

CHEMISTRY. CHEMICAL ENGINEERING**ХІМІЯ. ХІМТЕХНОЛОГІЯ**

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FOR HIGH-CONCENTRATED REVERSE EMULSIONS**

I.L. Kovalenko, V.P. Kuprin. Розробка емульгатора для висококонцентрованих зворотних емульсій. Зворотні емульсії знайшли широке застосування в гірничорудній промисловості як матриці емульсійних вибухових речовин і бурових промивних рідин. Визначальною характеристикою зворотних емульсій промислових вибухових речовин є висока стабільність і стійкість до кристалізації. **Мета:** Метою роботи є оцінка механізму дії емульгаторів типу SMO і деяких PIBSA-похідних, найбільш широко застосовуваних у світовій практиці, а також розробка ефективного вітчизняного емульгатора зворотних емульсій. **Матеріали і методи:** Напівдинамічним методом з використанням зворотного сталагмометра було визначено зниження міжфазного натягу на межі «вода / дизельне паливо» в присутності 0,5 % мас. сорбітану моноолеата різних виробників. З використанням обраних емульгаторів за допомогою динамічного міксеру були приготовлені емульсії на базі монорозчину аміачної селітри і дизельного палива такого складу, % мас.: аміачна селітра — 76,8; вода — 15,6; дизельне паливо — 6,0; емульгатор — 1,6. **Результати:** За результатами досліджень міжфазного натягу «вода / розчин ПАР в дизельному паливі», стійкості емульсій на монорозчині аміачної селітри і ІЧ-спектрів SMO різних виробників встановлено, що наявність в продукті домішок олеїнової кислоти, ді- і триолеатів призводить до зниження міжфазної активності, підвищення маслорозчинності емульгатора і зниження стійкості емульсій до кристалізації. На основі аналізу спектральних даних висловлено припущення щодо можливості специфічної взаємодії за механізмом «спектрального резонансу» між емульгаторами типу PIBSA-MEA, LZX і зародками кристалів нітрату амонію NH_4NO_3 в дисперсній фазі емульсії. Реалізовано амідування рослинних масел моноетаноламіном при знижених температурах (90...100 °C), і методом ІЧ-спектроскопії доведено наявність в продукті переважно амідів жирних кислот. Отримані аміни мають добру емульгуючу здатність як в динамічних, так і в статичних апаратах в різних режимах роботи. За спектральними даними показана можливість специфічної адсорбції отриманих амідів на зародках нітрату амонію, яка забезпечує гальмування процесів кристалізації емульсії.

Ключові слова: поверхнево-активна речовина, емульгатор, міжфазна активність, специфічна взаємодія, амід.

I.L. Kovalenko, V.P. Kuprin. Emulsifier development for high-concentrated reverse emulsions. The reverse emulsions have found broad application in ore mining industry as matrixes of emulsion explosive substances and boring washing waters. The defining characteristic of reverse emulsions of industrial explosive substances is the high stability and immunity to crystallization. **Aim:** The aim of this work is to assess the mechanism of emulsifiers effect like SMO and some PIBSA-derivatives, that are most abundantly used in world practice, and also to develop an effective domestic emulsifier of reverse emulsions. **Materials and methods:** Using the semi-dynamic method with use of the reverse stalagmometer it was determined the decreasing in interfacial tension on "water / diesel fuel" border in the presence of 0.5 wt % sorbitan monooleate of various producers. Emulsions with use of the chosen emulsifiers using the dynamic mixer on the basis of monosolution of ammonium nitrate and diesel fuel have been produced. The emulsions have the following composition, wt %: ammonium nitrate — 76.8; water — 15.6; diesel fuel — 6.0; emulsifier — 1.6. **Results:** By the researches results of the interfacial tension "surfactant water / solution in diesel fuel", the stability of emulsions using monosolution of ammonium nitrate and the IR spectrums of SMO of various producers it is established that presence in product of impurity of oleic acid, di- and trioleates leads to decreasing in interphase activity, increasing of emulsifier oil solubility and decreasing the resistance of emulsions to crystallization. On the basis of the spectral data analysis it is suggested about possibility of specific interaction on the mechanism of "spectral resonance" between emulsifiers of the PIBSA-MEA, LZX type and crystals nucleus of NH_4NO_3 ammonium nitrate in dispersed phase of emulsion. Amidation of vegetable oils by monoethanol amine is implemented at the reduced temperatures (90...100 °C). It was proved the availability mainly of fatty acids amides in product using the method of IR-spectroscopy. The obtained amides possess good emulsifying ability both in dynamic and in static devices in different duties. According to spectral data, the possibility of specific adsorption of the received amides on ammonium nitrate nucleus is shown. This provides inhibition of emulsion crystallization processes.

