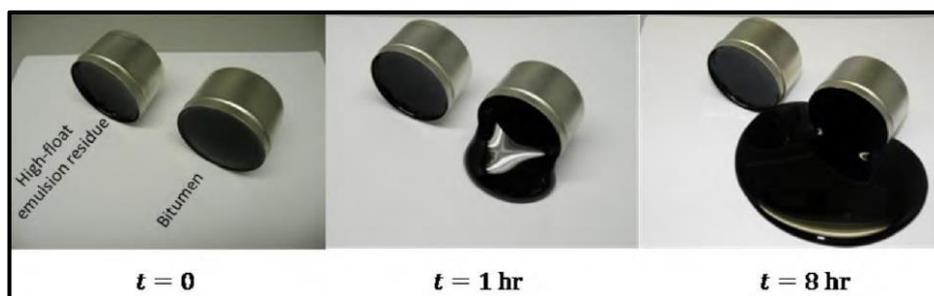


Figure 6: Specimens showing the “gel” structure of the residual binder of high-float emulsions [13]

As a result of these distinctive characteristics, aggregate particles can be coated with a thicker film of bitumen, there is less “bleeding” or “fating up” of the binder during the summer months, and the binder is less brittle and more

resistant to cracking, during the winter months. Such properties are most desirable in Canada and parts of the USA, where road surface temperatures can vary widely, such as from $-50\text{ }^{\circ}\text{C}$ in winter up to $+80\text{ }^{\circ}\text{C}$ in summer.

Other derivatives of tall oil are also used as anionic emulsifiers. Vinsol® resin is a thermoplastic natural resin that is extracted from pinewood stumps exclusively by a company called Pinova, Inc. in Brunswick, Georgia, USA. Similar products called Vinex® resin and Carbofen® resin are supplied by Industrial Oleochemical Products (IOP South Africa) and Polytrade (Brazil), respectively.

2.2. Cationic Emulsifiers

Cationic emulsifiers typically comprise a hydrocarbon chain and an amine functional group, as shown in Figure 2. An amine is an organic compound derived from ammonia, in which one or more of the hydrogen atoms in the ammonia molecule (NH_3) is replaced by an organic functional group, such as an alkyl or an aryl. The hydrocarbon chain is provided by a TOFA. These emulsifiers are normally manufactured in a specialist chemical plant by reacting the TOFA with the amine under pressurised conditions at high temperatures. There are a large variety of cationic emulsifiers available on the market and they are classified as monoamines, diamines, quaternary ammonium compounds, amidoamines and imidazoles.

3 EMULSION “BREAKING” AND ADHESION TO THE AGGREGATE

A fundamental property that is required of a bitumen emulsion is an ability to “break” and adhere on application. Once applied to the receiving surface, e.g. to the existing road pavement, in the case of spray-grade emulsions or to an aggregate, in the case of mixing-grade emulsions, the bitumen emulsion will undergo what is termed a “breaking” process, whereby the bitumen comes out of suspension or separates from the water phase of the emulsion. Then, the water will evaporate off the road surface (or be forced out by compaction equipment in cold-mix asphalt applications), thereby leaving a residue of bitumen that is bonded or adhered to the receiving surface.

Normally, depending on the final application of the emulsion, its breaking speed can be controlled to be either slow, medium or rapid. This can be done by adjusting the emulsion formulation with different types and/or levels of emulsifier. “Rapid-set” (RS) emulsions set quickly once they come in contact with the receiving surface. Such emulsions are used as tack coats and for surface dressing (or “chip-sealing”) operations. “Medium-set” (MS) emulsions are usually used for mixing with aggregates of low surface area, i.e. single sized, to produce open-graded mixes, while “slow-set” (SS) emulsions are mixed with aggregates of high surface area, i.e. that are well graded, to produce slurry seals and dense-graded mixes.

Figure 7 illustrates the breaking process of a typical bitumen emulsion. Once in contact with a solid surface, such as the road pavement or an aggregate, the emulsion will become unstable, causing the droplets to flocculate. This is precipitated by the physical and chemical changes imposed on the system, which overpower the electrostatic charges between the bitumen droplets, i.e. the emulsion irreversibly “breaks”. During flocculation, bitumen droplets approach closer to each other, thereby, leading them to adhere. Following this, the adhered bitumen droplets fuse together (i.e. coagulate) to form droplet chains, which finally, after complete water evaporation, combine to form a continuous bitumen film. This final step is termed emulsion coalescence or setting [5, 14].

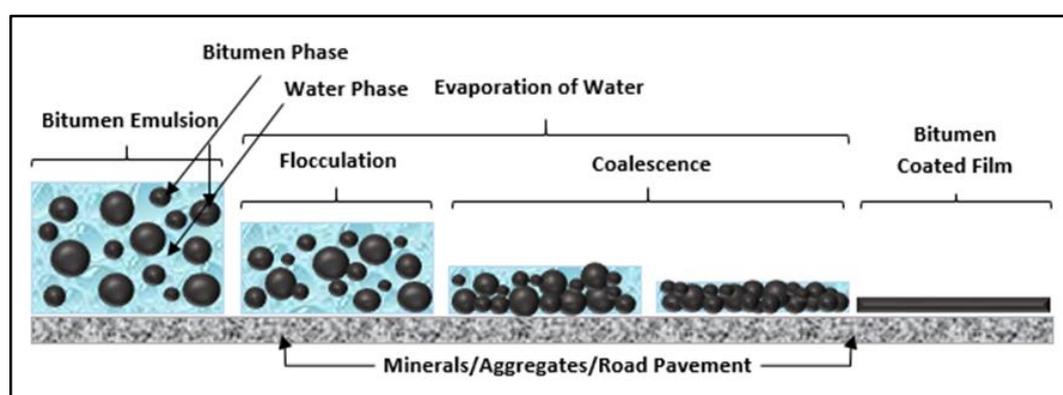


Figure 7: The breaking process of a bitumen emulsion

However, the property of strong adhesion is not always easy to obtain, and it appears to be influenced by minor variations in the composition of the emulsion [15] and by the aggregate type used. Good adhesion is usually achieved if the aggregate is completely “wetted” or coated by the bitumen, i.e. they are electrostatically bonded together. Poor adhesion is caused by premature coalescence occurring away from the surface or the presence of water at the interface of the aggregate and bitumen [6]. The former phenomenon can occur when a cationic emulsion is used on a dusty

