

INTRODUCTION TO ASPHALT EMULSIONS

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Public Works Canada Seminar
Charlottetown P.E.I.
November 16 – 17 1995

TABLE OF CONTENTS

	Page
Introduction to Asphalt Emulsions	1
Asphalt Emulsion Manufacture	1
Emulsion Theory	2
Emulsion Chemistry	4
Emulsion Types	6
Emulsion Tests and What They Mean	7
Emulsion Handling	9
New Emulsion Products	11
References	12
Appendix A Chemical Charts	13

INTRODUCTION TO ASPHALT EMULSIONS

Asphalt emulsions have been in use as a road building material since the 1920's, and its use has advanced steadily since then. Most emulsions in use are in maintenance applications but the trend is clearly including new construction. The total asphalt emulsion production makes up a very small amount of the total asphalt used for paving applications.

In general the asphalt emulsion business has been a relatively closed shop with little technology transfers occurring. The trend has slowly changed as the use of asphalt emulsions has expanded. Generally the engineer's experience with emulsion usage has been quite limited. The emulsion producers now see it as their responsibility to make the emulsion user aware of the economic and efficient capabilities of emulsions in all road building applications.

This paper has been designed with the end user of asphalt emulsions in mind. A number of basic questions will be answered.

What is emulsified asphalt?
How is it manufactured?
What are the various emulsion types?
How do you separate the various types?
How is it stored and handled?

The following topics will be discussed in greater detail:

Emulsion Manufacture
Emulsion Theory
Emulsion Chemistry
Emulsion Types
Emulsion Tests and Their Meaning
Emulsion Handling

The last section of the paper will deal with additives such as polymers (How they change emulsion properties and their benefits).

Asphalt Emulsion Manufacture

An asphalt emulsion is a product formed by the mixing of water and asphalt in a special process called emulsification. Emulsification is a technical process which involves the input of mechanical energy in the form of shearing, thermal energy to liquefy the asphalt cement and the addition of precise amounts of chemical stabilizers. The result is a dispersion of minute asphalt droplets in chemically treated water (oil in water emulsion).

The emulsion processing unit in a manufacturing plant consists of raw material storage facilities, chemical feed pumps, temperature and pressure sensors and proportion control equipment. The molten asphalt cement and the chemical water solution are pumped under pressure into a colloid mill.

The colloid mill is a high shear mechanical mixer which disperses the asphalt cement in the water phase. Depending on the size and type, the colloid mill requires from 30 to 1500 hp

motor and has an adjustable shearing chamber which is usually set at about 25 thousands of an inch clearance. This high speed pressurized shearing is necessary for the dispersion needed to homogenize the emulsion into small stable droplets (typically between 3 and 25 microns in size). The process is actually done at asphalt temperatures up to 170°C and at rates of manufacture up to 20,000 gallons per hour. Once the emulsion is produced, the finished product is pumped into storage tanks, tested and then shipped.

Emulsion Theory

This section is going to provide a more detailed look at the nature of asphalt particles in an emulsion, how they are stabilized and how they ultimately coalesce into a film on the aggregate surface.

An asphalt emulsion is a liquid, water based form of asphalt cement, which is prepared by processing molten asphalt cement. The emulsification process produces an emulsion which is a dispersion of small droplets of asphalt cement in water. The water is the continuous phase and the asphalt is the dispersed phase; therefore many of the properties of an emulsion of this type (oil in water emulsion) are similar to the properties of water. Emulsions of asphalt in water will conduct electricity, freeze, mix with water and remain immiscible with other oils.

Just for interest, two other oil in water emulsions commonly encountered are milk and latex paint. Milk is an emulsion of butterfat in a water solution of milk protein and lactose, which is milk sugar. The cow does the primary emulsification and the dairy homogenizers further disperse the fat globules into a more stable homogeneous state.

Water based paint is the other oil in water emulsion likely to be seen. Latex and other resins are dispersed in fine droplets to coalesce into a paint film upon evaporation of the continuous phase which is water.

