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**RESIDUAL BINDER OF ROAD BITUMINOUS EMULSIONS  
INVESTIGATED USING THE SUPERPAVE SYSTEM. REVIEW**

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The article reviews the features of the study of residual binder obtained from bituminous emulsions using the SUPERPAVE system. The need to add improving additives to bituminous emulsions, namely modifiers (polymeric and adhesive additives) and special additives of different effects (solvents, stabilizers, thickeners, defoamers) is characterized. It is determined that the effect of special additives with different effects on the properties of the residual binder of the emulsion is not fully investigated. It is shown that the method of obtaining residual binder from bitumen emulsions in the laboratory is especially important. Today, all methods of obtaining residual binder from an emulsion can be divided into high-temperature distillation methods and low-temperature evaporation. The literature review confirmed that the high-temperature and low-temperature performance characteristics of the residual binder of emulsions primarily depend on the amount and type of modifier and emulsifier used.

**Key words:** bitumen emulsion, residual binder, SUPERPAVE system, polymer, adhesive, binder distillation and evaporation.

### Introduction

The Superior Performing Asphalt Pavements (SUPERPAVE) system is currently the most advanced for the study of bitumen binders for road construction. According to this system, special attention is paid to the study of unmodified and modified petroleum road bitumen for asphalt concrete layers of road structures (Zeiada, 2022; Watson, 2003; Gou, 2024). However, other types of bitumen road binders are liquefied bitumen and bitumen emulsions. The use of the latter is particularly popular today. As a result of technological processes, so-called residual binder is obtained from liquefied bitumen after the diluent evaporates and from emulsions after their decomposition, which serves as an adhesive bond throughout the entire service life of the material or product. In this review, we will focus on the study of residual binders in bitumen emulsions. When the bitumen or the emulsion itself has been modified, the residual binder will be modified accordingly. However, the residual binder of emulsions consists not only of unmodified or modified bitumen, but also of an emulsifier with acid or alkali residues, depending on the charge of the emulsion itself. Accordingly, the residual binder obtained from the bitumen emulsion is different in composition from the bitumen binder for hot mix asphalt. Therefore, the purpose of this review was to establish the features of the study of residual binder from the emulsion using the SUPERPAVE system.

### Analysis of sources on the research topic

As refineries improve and the depth of oil refining increases, road builders are increasingly facing a decline in the quality characteristics of bitumen and, as a result, emulsions. Therefore, not only the original bitumen, but also emulsions require the addition of improving additives. Such "improvers" can be divided into two groups: modifiers and special additives with different effects. To meet the requirements of emulsions for a particular road technology, it is necessary to use modifiers - substances that affect the properties of the residual binder, but at the same time, modifiers may or may not affect the properties of

the emulsion itself. Special additives with different effects have a positive effect on the properties and characteristics of the emulsion itself, namely: the disintegration process, storage stability, viscosity, etc. In turn, they are characterized by a short or insignificant effect on the residual binder after the emulsion breaks down (Sidun, 2019; Sidun, 2023, Bidos, 2024).

Popular bitumen modifiers for emulsions and emulsion modifiers include adhesion additives and SBS (styrene-butadiene-styrene) or SBR (styrene-butadiene-rubber) polymers. Today, most bitumen is characterized by low adhesion properties to granite and other stone materials derived from igneous (volcanic) rocks (Pstrowska, 2022), and the cationic emulsifier, which is present in the emulsion in different amounts, may not fully ensure the necessary adhesion of the residual binder to this aggregate. Therefore, the modification of bitumen with adhesives is becoming an increasingly necessary operation before the emulsion is made. Moreover (Pyrig, 2024), it has been suggested that adhesives can act as inhibitors of bitumen aging. Adhesive modifiers of bitumen for emulsions are usually used, as a rule, of active rather than passive action. After all, adhesives with "passive adhesion" are used in hot technologies, where the binder has a low viscosity and as a "liquid" can cover the stone material well. "Active adhesion" refers to the formation and maintenance of a strong chemical bond between crushed stone and bituminous binder at low temperatures in the presence of water, which is a key difference over passive adhesion (Gunka, 2020). In the case of active adhesion, due to the action of a surfactant, water is displaced from the surface of the stone material and replaced by a bitumen binder. Modification with adhesion additives is possible only before emulsification, by homogenizing bitumen and surfactants in modifying tanks or by dosing into the bitumen flow in pipelines with subsequent homogenization in statomixers.

