

EMULSIFIERS





"You change and the world changes, you live and the world lives, you dance and the world dances, you are the world..." Filomena Falvo

To my daughter...

"The road to pursuing change is impervious, fraught, long, wide and bumpy, like the path of life. For a strange game of destiny the Star Asphalt has always dealt with roads and now, through the Filomena Falvo Foundation, its mission merges with the human spirit to create a single purpose. Roads finally become paths, paths become objectives".

This work is the result of the collaboration between Star Asphalt S.p.A., a leading company in the production of special additives for bitumen and bituminous conglomerates, and the "Falvo Filomena" Foundation. Together, we are developing totally eco-friendly and green industrial systems. All Star Asphalt products have the certifications required by the Reach legislation and have been created with a particular focus on respect for the environment. In collaboration with the "Falvo Filomena" Foundation, we aim to continue the constant work of experimentation and innovation to achieve goals that are consistent with truth and clarity, peculiar virtues of my daughter Filomena, to whom this writing is dedicated.

President Prof. Rosario Giovanni Falvo





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INTRODUCTION

For many years the bituminous emulsions are used in the field of road to "impregnate", "treat", "stabilize" and pave. In the pre-war period they represented the most effective way to better organize the roads. Although implemented with techniques and methodologies suitable for vehicular traffic at the time, the bituminous emulsions made it possible to obtain pavings bonded to the surface, impermeable and with good load-bearing capacity and represented the best technical solution against the accumulation of dust and mud on the mantle road. With the passage of time, and therefore during the post-WWII reconstruction, the road technique has evolved undergoing a substantial acceleration: this is how the first asphalt plants and the first pavers for paving appeared. The technical evolution and the increase of the vehicular traffic have determined the decadence of the primary role of binder of the bituminous emulsions. Nowadays, the increase in sensitivity towards environmental problems and the need to reduce harmful emissions into the atmosphere has led to a change that has also involved the road sector. In fact, new cold techniques have been added to the traditional and consolidated methodologies of hot laying, suitable for the recycling of floors and for superficial refurbishments. With the new-generation polymer-based bitumen emulsions it is possible to realize cold microtapes to roughen smooth surfaces and, above all, it is possible to intervene with in situ recycling techniques in the intermediate and deep layers of the pavement, consolidating and reinforcing the damaged areas.

In many road-building applications, bitumen emulsions are the safest and most environmentallyfriendly alternative to using hot bitumen as the risks of emissions and burns are avoided, and the production process is less energy intensive.





Bituminous emulsions

A bitumen emulsion is a dispersion of bitumen in water and in order for this dispersion to occur it is necessary the use of a mechanical shearing action and a surface active agent (emulsifier). From a scientific point of view, an emulsion is a thermodynamically unstable heterogeneous system consisting of at least two phases, one dispersed in the form of droplets in the other; the stability of such a system, which in itself is minimal, needs to be increased by means of suitable surfactants, having the property of lowering the surface tension at the interface between the phases, favoring the dispersion of the bitumen in water. As a consequence, the bituminous emulsions, in addition to the two main phases, must contain suitable agents that favor the maintenance of equilibrium.

A stable emulsion does not separate itself into its components. The main factor influencing the storage stability of the emulsion is the size of the particles, which in turn depends on the type and quantity of the emulsifiers used, the pH of the aqueous phase and the origin and gradation of the bitumen used.

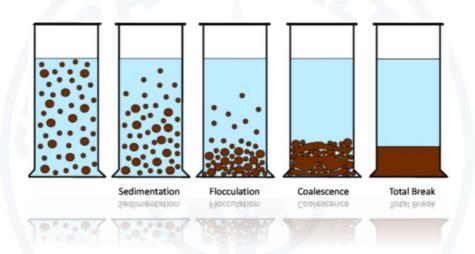


Figure 1. Evolution of storage stability of an emulsion.

According to the commonly accepted principle, an emulsion can be defined using three different classifications, respectively based on: ionic character, quantity of residual bitumen, breaking spead.





Bitumen

Bitumen is defined as the residual product of non-destructive distillation of crude oil. Bitumen is an engineering material used for various applications; the main application, however, is to be considered in the road construction sector.

Bitumens are generally characterized by colloids containing high molecular weight compounds, relatively insoluble and non-volatile known as "Asphaltenes", dispersed within a liquid, continuous and low viscosity phase, consisting of low molecular weight compounds called "Maltens". Asphaltenes are believed to be the component of the asphalt that gives the hardness, while the malteni provide ductility and facilitate adhesion. Maltens are mainly composed of oils (aromatic and saturated) and resins (compounds that represent a transition between asphaltenes and oils). Typically, bitumens contain between 5% and 25% by weight of asphaltenes.

Asphaltenes and resins have acidic and basic functional groups, so they are considered the most polar compounds in the bitumen which exhibit "interfacial" properties. When bitumen drops are dispersed in water, these polar compounds tend to migrate to the liquid-liquid interface, so they can be considered as natural surfactants. Asphaltenes and saturated compounds tend to destabilize the emulsion, while resins and aromatic compounds tend to stabilize the system.

Bitumen with a high content of asphaltenes and paraffins are difficult to emulsify. The paraffins tend to increase the viscosity of the asphalt and even at high temperatures the emulsion is not guaranteed. Saturated compounds tend to increase the time of emulsion rupture. Naphthenic and aromatic compounds increase the breaking rate of emulsions and improve their stability. Naphthenic bitumen have a high quantity of heterocyclic aromatic compounds, show a good acidity and not very high viscosity; this favors the stability of the emulsion and improves the degree of cohesion and adhesion on the stone aggregates. Paraffinic bitumens, however, have a low content of aromatic compounds, show a very low degree of acidity and very high viscosity, resulting in a reduced tendency to the emulsification process and a reduced compatibility with stone aggregates, for which it is often necessary to incorporate additional additives such as fluxes and adhesion promoters.