Keywords: surface-active substance, emulsifier, interphase activity, specific interaction, amide.

Introduction. The reverse emulsions ("water-in-oil") have found wide application in ore mining industry as matrixes of the emulsion explosive substances (EES) and boring flushing waters.

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The emulsion energy-condensed systems (EECS) used as matrixes of explosive substances represent the reverse emulsions of the high-concentrated aqueous solutions (85...90 wt %) of inorganic salts-oxidizers in hydrocarbon phase (diesel fuel, oils, etc.). Such systems are insensitive to shock, friction, spark and possess the high safety of the behavior, production and transportation. However, at temperatures of application of EES (10...50 °C) the dispersed phase of emulsion represents supersaturated solutions. It creates conditions for salts crystallization, emulsions destructions and, as a result, leads to loss of EECS detonation ability.

Technological and detonation parameters of industrial EECS depend on wide range of factors: composition and concentration limits of dispersed phase (aqueous solution of nitrate salts), nature of dispersion medium, technology of emulsification, etc. However, "the life term" of emulsion is mostly defined by type of the used emulsifier — the surface-active substance (SAS), that provide necessary dispersion and stability of system.

Classical ideas of influence on SAS emulsifying ability of its interphase activity and size of the hydrophilic-lipophilic balance (HLB) of molecule [1] are the cornerstone of the effective emulsifiers choice.

According to Kolganov and Sosnin [2], stable emulsions of the high-concentrated aqueous solutions of nitrate salts in hydrocarbon environments are formed on the basis of three SAS groups:

- esters of fatty acids and polyols (sorbite, sorbitan, glycerin, pentaerythritol, etc.);
- mixes of aminoamides and esters of fatty acids;
- condensation products of polyisobutylene and maleic anhydride.

At the same time, formation of high-disperse emulsion requires decrease in interfacial tension on "dispersed phase / dispersion medium" intersection (γ). According to Kruglyakov [1], the emulsions made by hashing and injection must have γ about 5 mJ/m².

In world practice, maximum application for obtaining EES matrixes has found the sorbitan monooleate (SMO) and products, obtained on the basis of polyisobutylene succinic anhydride (PIBSA) [2]. Mentioned compoundings are not manufactured in Ukraine and imported.

In respect of increasing demands of mining industry in effective EES as an alternative to trinitrotoluene materials the question of effective domestic EECS's development is of the most immediate interest. At this, the development of domestic emulsifiers has additionally to take in account the raw material availability, its cost, and also the manufacturing safety demands and the usage of SAS. Accounting written above, the ethoxylated surfactant based on animal and vegetable fats (zhyrinox and ryfox) have been synthesized in cooperation with LLC "Barva" (Ivano-Frankivsk). Due to change of groups quantity of ethylene oxide it was succeeded to reach the HLB necessary value (3...6) and interphase activity of emulsifier. Selection justification of structure and nature choice of these surfactants, that is the base of "Ukrainit" emulsifier, is given in [3].

Experience of industrial use of "Ukrainit" emulsifier has shown [4] that it provides sufficient stability of emulsion matrixes during obtaining the pourable EECS, used on open mining operations in pits.