The polymer modification of bitumen for emulsion production is aimed at improving its heat-resistant and crack-resistant properties, and giving the binder elasticity. Emulsion modification with a polymer can be performed before, during, and after emulsion production. Before production - bitumen is modified, as a rule, with thermoelastoplastic polymers such as SBS. Bitumen modification with such polymers is possible in modifying tanks using mechanical stirrers and/or in colloidal mills. In the case of emulsion production with a bitumen-polymer binder, the emulsion equipment must be retrofitted with heat exchangers to reduce the emulsion temperature at the outlet. The fact is that the required fluidity of the bitumen-polymer binder is achieved at temperatures above 180°C, which causes the emulsion to exceed the maximum permissible temperature of 95°C. In this case, the emulsion boils and the surfactant loses its emulsifying properties, which is unacceptable.

During and after emulsion production, modification is performed by SBR polymers - latexes, which are aqueous solutions containing 63-65 % of the polymer. The introduction of latex during production into an environment with a temperature of more than 100°C will cause the water of the latex dispersion medium to boil, so the conditions for such modification must take into account the almost instantaneous increase in the volume of the modified material and, accordingly, the pressure. The introduction of latex into the finished emulsion requires lowering the emulsion temperature below 70°C. In this case, the process of adding latex is arbitrary (automated, mechanized or manual), and in particular such a modification can be applied to a part of the batch during or after shipment. In any case, the latex-modified emulsion has increased requirements for storage conditions. Due to its lower density, the polymer will float and concentrate on the surface of the volume, which will lead to stratification of the emulsion and require its mandatory periodic stirring (Gunka, 2020; Salomon, 2006). Special additives with different effects include diluents, stabilizers, thickeners, and defoamers. As diluents, economically available petroleum-derived solvents with high flash points and gaseous transition and without damaging the bitumen structure (diesel fuel, kerosene, white spirit) are usually used. The purpose of adding diluents is to reduce the viscosity of bitumen. As a result, the emulsified diluted bitumen will show greater plasticity at low ambient temperatures. Diluents are added to bitumen before emulsification, taking into account their flammability and explosiveness. Stabilizers help to increase the density and viscosity of the emulsion dispersion medium, which in turn improves the homogeneity and stability during storage and

transportation of the emulsion. Solutions of  $\text{CaCl}_2$  and KCl salts are used as stabilizers. Emulsifier manufacturers recommend adding stabilizers to the aqueous phase before emulsification in the following cases: when the bitumen content in the emulsion is less than 50 % by weight, the emulsion will be transported over long distances, and in cases of long-term storage (more than 14 days). Thickeners for emulsions are also added to the aqueous phase before emulsification and act like an emulsifier, creating an increased charge on the surface of the dispersed bitumen and increasing the viscosity of the dispersed medium (much more than stabilizers). They are used to achieve a higher viscosity of the emulsion with a lower bitumen content than required for this purpose. Defoamers or anti-foaming additives are used to reduce foaming from an emulsion component such as an emulsifier during mixing or overloading of emulsions. These additives are fed into the aqueous phase prior to emulsification. In most cases, improving additives are used in the manufacture of fast-breaking emulsions for surface treatment, patching and slow-breaking emulsions for slurry surfacing. This is due to the direct contact of the products of such technologies with the moving component of transport and environmental influences, namely temperature, solar radiation and ultraviolet radiation, precipitation and various types of substances that can get on the road surface. The effect of special additives with different effects on the properties of the residual emulsion binder is not fully investigated and reviewed in the literature. However, the main influence on the residual binder of emulsions will be exerted by the modification with polymer and/or adhesive and the amount and type of emulsifier, acid or alkali used (Salomon, 2006). One of the first to pay attention to this was King (1993), who studied the residual binder of both cationic emulsions with HCL and anionic emulsions with NaOH with different amounts of emulsifier and SBS-type polymer modifier using the SUPERPAVE system. In addition, he simultaneously studied unmodified and modified bitumen from which the emulsions were made. As a result of the research, it was found that the polymer has the greatest positive effect on the residual binder of the emulsion (King, 1996).