Dissimilar liquids such as oil and water usually separate when mixed together, but the emulsification process in conjunction with a surfactant (emulsifier) shears the asphalt into fine droplets. The smaller the particles the greater the surface area. This increase in surface area and decrease in particle size brings the emulsion particles close to the world of colloidal chemistry, the chemistry of small particles. Such phenomena as Brownian movement of molecules start to affect the properties of the suspended particle if it is small enough.

One of the properties, that is expected from a suspended particle is that it will tend to settle out of suspension. Asphalt emulsions are no exception. To counter this tendency, asphalt emulsions are stabilized by thermal energy used to make asphalt cement a molten liquid, mechanical energy imparted through the shearing forces of a mill and chemical surface active agents. Asphalt emulsions used for road purposes have from 55 to 75% asphalt by weight dispersed in water. They also contain from 0.15 to 3.0% chemical emulsifiers usually added through the water phase.

In many ways the chemical surface active agent appears to be the most important ingredient in an asphalt emulsion. These agents are highly efficient emulsion stabilizers even when used in small amounts. These surfactants possess the unique property of altering the surface energy of their solvents dramatically. Later it will be shown that the quantity and nature of the surfactant is largely responsible for determining the character of the emulsion and the suitability of that emulsion for a specific application.

At the interface between the oil and water phase of any emulsion the hydrophilic soluble portion of the surfactant molecule orients itself toward the water. The oil soluble lipophilic portion of the surfactant molecule orients itself towards the asphalt. The chemical surfactant acts as a bridge between the two immiscible phases by lowering the surface tension and making the transition between them less abrupt.

Surface active agents are attracted by virtually all surfaces and will migrate to any interface which allows them to be in a more stable energy state. Therefore the orientation of surfactants at oil/water interfaces, water/air interfaces and water/solid interfaces is explained by kinetic energy properties of surface active molecules.

Asphalt droplets in an emulsion have the surface active emulsifier oriented at their surface. The emulsifier attaches itself to the interface in the colloid mill as soon as mechanical shearing forces of the mill expose the new asphalt surfaces. From that time on the stability of the asphalt emulsion is dependent upon the type of chemical design intended and the subsequent handling of the emulsion.

It is important to remember that asphalt in the emulsified state is in a transitional period. The emulsion is a vehicle for the deposition of an asphalt film onto a specific surface. Asphalt emulsions are inherently unstable by design. Emulsions are designed to become unstable at just the proper moment so that maximum benefit can be derived from the fluidity of the emulsion and the cohesive properties of the asphalt. Since asphalt cement is a semi-solid at application temperatures, at the chosen moment of emulsion breakage, the unstable asphalt droplets contact each other and coalesce to form a continuous film.

The asphalt forms this continuous film at a faster or slower rate depending upon a number of factors; the type of asphalt cement, the water content, the chemical surfactants and additives, the quantity of surfactant used, and the way in which the emulsion is handled. Handling includes all of the conditions of application. The temperature of the emulsion, the aggregate, the outside air temperature and humidity all affect the rate of emulsion deposition and rate of final cure. As the temperature increases, the rate of emulsion deposition and cure increases.

Since the surfactants used to stabilize the emulsion are attracted to any surface, a high surface area aggregate will cause a faster rate of breakage than a low surface area aggregate. A higher fines content results in faster breakage.

Antagonistic chemicals which may be present in the mixing water, the aggregate or intentionally added to the emulsion mix can cause precipitation of the surfactant and breakage of the emulsion.

The contact of the emulsion with other surfaces is increased with mixing of the emulsion and the aggregate. Mixing hastens emulsion breakage. Other than handling, the basic components of the emulsion also affect the rate of break and cure.

The asphalt cement itself is a great source of variability. Asphalt is also a type of colloid, a dispersion of asphaltene particles in the liquid oil and resin fraction of the asphalt. The chemical and structural complexity of the asphalt makes it very difficult to analyze, and very difficult to predict how it will perform in an emulsion. However, it is known that variation in the asphalt properties can cause variation in the finished emulsion.

A correlation can be drawn from experience, and these following seem to be significant influences; the crude source, the type of manufacture, whether it is distilled or extracted, or additives used in manufacture such as silicone or caustic soda. Blown asphalts or gel types often used in roofing are known to be notoriously difficult to emulsify.

