**Vol. 5, No. 1, 2023**

https://doi.org/10.23939/jtbp2023.01.049

**Iurii Sidun[1], Khrystyna Sobol[1], Volodymyr Bidos[1], Oleksii Hunyak[1], Iryna Protsyk[2]**

# CATIONIC OVER-STABILISED BITUMEN EMULSION IN ROAD CONSTRUCTION: REVIEW

*[1] Lviv Polytechnic National University,*
*Department of Highways and Bridges,*
*[2] Separate structured subdivision*
*Automobile and Road Vocational College*
*of Lviv Polytechnic National University,*
*volodymyr.m.bidos@lpnu.ua*



**This article describes the classification of cationic bitumen emulsions according to "reactivity" and breaking behaviour characteristics. The methods of researching the characteristics of breaking behaviour for bitumen emulsions of different "reactivity" in accordance with European and Ukrainian regulatory documents are presented. Available possible emulsifiers in Ukraine for over-stabilised bitumen emulsions are given with a description of road technology where they can be applied. The experience of using over-stabilised bitumen cationic emulsions in road construction is characterized. Namely, a literature review of the use of over-stabilised bitumen cationic emulsions in soil stabilization technologies, strengthening of base course materials with emulsion, and "cold recycling" technology was carried out. The regularities of the interaction of over-stabilised bitumen emulsion with finely dispersed mineral binders and fillers are reviewed.**

**Key words: rapid-, medium-, slow-setting bitumen emulsion, over-stabilised bitumen emulsion, soil stabilization, base course materials, "cold recycling" technology, Portland cement.**

## Introduction

Cationic bitumen emulsions (CBE) remain a popular material for road construction abroad and in Ukraine (Sidun, 2019; Sidun, 2019; Dołżycki, 2019; Pérez, 2013; Liu, 2020). One of the most important physical and technical properties of these emulsions is the breaking behaviour. Emulsion breakdown refers to the formation of a residual binder and an aqueous phase. Emulsion breakdown can be divided into planned and non-planned. Unplanned breakdown of the emulsion occurs after its production in case of non-compliance with the requirements for the composition of the emulsion, technological parameters of production. Also, breakdown can occur during improper preparation (unsufficient mixing, non-compliance with the temperature regimes) or long-term storage of emulsions in containers. Planned breakdown of the emulsion occurs when it is used as a material for certain road technologies. Bitumen emulsion begins to breakdown when it covers or mixes with mineral surfaces, materials, and final of breakdown will depend on its reactivity. According to reactivity, cationic bitumen emulsions are usually divided into three types: rapid-setting (CRS), medium-setting (CMS) and slow-setting (CSS). Therefore, the rate of emulsion breakdown will depend directly on its reactivity, which is regulated mainly by the type and amount of emulsifier in the emulsion and the pH of the emulsion itself. But the rate of planned emulsion breakdown will also depend on the reactivity of the mineral part with which it will interact. In this case, it is necessary to be guided by the principle of matching the reactivity of the emulsion with the reactivity of the surface or aggregate. Therefore, rapid-setting emulsions are used with non-reactive aggregates with a small surface area, and slow-setting ones are used with reactive aggregates with a large surface area. As for road technologies, as a rule, CRS is used for surface treatments, CMS for mixtures of porous grain composition, and

CSS for dense mixtures according to their grain composition (Grilli, 2012; Grilli, 2013; Grilli, 2018; Grilli, 2016; Pasetto, 2020; Sidun, 2022; Ouyang, 2018; Baldo, 2021; Vollis, 2017; Romeo, 2018; Garilli, 2019; Godenzoni, 2018).

