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ACIDS IN BITUMEN EMULSIONS

In the article there is proved the possibility of using ortho-phosphoric acid with special emulsifiers instead of hydrochloric acid – for the production of road cationic slow-setting bitumen emulsions. There is ascertained the difference between used for bitumen emulsions distilled binder (Nybit E85 bitumen), produced from heavy crude oil, and oxidized bitumens (grade 70/100 bitumen produced by JSC Mozyr Refinery and grade BND 60/90 bitumen of JSC UkrTatNafta), produced from light crude oil. The difference is analyzed between physical-mechanical indices of distilled and oxidized bitumens. Eight bitumen emulsion formulations were developed based on usage hydrochloric acid, three bitumens and three emulsifiers (Redicote E-11, Redicote 404 and Redicote E-4875), as well as four formulations based on usage of ortho-phosphoric acid, two bitumens and two emulsifiers (Redicote EM44 and Redicote C-320). There was investigated the influence of hydrochloric and ortho-phosphoric acids upon the physical-technical indices of road cationic slow-setting bitumen emulsions and the difference was ascertained between the indices of bitumen emulsions based on distilled and oxidized bitumens. Bitumen emulsion formulations were developed based on usage of ortho-phosphoric acid and special emulsifiers for the class of cationic slow-setting emulsions for slurry seal and microsurfacing mixtures.

Keywords: bitumen emulsion, hydrochloric and ortho-phosphoric acids, slurry seal and microsurfacing mixtures

1. Introduction

Bitumen emulsions found the broad-range usage in the road construction world-wide. The application of bitumen in a form of emulsion have a number of advantages: application of organic binding materials in a form of emulsion allows decreasing bitumen consumption for 20÷30% w/w due to formation of

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thinner bitumen film around the grains of mineral materials; absence of necessity for emulsion and aggregate pre-heating allows saving fuel-power resources; extension of road season due to road works performance at the temperature not less than 5°C; possibility of wet aggregate treatment and road works performance with wet base; emulsions storage is simple and does not require warehouses with complicated heating system. It is extremely important that emulsions allow working at as unfavorable weather conditions, as making impossible (even in presence of surfactants) to reach the necessary quality of works with application of hot mixes. It is possible to use road emulsions as a binder for plenty of road technologies. In spray applications the emulsion is used for surface dressing (chip seal), fog seal, scrub seal, graded aggregate seal, tack coat, prime coat, penetration macadam and dust control. In mix applications it is used for slurry seal, microsurfacing, cape seal, open-graded cold mix, dense-graded cold mix, soil stabilization, pre-coated chips, stockpile mix and RAP [1–2]. The results of theoretical investigations and practical application of bitumen emulsions have shown that the greatest effect is reached with cationic bitumen emulsions applied.

2. Analysis of recent investigations and publications

A lot of investigations were done on application and modification of cationic bitumen emulsions, both world-wise [3–6] and in the Ukraine in particular [7–8]. Still, the review of scientist's publications, both the domestic and foreign ones, has shown that the issues of application of this or that acid in an emulsion are cleared-up insufficiently. It is known that for the production of cationic bitumen emulsion it is possible to use hydrochloric, ortho-phosphoric and acetic acids. Let us address out attention to the first two ones – as the most used in production. In Ukraine there is widely used hydrochloric acid for emulsions – due to the worked-up technology of its application. (Though in the world-scale the usage of ortho-phosphoric acid is not a problem). Let us try to compare these acids. Hydrochloric acid is rather aggressive and highly corrosive, while that may lead to destruction of technological equipment. The labor safety during the working process shall be on the raised level. Besides, in the Ukraine it is required that acid implies getting license for work with precursors. Therefore, the usage of hydrochloric acid not just leads to increase of cost of technology, but also requires a whole chain of additional technological modifications, both that of the personnel's working place itself, and of the production equipment – at installation stage and in course of its operation.

Significant contribute into investigation of the problem of acid usage for emulsions was made by A. James [9–10]. He asserts that alternative acids can provide for advantages in operation indices at the stage of final application of emulsion. Reaction of acid with aggregate, along with resulting changes of pH make significant influence upon the cationic emulsions breakage. Besides, the

choice of acid makes influence upon the process, while the products received will potentially make influence upon the adhesion and rheology of the residual [11]. A. James together with T. Ng analyzed the usage of ortho-phosphoric acid for slurry seal and microsurfacing technologies and determined the peculiarities and advantages of application of this acid for the said technologies [12–13].