Asphalt must be heated to a temperature high enough to make it molten and function as a Newtonian fluid before manufacture. Variation in this temperature can influence the emulsion properties. The amount of asphalt in an emulsion and particle size of the dispersed asphalt droplets have an effect, largely on the emulsion viscosity which can result in different rates of set and mixing properties.

The water used in the emulsion manufacture as well as the water used in aggregate mixing might contain antagonistic chemicals, dissolved salts, or particulate contamination which could influence breakage. Water temperature also influences the emulsion breakage rate.

With regards to the surface active agents the following factors have the greatest effect on emulsions; the quantity of emulsifier, charge (which can be positive, negative or neutral), the temperature (which always increases rate of breakage), and the pH which has a different effect on different chemical types. There is generally an optimum pH, both above and below which the emulsion is less stable.

Many of the factors outlined here are primarily the concern of the emulsion manufacturer, who is able to vary his process as necessary to insure that the product reaching the user has consistent and reproducible properties.

The field influences such as aggregate size, temperature, and mixing water are normally under the control of the user and any change should be reported to the emulsion supplier so that the most suitable product can be recommended and produced for each application.

Emulsion Chemistry

The chemical surface active agents which serve as emulsifiers for asphalt emulsions are classified chemically by the electro-chemical charge which they attain when they dissociate in the water solution.

This portion of the paper will examine the chemical types of emulsifiers, and how the chemical type affects the emulsion interaction with different aggregate surfaces.

There are basically three different types of chemical surface active agents, each of which is capable of forming a stable emulsion when used in very small quantities. The nature of these chemicals is quite different and markedly affects the properties of the emulsion formed. The three basic types are called: Anionic, Cationic and Non-ionic. These names are a result of the way the chemicals react when their solution is subjected to a direct electrical current. The anionic chemical migrates to the anode, the cationic chemical to the cathode and the non-ionic chemical does not migrate at all.

The chemical emulsifiers impart their charge to the asphalt droplet in an emulsion, so that the emulsions have the same names and properties as the surfactants. The cationic emulsions are positively charged and are attracted to their opposite, or negative electrode. The anionic emulsions are negatively charged and are attracted to their opposite, or positive electrode.

Of all the factors influencing emulsion breakage, the most important one with regard to the electro-chemical charge on emulsions is the surface contact. Of course the evaporation of water, chemical reactions, and temperature were discussed earlier as factors affecting emulsion deposition, and these are certainly significant factors, but the surface contact of the aggregate with the emulsion is of greatest concern in the design and control of most applications.

The amount of aggregate is the largest ingredient in all mixes. Even slurry seal which is usually quite high in residual asphalt content only about 10% residual asphalt based on the dry weight of aggregate. The aggregate size, shape, gradation, porosity and fines content determine the character of the emulsion mix.

Virtually all aggregates have negatively charged surfaces. Negatively charged surfaces abound in our entire environment. Cationic emulsions which are positively charged see the surface of aggregate as a negatively charged cathode. Since opposite charges attract, the cationic emulsion particle is attracted to the stone surface. For many years this phenomenon has been exploited by the addition of cationic anti-stripping and adhesion agents to hot asphalt cement and cutback asphalts. The affinity of cationic emulsifiers for mineral surfaces is so great that water is displaced from the mineral surface and the cationic chemical is firmly bound electro-chemically to the stone surface.

The fine portion of mineral aggregate has the potential to present very great surface areas to the emulsion. One gram of a typical slurry seal aggregate will commonly have less than one square metre per gram surface area. A montmorillonite clay, by contrast, can have a surface area up to 200 square metres per gram. This great area has a high surface energy for the attraction of all types of surfactants. The negative charges exposed in all that surface make it especially attractive to the positively charged cationic emulsions.

Surface contact then, is increased by the amount of fine materials present in the aggregate. Fine clays or silty materials can absorb water from the asphalt emulsion and cause emulsion breakage by desiccation.

It was believed for many years that limestone had a positive surface charge. This misconception arose because many anionic emulsions, which are negatively charged were attracted to and coated limestone very well. Direct measurement of the charges on the surfaces of various stone types confirmed that virtually all of them are negatively charged including limestones. A few dolomites do exist with very high magnesium carbonate content which are positive and are compatible with anionic emulsions. For all practical purposes, mineral aggregate has a negative surface charge.

