Bituminous emulsions

NEW VERSATILE BITUMEN EMULSIFIER FOR COLD MIX APPLICATION: FROM LABORATORY CONCEPTION TO FIELD TRIAL VALIDATION

Jorda Eric, INOUBLI Raber
Arkema

Abstract

During last we worked to develop new surfactant technology for bitumen emulsion. Based on renewable raw materials, this new emulsifier allows to produce emulsions with outstanding coating/workability properties, particularly suited for cold mix applications. Purpose of this article is to follow the project from the scope of work to the field trial on a rural country road going through all steps from laboratory to industrial production. The scope of work was quite challenging with many specifications, technical expectations: Renewable raw materials Easy to handle emulsifier Versatile non-hazardous emulsion Fully coated and easy to handle cold mixes with any type of aggregates and bitumen Pavement good mechanical properties, moisture resistance Compatible with high RAP use. First generation developed using standard laboratory mix-design process showed some unacceptable weaknesses when applied at industrial scale. Industrial emulsion showed some creaming issues not observed at laboratory scale and stripping occurred on the mix when too much energy was applied during paving step. After this disappointing attempt, we had to reconsider all steps from laboratory formulation to final paving application with objective to make our evaluation process more representative of the critical parameters encountered. Observations made during the first industrial implementation were key element to build-up the new evaluation process including more stringent tests at every step of the process. Based on this experience, new formulation was developed step by step (synthesis, formulation, emulsion manufacturing, cold mix production, mix properties) and validated at each scale (laboratory, pilot, industrial). The outcome of this exciting project is a patented new surfactant recently commercialized. In this presentation, we propose to present the story of this new surfactant development from the market request to the successful jobsite with a focus on the importance of field trials in the innovation process for chemicals used in paving applications.

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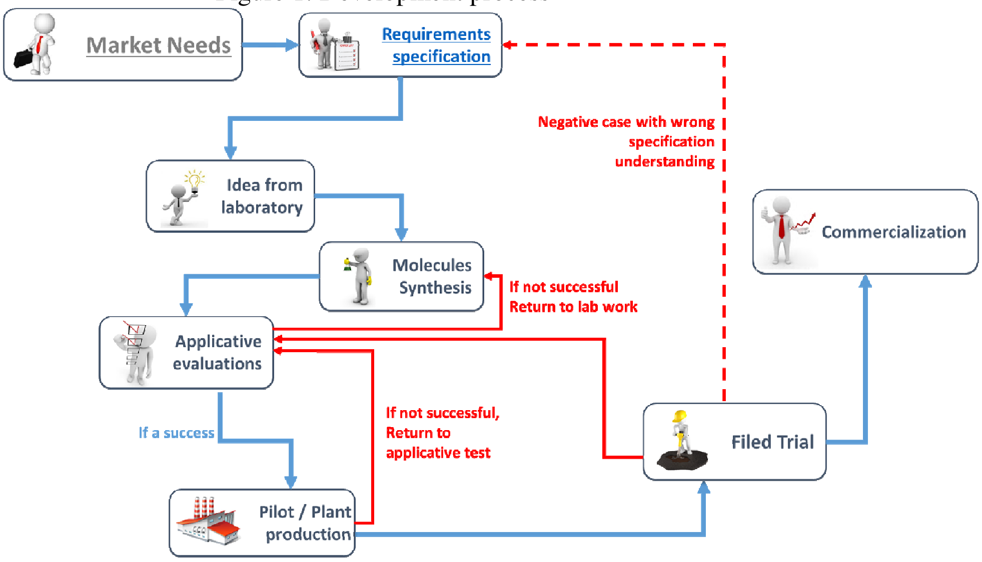
1. INTRODUCTION

Pavement preservation with bitumen emulsion is well known and used in southern Europe and more specifically in France. Market of surfactant for bitumen emulsion is growing and needs adaptations regarding the evolution of customer's request. We propose to focus on specific application (cold mix and especially grave emulsion for French market as defined by standard NF P98-138 [1]) and to detail the development process of a surfactant formulation as a function of evolution of market and also, as a function of specific link between R&D, production and final use.