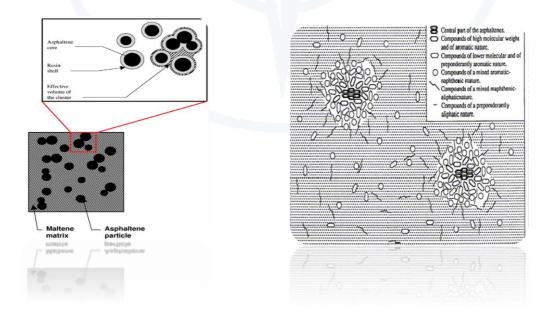


Figure 2. Representation of the structure of the bitumen.





Emulsifiers

The emulsifying agents, also known as surfactants, are necessary to guarantee the stability of the emulsion over time. The stability of the emulsion determines its appropriate use. Surfactants are chemical compounds with surface activity which, when dissolved in a liquid, in particular water, allow to reduce the surface tension by preferential adsorption to the liquid/vapor surface.

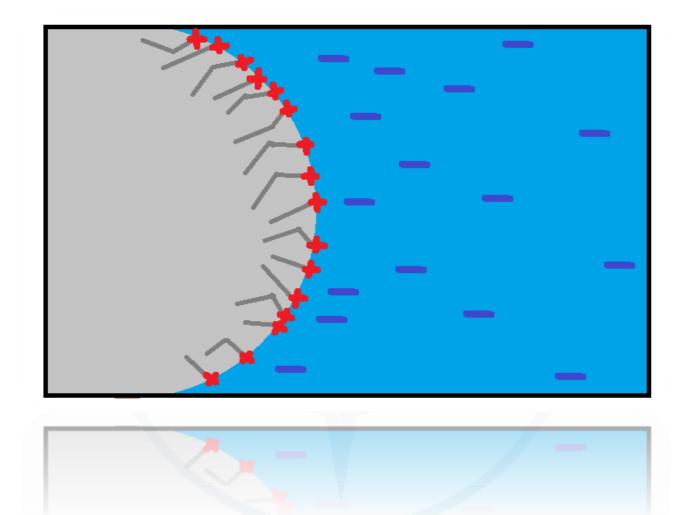


Figure 3. Representation of the water/bitumen interface.





There are numerous natural compounds that act as surfactants, but more commonly the chemical compounds are synthesized to produce the desired characteristics. They produce a surfactant that can be grouped according to the type of emulsion they produce. The types of surfactants are: anionic, cationic, amphoteric and non-ionic. The "surfactant" molecules are composed of two different parts, a "fat" or a hydrophilic fraction, with a great affinity towards the bituminous phase, and the other hydrophilic or polar, with a high affinity for water. This characteristic causes the surfactant to position itself at the interphase between the aqueous phase and the bituminous phase.

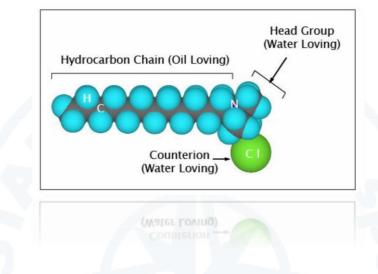


Figure 4. Representation of a cationic type emulsifier.

The emulsions are classified according to the charge provided by the surfactant: the cations provide a positive charge, the anions a negative charge. The anionic emulsifiers are those which have a negatively charged polar fraction, while the cationics are a positively charged polar fraction.





CLASSIFICATION OF BITUMINOUS EMULSIONS

Classification according to the ionic character

The surfactants used for bituminous emulsions are classified as anionic and cationic in relation to the electric charge which gives the bitumen particles. Based on this classification, bituminous emulsions are divided into:

1. Anionic bituminous emulsions (basic), with negative charge.

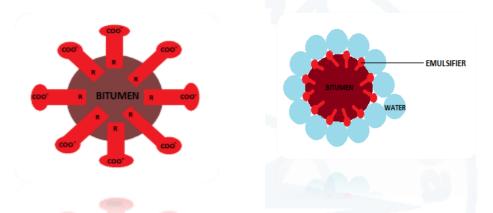


Figure 5. Schematization of the function of an anionic emulsifier.

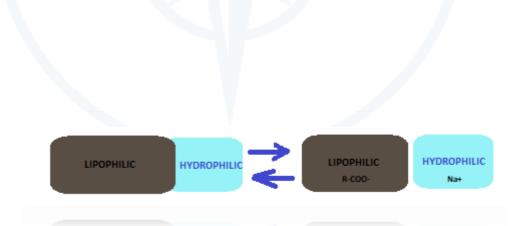


Figure 6. Schematization of the dissociation mechanism of an anionic emulsifier in water.





2. Cationic (acidic) bituminous emulsions, with positive charge.

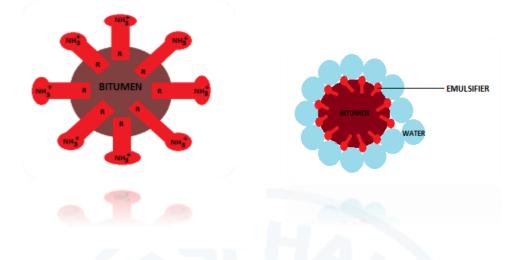


Figure 7. Schematization of the function of a cationic emulsifier.

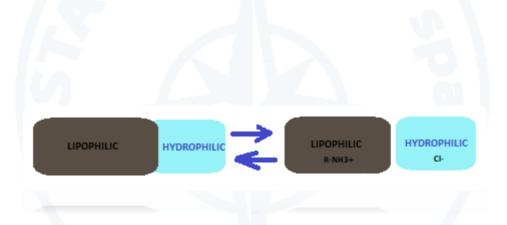


Figure 8. Schematization of the dissociation mechanism of a cationic emulsifier in water.