aggregate, where the dust causes the emulsion to break and then coat the dust particles before it has a chance to “wet” and coat the coarse aggregate particles. Many authors also claim that the electric charge at the surface of the aggregate can affect the level of adhesion achieved. These arguments are further described in the following paragraphs.

3.1. Effect of aggregate type

Aggregates constitute the largest part of the bituminous pavement structure, as they are used in both asphalt mix and pavement sealing applications. Their main function is to withstand and distribute the traffic induced loadings through the pavement structure and to provide a level of skid resistance at the surface of the pavement.

There are three main types of rock classification, depending on its formation process. Igneous rocks include basalt, dolerite, granite, andesite, porphyry, rhyolite and diorite. Sedimentary rocks include limestone, dolomite and sandstone (gritstone), while commonly used metamorphic type rocks include meta-quartzite, hornfels, schist and gneiss. The three rock types possess distinct physical, mechanical and chemical properties and since the breaking mechanism of emulsion involves interaction with an aggregate, the chemical characteristics of the aggregates are important.

Some authors [14] have argued that the breaking speed of an emulsion and the adhesivity of the residual bitumen to the aggregate is strongly influenced by the mineralogy of the aggregate and, in particular, to its silica (SiO_2) content. Rock types with high silica contents were originally considered as “acidic”, while the rock types with less silica content and, correspondingly, with more of the metallic oxides were considered as basic.

In the 1950s, Bellanger and Duriez [16] and Mertens and Wright [15] described how aggregates can carry different distributions of electro-positive to electro-negative surface charges. They claimed that “acidic” aggregates, i.e. those with high silica contents, generally possess an electro-negative charge, while “basic” aggregates have an electro-positive charge. A summary of their classification is shown in Figure 8. In addition, other authors [17, 18] have described how acidic and basic rocks can be classified as hydrophilic and hydrophobic, respectively, with regard to their affinity for water.

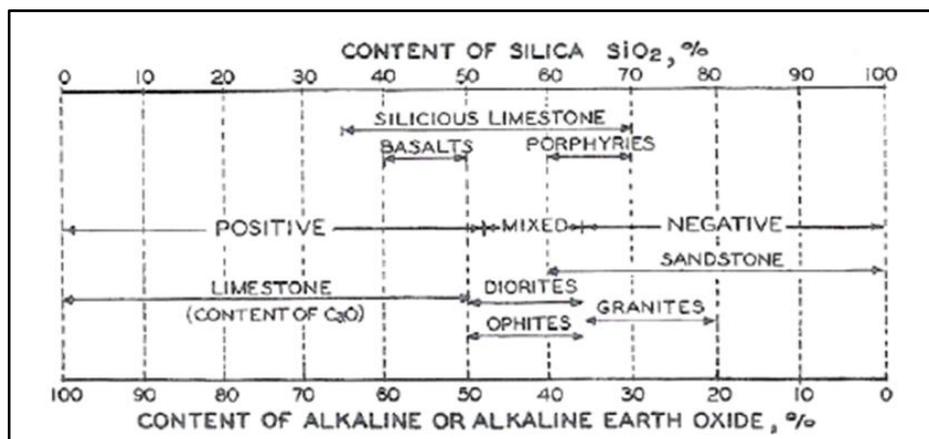


Figure 8: Classification of aggregates by silica content and surface charge [15]

Therefore, in order to obtain the desired emulsion break, cohesion and adhesivity properties, it would seem rational to select an emulsion with an electrical surface charge opposite to that of the aggregate. Consequently, negatively charged anionic emulsions would be preferred for coating the electro-positively charged surfaces of basic aggregates, whereas positively charged cationic emulsions would be preferred for the electro-negatively charged surfaces of acidic aggregates.

Despite this logic, some studies have disputed this electro-positive versus electro-negative classification. Research conducted by Dybaiski [19], following that of the Virginia Highway Research Council, and Schilling and Schreuders [20] found that all aggregates, including limestone, have negative surface charges. Schilling and Schreuders were able to explain that while limestone aggregate is electro-positive and siliceous aggregate is electro-negative, when they are both perfectly dry, both aggregates become negatively charged, when moistened with water. Plotnikova also found that the adsorption rates of anionic and cationic emulsifiers onto wet and dry aggregates are different [21].

Such findings in relation to the dry versus wet state of the aggregate might not appear to withstand scrutiny, considering that for bitumen emulsions the continuous phase is water and this, therefore, would be the first material to come in contact with the aggregate. Consequently, the aggregate being in dry or wet state should not make any difference to the degree of attraction between the aggregate and the emulsion.

However, these findings are noteworthy. It is easy to envisage aggregates having a relatively high moisture content when used in emulsion bound asphalt mix applications, such as slurry seals and in situ recycling. However, for chip seal work, it is easy to envisage the surface of the chip being either wet or fully dry, depending on the way it was prepared and the prevailing weather conditions. During summer months, it is common to see fully dry chippings being used, even if the chippings had been washed. On the other hand, if a graded aggregate is used, as in Canada, it is reasonable to assume that the fine portion of the aggregate will hold onto moisture longer.