It will be asked then, "Why do some anionic emulsions coat limestone very well and break rapidly in the presence of limestone?"

The explanation given by some researchers is that the surface of limestone, while negatively charged does have exposed calcium ions on the surface. These calcium ions react chemically with the anionic soap molecule, rendering it insoluble and forming a chemical bond with the surface.

The surface of limestone is still a net negative however, and the negative charge sites can be occupied by the positively charged ions of a cationic emulsion. Cationic emulsions are attracted to virtually all stone surfaces. Some emulsion compatibility tests were conducted to test the adhesion of anionic and cationic emulsions to the surfaces of various aggregates; gravels, chats

and limestones. The results showed that cationic emulsions rendered the surface of all the aggregates lipophilic and coated with asphalt. The anionic emulsions were shown to render some of the limestone lipophilic and coated with asphalt.

There are many factors in the design of emulsion mixes which may lead the emulsion user to choose one or the other type. Satisfactory results in every type of application have been obtained using all chemical emulsion types, including non-ionic emulsions. The recommendation in all cases is to consult with your emulsion supplier to determine which of the many formulations and emulsion types will best suit the specific job demands.

Emulsion Types

There are three major classifications of emulsion grades; Rapid Set, Medium Set, and Slow Set. These categories historically were made to conform to the older cutback asphalt designations: RC, MC and SC.

The terms “rapid, medium and slow” were meant to relate to the amount of time it took for the emulsions to cure. It was also related to the amount of mixing that could be performed before the emulsion broke. The mixing time and the rate of cure are still related today, the emulsions which allow the longest mixing time generally take the longest to cure, and emulsions which allow very short mixing time are those which set and cure most rapidly. As a rule the rapid, medium and slow categories have a relationship to the sensitivity of the emulsion to breakage.

The following is a list of the most commonly used emulsions both cationics and anionics:

<u>Cationics</u>	<u>Anionics</u>
CRS-1 (RS1K)	RS-1
CRS-2 (RS2K)	RS-2
CMS-2	MS-2
CSS-1	SS-1
CQS-1h	HF150
CRS-2P	HF250
	HF1000
	HFMS-2
	RS-2P
	HF150P

Today there are many more types of emulsions used nationally, and even more specialty grades, which have only local designations. For each of these grades there exists a test or tests which attempt to distinguish it from all other types.

Emulsion Tests and What They Mean

The nomenclature and the testing procedures have roots in the development of the products for field use. This section will look at the tests used for emulsions today and the reason some of the tests were developed.

The real justification for having any tests at all is the need to predict the field performance by checking certain properties in the laboratory. The following is a list of the major tests used today for emulsions and the performance characteristic which the test is supposed to identify.

Viscosity: The viscosity test measures the flowing ability of an emulsion which influences how the emulsion will pump and how it will run off a crowned road. Emulsion viscosity is very important in seal coat work. When the viscosity is too low the emulsion runs off to the shoulder and may form an unusually large wave or roll in front of the aggregate curtain during cover application. When the emulsion is too thick the application forms ridges and the aggregate does not retain a level mat. The thick emulsion material if not sprayed at an elevated temperature will also cause improper spray and streaking in the mat will occur.

Distillation Test: In this test the emulsion is heated and the water boiled away. Any oil distillates which are present and volatile at the test temperatures will be boiled away and collected in the graduated cylinder. Some components of the asphalt usually vaporize at the test temperature also, so it is not uncommon for the residue from the distillation to have slightly different properties than the original base asphalt. Of course, chemical additives often cause the residue to be different from the base asphalt also.

Settlement Test: The settlement test is meant to measure the storage stability of an emulsion. The test usually measures the amount of settlement after 5 days, however many specifications have a one day requirement if the emulsion is used immediately. The settlement test is performed at room temperature, so the actual settlement may be different than the settlement found in a hot storage tank.

Storage Stability Test: Determines the storage stability with respect to the asphalt particles settling out of the emulsion in 24 hours. This test can be used in place of the settlement test.

Sieve Test: This is a test of the homogeneity of asphalt emulsions, and is a complement to the settlement test. It is used to identify large particles, which may or may not have been detected in the settlement test. Such particles could clog spray nozzles and not allow a proper spray fan of emulsion.