Classification according to the breaking speed

By breaking an emulsion we mean the event for which the water separates from the bitumen, determining the phenomenon of grip. The time necessary for the separation of the emulsion depends on many factors such as: the climatic trend, the emulsion temperature, the chemical nature of the aggregates, the particle size of the bitumen particles, the type of application, the way the work is performed, etc. Therefore, we will talk about emulsions with a super rapid setting (SR), with a rapid setting (R), with a medium setting (M), with a slow setting (S) and over-stabilized (LL).

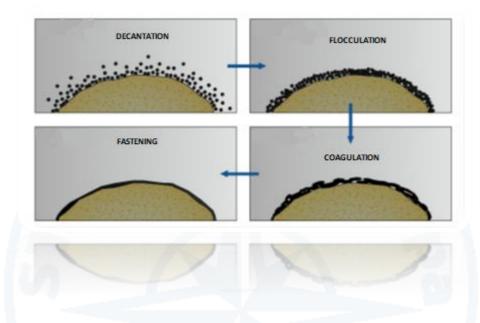


Figure 9. Schematization of the process of breaking a bituminous emulsion.





Classification according to the percentage of residual bitumen

A classification typology widely used in the road sector is based on the percentage volumetric ratio of the bitumen dispersed on the total bitumen. The percentage of residual bitumen of a bituminous emulsion varies between 50 and 69%.

NOMENCLATURE

Combining the three types of classification just illustrated, it is possible to characterize the bituminous emulsions through the following univocal nomenclature scheme: if you want to indicate, by way of example, a rapid setting cationic bituminous emulsion with 55% of residual bitumen, the EC R 55 notation will be used.

In the past, the following name was used based on the previous classification:

ECR 65 **R**apid setting **C**ationic bituminous **E**mulsion with **65%** of residual bitumen ECR 65 M **R**apid setting **C**ationic bituminous **E**mulsion at **65%** of residual **M**odified bitumen.

The new denomination of Cationic Bituminous Emulsions considers the following parameters:

- I. $C \rightarrow C$ ationic bituminous emulsion;
- II. Residual binder content (example 65%);
- III. $B \rightarrow Road Bitumen;$
- IV. $P \rightarrow$ Presence of Polymers (modified emulsions);
- V. $\mathbf{F} \rightarrow \mathbf{P}$ Presence of **F**luxant for more than 2%.

Setting index: from 1 (faster) to 12 (slower); example in Italy: class 2=super rapid setting.

Examples:

C 69 B2 69% Cationic Bituminous emulsion with residual bitumen, breaking class 2. C 65 BPF 6 65% Cationic Bituminous emulsion of residual bitumen with Polymers, with more than 2% of Fluxant, breaking class 6.





PROPERTY OF BITUMINOUS EMULSIONS

The bituminous emulsions are characterized by properties that are subdivided into:

- ✓ Intrinsic properties;
- ✓ Extrinsic properties.

Among the intrinsic properties of an emulsion are:

I. Viscosity;

- II. Stability to storage.
 - I. Viscosity is the ability of a fluid to resist sliding and changes in shape. It is strongly influenced by the working temperature that is decisive when it is necessary to ensure, for example, the coverage of the aggregates or the effectiveness of an attack hand. The viscosity depends mainly on the concentration of dispersed bitumen, from the original crude oil, from the emulsifier used. Other factors that influence the rheological properties of the emulsion are: the consistency and granulometry of the bitumen particles, and the manufacturing process (type of mill used).
 - **II.** A stable emulsion does not separate itself into its components. The main factor influencing the storage stability of the emulsion is its granulometry, which in turn depends on the type and quantity of the emulsifiers used, the pH of the aqueous phase and the origin and gradation of the bitumen used.

Among the extrinsic properties, closely related to the use of emulsions, we can distinguish:

- I. The breaking speed;
- II. Adhesion.

I. Process emulsion breaking.

In order to perform its binding functions, it is necessary for the emulsion to separate in its basic components, which involves flocculation and coalescence of the droplets and removal of water. For slow bursting emulsions, the main breaking mechanism is due to evaporation and/or water absorption by the aggregate, in the remaining part of the cases the occurrence of chemical aggregate-emulsion reactions contribute to the phenomenon of breakage. In many cases, this type of phenomenon is sufficient to eliminate water from the system; the speed of these processes depends on:

- Reactivity of the emulsion.
- The reactivity of the aggregate.
- Environmental factors (temperature, humidity, wind speed, mechanical action).
- Changes in pH.
- Emulsifying adsorption on the aggregate.





Flocculation time (rupture) and coalescence (polymerization) depends on the system, but in general flocculation is the fastest process in which some waters can be expelled from the system and a certain cohesive force develops, followed by the slower coalescence process, which translates into a continuous phase of bitumen.

Two extreme cases of emulsion failure can be considered:

Case 1: a sharp change in pH, the charge on the emulsion droplets is rapidly destroyed, followed by a rapid flocculation process, while the coalescence process occurs at a slower pace; this speed, in addition to the factors already mentioned, depends on the viscosity of the binder; coalescence is slower with viscous bitumen and low temperatures.

Case 2: loss of water, by evaporation or by absorption, usually preponderant with porous inerts, in this situation the predominant process is that of coalescence.

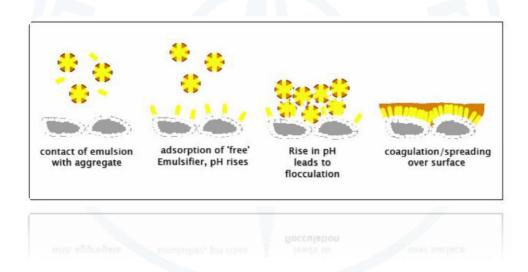


Figure 10. Representation of the phases of rupture of a cationic bituminous emulsion RS.