However, the technology of emulsion energy-condensed systems application in underground conditions of mines imposes special requirements to emulsions stability. The stick powder emulsion explosive substances must have guaranteed storage life not less than 6 months, and pourable have to stand repeated transfers of emulsions that assumes use of emulsifiers which will provide required stability of system.

The aim of this work is to assess the mechanism of emulsifiers effect like SMO and some PIBSA-derivatives, that are most abundantly used in world practice, and also to develop an effective domestic emulsifier of reverse emulsions.

Materials and Methods. The decreasing of interfacial tension on border "water/diesel fuel" in the presence of 0.5 wt % sorbitan monooleate of various manufacturers has been determined using the semi-dynamic method and using the back stalagmometer. Using the chosen emulsifiers and the dynamic mixer the emulsions have been prepared for which the "life time" τ at temperature of 25 °C, i.e. time of preservation of emulsion stability prior to mass crystallization were defined. Emulsions have

been prepared on the basis of monosolution of ammonium nitrate and diesel fuel of the following structure, wt %: ammonium nitrate — 76.8; water — 15.6; diesel fuel — 6.0; emulsifier — 1.6.

The choice of diesel fuel as hydrocarbon phase is caused by its wide use in emulsion EES structures [4]. The measurement results are given in the Table 1. For comparison the values for solution of oleic acid are given.

Table 1

Interfacial tension “water/diesel fuel” γ in the presence of 0.5 wt % SMO of various producers and “life time” of emulsions τ

| SMO product name | γ , mJ/m ² | τ , days |
|--|------------------------------|-------------------------|
| Jeemul-80 (Jeevika spakchem PVT, Indian) | 14.8 | 2 |
| SP-80 (Experse, SAR) | 13.2 | 2 |
| S 80 (Rugao Wanli Chemical Industry Co, China) | 11.9 | 3 |
| Lonzest SMO EG 215279 (Lonza, USA) | 9.8 | 6 |
| Oleic acid | 33.9 | emulsion is not forming |

All compounds given in table 1 are declared by producers as SMO (SPAN 80) CAS № 1338-43-8. However, as it seen from data of the table, they significantly differ on interphase activity. As ethers of sorbitan and fatty acids are obtained at high temperatures (up to 245 °C) in the presence of complex catalytic systems [5], in industrial product along with sorbitan monooleate can be found di-, three-, tetra-oleates of sorbitan, sorbite, oleic acid and products of their oxidation. The presence of such impurities can significantly change an interphase activity of SMO and, as a result, an emulsion stability.

The Lonzest product has the highest activity of the examined samples. It differs from others by more dark color and possesses smell of burned caramel. The analysis of SMO IR-spectrums, demonstrating maximum (Lonzest) and lowered (SP-80, Experse) interphase activity, has shown that these products have the identical maxima of absorption, corresponding to reference data (“Spectral Database for Organic Compounds SDBS” [6]).

However, in the Lonzest sample the absorption band, corresponding to ester groups ($\nu = 1742 \dots 1744 \text{ cm}^{-1}$) and absorption band of oleic acid ($\nu = 2924 \text{ cm}^{-1}$) have almost identical intensity (ratio 1/1.1).

In spectrum of SP-80, the absorption band corresponding to oleic acid is considerably more expressed ($\nu = 2924 \text{ cm}^{-1}$) – the ratio of absorption intensity of ester groups and oleic acid makes 1/1.75.

As it is known [7], oleic acid has hydrophilic-lipophilic balance of HLB = 1.0 and, unlike SMO (where HLB = 4.3), cannot function as emulsifier of reverse emulsions because of preferential dissolution in hydrocarbon phase and low interphase activity (Table 1).

It should be noted that crystallization resistance of the reverse emulsion of ammonium nitrate high-concentrated aqueous solution in diesel fuel is in direct dependence on interphase activity of emulsifier. The lower value γ , reached during emulsifier introduction, the longer “life term” of emulsion (Table 1). It can be caused by reduction of the emulsion globules linear size that contains ammonium nitrate supersaturated solution NH_4NO_3 . The author [8] has come to similar conclusion at research of nitrate salts crystallization regularity in reverse emulsions on the diesel fuel basis.