Particle Charge Test: The particle charge test is the valid accepted means of determining whether or not an asphalt emulsion is cationic. A cationic emulsion will break on the cathode. A determination of the pH of the emulsion is not an acceptable means of identifying a cationic emulsion. There are now newer cationic chemicals with a neutral or alkaline pH and there are non-ionic chemicals with an acid pH.

Demulsibility Test: The demulsibility test measures the comparative stability and rate of chemical break of an asphalt emulsion. While the demulsibility test was devised to determine setting speed, it has been found that many emulsions which in fact set very rapidly in the field, fail to pass this test because the emulsifier used to produce the emulsion was not antagonized by the chemical used in the test.

Cement Mixing Test: The cement mixing test was devised to predict which anionic emulsions could be used for soil stabilization. It was thought that since many soils have fine clayey material, the ability of an emulsion to mix with Portland cement could predict the ability to

mix with clay. This held pretty generally true until a number of cationic slow setting emulsions were developed which could coat the soils very well but couldn't mix with cement.

Classification Test: The classification test is used to classify cationic rapid setting emulsions by their ability to coat a standard Ottawa silica sand and cement.

Coating Test: The coating test determines the ability of an anionic or cationic medium setting emulsion to (1) coat an aggregate thoroughly, (2) withstand a mixing action while remaining as a film on the aggregate, and (3) resist the washing action of water after completion of the mixing.

Tests are also performed on the residual asphalt after the distillation procedure. Two of the most common tests performed are as follows:

Penetration Test: This test is run to ensure that the asphalt cement used to manufacture the emulsion meets specification.

Float Test: The float test is used to measure the ability of an asphalt residue from the distillation process to resist flow under low stress. Proponents of the "High Float" emulsions claim that the asphalt is made less temperature susceptible and provide better overall performance than conventional emulsions.

Emulsion Handling

There are four primary influences on the rate of breakage of an asphalt emulsion; evaporation, chemical antagonism, surface contact and temperature.

The typical asphalt emulsion has about 65% asphalt and 35% water. If the amount of water is reduced to very much below 25%, the emulsion can invert phases and become unstable and break. The mechanism is a little complex, but basically there is not enough water to surround each asphalt particle so they coalesce.

Any of the numerous chemical contaminants will cause the chemical emulsifier to dissociate from the surface of the asphalt droplet. Without the stabilizing effect of the surface active agent, the droplets become mutually attractive and will form one solid mass of asphalt. Many soluble salts can have this effect, such as the calcium carbonate found in hard water. Organic compounds like anionic detergents are often antagonistic to the chemical surface active agents used in the emulsion.

The contact of the emulsion to any foreign surface causes a number of things to happen. The surfactant by its nature leaves the surface of the asphalt to associate with the new surface. If the new surface is dry or porous, it will absorb the stabilizing water layer from the emulsion. The new surface has its own surface chemistry which may not be compatible with the chemistry of the emulsion.

All of these surface factors are useful and beneficial when considered as part of the design for the surface which has to be coated. Other surfaces introduced as particulate contamination can cause breakage in the storage tank or in a blending operation.

Increases in temperature can cause boiling and vaporization of the water phase. Temperature changes also effect the energy state of the emulsifiers used to stabilize the emulsion, as the temperature increases, activity increases, and hotter emulsions usually tend to break faster than the same emulsion would break if it were cool. Low temperatures which cause freezing of the water phase will usually cause the emulsion to break.

It is recommended that emulsions be stored in vertical tanks to minimize the exposure of the emulsion surface to air. Evaporation from the surface will cause a film of broken asphalt to form at the interface. Cylindrical tanks also have the benefit of allowing the broken skin to float up and down without becoming incorporated in the emulsion. Gentle agitation will keep the emulsion uniform during long periods of storage and will prevent the formation of a surface skin.

Heating is best accomplished in as slow and uniform a manner as possible. Even though the entire emulsion doesn't boil, localized sections can become overheated if the source is applied too rapidly. Live steam should never be used. Hot water exchange coils or electric heat are best. Emulsions should not be stored over 90°C and some mixing types are best stored and used around 25 to 30°C.