II. Adhesion.

Another fundamental property of the emulsions is adhesion, which depends on the electrostatic charge that the emulsifier gives to the bitumen globules. This property is strictly related to the temperature and the possible presence of dust.

In the presence of a stone material having alkaline characteristics (limestone) if a cationic (acidic) emulsion is used, a reaction occurs between the calcareous material and the emulsifier with the consequent formation of insoluble amine carbonate. On the other hand, if an anionic (basic) emulsion is used, an attraction of negatively charged bitumen globules occurs, resulting in the formation of an insoluble calcium soap. In the presence of a stone material having acidic characteristics (silica, quartzite, granites, porphyries), if a cationic (acidic) emulsion is used, an attraction of positively charged bitumen globules occurs with consequent formation of an insoluble amine globules occurs with consequent formation of an insoluble amine globules occurs with consequent formation of an insoluble amine silicate; if instead an anionic emulsion (basic) is used, no attraction phenomenon or reaction occurs: there is therefore no adhesion.



Figure 11. On the left a bituminous emulsion before the breaking and setting process; on the right a bituminous emulsion after the breaking and setting process.





PREPARATION OF BITUMINOUS EMULSIONS

Industrially, for the production of bituminous emulsions, equipment capable of generating a strong shearing action is required through which it is possible to obtain a bitumen dispersion with a degree of fineness in the order of microns. The equipment used consists of colloidal mills capable of creating a progressive enrichment of the dispersing phase. The emulsification of the bitumen takes place through a fragmentation of the same into particles of micrometric dimensions that are electrically charged and endowed with repulsive power towards each other. During the production process of a bitumen emulsion it is necessary to effectively and accurately monitor the dispersion energy, viscosity, temperature and dosage of the components necessary for obtaining the emulsion.



Figure 12. Bituminous emulsion packaging in our laboratories.

The main factors that influence the bitumen/water dispersion are: the amount of mechanical energy contributed by the mill (which influences the degree of bitumen fragmentation in very fine particles), the surfactant's ability to guarantee emulsification by creating a protective film around the bitumen particles (this film reduces the surface tension between the two phases). In order to ensure that the bitumen is adequately dispersed in the aqueous phase, it is also necessary that, during the emulsification process, its viscosity is at the optimum value of about 200 mPa·s. Around these





viscosity values, the bitumen is fragmented with the minimum cutting force, allowing the surfactant to bind perfectly on the surface of the bitumen globule.

Finally, the dosage of the components necessary for obtaining a bituminous emulsion must be evaluated accurately and with great precision. Even small variations in the quantity of the emulsifier and of the acid (in the case of cationic emulsions) or of the base (in the case of anionic emulsions), can significantly influence the final result.

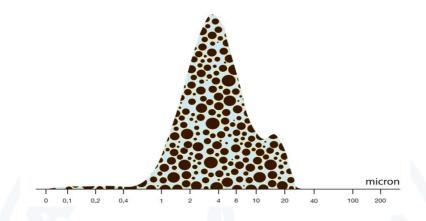


Figure 13. Particle distribution typical of the dimensions of bituminous emulsion drops.

Bitumen emulsions can be produced in batch or in line. In the batch production system, the aqueous phase is prepared in a tank in which water, emulsifier and other chemical additives (such as viscose, stabilizers...) are mixed, by adequately mixing the resulting soap solution; bitumen, on the other hand, is introduced into a dedicated tank and optionally added with fluxes, adhesion promoters... However, a correct dosage of the various components is essential for the quality of the resulting final emulsion and any automatic or semi-automatic control will make the production more efficient and reduce human error to a minimum. The production process of the cationic (acidic) or anionic (basic) bituminous emulsion is concluded when bitumen and soap solution are dosed in the colloidal mill.

In an in-line production plant, on the other hand, the aqueous phase system must be designed to provide sufficient reaction time for chemicals to ensure that the solution is neutralized before it comes into contact with the bitumen. The production process requires an automatic control, through the use of flow meters for all the dosages of material to be used, with the exception of the acid or base that must be controlled by the pH from the aqueous phase.

Special additional additives such as latex, SBS and adhesion promoters require special components and technical solutions; for example, the latexes are sensitive to cutting and can coagulate in pumps and lines, the bitumens modified with SBS, instead, usually require a production of the bituminous emulsion above the boiling point of the water and this involves a realization of the itself under pressure and cooling before release to atmospheric pressure in the storage tank.





The emulsification involves the formation of small bitumen droplets; to obtain a small particle size in the emulsion it is necessary to apply the right mechanical energy in order to prevent their coalescence at the end of the process.

The particle size of the resulting emulsion can be related to the design of the mill head, the speed of the mill rotor, the distance between rotor and stator, the dwell time in the mill, the concentration and type of emulsifier, and the temperature emulsification.

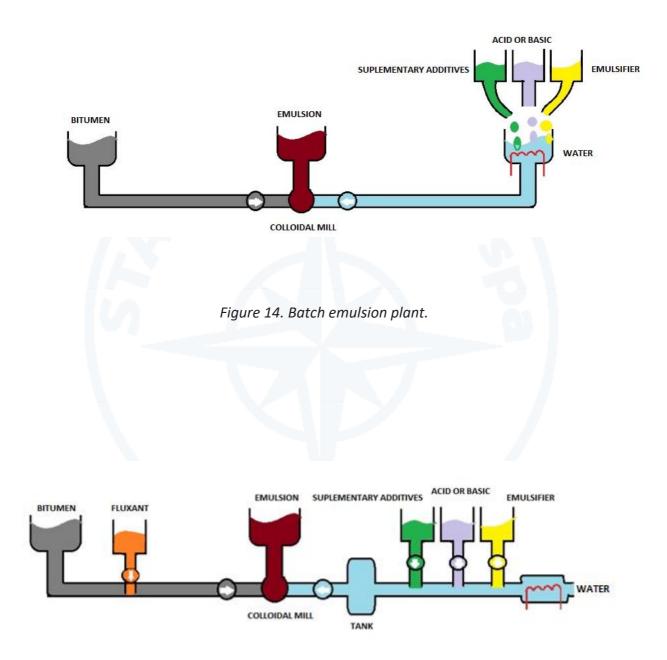


Figure 15. In-line emulsion plant.





