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Obtaining of Bitumen Emulsions using Nonionic Surface-Active Substances

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Abstract

Background: One of the trends concerning an effective use of large-tonnage and yet scarce binder as bitumen is a considerable introduction of bitumen emulsions in water into the practice of road and civil construction. **Methods:** The paper presents the experimental data on the research of bituminous emulsions, the physical-chemical properties of an original BND bitumen 60/90 from Zyuzeevsky NBZ and the bitumen residue there of. **Results:** The resulting emulsions were highly stable and were referred to slowly structured (slowly decomposing) ones, which may be used in the preparation of cold bituminous mineral mixtures of different density used for storage, the strengthening of soils, dust removal from roads. These emulsions had a viscous consistency that may be used for solving the problem of bitumen emulsions application to an inclined surface. Bituminous residues differ by the improvement of a film binder adhesion performance with mineral material (adhesion) without the use of additional adhesion additives. **Conclusion:** The use of such a component, which also has an emulsifying ability and an adhesion effect, an increased resistance to delamination and coalescence of an emulsion during storage, bitumen saving and the environmental rate.

Keywords: Bitumen Residue, Bituminous Emulsions, Emulsifier, Properties, Surfactant

1. Introduction

Road bitumen emulsions (BE) emerged in the early twentieth century with the use of an anionic surfactant as an emulsifier, which had its advantages and disadvantages. In the future, many countries refused from the use of anionic surfactants due to the transition to a cationic emulsions in the late 50-s. The transition to cationic bitumen emulsions is conditioned by the fact that they provide greater adhesion to stone material, even under adverse environmental conditions, which is related to the difference in the mechanisms of anionic and cationic emulsions decomposition - an anionic emulsion decomposes during the contact with a surface as the result of water evaporation and cationic emulsion decomposes by the chemical sorption of emulsifier ions, and the subsequent release of water. We may say that in France - the world leader in the production and application of bituminous emulsions - 97% of the total volume of produced emulsions are cationic ones, and a small portion of the anionic emulsions is used for special purposes, such as in the construction of coatings with a «sandwich» structure[1].

For more than 60 years of bitumen emulsions production different compositions and the technologies of their use in road construction were developed perfectly. They include quite a number of various components for different purposes.

Let's consider the component composition of bitumen emulsions for different purposes (Table 1)[2,3].

The most high-tech, precise and complete definition of the emulsion yields was presented in 1961 by R. Becher in the Theory and Practice of the emulsion: emulsion is a thermodynamically unstable heterogeneous system consisting of two immiscible liquids, at that the one is dispersed in the least amount, in the form of droplets the diameter of which is greater than 0.1 micrometer. The

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Table 1. Chemical composition of bituminous emulsions

Component name	Content, % wt.	Note
1	2	3
1. Bitumen	30–80	Viscous road bitumens with a penetration are used commonly (25 °C, 0.1 mm) 60–200; it is possible to use bitumen modified by polymers
2. Water	15–70	The use of hard water and the absence of mechanical impurities are not allowed. A large number of electrolytes can result in decay. Also decay may occur on the surface of solids. The hardness of used water should not exceed 6 mEq/l.
3. Emulsifier	0,15-3,0	Anionic and cationic emulsifiers. The obtaining of three classes of emulsions - EBC-1,2,3
4. Acid	0,1–1,0	Hydrochloric acid of 25–37%, the pH of the aqueous phase makes 1.5–3.5. It transfers emulsifier into ionic form, it allows to adjust the pH of an aqueous phase and an emulsion
5. Растворитель	0,5–3,0	The introduction of a variety of solvents in order to increase the stickiness emitted during the decay of the bitumen emulsion (as the film forming agent) and to facilitate its dispersion in water is possible
6. Modifier of a disperse phase	2,0–10,0	Polymers may act as a modifier of a dispersed phase. They serve as the polymers that are used for an extended temperature range performance of viscous bitumen with the simultaneous increase of their heat and crack resistance and flexibility
7. Stabilizer	0,05–0,5	Calcium chloride as 30–35% aqueous solution is often introduced as a stabilizer
8. Thinner (if necessary)	5–30	It is used to increase the penetration of bitumen up to the desired value. Vacuum gas oils, oil fractions are used, etc.

minimum stability inherent to this type of the system may be increased by the addition of special agents such as surfactants (emulsifiers)[4-8].