Many kind of surfactants are available for paving application. However, grave emulsion (particularly popular in France for base course construction and reprofiling of uneven pavements) needs surfactant with specific technical expectations [2]. These expectations have had many evolutions since the last 15 years and we had to adapt our R&D tools and process to follow this evolution.

In this paper, as shown by the figure 1, we propose to detail, through the development of New Surfactant formulation, the life of a project from laboratory synthesis to commercialisation with a particular focus on the importance of field trials.

Figure 1: Development process



2. DEVELOPMENT AND USE OF FIRST SURFACTANT GENERATION

2.1 Market specification evolutions:

Grave emulsion is well known and used in France since the end of last century. It was well appreciated to formulate base course and for this kind of application, classical slow setting emulsion with cationic amidoamine surfactant [3] were used to realise emulsion. These emulsions gave cold mix with good mechanical properties and non-complete coating aspect of aggregates. Nevertheless this drawback was not an issue because most of roads using grave emulsion as reprofiling layer or base course were generally covered by a wearing course (chip seal, microsurfacing or other…) having appropriate aspect.

In beginning of 2000's, we observed an evolution of market needs; two new specifications became more and more important for grave emulsion. The first one was the asphalt mix aspect: customer wanted to have blacker asphalt mix even if the pavement layer was meant to be covered by a surface treatment. The second was the workability. It became more common practice to store the asphalt mix for few days before use and asphalt mix was expected to keep acceptable workability. And, more surprisingly, these new needs could be at the expense of mechanical properties. Unfortunately, it was complicated to achieve these new specifications with classical amido-amine surfactant. Even if technically speaking, mechanical properties could be considered as more important than asphalt aspect, we should adapt our surfactant chemistry to the market needs.

2.2 Formulation adaptation:

Seeing these technical specification evolutions, we had to adapt our chemistry to fit them. We had the following technical pathway:

- Emulsion produced to evaluate surfactants: 60% of bitumen (160/220) of different origins, HCl to have pH 2, surfactant concentration between 10 and 20kg/t (adjusted to fit specifications).
- Asphalt content in the grave emulsion : 4.2%
- Improved coating aspect and workability: It seemed that those two parameters were linked and to improve them, we should favour coating rather than emulsion breaking. To fit these parameters, we propose to remove classical amido-amine surfactant by surfactant having lower reactivity with aggregate like non-ionic surfactant. This reactivity and stability parameter were measured by normalised cement test [4]. On the other side, we evaluated the coating quality (coating homogeneity, aspect) with the standard normalised test NF P98-257-1 [5]

With these targets, we developed a surfactant formulation with non-ionic molecules (Surfactant 1). As shown in table 1, slow setting emulsion with this Surfactant 1 gave good asphalt workability, stability and aspect. Nevertheless, mechanical properties (measured by Duriez compression test, NF P98-251-4) were very low.

Emulsion with Surfactant 1 did not fit specifications and to improve mechanical properties, we decided to formulate it with antistripping agent. Nevertheless, this antistripping agent should not disturb too much the emulsion behaviour. It was known that using amine surfactant could favour emulsion breaking and so decrease workability of the asphalt. Choice was to add an appropriated blend of specific fatty amine plus a fatty acid molecule. This blend was used as Surfactant 2.

Table 1. Cold mix applicative results as function specifications (run 1)

	Surfactant 1	**Surfactant 2**
Chemical nature	Non-ionic	Non-ionic + fatty amine + fatty acid 1
Emulsion Stability	**OK**	**OK**
workability	**OK**	**OK**
Coating quality	**OK**	**OK**
Mechanical properties	NO	**OK**

At this stage, we succeeded on targeting initial specifications. However with emulsion using surfactant 2, we observed an important foam on emulsion surface that could bring some issues in the storage at industrial scale.

We returned to the laboratory to investigate about this issue and found that the critical parameter leading to this foaming seemed to be the fatty acid length. We observed that we needed shorter acid molecule but long enough to have antistripping effect. This observation was new and could be useful for other formulations/applications and so it was patented (FR2992966) [7]. Several acids (different carbon chain length) were tried and the best compromise was obtained with fatty acid 2 (table 2).