Thus, the act mechanism of SMO emulsifier has classical nature, and lies in high interphase activity at the HLB optimum value. The presence in product of impurities of oleic acid, di- and trioleates leads to increase of γ , increase of oil solubility of emulsifier and resistance decrease of emulsions to crystallization.

The emulsifiers based on the PIBSA providing the increased resistance to crystallization of reverse emulsions based on the supersaturated solutions of ammonium nitrate behave a little differently. A number of authors associates it with formation of the high-viscosity structured layers on the

* interfacial tension “water/diesel fuel” 47.5 mJ/m²

interphase boundary [2]. Really, kinematic viscosity of PIBSA is in range 300...400 mm²/s at temperature of 100 °C.

However, the structural and mechanical barrier created by polymeric additive on the interphase boundary first of all prevents the coalescence (enlargement) of emulsion globules, and should not affect the crystallization of dispersed phase.

To prevent the crystallization of ammonium nitrate inside the emulsion globule, the additive must have the clear-cut hydrophilic group providing its penetration into aqueous phase of emulsion. At the same time, the action of hydrophilic group can be various:

1) the hydrophilic part of the SAS polymeric molecule or group which possess high hydration energy (–OH, –O–) can reduce solubility of the nanodimensional crystals nuclei of ammonium nitrate which are formed in supersaturated aqueous solutions i.e. foster crystals growth;

2) the hydrophilic group can possess ability to specific adsorption on the growing crystals, reducing their linear size and, according to Gibbs-Calvin equation (1), increases the extent of solution supersaturation demanded for mass crystallization i.e. slow down crystallization:

$$\ln \frac{C_r}{C_\infty} = \frac{4V_m \sigma}{d \cdot RT}, \quad (1)$$

where C_r and C_∞ — concentration of oversaturated and saturated solutions, respectively;

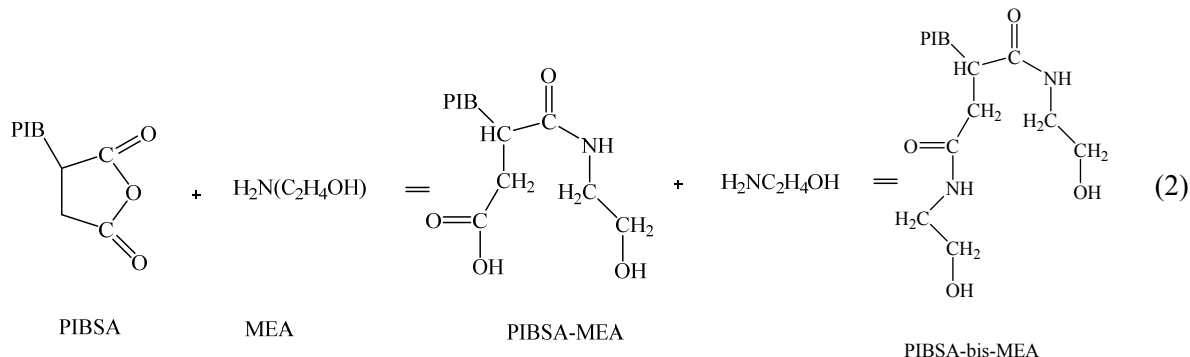
V_m — molar volume;

σ — boundary energy;

d — linear size of crystal.

So, it is shown in [8] that crystallization of potassium nitrate in reverse emulsions, using the derivatives of succinic acid as SAS, happens at supersaturation of solution in 3.5 times higher than in systems with usual nonionic emulsifiers.

According to [9] the maximum resistance of reverse emulsions to crystallization provides the emulsifier received as a result of polyisobutylene succinic anhydride interaction with monoethanolamine (MEA):



Product of interaction of one mole of PIBSA with two moles of MEA (PIBSA-bis-MEA) is known under the Lubrizol trademark (LZX) [10].