3.2. The chemical reaction during breaking of the emulsion

Assuming that the aggregates used in road construction can be either negatively or positively charged when they are used, then anionic and cationic emulsions will break and adhere to these aggregates differently.

Anionic Emulsion with negatively charged aggregate:

When an anionic emulsion is used to coat negatively charged aggregates, e.g. the moistened graded aggregate used in graded seals, known as “gravel seals” in Canada, or a dry high silica content rock type such as granite, there are no attractive forces between the bitumen droplets and the surfaces of the aggregates, i.e. both are negatively charged. Therefore, the breaking of the emulsion by chemical action will not occur. Accordingly, anionic emulsions rely on evaporation and the compressive force of compaction rollers and/or traffic for breaking to occur [20, 22 & 23]. As a result, such emulsion-aggregate combinations tend to be used more often in countries with dry warm climates, e.g. South Africa, Canada, USA and Australia.

Anionic Emulsion with positively charged aggregate:

If a dry limestone aggregate is being used, it will be positively charged and the anionic bitumen emulsion will break by means of an electro-chemical reaction [24]. The attraction between the positively charged aggregate and the negatively charged bitumen droplets will result in a breaking of the anionic emulsion and good adhesion between the bitumen and the aggregate. Accordingly, anionic emulsions are often used for chip seal applications in Canada and the USA.

Cationic Emulsion with negatively charged aggregates:

By contrast, the bitumen droplets in emulsions manufactured using cationic emulsifiers will be attracted to negatively charged aggregate surfaces, e.g. all moistened aggregates and dry high silica aggregates such as sandstone. It should be noted that sandstones and other high silica content aggregates are typically those with high PSV (Polish Stone Value) and AAV (Aggregate Abrasion Value) values and most often used for surface dressing applications in Europe. As the affinity of these aggregates for the bitumen droplets is greater than that for the water, the water in the system is displaced and the bitumen droplets coagulate at the surface of the aggregate to form a residual film of bitumen coating the aggregate, as shown in Figure 9 [20].

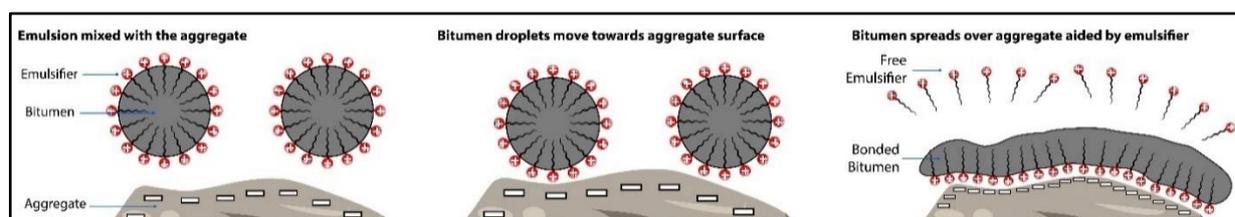


Figure 9: Breaking and adhesion of cationic emulsion to aggregate with a negative surface charge

Cationic Emulsion with positively charged aggregates:

Of course, if the aggregate being used were a dry limestone or basalt rock type and it was not moistened, it would have a positively charged surface and, as a result, the cationic emulsion would be slow to break and would have no affinity for the aggregate.

In summary:

When all factors are taken into consideration, cationic bitumen emulsions are the preferred emulsion type for surface dressing (chip-sealing) and tack coat applications in Europe, where a quick breaking of the emulsion and a quick build-up of cohesion is required, so that the road can be re-opened to traffic with a minimal delay. Anionic emulsions are much more suitable for “gravel seals” and/or chip sealing in countries like Canada and the USA, when mostly very dusty or graded aggregates are available. In addition, anionic emulsions work very well when making slurry seals with poor quality aggregates, where a stable system with a slow break is more desirable than a quick cohesion build-up. Cationic emulsion would break too quickly with such aggregates and would not give the level of coating or workability required. Anionic emulsions are, in general, more storage stable than cationic emulsions and lend themselves for use as water-proofing applications – something cationic emulsions are not suited to as they are more likely to break on the bristles of the brush during application.

In order to improve the breaking speed and, consequently, speed up the cohesion build-up of anionic emulsions (and cationic emulsions to a lesser degree), many authors have described the use of breaking agents. However, to date, these agents are not widely used throughout the industry and are not discussed in this paper. However, adhesion agents have been found to improve the degree of adhesion between the residual bitumen from an anionic emulsion and the aggregate. Such agents are used in the industry and are described in the following section.

3.3. Adhesion agents for anionic emulsions

Adhesion agents are very similar to emulsifiers in their make-up and typically comprise a hydrocarbon chain and an amine functional group head. These compounds are normally prepared from the higher molecular weight ethylene amines and fatty acids. Adhesion agents act as a contact bridge that bonds hydrophilic aggregate to hydrophobic bitumen. The amine head of the molecule adheres to the aggregate surface, while the hydrophobic hydrocarbon chain bonds to the bitumen.

When emulsions are used to coat aggregates or seal existing road pavements, the length of the hydrocarbon chain of the emulsifier and/or the adhesion agent being used is an important factor in the adhesion mechanism. Other influencing factors are the surface area of the aggregate, the surface polarity of the aggregate particles, i.e. positive or negative, and the acid/base interactions at the emulsion-aggregate interface. The degree of adhesion between a given emulsion or bitumen and an aggregate particle is dependant on its initial wettability (or ability to coat the aggregate) and by the degree of attraction between the residual bitumen and the aggregate [6].