Table 2. Cold mix applicative results as function of specifications (run 2)

	Surfactant 1	**Surfactant 2**	**Surfactant 3**
Chemical nature	Non-ionic	Non-ionic + fatty amine + fatty acid 1	**Non-ionic + fatty amine + fatty acid 2**
Stability	**OK**	**OK**	**OK**
Workability	**OK**	**OK**	**OK**
Foaming	-	YES	**NO**
Coating quality	**OK**	**OK**	**OK**
Mechanical properties	NO	**OK**	**OK**

In order to move to the next step, we partnered with a paving company to realize an industrial evaluation:

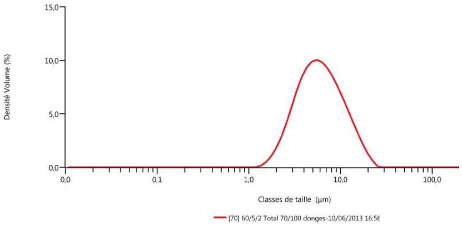
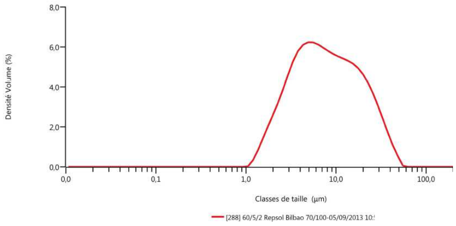
- Pilot plant scale production of emulsifier
- Emulsion industrial production
- Asphalt mix production and field trial

Working with the different bitumen grades available at our partner's plant we found out that variability was important and some bitumen were leading, at industrial scale, to unacceptable creaming.

It appeared that the industrial emulsion showing stability issue was also showing some degraded particle size distribution (table 3), not evidenced at laboratory scale.

Based on this observation, new emulsification conditions were set-up on our pilot unit to be more sensitive to bitumen variability.

Table 3. Effect of bitumen variability on industrial emulsion stability

Bitumen	Emulsion (60%, pH 2) particle size distribution	observation
1	 Average diameter = 5.8 µm	Emulsion stability OK
2	 Average diameter = 7.8 µm with large distribution	Bitumen skin on top and bitumen sediment (emulsion not stable)

Despite these observations, and after that our partner confirmed good mixing results at laboratory scale we decided to realise a field trial to evaluate the coating quality on a grave emulsion for reprofiling.

Our partner produced few tons of asphalt mix with Surfactant 3, bitumen 1 and limestone aggregates.

Results of this trial are detailed in next table:

Table 4. Field trial test (Grave emulsion with Surfactant 3)

Pictures and Remark / Observation	
 Area with good aspect (homogeneous, acceptable coating…)	 Area with stripping and dry aspect
 Presence of mastic, lumps	 Cracking on turns

As detailed on table 4, we observed strong asphalt stripping and important dry parts whereas it was not observed on asphalt produced at lab scale. Despite a full mix design process following state of the art procedures, it appeared that the intensity of stress endured by the mix during storage, transport and especially paving step (mechanical induced stripping) was underestimated. Taking into account the field test observations, we added a new test to our product qualification process: the reworking step. This test was pretty simple:

- Coating quality at initial time as described by standard test [5]
- Storage under predetermined constraint
- Energic mixing 2 hours after aggregate and emulsion blending + evaluation of coating quality
- Energic mixing 5 hours after aggregate and emulsion blending + evaluation of coating quality

With this test, we are able to simulate aggregate stripping during transport, storage and paving. Demonstration was done with partner's system (limestone aggregate with emulsion using Surfactant 3): at laboratory scale, asphalt has good aspect at initial time and presented important stripping after reworking test.

At the end of this project, we conclude that Surfactant 3 could not be used for grave emulsion. Nevertheless, we learned a lot about this experience and adapted our validation specification process as presented in table 5.