Since an asphalt emulsion is about two thirds asphalt and one third water, it follows that the temperature volume correction for emulsified asphalt should be about two thirds of the correction for asphalt alone. Asphalt cement when heated from 15°C to 85°C will increase in volume about 4.5%. Over the same temperature increase an asphalt emulsion will increase approximately 3.0% in volume.

Pumping should be as gentle as possible introducing as little shear into the system as possible. Positive displacement pumps are to be used when transferring emulsion. Centrifugal pumps are not recommended. Low speed pumps with sufficient clearances to avoid squeezing the particles are preferred. If care is taken to avoid suction leaks and to provide a net positive suction head, the entrapment of damaging air bubbles can be avoided.

Blending can often be accomplished successfully to mix old and new shipments or to alter the asphalt content by blending a high residue emulsion with a low asphalt content emulsion. Any blending should be done only with the assistance of the emulsion supplier. Many emulsions have different chemical properties even though they may have exactly the same designation. Mixing chemical types like anionic and cationic can result in quick breakage and complete coalescence.

Dilution with water should also be treated with caution because of the many possible chemical constituents of even potable water. Dilution also causes the surface active agent to change its' state of chemical equilibrium. Many emulsions are designed for easy dilution and may be treated that way readily.

The change in concentration of salts can cause the settling out of the colloidal particles. River deltas are formed by this salting out effect on other suspended particles, those of silt and clay. Some of these salts can also be present in water used for mixing emulsions with aggregate. While not usually a problem, awareness of the potential effect will alert the user to possible causes should a problem actually arise in the field.

Contaminants of any sort should be avoided because even if they do not have an immediate negative effect on the emulsion properties, they will often cause a change in the performance characteristics of the emulsion. This could cause two identical emulsions to give different

results on a project. Contaminants can have many different effects, a change in pH will often cause coagulation just as it will in natural systems. The worst aspect of chemical contaminants is the effect is unpredictable and often deleterious.

The safest way to store and handle emulsions is to avail yourself of the technical service provided by your emulsion producer and ask his advice on any new or unusual application.

New Emulsion Products

In recent years there have been a number of new products which have been developed to improve and expand the use of asphalt emulsions in the road construction business as well as the industrial market. One of these new emulsions is the polymer modified type for both anionic and cationic. With the addition of a small percentage of polymer to the base asphalt used to make the emulsions, the properties of that asphalt cement can be dramatically improved. There are many different types of polymers being used such as polyethylene, EVA (ethylene vinyl acetate) and SBS (styrene butadiene) polymers.

The following six engineering properties are typically improved by the addition of polymers to the asphalt cement; higher viscosity, lower temperature susceptibility, higher tensile strength after elongation, improved elastic recovery, increased durability and improved adhesive properties.

The improved properties of the base asphalt due to polymer modification allow asphalt emulsions to be used in areas where normally asphalt emulsions are not used. Traditionally asphalt emulsions used in seal coats have had limited application. With polymer modification the seal coats can be applied to high speed roads, and heavy and high traffic volume areas. Loss of cover aggregate is dramatically reduced. Improved cohesiveness and elastic properties give a seal coat designed with polymer modified emulsions exceptional resistance to wear and tear. The polymer modified residual asphalt gives enhanced adhesive properties both in initially securing the aggregate and then retaining it under long term action of water and heavy traffic loads.

The polymer modified emulsions are applied using the standard equipment used for spraying conventional asphalt emulsions. Polymer modified emulsions have made great inroads in the area of slurry surfacing and microsurfacing. Although there is a higher initial capital cost for using modified emulsions, the long term benefits save many because of decreased maintenance costs such as resurfacing and traffic delays.