Regarding the regulatory framework in Europe, the determination of CBE decay characteristics is regulated by EN 13808. It states that there are three possible methods for determining decay characteristics: according to EN 13075-1:2020, EN 13075-2:2020 and EN 12848:2020. BEs of rapid-setting and medium-setting should be tested according to the method according to EN 13075-1:2020 to the mineral filler method by the index of breaking behaviour. If the CBE is slow-setting or over-stabilised, than it must be tested according to EN 13075-2:2020 by the indicator of time to breakdown by breakdown time while mixing with the filler of fine fractions; EN 12848:2020 by the indicator of bitumen emulsions stability during mixing with cement. It is worth mentioning, that in EN 13808 the term over-stabilised CBE (COS), which should be slower than CSS in terms of decay rate. As a consequence, according to EN 13808 CBE can be assigned from 2 to 10 classes depending on the determined characteristics of decay. CRS and CMS can be assigned to classes from 2 to 5, the breaking behaviour indicator for them is the amount of mineral filler, which is necessary for the breakdown of the emulsion according to EN 13075-1:2020. CSS and COS belong to classes from 6 to 10. From class 6 to 8, the breaking behaviour characteristic is established according to EN 13075-2:2020, which also states the necessity to mix emulsion with mineral fillers, but unlike EN 13075-1:2020, in this method the emulsion is diluted with water and the characteristic of breaking behaviour is directly the breakdown time. In turn, class 9 and 10 are set according to EN 12848:2020, using a method that is fundamentally different from the ones mentioned, since CBE is mixed with cement under specified conditions, then filtered through a sieve and the mass of the coagulated material (bitumen and cement) remaining on the sieve is determined. According to EN 13808, the CBE marking mentions the emulsion class, but does not directly report its type of reactivity.

Analyzing the given above, it might be concluded, that COS can be attributed to a separate type of CBE in terms of reactivity and associated with classes 8 and 10 according to the breaking behaviour characteristics, since the requirements for these classes are the most extreme from the point of view of reactivity.

According to the Ukrainian regulatory document DSTU B V.2.7-129:2013, there is no mention of COS at all, and the determination of the breaking behaviour characteristic occurs for all types of CBE by reactivity on the basis of two equivalent and interchangeable methods: the breaking behaviour index and the miscibility of the emulsion with mineral materials. The determination of the breaking behaviour index according to DSTU B V.2.7-129:2013 is similar to the method according to EN 13075-1:2020, the second method consists in the miscibility of the emulsion with mineral materials of porous and dense grain compositions and visual assessment of the ability of the emulsion to create homogeneous mixtures with them to cover the grains of mineral material with a uniform film of binder.

Therefore, COS has the longest decay time and the slowest breakdown rate among other classes. COS make it possible to mix with mineral materials for a relatively long time and create homogeneous mixtures with them, uniformly covering the grains of the mineral material. Such emulsions can be used for such road technologies as: cold recycling, impregnation technologies, stabilization and strengthening of soils, cold emulsion stored mixtures and others. The determining factor for creating such emulsions is the amount and type of emulsifier used. For the production of COS, emulsifiers for CSS can be used, but with their higher dosage in CBE. However, it is more promising to use special emulsifiers called cationic super stable emulsifiers (CSSPE), which will allow to reduce the amount of surfactant in the emulsion and the acid, which the emulsifier needs for the reaction. Therefore, with the correct selection of emulsifiers and their dosages, it is possible to achieve the necessary technical, economic and environmental benefits for COS.

## Analysis of sources on the research topic

Currently, there is a small selection of CSSPE emulsifiers for CBE on the market. Instead, the list of “slow-setting” emulsifiers for emulsions is quite wide, in contrary to surfactants for over-stabilised emulsions. In the Table 1 shows the Swedish CSSPE for COS, from the Nouryon company: Redicote E-4868, Redicote E-4875, Redicote E-4868 NPF, Redicote E-4880, slow-setting emulsifiers from the same company: Redicote E-4875 NPF, Redicote E-47 NPF, and the Italian-produced emulsifier ProActive Q-2830 of the ProActive company, which can be used with increased dosage in the production of COS.