The properties of emulsions are largely dependent on the emulsifying and stabilizing properties of an emulsifier. At low emulsifier content emulsion may not be obtained or are obtained as polydisperse and unstable ones. The gelling of emulsions and their destruction at stirring is observed often at excess.

The following definitions concerning surfactants were accepted at the III-rd International Congress[9]

- Anionic surfactants in aqueous solutions are dissociated to form a negatively charged ion (anion) of a molecule organic residue;
- Cationic surfactants in aqueous solutions are dissociated with the formation of a positively charged ion (cation) of an organic molecule residue;
- Ampholytic surfactants in aqueous solutions depending on environment are dissociated to form an organic residue of an anion or a cation molecule. In an acidic environment, they exhibit cationic properties and in alkaline environment they demonstrate anionic properties;
- Non-ionic surfactants in aqueous solutions do not form ions. Their solubility is conditioned by the presence of polar functional groups.

Macromolecular (polymer) surfactants composed of a large number of repeating units, each of which has a polar and nonpolar groups are included in a separate group.

Let's note a few illustrative families, illustrating them with examples in each class.

1) Anionic surfactants are ionized in aqueous solution with the formation of negatively charged organic ions responsible for the surface activity, which contain salts and the sulfates and fatty acids, organophosphates, "tall oil" - the residual distilled product obtained in the paper industry as the waste softwood treated in a manner called "in sulphate". There is the following general formula: R - COONa (or R - COOK), wherein R - is a characteristic chain of the fatty acid; it has a non-polar part of a molecule and is a lipophilic one. COONa group is presented by a polar hydrophilic part. In the solution of a continuous aqueous phase soap molecules ionize Na+ (or K +) ions as cations, adsorbed by water, and other molecules - R - COO- ions are presented by anions, adsorbed bitu-

men droplets. This active substance in the form of a paste was often used when only anionic emulsions were present at the market. The use of anionic emulsions in roadworks is severely restricted nowadays.

2) Cationic surfactants are ionized in aqueous solution to supply the positively charged organic ions responsible for the surface activity. Despite the fact that this discover was made long ago the first molecule of hexodelamin hydrochloride CH3- (CH2) 15NH3 + Cl^- in 1896 was prepared by Kraft, which were widely used later due to their bacteriostatic properties as corrosion inhibitors, flotation agents, emulsifiers, but especially as textile softeners in an economic application[7,10]. Cationic surfactants provide a significant positive effect in the processing technology of various mineral materials by petroleum bitumen and at the activation (hydrophobic development) of mineral powders in the process of grinding, which is important to achieve the required quality of asphalt concrete, and an increased efficiency of road surfaces. They also help to mix uniformly the finest particles, thus improving the treatment of mineral materials by a binder, thereby reducing the energy costs of mixing processes.

Their area of application is extended to all negatively charged surfaces. In addition to hydrocarbonate radical, most of these molecules have a positively charged nitrogen atom, which may be either aliphatic or heterocyclic one.

The use of cationic emulsions is various. For example the emulsions modified by the polymer with a quick decomposition used in the surface layers are widespread. In this case, such compounds as alkylamines, alkylamidoamines, nitrogen containing heterocycles of imidazoline, the molecules of which shall be in a salt form are used as the surfactants. For this purpose, various types of organic acids are used - acetic, formic, lactic one - but hydrochloric acid is used in practice[11].

Bitumen emulsions used in the impregnation or cooking of cold asphalt mixes without fine granular elements have an average decay period[8,12].