GOOD PRACTICES FOR THE MANAGEMENT OF BITUMINOUS EMULSIONS

Improper storage and handling can compromise the quality and performance of the emulsion. There are numerous good management practices to ensure the performance of bituminous emulsions once in place.

Storage:

- Store at a temperature between 20 and 60°C.
- Do not allow the emulsion to freeze.
- Do not allow the emulsion temperatures to exceed the boiling point of the water.
- Store the emulsion in vertical tanks.
- Mix the material every two weeks.
- Protect the pump, valves and lines from freezing.
- Storage conditions.

Freezing breaks the emulsion and separates the bitumen from the water; this involves the formation of two layers inside the storage tank, none of which will be suitable for the intended use.

Furthermore, an emulsion should not overheat because at high temperatures the degree of water evaporation increases, causing the characteristics of the emulsion to vary. It is therefore advisable to keep a bituminous emulsion between 20 and 60°C.

• Type of tanks.

The horizontal tanks have a high interface surface: exposing the emulsion to the air favors the formation of a superficial film.

Vertical tanks are better because they minimize the surface exposed to air.



Figure 16. Storage silos of a bituminous emulsion.





• Agitation.

It is necessary to keep an emulsion moving while not subjecting it to mechanical stress. A slight agitation is therefore advisable. The propellers should be large and rotate slowly to gently circulate the material and ensure proper mixing.

• Pumping line.

Avoid repeated pumping and recirculation to avoid continuous contact with the air, which causes instability; It is also important to pump from the bottom of the tank to minimize contamination and the possible formation of a surface film. It is advisable to place inlet pipes and conduits on the bottom of the tank to avoid foaming. It is important to protect pumps, valves and lines from freezing in winter.

Treatment:

- Do not mix anionic and cationic emulsions.
- Do not load material with high temperature, above 100°C.
- If necessary, dilute the emulsion by adding hot water.
- Wear appropriate personal protective equipment (PPE) to safely handle the emulsion.
- Bituminous emulsions are classified as non-hazardous materials.

• Security procedures.

Safety procedures are important when handling bitumen emulsions. Workers must work in adequately ventilated areas to avoid exposure to fumes, vapors and mists; it is necessary to wear the appropriate personal protective equipment (PPE).

Emulsion tests:

- Make sure the tester understands when the emulsion breaks.
- Understand why emulsions are demulsified.
- Understand how the characteristics vary according to the different applications and productions.
- To obtain results that show how the emulsion behaves in action.
- Be sure to perform the tests according to standardized methods.
- Make sure you get consistent results.





• Production batch analysis.

Sampling is a critical aspect of the management of bituminous emulsions. A good sampling promotes good tests so it is important to take samples for certification from the original tank and test them within two days of collection.

All tests must be performed according to the methods and procedures established by current regulations.



Figure 17. Laboratory tests on bitumen emulsions in our laboratories.





OUR EMULSIFIERS

EMULSIFIERS FOR CATIONIC BITUMINOUS EMULSIONS

1) StarAcid TD6 is an amine-based surfactant used to produce super-fast breaking emulsions according to UNI EN 13075-1 standards. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45°C and subsequently saponified with hydrochloric acid, bringing the pH of the final solution to a value of about 2. The dosage percentages are a function of the working conditions: they vary from 0.15% to 0.25% on the weight of the final emulsion.

StarAcid TD6 it is used for treatments and patches and holes maintenance applications.



Figure 18. Example of treatment of patches and holes.





Formulation type for treatment of patches and holes

BITUMEN 70/100	60% W.W.
WATER	40% W.W.
STARACID TD6	0.2% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=7
	FINAL EMULSION
EMULGEL PV	0.2% W.W.
	OVER SOAPY SOLUTION

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24





Breaking index (MINERAL FILLER)

It is a dimensionless number corresponding to the quantity in grams of the reference filler, necessary to coagulate 100 g of bituminous emulsion.

PRINCIPLE (UNI EN 13075-1)

A reference filler is added at uniform speed to a specified amount of mixed bitumen emulsion. When the emulsion has completed the break, the amount of filler added is determined by weighing. The mass in grams of the filler multiplied by 100 and divided by the quantity in grams of emulsion, represents the dimensionless rupture index of the same (BV).

> Formulation BV= (100 x m_f)/m_e

where:

 $m_f = m_2 - m_e - m_1 \rightarrow$ amount of filler in grams added; $m_e \rightarrow$ amount of emulsion in grams.

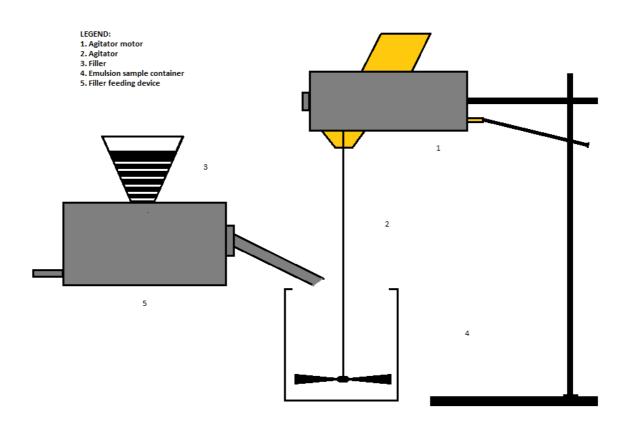


Figure 19. Schematization of the instrumentation necessary for the process of determining the rupture index of a bituminous emulsion.