Khan, et al. [6] have investigated the adhesion of bitumen droplets of an emulsion to an aggregate surface. They found that the addition of very small quantities (0.02 %) of adhesion agents to the water phase resulted in improved adhesion. Khan explained that the adhesion agents used were more effective than the emulsifiers used at forming a bond with the aggregate, due to their stronger affinity towards the aggregate surface. As the emulsifier molecules tend to have a longer hydrocarbon chains than that of the adhesion agent, they are more attached to the oil phase (i.e. bitumen droplets) of the emulsion. As a consequence, the adhesion agents are able to move more quickly than the emulsifier ions onto the aggregate surface. As illustrated in Figure 10, the formed layer of adhesion agent molecules then act to attract the bitumen droplets, thereby, allowing the droplets to settle and adhere to the mineral surface.

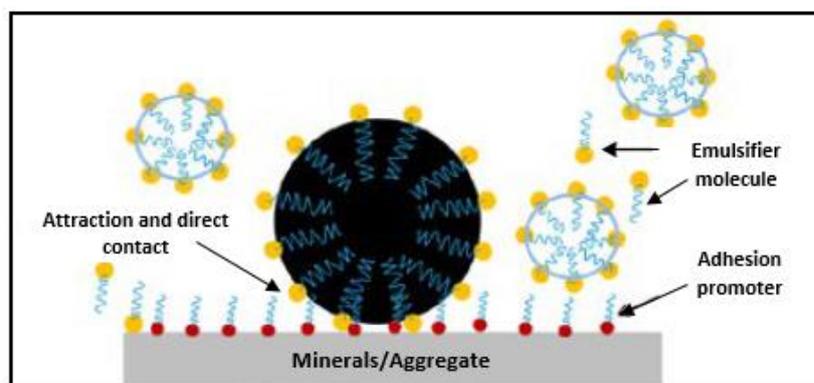


Figure 10: Proposed mechanism of adhesion between bitumen-mineral surface in the presence of emulsifier and adhesion promoter [6]

Mertens found that alkanolamine based adhesion agents greatly improve the adhesion of anionic bitumen emulsions [15]. Schilling describes how the addition of an aqueous solution of a poly-carboxylic acid-polyethylene amine type compounds to the anionic emulsions, prior to application, improves adhesion substantially, even with highly acidic (i.e. negatively charged) aggregates [25].

4 TYPICAL APPLICATIONS OF ANIONIC EMULSIONS

Despite the dominant use of cationic emulsions in road construction applications, anionic emulsions are still widely used throughout North America, Africa and Australia for a range of road maintenance techniques, including pavement sealing, gravel seals, tack coating, slurry sealing and in situ pavement recycling. The majority of emulsions used for such applications in Europe are cationic. Anionic emulsions are also used as a waterproofing material in the construction industry worldwide (e.g. for roofing applications).

The performance requirements for spray grade emulsions, such as gravel seals and tack-coats are much different than those for mixing grade emulsions used to make slurry seals and for in situ pavement recycling. Spraying emulsions are usually formulated to break rather fast on the road. In addition, since they are going to be sprayed, viscosity is

also an important parameter. Mixing grade emulsions are usually designed to be more stable, so as to allow full coating of the aggregate and a degree of mix workability before the emulsion breaks.

4.1. Surface Dressing

Surface dressing or “chip sealing”, as it is called in some countries, is one of the most commonly used road maintenance techniques throughout the world. It is a two-step process, consisting of the application of a layer of bitumen emulsion onto the existing pavement surface, followed by a layer of single size aggregate chippings (see Figure 11). When the emulsion breaks, it leaves a residual layer of bituminous binder that has two functions. Firstly, it acts as an impermeable membrane to seal the pavement from any water ingress and, secondly, it acts as a glue to bind the chippings to the receiving surface. The chipping then act to provide a new surface texture and impart an increased degree of skid resistance to the road user.



Figure 11: Applying the chipping to the surface dressing binder

The cover aggregates used for surface dressing applications can be classified into three sub-groups, depending on the amount of fine aggregate present (i.e. passing the 75 micron sieve):

1. Washed chips are clean, single sized coarse aggregates having a fines content of 0 to 1 %, by mass. This is usually achieved by passing the aggregate through a washer at the quarry, sometimes twice;
2. Unwashed (dirty) chips usually have a fines contents of 1 to 3 %. The general gradation is still that of a single size stone, or close to it, but they have not been washed; and
3. Graded aggregate has a continuous grading, so it typically contains a coarse aggregate fraction, a fine aggregate fraction and a fines fraction. The fines content is usually of the order 2 to 7 %, by mass.

The function of the bitumen emulsion in a surface dressing system is the same regardless of the gradation of the cover aggregate, i.e. it has to spray and cover the receiving substrate uniformly, achieve a good bond to it, have sufficient stability to wet the cover aggregate and then break and cure quickly to create a strong bond to the cover aggregate particles. Anionic emulsions are widely used for chip sealing applications in North America and, particularly, in Canada, where washed single sized aggregates are typically not available locally. The most commonly used emulsions are the “High Float” anionic emulsions. These emulsions can be sub-classified as either “rapid set”, “fast medium set” or “slow medium set”, depending on the breaking speed of the emulsion. Each of these emulsion types can be polymer-modified or not.

High float “fast medium set” emulsions are preferably used with unwashed chips. These types of emulsion have sufficient wetting capability to grip the stone even if a dust film is present. High float “slow medium set” emulsions are preferably used with graded aggregates that have a high surface area. These high float emulsions are designed to wet a high amount of fines before breaking. A softer emulsion residue binds many of the finer particles and then stiffens slightly, similar to mortar. Whereas in Canada, chip seals that use graded aggregates are known as “graded seals” or “gravel seals”, in other countries, this surface treatment technology is known as “Otta seal”.

