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# Practical Aspects of Development of Universal Emulsifiers for Aqueous Bituminous Emulsions

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**Abstract:** A highly promising approach to the improvement of the properties of bituminous compositions for road building (BCRB) is introduction of surfactants that increase the strength of the adhesive bond between bitumen and the rock material surface and provide required rheological properties of BCRB as a result of emulsification of the bitumen binder in the aqueous medium. The performance characteristics, including the breaking rate of a bituminous emulsion (BE) are controlled by introducing modifying additives both into the dispersed phase and into the dispersion medium. The additives used for dispersion medium are usually stabilizers, organic and inorganic acids, or polymers and this issue has been comprehensively studied. The effect of petroleum fraction-based products on the BE properties is less studied. Only few studies dealing with BE modification with petroleum-based products were performed in Russia. Russian industry produces a limited range of surfactants and many of them, while having high emulsifying capacity, do not promote adhesion. Furthermore, they are rather expensive due to complex and multistage processes for their production.

**Key words:** Bitumen · Amines · Emulsification · Physico-chemical properties · Roadbed durability

## INTRODUCTION

The cationic bituminous emulsions (BE) were developed back in the early 20th century [1-3], but their industrial application started only in 1953. For a number of reasons, in Russia, they remain a new type of organic binder materials [4-9]. Long-chain aliphatic amines prepared via a complicated industrial process find wide practical use for the fabrication of bituminous emulsions for various purposes [1-3]. This paper presents results on the synthesis of similar amines from non-target products of the JSC Nizhnekamskneftekhim.

Apart from advantages of bitumen as an organic binder material, BE have a number of useful properties, namely, a much lower viscosity in the temperature range from 0 to 100°C and higher adhesive capacity to the rock material surface. A highly important indicator of the BE quality is the breaking rate according to which emulsions are classified as fast-, medium- and slow-breaking emulsions, classes 1, 2 and 3, respectively.

Long-chain aliphatic amines prepared via a complicated industrial process find wide practical use for the fabrication of bituminous emulsions for various purposes. This paper presents results on the synthesis of similar amines from non-target products of the JSC Nizhnekamskneftekhim. A facile and cost-effective process for the synthesis of new compounds for preparing bituminous emulsions and for manufacture of high-quality BCRB based on them is a topical issue.

Ethylene bonds are known to be highly reactive towards addition reactions. One such reaction is the Prilezhaev reaction consisting in oxygen addition to the double bond under the action of perbenzoic acid to give oxiranes. However, perbenzoic acid is an expensive compound whose handling is dangerous. It is possible to replace perbenzoic acid for this reaction by peracetic acid, which is used at the instant of formation upon the reaction of glacial acetic acid with hydrogen peroxide:

$$CH_3C(O)OH + HO\text{-}OH \longrightarrow CH_3C(O)OOH + H_2O \quad (1)$$

For accelerating the reaction, minor amount of a strong inorganic, most often sulfuric, acid is added to the reaction mixture. In this case, peracetic acid is formed within 1-2 hours at 40-60°C.

The oxidation of olefins with peracetic acid can be represented as follows:

$$RCH{=}CHR_1 + CH_3C(O)OOH \longrightarrow \underset{\diagdown\,O\,\diagup}{RCH{-}CHR_1} + CH_3COOH \quad (2)$$

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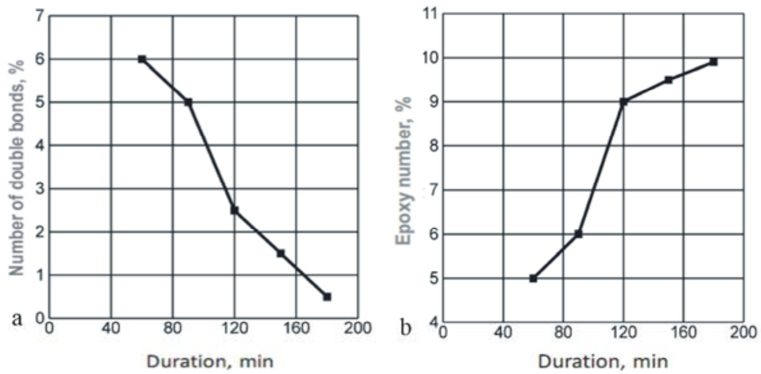