The emulsions with a slow decay are used in the production of mixtures at stationary mixers, or on site using selected materials, as well as in the cold asphalt mixtures of immediate application with a mineral part[13].

3) Surfactants - the ampholytes the composition of which is similar to amphoteric products, i.e. this is the surfactant containing two or more functional groups which may be ionized in aqueous solution depending on environmental conditions, providing the composition with an anionic or cationic nature of the surface material. These products exhibit their ionic character depending on pH: they are the anions above an isoelectric point, and the cations below this point. In addition to synthesis products this group has amino acids contained in plant (soy lecithin) and animal proteins (milk casein). Schematically, these molecules may be represented in the following form: NH2-R-COOH.

4) Non-ionogenic surfactants are the surfactants which do not form ions in an aqueous solution. The solubility of non-ionogenic surfactants in water is performed due to the presence of functional groups in their molecules with a strong affinity for water. It may be assumed as a classification system, the type of communication connection for hydrophilic and lipophilic groups.

The use of nonionic surfactant, as emulsifiers, is of great interest as they are compatible with all ionic surfactants, despite the pH conditions contained not only in the aqueous phase, but, as noted above, in the bitumen phase. Due to this one may observe the maximum affinity of two phases resulting in a highly dispersed emulsion with increased resistance to delamination and coalescence. Unlike cationic emulsions, during the preparation of emulsions based on nonionic surfactant an acid is not used, but it removes a negative effect on the soil. So, from the standpoint of industrial safety the use of nonionic surfactants is certainly preferable than anionic and cationic emulsifiers.

So to the tasks solved by emulsifier systems include the following ones[13]:

I - The drop of stress at the interface between the bitumen and aqueous phases and thereby the decrease in the volume of mechanical work during the manufacture of bitumen emulsions (bitumen dispersed in an aqueous phase, i.e. during emulsification);

II - The formation of a protective solvate shell around the individual emulsified bitumen particles, preventing the merger of bitumen particles;

III - The control of dispersed bitumen from emulsion on the surface by sedimentation;

IV - the creation of the layer increase possibility for a deposited bitumen in the terms of water displacement from emulsion.

Anionic emulsifiers are limited in their performance qualities, since they solve the problems I and II well, whereas the problem III and IV are solved only in an unsatisfactory extent. Correctly selected components of an emulsifier allows not only to spend a quality emulsification of bitumen, but also be sure in a given rate of decay on the surface of any nature.

2. Materials and Methods

During the preparation of BE in water A special attention was paid to the choice of surfactant components, which are used as the nonionic surfactants and alcohol ethoxylation products (AEP) of the two marks A and B differing by the degree of substitution.

The selection of these components was not an accidental. Thus nonionic surfactants are the ethoxylates of natural higher fatty alcohol fractions of C_{12}-C_{14} hydrocarbons, wherein the ratio of hydrocarbon units with respect to the bitumen and oxyethylene units in relation to the aqueous portion is most optimal. In its turn, at the selection of the following component we proceeded from the the fact that the AEP is a water soluble polymer when it is administered in order to obtain a stable BE demonstrating a significant resistance to abrasion during deformation.

The preparation of BE was carried out using the bitumen of 60/90 grade produced by OJSC "Tatnefteprom-Zyuzeevneft" whose properties were shown in Table 2.

Table 2. Qualitative characteristics of BND 60/90 bitumen according to GOST 22245-90 "Viscous bitumen for roads"

Name of indices	The standard according to GOST 22245-90	Actual meaning
1	2	3
1. The depth of the needle penetration, 0.1mm - at 25°C - at 0°C	within 61 – 90 No less than 28	74 20
2. Softening point, °C	No less than 47	49
3. Elongation, cm - at 25°C - at 0°C	No less than 55 No less than 4,0	More than 100 0,5
4. Brittleness temperature, °C	No more than - 17	–14
5. Flash point, °C	No less than 230	230
6. Penetration index range	from –1,0 to +1,0	–0,8
7. Adhesion of bitumen with mineral material (adhesion), points	-	3

3. Results

The obtained EB bitumen phase with the content of 40 and 60% wt. of water, respectively, with the introduction of the latest selected components were highly stable and were referred to slow structuring (slowly decomposed). This type of emulsion is used in the preparation of cold bituminous mineral mixtures of different density used for storage, strengthening of soils, dust removal from roads.