2) StarAcid A14 is an amine-based surfactant used to produce fast and medium breaking emulsions according to UNI EN 13075-1 standards. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45°C and subsequently saponified with hydrochloric acid, bringing the pH of the final solution to a value of about 2. The dosage percentages are a function of the working conditions: they vary from 0.3% to 0.6% on the weight of the final emulsion.

StarAcid A14 is used for different types of applications:

• **Tack coat**: such a treatment involves applying a quantity of bituminous emulsion on a surface already treated to obtain a good adhesion with the next layer.





Figure 20. Examples of treatment for attack hands.

Formulation type for tack coat

BITUMEN 70/100	55% W.W.
WATER	45% W.W.
STARACID A14	0.3% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION





• **Surface treatment:** achievable through the application of the emulsion followed by the laying of stone covering aggregates according to pre-established dosages. The roughening surface treatment can be realized in mono-layer or double-layer.





Figure 21. Examples of surface treatment.

Formulation type for surface treatment

BITUMEN 70/100	65% W.W.
WATER	35% W.W.
STARACID A14	0.5% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION
STARLATEX A	4.0% W.W.
	OVER EMULSION





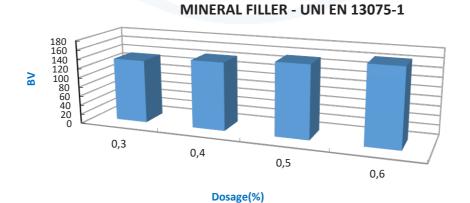
• **Cold plastic asphalt**: aggregate-emulsion mixtures produced and used at room temperature. In the realization of this asphalt type it is possible to use aggregates with a low content of bituminous ends and emulsions at medium breaking speed with fluxant.



Figure 22. Examples of cold plastic asphalt.

Formulation type for cold plastic asphalt

BITUMEN 70/100	65% W.W.
STARDOPE 130P	0.5% W.W.
	OVER BITUMEN
STAROIL VG30	15%
	OVER BITUMEN
WATER	35% W.W.
STARACID A14	0.6% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION







1) StarAcid SQ30 is a surfactant based on quaternary ammonium salts used to produce slow breaking rate emulsions according to UNI EN 13075-1 standards. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45°C and subsequently saponified with hydrochloric acid, bringing the pH of the final solution to a value of about 2-5. The dosage percentages are a function of the working conditions: they vary from 1.0% to 1.4% on the weight of the final emulsion.

StarAcid SQ30 is used for different types of applications:

• **Prime coat**: such a treatment involves applying a quantity of emulsion on a porous surface that has never been treated before with a binder. The bituminous emulsion penetrates the treated surface and impregnates it.



Figure 23. Example of treatment by impregnation coat.

Formulation type for prime coat

BITUMEN 70/100	55% W.W.
WATER	45% W.W.
STARACID SQ30	1.0% W.W.
	OVER EMULSION
pH=5 FINAL EMULSION*	

*If it necessary use hydrochloric acid to reach final emulsion pH between 2 and 5.





• **Slurry Seal or Microsurfacing**: for Slurry Seal we mean a mixture of aggregates, bitumen emulsion, water, cement and any additional additives, having a fairly fluid consistency and usable for the realization of rather thin carpets.



Figure 24. Examples of treatment of the Slurry Seal type.

Formulation type for slurry seal or microsurfacing	
	A Contract of the second s
BITUMEN 70/100	65% W.W.
STARDOPE 130P	0.4% W.W.
	OVER BITUMEN
WATER	35% W.W.
STARACID SQ30	1.1% W.W.
	OVER EMULSION
STARLATEX A	5.0%
	OVER EMULSION
pH=5 FINAL EMULSION*	

*If it necessary use hydrochloric acid to reach final emulsion pH between 2 and 5.





• **Cold recycling:** it is carried out by mixing, at room temperature, RAP with the bitumen emulsion.

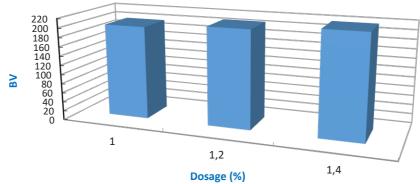


Figure 25. Example of cold recycling treatment.

Formulation type for cold recycling treatment

BITUMEN 70/100	60% W.W.
WATER	40% W.W.
STARACID SQ30	1.3% W.W.
	OVER EMULSION
pH=5 FINAL EMULSION*	

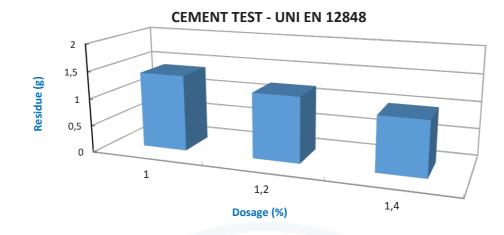
*If it necessary use hydrochloric acid to reach final emulsion pH between 2 and 5.



MINERAL FILLER - UNI EN 13075-1







Mixing stability with cement (CEMENT TEST)

It represents the mass in grams of the coagulated material (bitumen + cement) produced when a bituminous emulsion is mixed with the standard test conditions.

PRINCIPLE (UNI EN 12848)

The bituminous emulsion is mixed with cement and, when it is broken, poured through a sieve sized; the quantity of material retained on the sieve, weighed, establishes the breaking speed. It is applied to cationic bituminous emulsions and to slow and over-stabilized anionic bituminous emulsions.

Formulation Sc(g)= m₂-m₁

 $m_1 \rightarrow$ mass in grams of sieve and plate;

 $m_2 \rightarrow$ mass in grams of sieve and plate after drying.





2) StarAcid SP453 is an amine-based surfactant used to produce slow-breaking emulsions according to the UNI EN 13075-1 standards. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45 ° C and subsequently saponified with hydrochloric acid, bringing the pH of the final solution to a value of about 2. The dosage percentages are a function of the working conditions: they vary from 1.4% to 2.0% on the weight of the final emulsion.