*Table 1*

**Possible emulsifiers for over-stabilised bitumen emulsions**

| Available emulsifiers in Ukraine | Recommended dosage of emulsifier in bitumen emulsion | Recommended use of emulsifiers in road technologies |
|---|---|---|
| Over-stabilised emulsifiers | | |
| Redicote E-4868 (Fatty amines)<br>Redicote E-4875 (Fatty amines) | 0.8–1.2 | Conventional slurry (Super-stable emulsions for hot climates) Produce "super-stable" cationic slow set emulsions for the most reactive aggregates and hot conditions |
| Redicote E-4868 NPF | 0.8–1.2 | Emulsifier for cationic slow-setting emulsions suitable for tack, prime, slurry seal, cold mix and sealcoats |
| Redicote E-4880 (Fatty amines) | 1.0–1.5 | Cationic super slow setting emulsifier providing extended workability for virgin and recycled cold mixes produced in plant |
| Over-stabilised/ slow-setting emulsifiers | | |
| Redicote E-4875 NPF (Fatty amines) | 0.8–2.0 % | Emulsifier for cationic slow-setting emulsions suitable for tack, prime, slurry seal, cold mix and sealcoats |
| Redicote E-47 NPF (Fatty amines) | 1.4–1.8 % | Nonionic emulsifier for the production of slow-setting emulsions from bitumen, tall oil pitch, dust oils and resins |
| ProActive-Q-2830 (based on an aqueous solution of quaternary ammonium salt)<br>iACID SSQ-2830 (based on an aqueous solution of quaternary ammonium salt) | 0.8–1.2 | Slow-setting / "Over-stabilised" bitumen emulsion for "Rap-Recycling" |

A review of literature sources showed that COS is used for road mixtures in which finely dispersed mineral material is present, which can act as a binder (usually Portland cement) or a filler. The main technologies where over-stabilised emulsions are used are as follows: stabilization of soils, binding of base materials with emulsion, cold in-plant recycling. All these technologies involve performing technological operations after mixing the materials with bitumen emulsion, therefore, in order to delay the decay as much as possible, over-stabilised cationic bitumen emulsions are used. The technology of cold in-plant recycling involves transporting the finished mixture to the construction site, so it is necessary to ensure the immediate placing of the mixture. In addition, in these technologies it is possible to use a composite binder of bitumen emulsion and cement, and over-stabilised emulsions show good miscibility with cement (Grilli, 2012; Grilli, 2013; Grilli, 2018; Grilli, 2016; Pasetto, 2020; Sidun, 2022; Ouyang, 2018; Baldo, 2021; Vollis, 2017; Romeo, 2018; Garilli, 2019; Godenzoni, 2018).

The article (Ouyang, 2018) mentions that COS is usually used in mixtures containing Portland cement, as the reactivity of COS ensures the necessary mixing time (which is an important technological parameter) and the necessary physical and mechanical properties of materials obtained from such mixtures. It was also found out that the rheological properties of COS change slightly due to an increase in pH value and $Ca^{2+}$ concentration. Authors (Ouyang, 2018) thoroughly describe the COS decomposition process and the role of finely dispersed materials such as Portland cement and limestone for road mixes reinforced with a complex binder (Portland cement and bituminous emulsion). Three stages of the breakdown process (cracking) of the emulsion at constantly increasing pH and $Ca^{2+}$ concentration were established: coalescence of small drops of bitumen together with captured water; trapped water diffusion from the combined bitumen drops; complete breakdown. It was also investigated that there are two ways of breakdown when COS is mixed with fine solid material. One is the coalescence of bitumen droplets, and the other is direct drip adhesion to the cement surface. In the mixing of COS with limestone powder under the action of alkali ions and $Ca^{2+}$ ions, the coalescence of bitumen droplets dominates. When mixing COS with cement, direct droplet adhesion to the cement surface dominates. This difference is due to the fact that the adsorption capacity of Portland cement is much higher than that of limestone powder. Also, the adsorption capacity of cement with anionic emulsions is better than with cationic emulsions. This is probably because there are more components in cement with positive zeta potential than with negative. OH and $Ca^{2+}$ ions released during cement hydration cannot significantly destabilize COS. However, emulsions with better resistance to OH and $Ca^{2+}$ ion penetration still have better mixing stability.