EB have a viscous consistency, in contrast to an emulsion containing a cationic emulsifier. It was found that at the increase of ethoxylate content, the increase of stability with the increase of viscosity characteristics was observed. EB stability was also influenced by AEP concentrations change. One problem of bitumen emulsion use is its application on an inclined surface. In order to solve this problem it is recommended to increase the viscosity of emulsion by applying ethoxylates of higher natural fatty alcohols.

Then the studies were carried out concerning a bitumen binder. It was found that with the increase of an injected AEP component bitumen showed a significant improvement of adhesion and strength properties up to 1 point, whereas original bitumen has 3 points. The improvement of physical-chemical properties (Table 3) with the increase of surfactant is also revealed.

According to physical and chemical parameters bitumen of the grade BND 60/90 must comply with the requirements and standards: GOST 22245-90 "Viscous bitumen for roads":

- by penetration, 0.1 mm, at 25 °C the samples 5, 10, and 15 do not correspond;
- by softening temperature, °C, all samples meet the requirements without an exception;
- by elongation, cm at 25 °C, all samples meet the requirements without an exception.

Thus, based on these data (Table 3), we can say that the selection of additives for the adjustment of the emulsifying and adhesion-strength properties in order to produce nonionic EB had a positive effect on such factors as the softening point, elongation and penetration.

Table 3. Physical-chemical properties of bitumen residue property

Sample number	AEP A/B amount in water, % wt.	The volume of ethoxylate in water, wt %	Adhesion*, point	Softening temperature*, °C	Elongation at 25°C *, cm	Penetration at 25°C *, 0,1 mm
1	2	3	4	5	6	7
1	0,75	1	2 / 1-2	47/47,8	>100/91	92/90
2	1,00	1	2 / 1-2	48,2/49	90/85	89/85
3	1,25	1	1-2 / 1	50,1/51	83/80	83/80
4	1,50	1	1 / 1	53/54,3	80,9/75	79/76
5	1,75	1	1 / 1	53,6/54,7	80,1/74,9	78/74
6	0,75	2	2 / 2	47/47,2	>100/92	93/90
7	1,00	2	2 / 1-2	48/49,1	>100/89	90/87
8	1,25	2	1-2 / 1	50/50,8	>100/82	85/81
9	1,50	2	1-2 / 1	51/52,2	>100/81	81/77
10	1,75	2	1 / 1	51,6/52,7	>100/80,5	78,4/75,1
11	0,75	3	3 / 2	46,8/47	>100/92	93/80
12	1,00	3	2 / 2	47/47,6	>100/87	90/85
13	1,25	3	2 / 2	49,2/50	>100/84	85/81
14	1,50	3	2 / 1-2	50/50,7	>100/82,4	82,6/79
15	1,75	3	2 / 1-2	50,8/51,1	>100/81	78,7/76,2
Requirements according to GOST 22245-90	-	-	-	No less than 47	No less than 55	within 61÷90

* the fraction shows the value of the indicator depending on the applied AEP A and B.

4. Conclusions

According to study results AEP and ethoxylate influence is determined on the properties of the emulsions and the properties of the bitumen residue. In particular, with the introduction of additives, not only the increase in the values of bitumen adhesion with mineral material but also its brittleness temperature increase are observed.

5. Summary

The obtained results indicate not only the use of properly selected additives during the preparation of highly dispersed emulsion without an emulsifier with increased resistance to delamination and coalescence nor about the high mechanical strength of the bitumen film on the surface of a stone material, which is necessary for the preparation of high-quality road surfaces with high overhaul period.

6. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

7. Acknowledgement

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