In turn, the works (Takamura, 2000; Takamura, 2001; Hanz, 2010; Islam, 2015; Malladi 2018) showed that the method by which residual binder is obtained from bitumen emulsions in the laboratory is especially important. The US standards (ASTM D244-09, ASTM D6934-08, ASTM D6997, ASTM D-6014, ASTM D7403-19, ASTM D7497-21 and others) suggest distillation at high temperatures of 177°C, 260°C or no higher than 160°C (Marasteanu; 2003), and at relatively low temperatures (approximately 60°C according to ASTM D7497-21). It has been proven that the use of high-temperature methods leads to a harder residue and is not suitable for polymer-modified emulsions (Sun, 2020; Ge, 2020). In the European regulatory framework (EN 13808), there are concepts of residual, reconstituted, stabilized and aged binders from cationic bitumen emulsions. Stabilized and aged binders are prototypes of the emulsion binder that should be used for durability assessment. The presence of methods in EN 1431 for the preparation of stabilized and aged binders can be compared with the methods of process (RTFOT) and operational (PAV) aging in the SUPERPAVE system. Accordingly, the so-called residual binder according to EN 1431 is obtained by distillation (EN 1431), and the reduced binder by evaporation (EN 13074-1). To summarize, all methods of obtaining residual binder from an emulsion can be divided into high-temperature distillation and low-temperature evaporation methods - which are recommended for setting the parameters of residual binder immediately after the emulsion breaks down.

After the residual binder is extracted from the emulsion, it is tested using standard methods in the SUPERPAVE system. Dynamic viscosity is determined using a Brookfield Viscometer, process aging using a Rolling Thin Film Oven (RTFOT) and operational aging using a Pressure Aging Vessel (PAV), high-temperature performance using a Dynamic Shear Rheometer (DSR), and low-temperature performance using a Bending-Beam Rheometer (BBR) and Direct Tension Test System (DTT). The purpose of these studies is to establish the PG grade according to AASHTO MP1, and additional analysis can also be performed according to AASHTO MP1a (Clyne, 2003; Basu, 2003). The indicated parameters according to the SUPERPAVE system undergo significant changes depending on the composition of emulsions, primarily due to the amount and type of modifier and emulsifier used (King, 1993; King, 1996; Marasteanu, 2006; Cho, 2015; Wasiuddin, 2022; Mitchell, 2010; You, 2020; Rahman, 2019).

## Conclusions

The article considers modifiers and special additives of different effects that change the properties of the residual binder of the emulsion. The effect of modifiers on the quality indicators of the SUPERPAVE binder is quite researched, but the literature review did not reveal the effect of special additives of different effects on the binder in this system.

The problem of obtaining residual binder from an emulsion in the laboratory is reviewed in view of the European and American regulatory frameworks. As a result, it was found that for SUPERPAVE tests it is necessary to use low-temperature evaporation rather than high-temperature distillation methods.

The literature review confirmed that the high-temperature and low-temperature performance characteristics of residual binder emulsions primarily depend on the amount and type of modifier and emulsifier used.