The Otta seal technology was first developed and trialled in Norway’s Otta Valley in 1963. Since then, it has been used in northern Europe, Africa and other locations as an economical and practical alternative to traditional bituminous surface treatments. Otta sealing involves placing a graded aggregate on top of a relatively thick film of relatively soft bituminous binder. The binder works its way into the aggregate with rolling and trafficking. In this manner, the graded aggregate relies both on mechanical interlocking and bitumen binding for its strength. Trafficking of the seal immediately is desirable and its final appearance is formed after four to eight weeks giving a “premix” like appearance in the wheel paths [26].

Figure 12 illustrates the difference in the composition and structure of a single Otta seal in comparison to a single chip seal.

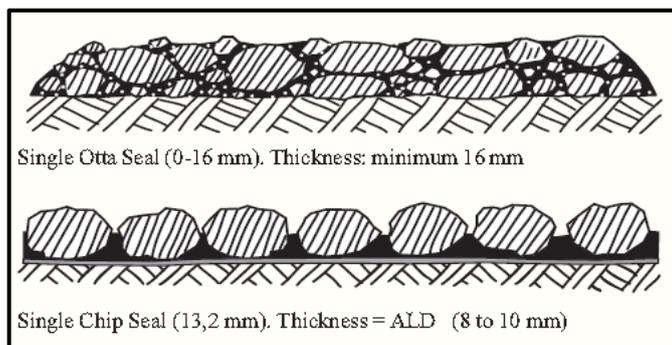


Figure 12: Composition and structure of a single Otta seal compared to a single chip seal [26]

Aggregates of relatively lower quality may be used for Otta seals compared to those typically specified for conventional chip seals. The aggregate grading is relatively relaxed and allows for a rather wide grading envelope depending on the level of traffic expected. Generally, for roads carrying light traffic (<100 vehicles per day), a 'coarse' grading should be chosen while a 'dense' grading should be used for roads carrying greater than 100 vehicles per day. Otta seals, like with chip seals, can be applied in single or double layers.

4.2. Tack coating

Tack coats and bond coats are a layer of bitumen emulsion applied between two layers of asphalt. As their names imply, their function is to improve the degree of adhesion between the two layers. The only difference between a tack coat and a bond coat is that the emulsion used in the bond coat will typically contain a percentage of polymer and, as a result, will generally achieve a greater bond strength.

The main characteristics expected from tack coat emulsions are storage stability and quick breaking. The emulsion viscosity must be relatively low to provide good wetting of the existing surface and to also have the ability to penetrate through the remaining layers of dust or fines on the existing old surface [7]. The emulsions are usually applied at a rate of 0.2 to 0.5 kg/m², with the emulsion having a residual binder content between 40 and 50 %.

There is broad variation in the types of emulsion used for tack coats worldwide. Often the choice between the use of an anionic or a cationic tack coat emulsion depends on the type of emulsion (i.e. cationic or anionic) that is available locally, as typically an emulsion plant will only produce one or the other. Then, over time, customers got used to specifying one type over the other. The anionic versions are mainly manufactured using distilled tall oils, liquid rosin or lignin-based emulsifiers.



Figure 13: Tack coat application

4.3. Fog sealing

A fog seal is a light application of diluted anionic or cationic emulsion onto an existing pavement surface to replace binder lost from the surface over time due to the effects of binder aging and trafficking. Fog seals are also used as a preventative maintenance technique on surface dressings that are beginning to show signs of chip loss at the onset of winter. Once the fog seal emulsion breaks, it leaves a sufficient residue of new bitumen that will help prevent or minimise any further chip loss.

A number of different types and grades of emulsions can be used in fog seals. In Europe, cationic emulsions are used, whereas anionic emulsions are used in countries like Canada, USA and South Africa. In some countries, the emulsion is diluted 50/50 with water, while in other countries, a tack coat emulsion is used.

4.4. Dust suppression

Dust suppression or dust control is the process whereby emulsion is applied to an unpaved road to reduce the amount of fine particles (i.e. dust), emitted into the air when the road is trafficked. It is an effective treatment on gravel roads, soil based roads, quarry roads, mine roads and construction sites. The light application of emulsion also provides some protection to the road surface. Typically, the emulsions used are highly diluted, even up to 95 %. Emulsions manufactured with specific slow set anionic emulsifiers are most commonly used. However, in the USA and Australia, it is often the more commonly available anionic tack coat emulsion that is used.



Figure 14: An untreated gravel road before and after a dust suppression emulsion is applied

4.5. Priming

In order to prepare a granular or untreated roadway for an asphalt layer such as a hot-mix asphalt, a surface dressing or a graded seal, an application of a prime coat emulsion (or a hot binder that is highly fluxed with a hydrocarbon based solvent) is often used. The function of such prime coats is to penetrate quickly into the granular surface and bind the granular material together, thereby providing partial waterproofing to the layer. It also serves as a bond between the existing surface and the new pavement layer. In addition, a prime coat provides a temporary riding surface for construction vehicles before an overlay is placed.