Fig. 1: Kinetics of variation of the content of double bonds (a) and epoxide number (b)

Table 1: Characteristics of $C_{26\text{-}28}C_{20\text{-}26}$ α-olefin oxides

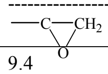
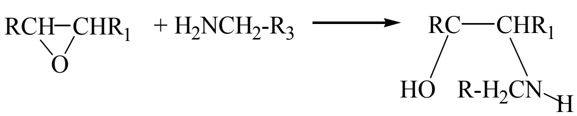
| Oxide type | Content,%  | Content,% C=C |
|---|---|---|
| $C_{26\text{-}28}$ | 9.4 | 0.3 |
| $C_{20\text{-}26}$ | 14 | 0.25 |

Table 2: Comparative characteristics and designations of the amination products

| Amine characteristics | Designation | Content of NH groups,% |
|---|---|---|
| Product of reaction of HMDA with $C_{20\text{-}26}$ olefins | Surf-1 | 8 |
| Product of reaction of PEPA with $C_{26\text{-}28}$ olefins | Surf-2 | 65 |
| Product of reaction of PEPA with $C_{20\text{-}26}$ olefins | Surf-3 | 66 |

The olefin oxides thus formed serve as the starting compounds for the preparation of long-chain aliphatic amines



We studied the oxidation of non-target $C_{20\text{-}26}$ and $C_{26\text{-}28}$ α-olefin fractions The considerable amount of impurities present in these fractions can have a substantial influence on the course of both oxidation and amination reactions. During selection of the optimal conditions, it was found that oxidation is not accompanied by the formation of glycol acetates (side products); therefore, the process was carried out in the absence of an inert solvent.

As a result of investigations, the optimal ratio between the reaction components was found to be: $H_2O_2$: $CH_3COOH$ : $H_2SO_4$: $C_{20\text{-}26}$ or $C_{26\text{-}28}$ α-olefin fraction = 3: 2 : 0.1 : 1 (mole/mole)

Sulfuric acid was used in the concentrated form and hydrogen peroxide was a 52% solution. The oxidation was carried out at a temperature of 70-75°C with vigorous stirring; the reaction was monitored based on the epoxide number and the content of double bonds.

As soon as in two hours after onset of the reaction, the epoxide number approaches a maximum, while the content of double bonds decreases to the minimum, i.e., the oxidation was actually completed. The results indicate that the oxidation of α-olefin fractions may be carried out without a solvent, which is favorable from economic and production technology standpoints.

The resulting products were aminated by hexamethylenediamine (HMDA) and polyethylenepolyamine (PEPA). The amination was carried out at 150-160°C for 5 hours; the amine to olefin oxide ratios were calculated from the epoxide number of the oxide. At the end of the reaction, the content of the NH groups in the product and its ability to form aqueous emulsions were determined. Comparative characteristics and designations of the amination products are summarized in Table 2.

Important characteristics of the surfactant efficiency in stabilizing artificial aqueous dispersions (among these, also bituminous emulsions) include the hydrophilic-lipophilic balance (HLB), the critical micelle concentration (CMC), the limiting adsorption, the limiting surfactant concentration ensuring the formation of aqueous dispersions, the temperature dependence of surface tension, the viscosity ratio of the dispersed phase and dispersion medium and the method for surfactant introduction.