StarAcid SP453 It is used for different types of applications:

- Prime coat.
- Slurry Seal o Microsurfacing.
- Cold recycling.

Formulation type for prime coat

BITUMEN 70/100	55% W.W.
WATER	45% W.W.
STARACID SP453	1.5% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION

Formulation type for slurry seal or microsurfacing

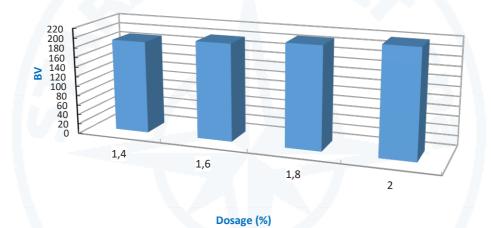
BITUMEN 70/100	65% W.W.
STARDOPE 130P	0.4% W.W.
	OVER BITUMEN
WATER	35% W.W.
STARACID SP453	1.6% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION
STARLATEX A	5.0%
	OVER EMULSION





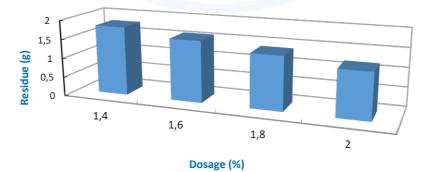
Formulation type for cold recycling treatment

BITUMEN 70/100	60% W.W.
WATER	40% W.W.
STARACID SP453	1.9% W.W.
	OVER EMULSION
HYDROCHLORIC ACID	pH=2
	SOAPY SOLUTION



MINERAL FILLER - UNI EN 13075-1

CEMENT TEST- UNI EN 12848







EMULSIFIERS FOR ANIONIC BITUMINOUS EMULSIONS

1) StarBas G is a mixture of fatty acids used to produce emulsions with a rapid and medium breaking speed according to ASTM D244-00. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45°C and subsequently saponified with sodium hydroxide, bringing the pH of the final solution to a value of about 12. The dosage percentages are a function of the working conditions: they vary from 0.3% to 0.6% on the weight of the final emulsion.

StarBas G It is used for different types of applications:

- Tack coat.
- Surface treatment.

Formulation type for tack coat

BITUMEN 70/100	55% W.W.
STARPITCH THL	3.0%
	OVER BITUMEN
WATER	45% W.W.
STARBAS G	0.3% W.W.
	OVER EMULSION
SODIUM HYDROXIDE	pH=12-14
	SOAPY SOLUTION

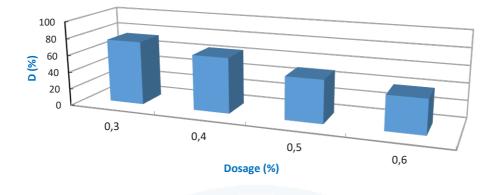
Formulation type for surface treatment

BITUMEN 70/100	65% W.W.
STARPITCH THL	3.0%
	OVER BITUMEN
WATER	35% W.W.
STARBAS G	0.6% W.W.
	OVER EMULSION
SODIUM HYDROXIDE	pH=12-14
	SOAPY SOLUTION





DEMULSIVITY - ASTM D 244-00



Mixing stability with solutions of calcium chloride or sodium dioctyl sulphosuccinate (DEMULSIVITY)

It represents the mass in grams of coagulated material produced when a bituminous emulsion is mixed with aqueous solutions of calcium chloride (for anionic emulsions) or sodium dioctyl sulfosuccinate (for cationic emulsions) under the test conditions defined by the specified standard.

PRINCIPLE (UNI EN 12848)

The bituminous emulsion is mixed with solutions of calcium chloride or dioctyl sulphosuccinate sodium and, when it is broken, poured through a sieve sized; the quantity of material retained on the sieve, weighed, establishes the breaking speed. It is applied to anionic and cationic bituminous emulsions with medium and rapid breaking speed.

<u>Formulation</u> D(%)= (A/B)x100

 $A \rightarrow$ weight of the demulsivity residue;

 $B \rightarrow$ weight of the distillation residue in the sampling of 100 g of emulsion.





2) StarBas NP1034 is an anionic surfactant used to produce slow breakage emulsions. It can be used both to obtain emulsions modified with elastomers in aqueous phase, and with modified bitumen. Said surfactant is dissolved in water at a temperature of 40-45°C and subsequently saponified with sodium hydroxide, bringing the pH of the final solution to a value of about 12. The dosage percentages are a function of the working conditions: they vary from 1.5% to 3.0% on the weight of the final emulsion.

StarBas NP1034 It is used for different types of applications:

- Impregnation.
- Waterproofing.





Figure 26. Examples of waterproofing treatment.

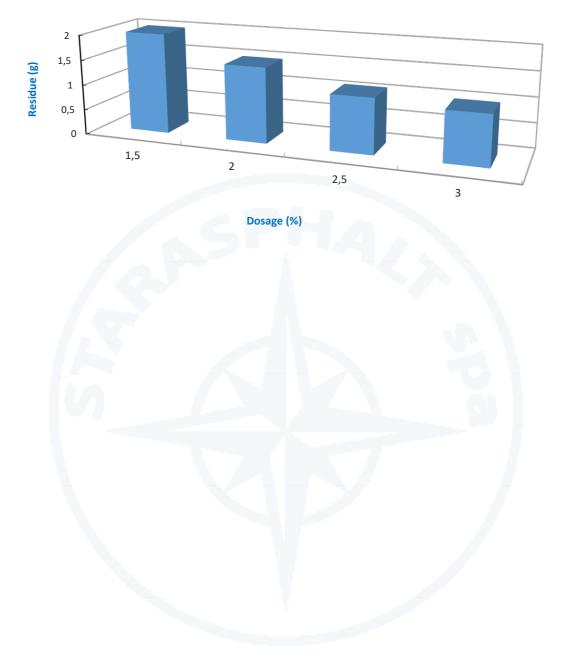
Formulation type for impregnation and waterproofing