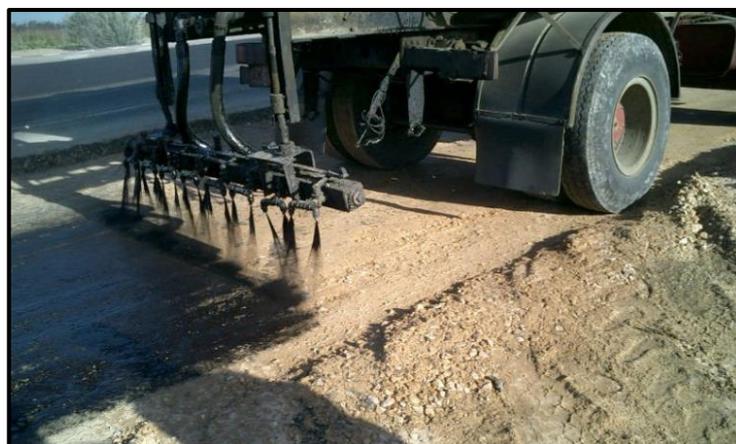


Figure 15: Prime coat application [27]

Traditionally penetrating priming binders were cutback bitumen. With increasing knowledge of the chemistry of emulsions and control over breaking and setting characteristics, specially formulated penetrating grade, slow-set cationic and anionic emulsions are now used in countries like Canada, the USA and Australia, including some that are solvent-free [28].

It is interesting to note that, in Australia, rapid-set anionic grades are found to be suitable for use in dry and warm conditions and but only with certain aggregates [29], while cationic rapid set emulsions can be applied to pavements consisting of a wide range of aggregate types and in cooler, damper conditions. This is very much in agreement with the breaking scenarios described in Section 3.2.

4.6. Seal coating

The seal coating process involves applying a special mixture of emulsion and fine aggregate/filler materials onto an old asphalt to renew its surface. The seal coat material fills small voids and cracks, thereby sealing the asphalt from any water ingress and giving it a new bituminous finish. Seal coating can be applied using specialist distributors or by hand, as it is easily spread using squeegees or brushes as shown in Figure 16.



Figure 16: Driveway sealing by hand application [30]

Anionic emulsions have been used for driveway sealing applications in Europe in the past, and specifically the UK and Ireland. However, it was necessary to use naphthenic type bitumen sourced from Venezuela, which is now less available than the alternative paraffinic type bitumen. However, the application is still commonly used in the USA and Australia, where climatic conditions favour the breaking of the anionic emulsions that are used.

4.7. Joint sealing

In pavement construction, joints occur at the interface between two adjacent layers of asphalt. There will also be a joint between the asphalt layer and other components such as kerbs, manhole covers, concrete footpaths, etc. Over time, due to the effects of oxidative aging, weathering and traffic use, these joints can open up as the asphalt is eroded away. This allows water ingress which, in turn, damages the asphalt further. As a consequence, it is now considered best practice for all joints to be sealed at the construction stage by the application of either a hot bitumen or a cold applied bitumen emulsion. The emulsions used can be cationic or anionic and usually contain modifiers such as fillers or polymers.



Figure 17: Sealing the vertical edge of a longitudinal joint with a hot binder

4.8. Slurry sealing and Micro-surfacing

Slurry seals and micro-surfacings consist of a mixture of fine aggregates and emulsion that are applied to an existing pavement to provide a new thin overlay surfacing. Sometimes, a small percentage of coarse aggregate and/or cement is added, depending on the performance levels being targeted. In general terms, slurry seals use poorer quality aggregate, have a slower setting time and are used on low traffic volume roads, whereas micro-surfacings use higher quality aggregates, have a quicker setting time and are used on high traffic volume roads, even motorways.

Slurry seals and micro-surfacings are always applied by specialist trucks that use a screed attached to the back of the truck to spread the slurry mixture across the width of the pavement lane. The slurry mixture is blended by a pug-mill mixer located on the truck directly in front of the screed. The breaking speed of the mixture on the road depends on many factors such as the prevailing weather conditions, the type of aggregate and the type of emulsion used.



Figure 18: Applying a cationic micro-surfacing on a motorway in France

The disadvantage with using anionic emulsions for these systems is that they are dependent on atmospheric conditions for adequate curing by evaporation. On the other hand, micro-surfacing systems made using cationic emulsion can typically be reopened to traffic as quickly as twenty minutes after application. However, anionic systems still have the advantage over cationic systems in that they allow the use of poorer quality aggregates (i.e. with higher clay contents), which are often the only type that are available locally. This is the reason that such systems are still widely used in countries such as Australia, Canada and the USA.

4.9. Emulsion Bound Cold-Mixes

Emulsion bound cold-mixes are manufactured by coating graded aggregates with a bitumen emulsion using a specialist cold-mix plant consisting of aggregate hoppers and a pug-mill mixer. In contrast with hot-mix aggregate, because they are bound with an emulsion, the aggregates being used do not need to be heated; hence, the term “cold-mix” was coined. Emulsion bound cold-mixes do require a time period to “cure”, in order to achieve their final mix strength. However, once they have cured, they can provide performance levels that are similar to conventional hot-mix asphalts [31, 32].

The emulsion used can be either anionic or cationic and, once again, this very much depends on the country in question. The main challenge is to have an emulsion that is sufficiently stable so that it coats all of the aggregate particles before the emulsion breaks. The cold-mix should also remain sufficiently workable for it to be laid evenly and homogeneously, but gain in cohesion as quickly as possible, once it is compacted into place.



Figure 19: Laying (anionic) emulsion bound cold-mix in Canada [33]

In Canada, cationic and anionic medium set emulsions containing a small quantity of solvent are commonly used for open graded cold-mixes. The addition of a solvent to the binder (before the emulsification process) helps the mixture to flow evenly through the paver screed and provides the mix with flexibility. The selection of emulsion to be used depends on a number of factors, including environmental conditions (temperature and humidity), traffic volumes and type, type of aggregate and the existing road surface conditions. Typically, the most common anionic emulsions used are MS-2 (i.e. medium set with class 2 viscosity) and MS-2h (i.e. as MS-2 but made using a harder class of bitumen) [33].

For dense graded cold-mixes, the most widely used grades of anionic emulsion in North America are SS-1, MS-2 and high float medium-setting (HFMS). HFMS emulsions give better aggregate coating and bitumen retention under extreme temperatures conditions [28, 34 & 35].