Table 5. Evolution of project specifications

First specifications setting	2nd specifications setting after customer laboratory evaluation	3rd specifications setting after customer field trial
Stability	Stability	Stability
workability	workability	workability
Coating quality	Coating quality	Coating quality
Mechanical properties	Mechanical properties	Mechanical properties
	Foaming	Foaming
	Bitumen versatility	Bitumen and aggregates versatility
		Reworking

3. DEVELOPMENT AND USE OF NEW GRAVE EMULSION SURFACTANT TO FIT MARKET NEEDS.

3.1 Market and technical specification:

During last ten years, grave emulsion market grew bigger and specifications shifted more and more to versatile surfactants giving good aspect (black) despite limited mechanical properties. Thanks to our field experience with first generation, we carried-on the project with clear specification as mentioned in table 5 and moreover, by adding new one as use of renewable raw materials.

3.2 Technical development of new grave emulsion surfactant:

As mentioned previously, we had the objective to develop surfactant formulation based on renewable raw materials and targeting all applicative properties detailed on table 5.
Process was adapted from what we learnt from previous experience:

- 1st: chemical surfactant formulation based on renewable materials
- 2nd: investigation on emulsion at lab scale
- 3rd: investigation on asphalt mix at lab scale
- 4 : checking on emulsion and asphalt at lab scale by paving partner
- 5: Field trial
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On literature, it is well known that lignin-based surfactant could be used to realise cationic bitumen emulsions. For example, many patents claimed use of lignin or derivatives ([8], [9],[10]). Lignin based surfactant gave good asphalt coating quality but limited moisture resistance properties. We worked then on a new product design at laboratory scale with clear target:

- Make stable surfactant formulation (at temperature between -10 to 50°C).
- Make sure that surfactant formulation has "acceptable" HSE profile
- Make sure that cationic bitumen emulsion obtained with this formulation was stable
- Make sure that emulsion was not classified
- Improve as much as possible the application properties

Many surfactants and emulsions formulations were realised as detailed on next few tables. We started by the objective to have surfactant formulation given stable soap (with concentration to target bitumen emulsion at 14kg/t of surfactant). After this first selection, we realised emulsions (60% Bitumen / 14-16kg/t of Surfactant 4 / pH 2) with selected surfactant formulations to make final selection based on emulsion properties.

Table 6a. Soap aspect and stability

Soap with Surfactant formulation (to have 14kg/t)	Lignine derivative A		Lignine derivative B		Lignine derivative C	
	Aspect	Picture	Aspect	Picture	Aspect	Picture
Surfactant formulation (lignine derivative + additif A)	OK		Soap OK but some deposit easiely re dispersable		ok	
Surfactant formulation (lignine derivative + additif B)	OK		Soap with too important deposit		ok	
Surfactant formulation (lignine derivative + additif C)	OK		Soap OK but some deposit easiely re dispersable		ok	

Three lignin derivatives (with different chemical natures) were tried with different additives / cosurfactant (A, B and C, with different chemical natures). We observed stable soap with lignin A and C. Lignin B given deposit after few hours or days, it looks like lignin B was not compatible with co-surfactants selected. Based on these observations, we decided to continue investigation with the lignin A and C to realise bitumen emulsions (properties detailed on table 6b).

Table 6b. Emulsions characterizations

Surfactant formulation		Emulsion aspect		Emulsion stability		Particules zise (µm)
Lignine derivatives	additive	day 1	day 7	Sieving residues (‰, 500µm filter)		d(50)
Lignin A	a	viscous	viscous	0,1		15,3
	b	Gel	broken	-		-
	c	OK	OK	9,5		13,1
Lignin C	a	OK	OK	0,07		6,2
	b	OK	OK	0,07		4,9
	c	OK	viscous	0,5		8,9

Emulsions with lignin derivative A seem to be less stable than derivative C and even when emulsion aspect seems good, stability is not acceptable (>1‰). We can link that to chemical nature of the lignin: lignin A has probably better electrostatic and sterical behavior to stabilize bitumen droplet.
Now with lignin C, it seems that surfactant formulations with additives (co surfactant) a and b could be considered as potentially interesting, both of them give good emulsion aspect, stability and particle size. To continue investigation, surfactant formulation choice was done on HSE profile: formulation Lignin C + additive b has not the pictogram "human toxicity" whereas it was the case foe formulation Lignin C + additive a.
Regarding surfactant properties, HSE profile and emulsion properties, we decided to continue the study with the surfactant formulation Lignin C + additive b and for next step, this formulation will be named Surfactant 4.