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APPENDIX A

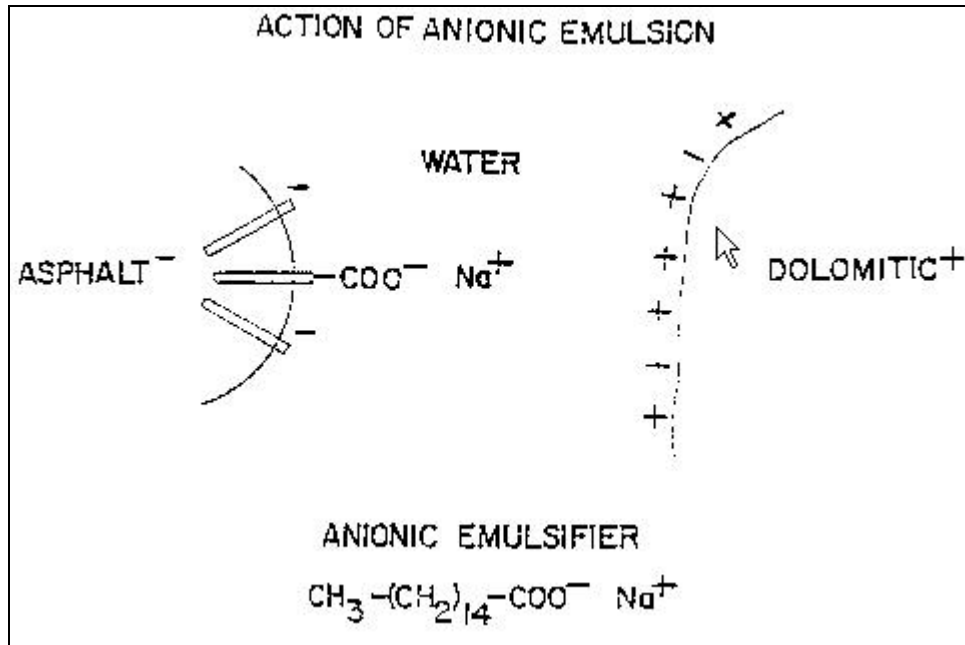


Figure A-1: Illustrating an Anionic Emulsifier and the Electrical Charges on Anionic Asphalt Emulsion Globules and on Some Dolomitic Aggregates

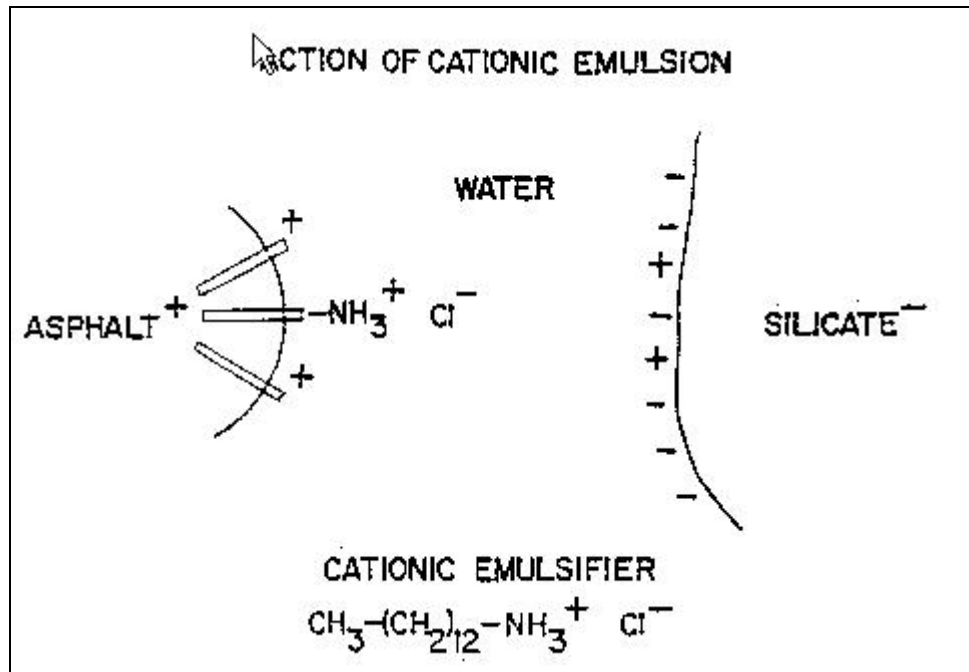


Figure A-2: Illustrating A Cationic Emulsifier and the Electrical Charges on Cationic Asphalt Emulsion Globules and Siliceous Aggregates