It was established in article (Romeo, 2018) that the use of over-stabilised bitumen emulsion maximize the suitability of the mixture for cold recycling, when made with special additives that delay the decomposition process. Due to these specific characteristics, a minimum amount of cement is required to promote the development of breakdown process. Hydration of cement, which absorbs water, changes the thermodynamic equilibrium of the system, causing emulsion breakdown. The total amount of filler in the mixtures was kept constant and the minimum amount of cement was set at 1 % of the mass of dry aggregate, taking into account the characteristics of the emulsion. Authors suggest that the evaluation of the effectiveness of mixtures should be based on the hypothesis that 1 % cement addition does not work as an active filler, but contributes to the development of the emulsion breakdown process. Therefore, cement is necessary to neutralize additives used to over-stabilise the bitumen emulsion and to stop the degradation process.

The article (Grilli, 2012) states that the improved composition of the COS emulsion is essential, especially for the type of “full depth” recycling. During the mixing and compaction stages, the bitumen emulsion and additional water work together as a single liquid phase that reduces internal friction, facilitating the homogenization and compaction processes. Therefore, the use of over-stabilised emulsions cannot be overestimated, since the use of standard emulsions will lead to early breakdown of the emulsion and the formation of bituminous clots within the mixture.

Garilli (Garilli, 2019) investigated the time and temperature dependence of several related phenomena affecting cold recycling mixes, such as COS breakdown and setting, water evaporation, cement hydration, and hardening. The authors recommend that the modified bending beam rheometer (BBR) test is a good approach to analyze the behavior of bitumen-cement emulsions as a function of various parameters (emulsion/cement ratio, setting time and temperature).

In the article (Godenzoni, 2018), it is stated that the layers made from cold recycling mixtures using COS and cement are characterized by a clear time and temperature dependence (behavior is similar to asphalt concrete). In particular, it was established that after 3–5 years after construction the stiffness of the layers made from these mixtures increases. However, in the future, the stiffness decreases mainly due to the occurrence of stresses from the vehicle loads.

The article (Grilli, 2018) indicates that the relationship between indirect tensile strength and COS dosage has a bell-shaped trend for the cold recycling technology, which emphasizes the importance of choosing the correct bitumen/cement ratio to control the resistance to breakdown of cement-bituminous materials.

The article (Baldo, 2021) proposes the use of industrial waste (electric arc furnace steel slag, coal fly ash and glass waste) as a substitute for traditional stone materials in combination with a combined binder (bitumen emulsion and Portland cement) for cold recycling technology. The over-stabilized bitumen emulsion of the C60B10 grade according to EN 13808 acts as an organic binder in the combined composition, which allows for optimal mixing of finely dispersed materials obtained from coal ash.

In work (Vollis, 2017) there is a study on the use of an over-stabilised emulsifier for the production of cationic bitumen emulsions. The typical characteristics of the emulsifier are given and the difference between the physical and technical indicators of stable and slowly-setting bitumen emulsions is shown.

In general, enough information was found from open sources regarding over-stabilised emulsions for road technologies. However, some scientists identify COS with CSS (Teja, 2011; Salomon, 2006), others in their articles do not mention the grade of used emulsion according to EN 13808, for particular pavement construction technology. Instead, they outline the direct functions performed by the emulsion, as a component of a certain mixture or indicate the role of the emulsion in a certain technological process (Wang, 2013; Lesueur, 2004; Cheng-Tsung, 2009; Seyed Morteza, 2009).

## Conclusions

1. Cationic bitumen emulsions were analyzed for their reactivity and disintegration characteristics in accordance with European and Ukrainian standards.

2. Popular emulsifiers for over-stabilised bitumen emulsions are given, depending on the application technology.

3. A literature review was conducted regarding the features of the use of over-stabilised bitumen emulsions, and it was established that such emulsions are most often used in mixtures made by cold recycling technology using Portland cement.

## References

Sidun, I., Solodkyy, S., & Vollis, O. (2019). Acids in bitumen emulsions. JCEEA, t. XXXV, z. 65 (3/18). 83–90. DOI: 10.7862/rb.2018.45.

Sidun, I., Solodkyy, S., Vollis, O., Gunka, V., Pyryk, R., & Shits, I. (2020). Orto-phosphoric acid as an alternative to hydrochloric acid – for cationic bitumen road emulsions. Review. Theory and Building Practice. 2(1), 88–93. URL: https://doi.org/10.23939/jtbp2020.01.088.