As stabilizers of aqueous dispersions, surfactants with HLB in the range from 10 to 18 were found to be preferred. Table 3 presents the calculated HLB values for the obtained surfactants and, for comparison, the same characteristics for the commercial emulsifier Peral-414. It can be seen from the Table that the HLB of the obtained

Table 3: Key colloid-chemical properties of the synthesized surfactants

| Characteristics | Surf-1 | Surf-2 | Surf-3 | Peral- 414 |
|---|---|---|---|---|
| Cloud point, °C | 34 | 28 | 12 | 10 |
| HLB | 14 | 15 | 17 | 16 |
| Amine number: initial | 149 | 220 | 243 | 248 |
| after thermal conditioning | | | | |
| (24 h at 100°C) | 147 | 217 | 238 | 235 |
| CMC, g /l | 0.24 | 0.08 | 0.06 | 0.07 |
| Interfacial tension of a 0.1% | | | | |
| solution of the surfactant, MN/m | 7 | 5 | 4 | 5 |

products fall in the selected range, which implies that these products can, in principle, be used for bitumen emulsification.

As regards other characteristics, the surfactants were also roughly at the level of the commercial sample, while in thermal stability, the new products were even superior.

The quality of the obtained emulsions depends to a large extent, all other factors being the same, on the industrial process used to prepare them and on process engineering. The process characteristics include: the stirring intensity and, hence, the type of stirrer, the method of combining the aqueous and organic phases, the order of introducing the surfactant and the neutralizing agent, the viscosity ratio between the dispersed phase and dispersion medium, emulsification temperature and the cooling conditions of the resulting emulsion.

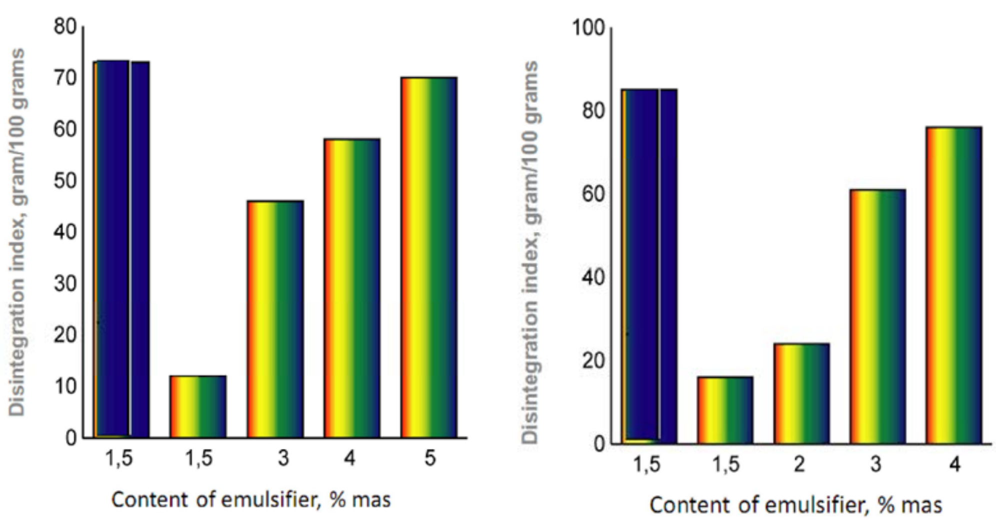
We utilized the commonly accepted approach to the preparation of emulsions by introducing the organic phase into the aqueous phase and intense mechanical action on the system. The emulsifier was added to the system by two alternative procedures.

According to the first one, the specified amount of the surfactant was added to a heated bitumen and the required amount of hydrochloric acid was added to the aqueous phase. According to the second procedure, the surfactant pre-neutralized by hydrochloric acid to pH of 1.5-2 was added to the aqueous phase, which was then heated to the specified temperature and a bitumen melt was gradually added to it with vigorous stirring. The dispersions obtained using a milling stirrer are inferior in stability to commercial bituminous emulsions even when the surfactant Peral 417 is used.

Among the laboratory vessels, the best stirring intensity was provided by colloid mills and rotary-pulse or acoustic (ultrasonic) dispersers. Therefore, in the measurements of the emulsifying properties of surfactants, a rotary pulse acoustic device was used for mixing.