The purpose of this work is determination of the efficiency of ortho-phosphoric acid application for production of slow-setting cationic bitumen emulsions (based on the accessible materials), as well as determination of its influence on the emulsion quality.

3. Main part

For the production of bitumen emulsions based on hydrochloric and ortho-phosphoric acids there were taken popular in Ukraine raw materials, namely: oil distilled-bitumen grade Nybit E85 produced by Nynas (Sweden), oil viscous oxidized road bitumen grade 70/100 produced by JSC Mozyr Refinery (Belarus Republic), oil viscous oxidized road bitumen grade BND 60/90 JSC UkrTatNafta (Ukraine), emulsifiers Redicote E-11, Redicote 404, Redicote E-4875NPF, Redicote EM44 and Redicote C-320 produced by AkzoNobel (Sweden).

Physical-mechanical properties of bitumens are presented in Table 1. Penetration (Pen) and Ductility (D) were determined at 25 ºC.

According to Table 1, the difference between the oxidized bitumens and the distilled ones consists in the fact that the first ones have the larger plasticity interval (Softening Point is higher, while Fraaß breaking point is lower). For their part, distilled bitumens have substantially lower paraffin content and perceptibly higher total acid no., while that can be explained by differences in crude-oil and its processing technology.

Table 1. Physical-mechanical indices of bitumens

No	Type of bitumen	Name and value of indices					
		Softening Point, ºC	Pen, 0,1mm	D, cm	Fraaß breaking point, ºC	Paraffin content, % mass	Total acid no., mg KOH/g
1	Nybit E85	47	80	>100	-11	0,5	3,5
2	70/100 Mozyr Refinery	48	75	100	-21	4,5	0,6
3	BND 60/90 UkrTatNafta	49	72	84	-18	5,4	0,5

Production of bitumen emulsions was done on Danish laboratory batch bitumen-emulsion plant type DenimoTech SEP-0,3R (figure 1). Bitumen

emulsion formulations were developed for getting cationic slow-setting emulsions (CSS) intended for usage in slurry seal and microsurfacing technologies. Formulations with hydrochloric acid are presented in Table 2, while with ortho-phosphoric acid – in Table 3.

Fig. 1. Lab bitumen emulsion plant SEP-0,3R of Danish company DenimoTech

Table 2. Formulations of bitumen emulsion based on hydrochloric acid

No of formulation and type of bitumen	Components of emulsions, % w/w					
	Bitumen	Emulsifier Redicote E-11	Emulsifier Redicote 404	Emulsifier Redicote E-4875NPF	Hydrochloric acid in water phase till pH	Water
1.1) Nybit E85	61,0	1,1	–	–	2,5	till 100
1.2) Nybit E85	61,0	–	1,1	–	2,5	till 100
2.1) 70/100 Mozyr Refinery	61,0	1,1	–	–	2,5	till 100
2.2) 70/100 Mozyr Refinery	61,0	–	1,1	–	2,5	till 100
2.3) 70/100 Mozyr Refinery	61,0	–	–	0,8	2,0	till 100
3.1) BND 60/90 UkrTatNafta	61,0	1,1	–	–	2,5	till 100
3.2) BND 60/90 UkrTatNafta	61,0	–	1,1	–	2,5	till 100
3.3) BND 60/90 UkrTatNafta	61,0	–	–	0,8	2,0	till 100

Table 3. Bitumen emulsion formulations based on ortho-phosphoric acid Formulations of bitumen emulsion based on hydrochloric acid

No of formulation and type of bitumen	Components of emulsions, % w/w				
	Bitumen	Emulsifier Redicote EM44	Emulsifier Redicote C-320	Ortho-phosphoric acid in water phase till pH	Water
4.1) 70/100 Mozyr Refinery	61,0	1.1	–	2,5	till 100
4.2) 70/100 Mozyr Refinery	61,0	–	1,1	2,5	till 100
5.1) BND 60/90 UkrTatNafta	61,0	1.1	–	2,5	till 100
5.2) BND 60/90 UkrTatNafta	61,0	–	1,1	2,5	till 100

According to recommendations [12-13], production of efficient emulsions for slurry seal and microsurfacing technologies is possible not only based on high-acidic bitumen (in our case Nybit E85), but also on low-acidic one – with application of special emulsifiers. As those latter ones, there were taken the recommended by AkzoNobel emulsifiers – Redicote EM44 and Redicote C-320. These two emulsifiers are intended for rapid-setting emulsions, but in combination with ortho-phosphoric acid they provide for getting high-quality slow-setting emulsions.