4.10. Cold-Mix Recycling

Cold mix recycling is a process whereby reclaimed asphalt planings (RAP) and/or reclaimed aggregate materials are coated with a new bituminous binder either in situ at the road-works or at a central mixing plant, to produce a new cold-mix asphalt. The new binder can be in the form of a hot paving-grade binder or an anionic or cationic emulsion.

The in situ recycling process is performed by a ‘train’ of equipment consisting of a water tanker, an emulsion tanker, a milling machine, a sheep’s-foot roller, a grader, a steel-drum roller and a pneumatic tyred roller, as shown in Figure 20. In this process, the milling machine mills up and pulverises the existing pavement material while homogeneously mixing it with the added water and bitumen emulsion. If required, virgin aggregate and/or cement can also be incorporated into the mix by spreading it onto the existing pavement in advance of the recycling train.



Figure 20: Sequence of machinery used for the cold in-place recycling process

With in-plant cold recycling, the RAP from the old pavement is transported to a central mixing plant, where it is mixed with the bitumen emulsion to produce a new cold mix that is suitable for further paving.

The emulsion type and grade of emulsion to use is determined by a laboratory design that is performed on representative samples of the RAP or recycled aggregate that are to be used in the project, in accordance with the local specifications. In Canada, SS-1, SS-1h and HFMS-2s anionic emulsions are used [34], while cationic emulsions are now mainly used in Europe and the USA.

4.11. Soil Stabilisation

A process that is similar to cold mix recycling is soil stabilisation using a bitumen emulsion to form a pavement foundation layer. The engineering properties of the existing soil or subgrade material are improved by thoroughly mixing into it a specified amount of bitumen emulsion. The emulsions used must break relatively slowly to allow adequate mixing. Therefore, slow-setting grades of both cationic and anionic emulsions are used for this process.

4.12. Industrial water-proofing

Anionic emulsions have a proven track record as a water-proofing material in the industrial and construction industries. Other industrial applications include use as insulation bonding, a vapour barrier, industrial floor screed, protection against corrosion, sound insulation of ventilation ducts and heat insulation. Some of the reasons such anionic emulsions have been found most suitable for the above applications include their ability to adhere to most clean surfaces (including concrete, metal and wood), their residual film of bitumen remains flexible, they have excellent resistance to oxidation and water and they do not flow or “creep” over time.

Such emulsions are available in several grades, depending on their final viscosity and whether they contain an addition of resin. One of the most commonly used anionic emulsion for industrial waterproofing applications is known by its commercial name Flintkote®. The original Flintkote® formulation was developed by an American company of the same name in the 1920s but has been adapted over the years. The emulsion is pasty in nature, is typically applied at a rate of 700 to 800 g/m² and dries in about 2 to 3 hours.

5 CONCLUSIONS

Over the past fifty years, the use of anionic emulsions in Europe, for road construction and road maintenance purposes, has been almost completely replaced by the use of cationic emulsions. However, anionic emulsion are still widely used in some countries for various applications, including road construction and maintenance techniques. The objective of this literature review was to establish the state of the art of anionic emulsions worldwide and to identify the reasons why these emulsion are still favoured over cationic emulsions in some countries.

The literature review has demonstrated that there are many uses for anionic emulsions worldwide and, indeed, that there are applications in which it has its own niche. The main reason why anionic emulsions are more suitable than cationic emulsions for certain applications is their increased stability, i.e. they are slower to break, even when mixed with fine aggregate. Anionic emulsions have also been found to have a greater affinity for certain aggregate types, given certain conditions, e.g. the moisture content of the aggregate. These are valuable findings and suggest that there may be scope for the development of such anionic based applications in Europe and in other countries where cationic systems are currently favoured.

Based on the literature review conducted, it is recommended that further research should be undertaken in the following areas:

- The use of graded seals on low traffic volume roads in Europe;
- The use of anionic emulsions for the manufacture of cold-mix asphalts in Europe, when increased mix stability is required;
- The degree of adhesion that is achieved between various types of anionic emulsions with European aggregates, in both a dry and moistened state; and
- The use of adhesion agents in anionic emulsions, for a range of aggregate types.

Such research would help to establish if the use of anionic emulsions may be advantageous over use of the cationic emulsions for any of the typical road construction and road maintenance applications currently in use in Europe.

ACKNOWLEDGEMENTS

The authors would like to thank all those individuals who provided help and funding, including:

- Liam Henry, COO of Colas Ireland and General Manager of Chemoran;
- The staff at the Document Department of the CST Laboratory of Colas;
- Barry McNamee, Technical Manager of ICB Emulsions;
- Paul Cadel, Product Services Manager, Colas Limited;
- Tony Kucharek, Technical Director, McAsphalt Research Centre;
- Kobus Lowe, Technical Manager, Colas South Africa;
- Jean-Baptiste Izart, Commercial Manager for Special Products, Aximum.
- Kanjana Yindee, Technical Product Manager, SAMI Bitumen Technologies.