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## References

- Zeiada, Waleed & Liu, Hanqi & Ezzat, Helal & Underwood, Shane & Al-Khateeb, Ghazi & Shanableh, Am & Samarai, Mufid. (2022). Review of the Superpave performance grading system and recent developments in the performance-based test methods for asphalt binder characterization. *Construction and Building Materials*. 319. 126063. 10.1016/j.conbuildmat.2021.126063.
- Watson, Donald. (2003). Updated Review of Stone Matrix Asphalt and Superpave® Projects. *Transportation Research Record*. 1832. 217-223. 10.3141/1832-26..
- Gou, Guotao & Gou, Mingjie & Jing, Hongwei. (2024). Experimental Study on the Influence of the Superpave and Marshall Design Methods on the Pavement Performance of Asphalt Mixtures. *Journal of Engineering Science and Technology Review*. 17. 58-64. 10.25103/jestr.174.08.
- Sidun I., Vollis O., Solodkyy S., Gunka V. (2019). Cohesion of Slurry Surfacing Mix with Slow Setting Bitumen Emulsions. In: Blikharskyy Z., Koszelnik P., Mesaros P. (eds) *Proceedings of CEE 2019*. CEE 2019. *Lecture Notes in Civil Engineering*, vol 47. Springer, Cham 10.1007/978-3-030-27011-7\_53
- Sidun, I., Vollis, O., Bidos, V., Turba, Y. (2023). Versions of Orthophosphoric Acids for Slurry Surfacing Mix. In: Blikharskyy, Z. (eds) *Proceedings of EcoComfort 2022*. EcoComfort 2022. *Lecture Notes in Civil Engineering*, vol 290. Springer, Cham. [https://doi.org/10.1007/978-3-031-14141-6\\_40](https://doi.org/10.1007/978-3-031-14141-6_40).
- Bidos, Volodymyr & Sidun, Iurii & Sobol, Khrystyna & Balabukh, Yaroslav & Rybchynskiy, Sergii. (2024). Breaking behavior of cationic bitumen emulsions. *IOP Conference Series: Earth and Environmental Science*. 1376. 012010. 10.1088/1755-1315/1376/1/012010.
- Pstrowska K., Gunka V., Sidun I., Demchuk Y., Vytrykush N., Kułazyński M., Bratychak M. Adhesion in bitumen/aggregate system: adhesion mechanism and test methods // *Coatings*. – 2022. – Vol. 12, iss. 12. – P. 1934-1934-19. <https://doi.org/10.3390/coatings12121934>
- Pyrig, Yan & Galkin, Andrey & Zolotarev, Victor. (2021). Improvement of the method of evaluation of bitumen binder adhesion. *Bulletin of Kharkov National Automobile and Highway University*. 2. 57-67. 10.30977/BUL.2219-5548.2021.92.2.57.
- Gunka, Volodymyr & Demchuk, Yuriy & Sidun, Iurii & Miroschnichenko, Denis & Nyakuma, Bemgba & Pyshyev, Serhiy. (2020). Application of phenol-cresol-formaldehyde resin as an adhesion promoter for bitumen and asphalt concrete. *Road Materials and Pavement Design*. 10.1080/14680629.2020.1808518.
- Gunka, Volodymyr & Astakhova, Olena & Hrynchuk, Yuriy & Sidun, Iurii & Reutskyy, Volodymyr & Mirchuk, Iryna & Poliak, Olha. (2024). A Review of Road Bitumen Modification Methods. Part 1 – Physical Modification. *Chemistry & Chemical Technology*. 18. 295-304. 10.23939/chcht18.02.295.
- Salomon, D. (2006) Asphalt emulsion technology, in: *Transportation Research Board, Characteristics of Bituminous Materials Committee, Transportation Research Circular E-C102*, Washington, DC.
- King, G. & Lesueur, Didier & King, Helen & Planche, Jean-Pascal. (1993). SHRP test evaluation of High Float and Polymer Modified Bitumen emulsion residues. *Conference: 1st World Congress on Emulsion*, Paris, France.
- King, G., Lesueur, D., King, H., and Planche, J. P., (1996). "SHRP test evaluation of high float and polymer modified bitumen emulsion residues." *Proc., Eurobitume/Eurasphalt Congress*, Strasbourg.

Takamura, K., "Comparison of Emulsion Residues Recovered by Forced Airflow and RTFO Drying," ISSA/AEMA Proceedings, March 12-15, 2000, pp. 1-17.

Takamura, K. Forced Air Drying and Superpave Analysis of Emulsion Residue. Proc., ISSA 39th Annual Meeting, Maui, Hawaii, March 2001

Hanz, Andrew & Arega, Zelalem & Bahia, Hussain. (2010). Rheological Behavior of Emulsion Residues Produced by Evaporative Recovery Method. Transportation Research Record: Journal of the Transportation Research Board. 2179. 102-108. 10.3141/2179-12.

Islam, Mohammad & Salehi Ashani, Saeid & Wasiuddin, Nazimuddin & King, William. (2015). Effects of Curing Time, Temperature, and Vacuum Pressure on Asphalt Emulsion Residue Recovered by Vacuum Drying Method. Journal of Testing and Evaluation. 43. 20140014. 10.1520/JTE20140014.

Malladi, Haritha & Asnake, Meron & LaCroix, Andrew & Castorena, Cassie. (2018). Low-Temperature Vacuum Drying Procedure for Rapid Asphalt Emulsion Residue Recovery. Transportation Research Record: Journal of the Transportation Research Board. 2672. 036119811879191. 10.1177/0361198118791913.

Sun, Yang & Yue, Jin-Chao & Wang, Riran & Li, Rui-Xia & Wang, De-Cai. (2020). Investigation of the Effects of Evaporation Methods on the High-Temperature Rheological and Fatigue Performances of Emulsified Asphalt Residues. Advances in Materials Science and Engineering. 2020. 1-12. 10.1155/2020/4672413.

Ge, Dongdong & Zhou, Xiaodong & Chen, Siyu & Jin, Dongzhao & You, Zhanping. (2020). Laboratory Evaluation of the Residue of Rubber-Modified Emulsified Asphalt. Sustainability. 12. 10.3390/su12208383.

Clyne, T. R., Marasteanu, M. O., & Basu, A. (2003). Evaluation of asphalt binders used for emulsions (No. MN/RC-2003-24).