Dołżycki, B., Jaskuła, P. (2019). Review and evaluation of cold recycling with bitumen emulsion and cement for rehabilitation of old pavements. *Journal of Traffic and Transportation Engineering*, *6*, 311–323. URL: https://doi.org/ 10.1016/j.jtte.2019.02.002.

Pérez, I., & Rodríguez, L., Val, M. (2013). Mechanical properties and behaviour of in situ materials which are stabilised with bitumen emulsion. Road Materials and Pavement Design. 14. 221–238. DOI: 10.1080/14680629.2013.779301.

Liu, Z., Huo, J., & Wang, Z. (2020). Investigation on Properties of Cement Bitumen Emulsion Mortars (CBEM) in Consideration of Emulsifier Types. *Advances in Materials Science and Engineering, 2020*, 1–10. URL: https://doi.org/10.1155/2020/4820938.

Grilli, A., A Graziani, A., Bocci, M. (2012). Compactability and thermal sensitivity of cement–bitumen-treated materials, Road Materials and Pavement Design, 13:4, 599–617. DOI: 10.1080/14680629.2012.742624.

GrillI, A., Bocci, M., Graziani, A. (2013). Influence of reclaimed asphalt content on the mechanical behaviour of cement-treated mixtures, Road Materials and Pavement Design, 14:3, 666–678. DOI: 10.1080/14680629.2013.794367.

GrillI, A., Cardone, F., Bocci, M. (2018). Mechanical behaviour of cement-bitumen treated materials containing different amounts of reclaimed asphalt, European Journal of Environmental and Civil Engineering, 22:7, 836–851. DOI: 10.1080/19648189.2016.1219972.

Grilli, A., Graziani, A., Bocci, E., Bocci, M. (2016). Volumetric properties and influence of water content on the compactability of cold recycled mixtures. Materials and Structures, 49 (10), 4349–4362. DOI: 10.1617/s11527-016-0792-x.

Pasetto, M., Baldo, N. (2020). Cold Recycling with Bitumen Emulsion of Marginal Aggregates for Road Pavements. Lect. Notes. Civ. Eng., vol. 48, 155–163. DOI: 10.1007/978-3-030-29779-4_15.

Sidun, I., Bidos, V., Vollis, O., Stanchak, S., Hunka, V. (2022). Over-stabilised cationic bitumen emulsions – a new type of emulsions for Ukraine. Advance in Petroleum and Gas Industry and Petrochemistry, APGIP-11, Lviv. URL: http://apgip.lviv.ua/wp-content/uploads/2022/05/apgip-11-abstracts.pdf.

URL: https://www.nouryon.com.

URL: https://aron.ua/.

Ouyang, J., Hu, L., Li, H., Han, B. (2018). Effect of cement on the demulsifying behavior of over-stabilized asphalt emulsion during mixing. Construction and Building Materials. 177. 252–260. DOI: 10.1016/j.conbuildmat.2018.05.141.

Baldo, N. et al. (2021). IOP Conf. Ser.: Mater. Sci. Eng. 1203 022111. DOI: 10.1088/1757-899X/1203/2/022111.

Vollis, O., Sidun, I. (2017). Ultra-resistant emulsifier for cationic bitumen emulsions. Bulletin of the Kharkiv National Automobile and Road University, 79, 62–65. URL: http://nbuv.gov.ua/UJRN/vhad_2017_79_13.

Romeo, E., Betti, G., Marradi, A., Tebaldi, G. (2018). Effect of active fillers on cracking performance of bitumen-stabilised materials, Road Materials and Pavement Design, 19:7, 1563–1574. DOI: 10.1080/14680629.2017.1325773.

Garilli, E., Autelitano, F., & Giuliani, F. (2019). Use of bending beam rheometer test for rheological analysis of asphalt emulsion-cement mastics in cold in-place recycling. Construction and Building Materials. 222. 484–492. URL: 10.1016/j.conbuildmat.2019.06.141.

Godenzoni, C., Graziani, A., Bocci, E., Bocci, M. (2018). The evolution of the mechanical behaviour of cold recycled mixtures stabilised with cement and bitumen: field and laboratory study, Road Materials and Pavement Design, 19:4, 856–877. DOI: 10.1080/14680629.2017.1279073.