BITUMEN 50/70	55% W.W.
STARPITCH THL	3.0%
	OVER BITUMEN
WATER	45% W.W.
STARBAS NP1034	2.5% W.W.
	OVER EMULSION
SODIUM HYDROXIDE	pH=12-14
	SOAPY SOLUTION
EMULGEL PV	0.2%
	OVER SOAPY SOLUTION
STARLATEX B	5.0%
	OVER EMULSION





CEMENT TEST- UNI EN 12848





ADDITIONAL ADDITIVES FOR BITUMINOUS EMULSIONS



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CALPARK

EMULGEL PV It is a viscosizing additive used for the production of very stable cationic and anionic bituminous emulsions, slow, medium and fast breaking speed. It is added to the soapy solution, at a temperature of 40-45°C, saponifying with hydrochloric acid or with caustic soda, respectively for cationic or anionic bituminous emulsions. Its dosage ranges from 0.05% to 0.30% on the weight of the soap solution.



EMULSTAB It is a liquid additive used for the production of stabilized cationic bituminous emulsions, slow, medium and fast breaking speed. It is added to the aqueous solution, before the emulsification process. Its dosage varies from 0.3% to 0.6% on the weight of the final emulsion.







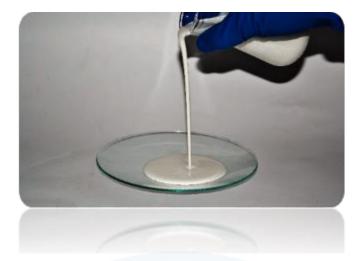
ANTIFOAM It is a liquid additive specially formulated to prevent, control or destroy the foam in liquid systems. In addition to exerting an effective action against the foam during the mixing phase, it results to be an excellent deaerant to the finished product. It is introduced into the soapy solution, at any stage of processing, without causing problems to the final preparation. Its dosage ranges from 0.05% to 0.10% on the weight of the soap solution.



STARFLUX It is a liquid additive based on hydrocarbon oils for the production of cationic and anionic bituminous emulsions. Its addition to bitumen, before the emulsification process, gives the final emulsion greater physical stability and, above all, facilitates its application. It is added directly into the emulsion bitumen tank, before the emulsification process. Its dosage varies according to the bitumen used for the preparation of the emulsion; normal, ranges from 1.0% to 5.0% on the weight of the bitumen.







STARLATEX A

It is an aqueous dispersion of copolymers based on butadiene and styrene used for the modification of cationic bituminous emulsions in order to give elasticity to the final bitumen. Its use guarantees the production of bituminous emulsions which, when broken, have a particularly elastic residual bitumen. These emulsions are intended for applications that require high mechanical characteristics, therefore higher stability to deformation and wider plasticity range. It is added to the water tank of the emulsion plant before the emulsification process or alternatively it can be added to the already produced bitumen emulsion. Its dosage varies according to the modification required; normally it varies from 2.0% to 5.0% on the weight of the final emulsion.

STARLATEX B

It is an aqueous dispersion of styrene-acrylic copolymers used for the modification of the anionic bituminous emulsions in order to give elasticity to the final bitumen. Its use guarantees the production of bituminous emulsions which, when broken, have a particularly elastic residual bitumen. These emulsions are intended for applications that require high mechanical characteristics, therefore higher stability to deformation and wider plasticity range. It is added to the water tank of the emulsion plant before the emulsification process or alternatively it can be added to the already produced bitumen emulsion. Its dosage varies according to the modification required; normally it varies from 2.0% to 5.0% on the weight of the final emulsion.







STARPITCH THL It is an acidifier based on bituminous fatty acids for the production of anionic bituminous emulsions. Its addition to the bitumen increases its acidity, making the values compatible with the characteristics of emulsifiability. It is added to the bitumen tank of the emulsion plant with a dosage ranging from 1.0% to 3.0% on the weight of the bitumen.







CONCLUSION

Our range of emulsifiers allows to realize bitumen emulsions for different uses and objectives. The wide range of emulsifiers developed in our laboratories allows, in fact, to work with all types of aggregates and bitumen and in conjunction with the most diverse climatic conditions. Our products, classifiable on the basis of their dissociation behavior in water, first favor the dispersion of the bitumen, then, following the breakage, they favor the adhesion of the bitumen to the stone material. In particular they are characterized by the liquid or pasty consistency that allows different types of handling, storage and dosage.

The wide range of Star Asphalt emulsifiers is summarized in the following table, which also explains the possibilities of use.

EM	ULSIFIERS	Surface treatment	Treatment of patches and holes	Cold recycling	Slurry Seal	Impregnation	Waterproofing	Tack coat
	STARACID TD6		•					
CATIONIC	STARACID A14	•						•
	STARACID SP453			•	•	•		
	STARACID SQ30	7		•	•	•		
ANIONIC	STARBAS G	•						•
	STARBAS NP1034					•	•	

Table 1. Applications of the Star Asphalt range of emulsifiers.





FINAL CONSIDERATIONS

The purpose of this "booklet" is to suggest the appropriate improvements in order to guarantee a high quality level of our roads, eliminating improvisation, coordinated with these indispensable for the managerial responsibility of the operators involved in the construction of road paving.

The StarAsphalt S.p.A. is constantly looking for innovative solutions and undisputed advantages on several fronts for the community, proposing advanced performance additives studied in its laboratories and realized in its production sites, in compliance with Regulation (EC) no. 1907/2006 concerning the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and the establishment of the European Chemicals Agency, resulting from the use of diversified products that are less and less harmful to humans and for the environment.

Considering the amount of the treated aspects and the continuous development of products and technological innovations, the following writing will be in continuous evolution.



NOTE

NOTE





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