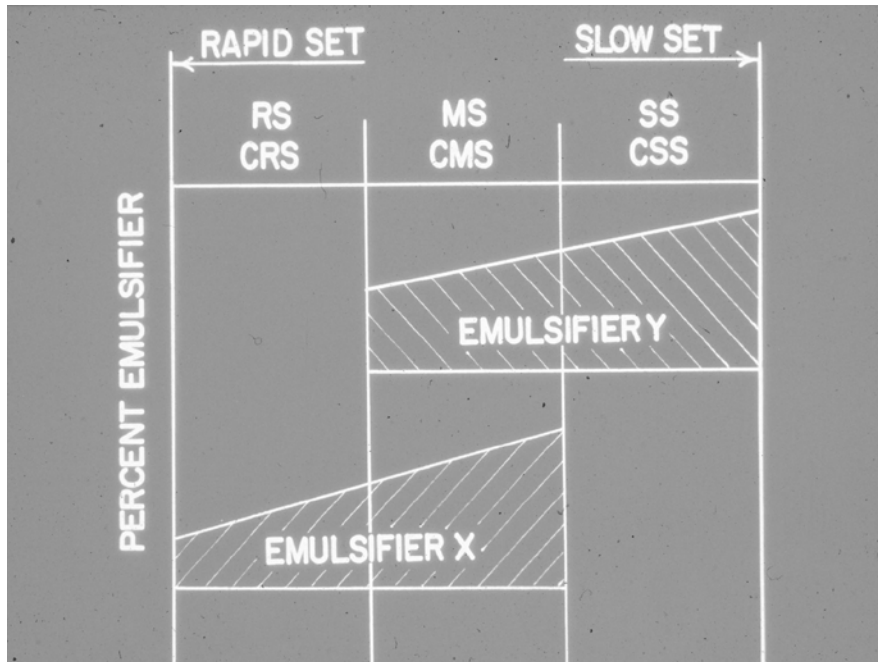


Figure A-3: Illustrating that Emulsion Stability is Increased by Increasing the Quantity of Emulsifying Agent

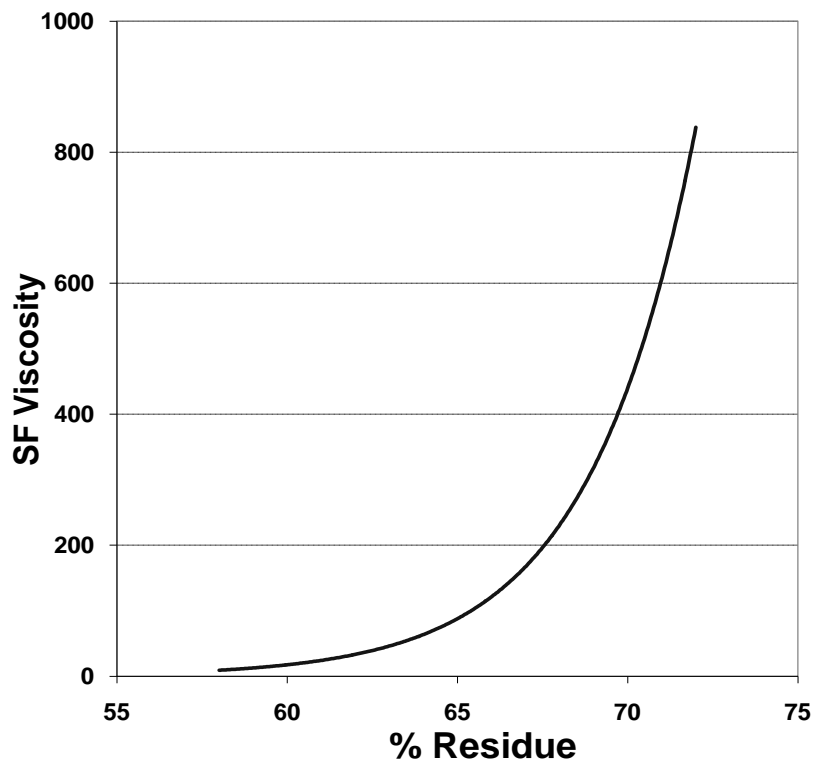


Figure A-4: Influence of Asphalt Content on Emulsion Viscosity