Teja, K. (2011). Improvement of silty soil as subgrade material by stabilizing with bituminous emulsion, Int. J. Engg. Res. Indu. Appls. 8(III). ISSN 0974-1518.

Salomon, D. (2006). Asphalt emulsion technology, in: Transportation Research Board, Characteristics of Bituminous Materials Committee, Transportation Research Circular E-C102, Washington, DC. URL: https:// onlinepubs.trb.org/ onlinepubs/circulars/ec102.pdf.

Wang, F., Liu, Y., Hu, Sh. (2013). Effect of early cement hydration on the chemical stability of asphalt emulsion. Construction and Building Materials. 42. 146–151. URL: 10.1016/j.conbuildmat.2013.01.009.

Lesueur, D., Potti, J. (2004). Cold mix design: A rational approach based on the current understanding of the breaking of bituminous emulsions, Road Materials and Pavement Design, 5:sup1, 65–87. DOI: 10.1080/14680629.2004.9689988.

Cheng-Tsung, L., Ming-Feng, K., Der-Hsien, Sh. (2009). Composition and reaction mechanism of cement–asphalt mastic, Construction and Building Materials, 23(7), 2580–2585, ISSN 0950-0618. URL: https://doi.org/ 10.1016/ j.conbuildmat.2009.02.014.

Seyed Morteza, M., Safapour, P. (2009). Base Course Modification through Stabilization using Cement and Bitumen. American Journal of Applied Sciences. 6. 10.3844/ajas.2009.30.42.

**Ю. В. Сідун[1], Х. С. Соболь[1], В. М. Бідось[1], О. М. Гуняк[1], І. М. Процик[2]**

[1] Національний університет "Львівська політехніка",
кафедра "Автомобільні дороги та мости",
[2] Відокремлений структурний підрозділ
"Автомобільно-дорожній фаховий коледж
Національного університету "Львівська політехніка"

## КАТІОННІ НАДСТІЙКІ БІТУМНІ ЕМУЛЬСІЇ В ДОРОЖНЬОМУ БУДІВНИЦТВІ: ОГЛЯД



Описано класифікацію катіонних бітумних емульсій за "реактивністю" та характеристиками розпаду. Наведено методи досліджень характеристик розпаду для бітумних емульсій різної "реактивності" відповідно до європейського та українського нормативних документів. Приведено доступні емульгатори в Україні для надстійких бітумних емульсій з описом дорожньої технології, де вони можуть бути застосовані. Виділено два типи можливих емульгаторів для надстійких бітумних емульсій: суперстабільні емульгатори та повільно розпадні. Проведено літературний огляд використання надстійких бітумних катіонних емульсій у технологіях стабілізації грунтів, укріплення матеріалів основи емульсією, технологія "холодного ресайклінгу". Оглянуто закономірності взаємодії надстійкої бітумної емульсії із тонкодисперсними мінеральними в'яжучим та наповнювачами, встановлено, що таким емульсіям притаманний найдовший з-поміж інших класів емульсій час розпаду і найповільніша швидкість розпаду. Надстійкі бітумні емульсії дають змогу протягом відносно довгого часу змішуватись з мінеральними матеріалами і створювати з ними однорідні суміші, рівномірно вкриваючи їх зерна. Загалом виявлено достатньо інформації з відкритих джерел щодо надстійких бітумних емульсій для дорожніх технологій, проте деякі науковці ототожнюють їх із бітумними емульсіями повільного розпаду. Інші у своїх статтях не згадують клас використаної емульсії згідно з нормативними документами. Натомість вони окреслюють безпосередні функції, що виконує емульсія як складник певної суміші, чи вказують на роль емульсії в певному технологічному процесі влаштування шарів дорожньої конструкції. Як наслідок, через застосування тієї чи іншої бітумної катіонної емульсії в певній технології, ми можемо опосередковано дізнатись її реактивність, а після цього припустити, чи вона належить до надстійких.

**Ключові слова: бітумні емульсії швидкого, середнього, повільного розпаду, надстійка катіонна бітумна емульсія, стабілізація грунтів, матеріали основи, технологія "холодного ресайклінгу", портландцемент.**