Basu, A., Marasteanu, M. O., & Hesp, S. A. M. (2003). Time-Temperature Superposition and Physical Hardening Effects in Low-Temperature Asphalt Binder Grading. Transportation Research Record, 1829(1), 1-7. <https://doi.org/10.3141/1829-01>.

Cho, Seong & Im, Jeong. (2015). Mathematical Approach in Rheological Characterizing of Asphalt Emulsion Residues. Mathematical Problems in Engineering. 2015. 1-13. 10.1155/2015/797808.

Marasteanu, Mihai & Clyne, Timothy. (2006). Rheological Characterization of Asphalt Emulsions Residues. Journal of Materials in Civil Engineering - J MATER CIVIL ENG. 18. 10.1061/(ASCE)0899-1561(2006)18:3(398).

Wasiuddin, Nazimuddin & Islam, Mohammad. (2022). Establishing Correlations Between Force Ductility and DSR Parameters of Asphalt Emulsion Residues. 10.1007/978-3-030-46455-4\_91.

Mitchell, M. & Link, R. & Prapaitrakul, Nikornpon & Han, Rongbin & Jin, Xin & Epps Martin, Amy & Glover, Charles. (2010). Comparative Study on Recovered Binder Properties Using Three Asphalt Emulsion Recovery Methods. Journal of Testing and Evaluation - J TEST EVAL. 38. 10.1520/JTE102739.

You, Lingyun & Dai, Qingli & You, Zhanping & Zhou, Xiaodong & Washko, Sarah. (2020). Stability and rheology of asphalt-emulsion under varying acidic and alkaline levels. Journal of Cleaner Production. 120417. 10.1016/j.jclepro.2020.120417.

Hanz, Andrew & Johannes, Petrina & Bahia, Hussain. (2012). Development of Emulsion Residue Testing Framework for Improved Chip Seal Performance. Transportation Research Record: Journal of the Transportation Research Board. 2293. 106-113. 10.3141/2293-13.

Rahman, Md Nafiur & Sarkar, Md Tanvir & Elseifi, Mostafa. (2019). Rheological and Molecular Characterization of Rubberized Asphalt Emulsion. MATEC Web of Conferences. 271. 03001. 10.1051/mateconf/201927103001.

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### **ЗАЛИШКОВЕ В'ЯЖУЧЕ ДОРОЖНІХ БІТУМНИХ ЕМУЛЬСІЙ ДОСЛІДЖЕНЕ З ВИКОРИСТАННЯМ СИСТЕМИ SUPERPAVE. ОГЛЯД.**

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У статті оглянуто особливості дослідження залишкового в'язучого отриманого із бітумних дорожніх емульсії за системою СУПЕРПЕЙВ. Окреслено різницю між вихідним бітумним в'язучим для емульсії і залишковим, яке виділене з бітумної дорожньої емульсії. Охарактеризовано потребу додавання покра-

щуючих добавок до бітумних емульсій, а саме модифікаторів (полімерів та адгезійних добавок) та спеціальних добавок різної дії (розріджувачі, стабілізатори, згущувачі, піногасники) та детально описано про їх застосування. В більшості покращуючі добавки використовують під час виготовлення швидкорозпадних емульсій для поверхневої обробки, ямкового ремонту та повільнорозпадних для литих емульсійно-мінеральних сумішей. Але вплив спеціальних добавок різної дії на властивості залишкового в'язучого емульсії є не до кінця дослідженим і оглянутим в літературних джерелах. Показано, що особливо важливим є метод яким отримують залишкове в'язуче з бітумних емульсій в лабораторних умовах. На сьогодні всі методи отримання залишкового в'язучого з емульсії можна розділити на високотемпературні методи дистиляції та низькотемпературні випаровування, які і рекомендуються для встановлення параметрів залишкового в'язучого зразу після розпаду емульсії. Адже після розпаду емульсії необхідно вірно встановити марку в'язучого за системою СУПЕРПЕЙВ. Для цього залишкове в'язуче випробовують за стандартними методами системи СУПЕРПЕЙВ: динамічною в'язкістю, технологічним та експлуатаційним старінням, високотемпературними та низькотемпературними експлуатаційні характеристиками. Огляд літературних джерел підтвердив, що високотемпературні та низькотемпературні експлуатаційні характеристики залишкового в'язучого емульсій в першу чергу залежать від кількості та типу використаного модифікатора і емульгатора.

**Ключові слова:** бітумна емульсія, залишкове в'язуче, система СУПЕРПЕЙВ, полімер, адгезив, дистиляція та випаровування в'язучого.