At laboratory scale, the Surfactant 4 was evaluated thoroughly in order to maximize our chance of success:
- Emulsion properties (60% Bitumen / 14-16kg/t of Surfactant 4 / pH 2).
- Emulsion with 8 different bitumens (coming from different refineries)
- Asphalt mix with different source of aggregates with a particular focus on basalt and limestone
- All asphalt mix characterisations (coating, stripping, workability, mechanical properties (R, r/R with Duriez test)…). As a comparison, we introduce on the study a competitor surfactant reference already used on this market (Ref).

Evaluation results were detailed in table 7:

Table 7. Global evaluation of asphalt mix obtained with bitumen emulsion with 14kg/t of Surfactant 4

	Emulsion	Basalt *St Yvoine* Massif central (4,2% of bitumen)				Limestone *Sirolaise* Fr Southeast (4,2% of bitumen)			
		Coating properties		Duriez test		Coating properties		Duriez test	
		coating	coating evaluation after rehandling (5h)	R (Mpa)	r/R moisture resistance	coating	coating evaluation after rehandling (5h)	R (Mpa)	r/R moisture resistance
Surfactant 4	60% bitumen (160/200) pH 2	Complete coating Black aspect	Good workability No stripping Black aspect	5,00	0,58	Complete coating Black aspect	Good workability Slight stripping on coarse aggregates Black aspect	7,40	0,57
Competitor Ref		Complete coating Black aspect	Good workability No stripping Black aspect	4,20	0,50	Complete coating Black aspect	Good workability Slight stripping on coarse aggregates Black aspect	6,90	0,55

Laboratory evaluation results were good and achieved all specifications defined previously. It was important to observe that we have good workability and very limited stripping after reworking (main reason of issues encountered in our previous project). Surfactant 4 was patented by Arkema.

With these results, clear objective was now to confirm them by field trial with our paving partner. Our results were first confirmed at partner laboratory scale with bitumen and aggregate available for field trial. This step at laboratory was a success and we decided to go for a field test:

- Emulsion with concentration of Surfactant 4 between 8 and 10kg/t
- Two mix productions with two different aggregates (limestone and diorite)

Table 8. Field trial test (Grave asphalt with Surfactant 4)

Limestone	Diorite
	
Good black coating aspect, stripping very limited even after production and good workability even after storage	Good black coating aspect, stripping very limited even after production and good workability even after storage

	
Good aspect of pavement layer	Good aspect of pavement layer

The field trial was a success, validating the improved mix design process that was set-up thanks to the first generation development project.
However, even if this new surfactant is relevant for reprofiling and maintenance materials, leading to good workability, good coating and fair mechanical properties, there is still room for improvement to reach the expectations for more demanding paving materials. In terms of innovation, a second step is already targeted:

- Perform/adapt this surfactant for:
    - Cold mix for base course: Technically speaking, it was known that emulsion breaking will favor the adhesion (r/R) but has a tendency to decrease coating quality (workability and aspect). An appropriate balance is achieved for maintenance material (r/R=0.5) with the new surfactant developed. Next objective will be to achieve mixes for base course (increasing market) with good moisture resistance and mechanical properties (r/R>0.75) and without negative effect on coating quality (solution not available on the market).
    - Recycling: Demand for cold recycling solutions that can take advantage of existing RAP binder is growing. Adaptation of this kind of surfactant formulation to be used or combined with rejuvenating solution might be a solution.
    - Bitumen variability: Adaptation to anticipate the new 2020 regulation on fuel oil and the impact on bitumen quality. This point imply to have a better understanding of relation between bitumen composition and emulsionability.

4. CONCLUSIONS

For a chemical company, development of a new additive like a new surfactant could be a long way, especially for such a complicated application as cold mix asphalt. Define the right scope of work and more specifically the relevant mix design process could be very difficult without easy access to field trial. It requires real anticipation of application challenges at every stage, from the chemical synthesis to final field test. Updating constantly laboratory mix design process by learning from field experience is a key aspect of new product development and the only way to address the next challenges.

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