REFERENCES

- [1] Shell Bitumen, The Shell Bitumen Handbook, Sixth edition, 2015. London: ICE Publishing
- [2] Hoiberg, A., Bituminous materials: Asphalt, Tars and Pitches - Volume II: Asphalts, Part One. 1st edition, 1965, John Wiley & Sons.
- [3] SFERB, Bitumen Emulsion, English Edition, 2008, Paris, SFERB.
- [4] Western Asphalt Products, 2019. Asphalt emulsion. [Online] Available at: <https://westernasphalt.ca/what-is-emulsion/> [Accessed 03 April 2019].
- [5] James, A., Overview of Asphalt Emulsion, Asphalt Emulsion Technology, Transportation Research Circular Number E-C102, 2006.
- [6] Khan, A., Redelius P., et al, Effects of surfactants and adhesion promoters on the bitumen-minerals interfacial bond during breaking of bitumen emulsions, 2018 [Online] Available at: <http://kth.diva-portal.org/smash/record.jsf?pid=diva2%3A1184457&dsid=-1221> [Accessed 1 December 2018].
- [7] Redelius, P. & Walter, J., Bitumen Emulsions, Emulsions and Emulsion Stability, 2006, pp. 384-412.
- [8] Johnson, R. A., Juristovski, A. G., Physical Properties of Tall Oil Modified Cement Binder, Physical Properties of Asphalt Cement Binders, John C. Hardin, ed. 1995, Philadelphia, ASTM.
- [9] HARRPA, Circular: HARRPA's Crude Tall Oil Biorefineries, 2017. [Online] Available at: <http://www.circulargy.eu/project/harrpa-biorefineries> [Accessed 3 March 2019].
- [10] McConnaughay, K., Asphaltic Paving Composition, United States, Patent No. 2,855,319, 1958.
- [11] ASTM Standard D 139-16, Standard Test Method for Float Test for Bituminous Materials, ASTM International, West Conshohocken, PA, 2016, DOI: 10.1520/D0139-16
- [12] Anderson, M., Asphalt emulsions and cutbacks, MS-26 The Asphalt Binder Handbook, 1st ed, Asphalt Institute, 2011, pp. 119-150.
- [13] Suda, J., High-Float Emulsion Residue: A New Rheological Model Based on the Existence of a Yield Stress - Master degree thesis, 2016. Canada: University of Alberta.
- [14] Hanz, A., Arega, Z. & Bahia, H., Advanced Methods for Quantifying Emulsion Setting and Adhesion to Aggregates, 2008 [Online] Available at: https://uwmarc.wisc.edu/files/2008_ISAET_Hanz_Quantification_of_Emulsion_Setting_and_Adhesion_paper.pdf
- [15] Mertens, E. W., Wright, J. R., Cationic emulsions: How they differ from conventional emulsions in theory and practice, 1959, Highway Research Board proceedings, 38, pp 386 - 397, Washington, D.C.
- [16] Bellanger, J., Duriez, M., La rupture des émulsions de bitume et l'adhévisité des résidus, Revue Générale des Routes et des Aérodrômes, Volume No. 309, 1957, pp. 41-55.
- [17] Highway Research Board, State of the Art: Effect of Water on Bitumen-Aggregate Mixtures, 1968, Washington, D.C.: Highway Research Board.
- [18] Huang, S. et al., Evaluation of Different Techniques for Adhesive Properties of Asphalt-Filler Systems at Interfacial Region. Journal of ASTM International, Vol. 2(5), 2005, pp. 1-15.
- [19] Dybaiski N., J., The Chemistry of Asphalt Emulsion, Fifty fifth Annual Meeting Transport Research Board, 1976.
- [20] Schilling, P. & Schreuders, Improved quick-set slurry seal emulsifiers with tall oil derivatives. Transportation Research Record, Issue 1171, 1988, pp. 98-107.
- [21] Plotnikova, I., Control of the interaction process between emulsion and mineral aggregate by means of physio-chemical modification of their surfaces, First World Congress on Emulsion, Paris, 1993.
- [22] Downey, M. R. P. & Schmitt, P. H., Emulsion Breaking Process. United States of America, Patent No. 3,257,231, 1966.
- [23] Gorman, J. L., Crawford, R. J. & Harding, I. H., Bitumen emulsions in road construction: a review. Road & Transport Research, 13(1), 2004. 2004, pp. 25-38.
- [24] Gaestel, C., The Breaking Mechanism of Cationic Bitumen Emulsions. SCI Road and Building Material Group, 1967, pp. 221-224.
- [25] Schilling, P., Anionic and cationic asphalt emulsions prepared with modified tall oil. Bordeaux, Colas SA, 1997.
- [26] Øverby, C., A Guide to the Use of Otta Seals, Publication no. 93, Norwegian Public Roads Administration, 1999.

- [27] APANM, Use of Prime Coat. 2019 [Online] Available at: <http://www.apanm.org> [Accessed 16 July 2019]
- [28] Simpson, P. L., Overview of Asphalt Emulsion Application in North America, Asphalt Emulsion Technology, Transportation Research Circular Number E-C102, 2006.
- [29] Puma Bitumen, Puma Bitumen- Bitumen Emulsions, 2015
- [30] Asphalt Maintenance and Paving, Driveway Seal Coating. [Online] Available at: <https://www.teamasphalt.com>, 2019 [Accessed 28 June 2019].
- [31] Lundberg, R., Jacobson, T., Redelius, P. and Östlund J.A., Production and durability of cold mix asphalt, 6th Eurobitume Congress, Prague, 2016, dx.doi.org/10.14311/EE.2016.074.
- [32] Delfosse, F., Béghin, A., Belkahia, A., Gaudefroy, V., Gueit, C., Odie, L., Comportement et étude des grave-émulsion, RGRA No. 954, 2018.
- [33] Croteau, J., Boston, B. & Davidson, K., Usage of emulsion mixes to mitigate the effect of subgrade movements. Proceedings of the Annual Conference of Canadian Technical Asphalt Association, 1999.
- [34] McAsphalt, Dense Graded Cold Mixes - Technical Bulletin, 2019 [Online] Available at: <http://www.mcasphalt.com> [Accessed 24 July 2019].
- [35] Asphalt Institute, Asphalt Cold-Mix Recycling. 1st ed. Maryland, Asphalt Institute, 1983.