Physical-mechanical indices of bitumen emulsions based on hydrochloric acid are presented in Table 4, while based on ortho-phosphoric acid – in Table 5.

Table 4. Physical-technical indices of bitumen emulsions based on hydrochloric acid

Index	Requirements according to [14]	Bitumen emulsions							
	ECS-60 (CSS)	1.1	1.2	2.1	2.2	2.3	3.1	3.2	3.3
Appearance	Homogeneous dark-brown liquid	Fits the requirements							
Hydrogen ions concentration, pH	1.5-6.5	2.52	2.60	2.95	2.99	2.86	2.83	2.82	2.93
Homogeneity (sieve No.014 residue), %, at most	0.25	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Content of residual binding agent	58–62	61	61	61	61	61	61	61	61
Assumed viscosity at 25 ºC. (apparatus with hole diameter of 4 mm), s	5–25	7	8	6	6	7	6	7	6

Stability during storage: sieve No.014 residue, %, at most - after 7 days - after 30 days		 0.3 0.4	 0.07 0.12	 0.06 0.14	 0.06 0.14	 0.04 0.12	 0.06 0.14	 0.05 0.15	 0.06 0.17	 0.07 0.15
Adhesion of residual binding agent to macadam, points, no less		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Miscibility with mixtures of grained composition	porous	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
	dense	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Breaking index, %		180-230	189	191	196	201	197	204	198	201

Table 5. Physical-technical indices of bitumen emulsions based on orthophosphoric acid

Index		Requirements according to [14]	Bitumen emulsions			
		ECS-60 (CSS)	4.1	4.2	5.1	5.2
Appearance		Homogeneous dark-brown liquid	Fits the requirements			
Hydrogen ions concentration, pH		1.5-6.5	3.42	3.23	3.44	3.26
Homogeneity (sieve No.014 residue), %, at most		0.25	0.01	0.01	0.01	0.01
Content of residual binding agent		58–62	61	61	61	61
Assumed viscosity at 25 ºC. (apparatus with hole diameter of 4 mm), s		5–25	7	8	6	7
Stability during storage: sieve No.014 residue, %, at most - after 7 days - after 30 days		 0.3 0.4	 0.12 0.28	 0.13 0.29	 0.14 0.28	 0.12 0.26
Adhesion of residual binding agent to macadam, points, no less		5.0	5.0	5.0	5.0	5.0
Miscibility with mixtures of grained composition	porous	Yes	Yes	Yes	Yes	Yes
	dense	Yes	Yes	Yes	Yes	Yes
Breaking index, %		180-230	228	215	226	215

All the bitumen emulsions produced correspond to [14] for the grade ECS-60 (emulsion cationic road slow-setting with bitumen content from 58 to 62%) and can be applied for slurry seal and microsurfacing technologies.

From Table 4 one can see not large difference between the values of breaking index and pH of bitumen emulsions on distilled and oxidized bitumens with hydrochloric acid. Due to higher total acid number of distilled bitumens these indices of bitumen emulsions on Nybit E85 bitumen are lower than in emulsions on oxidized bitumens.

The main difference in physical-technical indices of emulsions on hydrochloric and ortho-phosphoric acids consists in the lower values of breaking index and emulsion pH, while it means higher reactivity of this emulsion. The worse indices of stability during storage mean (in emulsions on ortho-phosphoric acid) the possibility of worse bitumen emulsification during the emulsion production, i.e.: there is possibility of rapid emulsification of bitumen droplets after milling by colloid mill, while due to this phenomenon the droplets are from the very beginning larger than in the systems on hydrochloric acid. Besides, in course of testing on miscibility with mixtures of grained composition and breaking index there was noticed the increased stickiness and darker coloring of mixes on ortho-phosphoric acid – in comparison with the systems on hydrochloric acid. In general, based on the testing done, it is possible to confirm the efficiency of using ortho-phosphoric acid for production of slow-setting cationic bitumen emulsions.

4. Conclusion

1. There was ascertained the difference of physical-mechanical indices of distilled and oxidized bitumens.
2. There were developed formulations of bitumen emulsions on distilled and oxidized bitumens based on usage of hydrochloric and ortho-phosphoric acids and special emulsifiers.
3. There was determined difference between physical-technical indices of emulsions on different acids.
4. There was proved that the usage of ortho-phosphoric acid and special emulsifiers provides for production of cationic slow-setting emulsions for slurry seal and microsurfacing mixtures.

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