As a result of transformations of PIBSA, the hydrophilic-lipophilic balance of emulsifier changes from 2 to 4 that provides increase of its emulsifying ability. At the same time, authors [11] on the basis of IR-Fourier spectroscopy results have established that strong interaction is observed in system “saturated ammonium nitrate solution — LZX”, unlike SMO. However, the nature of such interaction is insufficiently clear.

Authors [8...11] consider that formation of zwitterionic main group LZX provides decrease in energy of system due to Coulomb interaction between ions of ammonium nitrate and lyophilic part of emulsifier molecule.

In our opinion, sharp stopping of ammonium nitrate crystallization in the presence of LZX and PIBSA-MEA additives is caused by specific adsorption of SAS on the growing crystals faces as

a result of the “spectral resonance” phenomenon [12], arising at coincidence at least one strip of dissipation of electromagnetic wave energy of the contacting substances.

The similar assumption has been stated in [13] for the first time based on analysis of the fluctuation theory of E. Lifshits.

So, authors [14] have found strengthening of interaction at coincidence of absorption bands in IR range of adsorbate and adsorbent spectra. Moreover, at increasing the gap between contacting bodies the contribution of spectral range to interaction energy experiences the “bathochromic shift” to microwave and low-frequency band inclusive. At approach of molecule to surface, the spectral range defining interaction changes from zero frequencies and static dielectric permeability (Coulomb electrostatic attraction) to valence band where becomes effective exchange interaction.

The IR-spectra analysis of emulsions based on the ammonium nitrate solutions [10,15] shows that characteristic frequencies of groups $\nu(\text{NH})$ and $\delta(\text{H}_2\text{O})$ changed depending on concentration of salt in the range of $3221 \dots 3233 \text{ cm}^{-1}$ and $1651 \dots 1660 \text{ cm}^{-1}$, respectively. At the same time, for NH_4^+ ion the range of absorption lies in the range of $3030 \dots 3335 \text{ cm}^{-1}$.

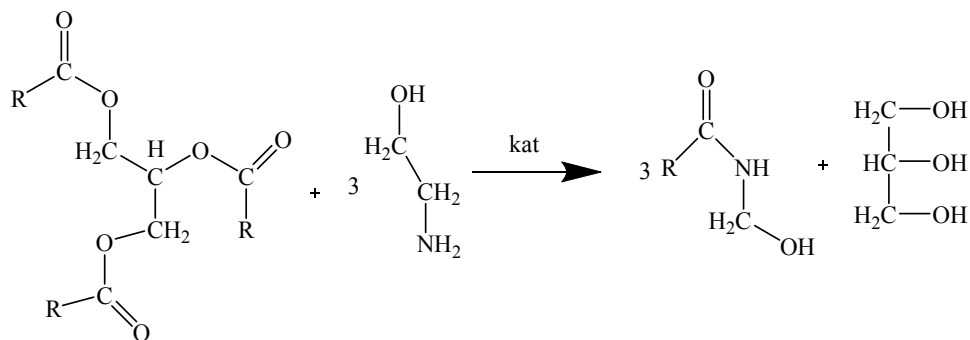
Comparison of PIBSA and PIBSA-MEA IR-spectra [16] shows that release of succinic anhydride at interaction of PIBSA with monoethanol amine is followed by formation of amide group with characteristic frequency of valent fluctuations $\nu(\text{NH}) = 3150 \dots 3300 \text{ cm}^{-1}$ which practically matches the frequency of absorption of NH_4^+ .

Thus, PIBSA-MEA and, respectively, LZX have in IR-spectra coinciding characteristics of frequency with absorption bands of ammonium nitrate crystals nuclei. And the specific interaction is available between them based on the mechanism of “spectral resonance” which leads to stopping of crystallization processes.

The stated observations have formed the basis of domestic emulsifier reverse emulsions development of energy-condensed systems based on ammonium nitrate.