The procedure for preparation of dispersions was as follows: first, the primary emulsion was obtained using a disk mixer and then the dispersion was treated with an acoustic disperser.

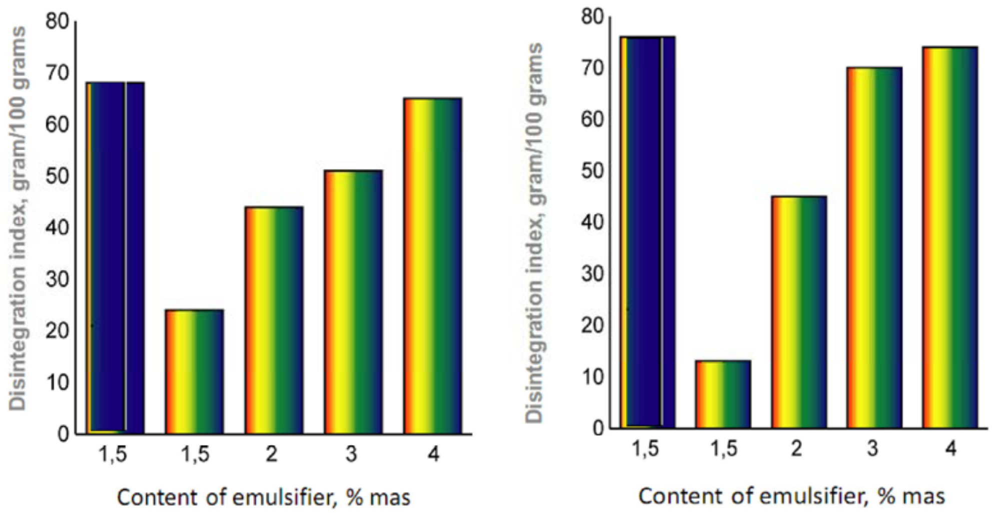
While comparing the results, it can be noted that the stability of dispersions and the surfactant concentration that provides an acceptable stability are somewhat lower for emulsions prepared by the first procedure than for emulsions obtained by the second procedure. In our opinion, this is due to differences in the mechanisms of formation of the interface and surfactant adsorption at the interface. Once the surfactant has been introduced in the organic phase, during emulsification its hydrophilic groups have to be aligned at the interface, to react with the neutralizing reagent and to provide stabilization of




a) Surf-1. Content of water 50%

b) Surf-2 Content of water 50%

Fig. 2: Properties of bituminous emulsions




c) Surf-3 Content of water 50% г) Peral-414 Content of water 50%

Fig. 3: Properties of bituminous emulsions

the particle. In view of the permanent surface renewal, these processes should occur at a rate comparable with the rate of interface formation. It should be borne in mind that the alignment of molecules during the formation of the adsorption layer is retarded upon increase in the bitumen viscosity. Some of the amine-containing hydrophilic groups may react with acidic components of the bitumen and the reaction products cannot participate in the interface formation.

While analyzing the foregoing, note that the synthesized surfactants are comparable with foreign Peral-417 sample as regards the colloid-chemical characteristics and the threshold concentration resulting in the formation of stable dispersions. The rate of emulsion breaking depends on the surfactant concentration and the amount of neutralizing agent (decrease in the surfactant concentration leads to an increase in the breaking rate).

## CONCLUSIONS

This study demonstrated the possibility of using non-target products of the regional plant JSC Nizhnekamskneftekhim: $C_{20-26}$ and $C_{26-28}$. alpha-olefin fractions as components for surfactant production. The hydrolytic and thermal stability of the synthesized compounds under conditions of BCRB preparation and application were studied. The synthesized surfactants are not inferior in performance characteristics to a commercial sample of emulsifying agent (Germany), which attests to good prospects of further research aimed at the development of formulations and processes for the preparation of bituminous emulsions based on them.

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