Recently, widespread development met the SAS synthesis of vegetable oils and alkylolamide products processing [17...19]. The monoethanolamida of vegetable oils fatty acids providing highly stable reverse emulsions [19] are of special interest. However, synthesis of these compounds requires either high temperatures [19] or use of solvent (toluene) with its subsequent stripping [18].

In this work, the fatty acids, which are part of sunflower-seed oil, treated to amidation:



Synthesis was carried out at stoichiometric mixture ratio of components at different temperatures ($90 \dots 130 \text{ }^\circ\text{C}$). The one-percentage excess of monoethanol amine was used as the catalyst. The formed glycerin was not separated. Oleic acid was subjected to amidation by monoethanol amine for comparison under the same conditions. The reaction path control kept by change of acid number.

The analysis of the received products IR-spectra has shown (Fig. 1 (curve 1), Table 2) that in case of vegetable oil amidation it is possible to receive mainly the amides of fatty acids (AFA) at temperatures of $90 \dots 100 \text{ }^\circ\text{C}$. Using the oleic acid as raw feedstock in the same temperature mode leads to formation of aminoethers (AET) and AFA mix. Presence of absorption bands in IR spectrum (Fig. 1 (curve 3), Table 2) specifies it. These bands are characteristic for valent fluctuations of $\text{C}=\text{O}$ esters ($\nu = 1742 \text{ cm}^{-1}$), and $\text{C}-\text{O}-\text{C}$ ester group ($\nu = 1185 \text{ cm}^{-1}$). The fixed absorption band of

1062 cm^{-1} corresponds to valent fluctuations of C–O in MEA, because the synthesis is conducted with a little surplus of the MEA.

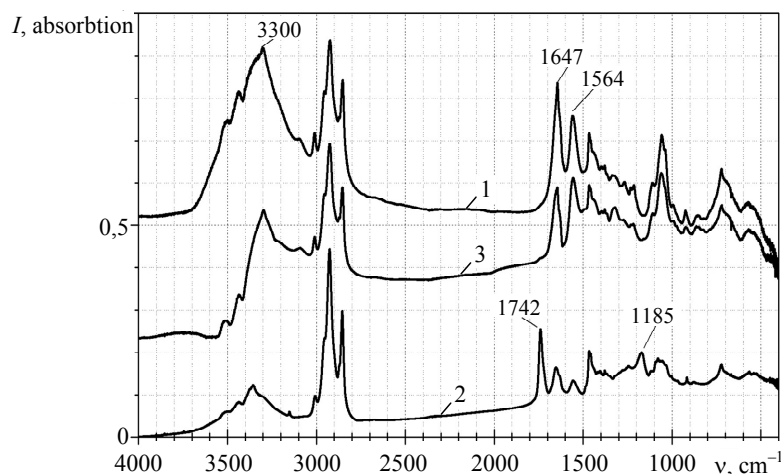


Fig. 1. The IR-spectra of products of amidation: 1 – sunflower-seed oil (laboratory facility); 2 – sunflower-seed oil (industrially); 3 – oleic acid (laboratory facility)

The results of AFA laboratory synthesis based on sunflower-seed oil have been reproduced using industrial equipment at the LLC “Antratsit” (Dnipropetrovsk region). As it seen of Fig. 1, the product obtained in industrial conditions (curve 3), is identical to laboratory one (curve 1).

Table 2

Reference of characteristic absorption bands of sunflower-seed oil amidation products (sample 1) and oleic acid (sample 2)

| Absorption bands frequencies, cm^{-1} | | Structural fragment and fluctuations type |
|--|----------|---|
| Sample 1 | Sample 2 | |
| 3300 | – | $\nu_{\text{as}}(\text{N-H})$ of the associated secondary amides |
| 3014 | 3014 | $\nu(\text{C=C})$ of oleic acid radical |
| 2928 | 2928 | $\nu_{\text{as}}(\text{CH}_2)$ of hydrocarbon radical |
| 2856 | 2856 | $\nu_{\text{s}}(\text{CH}_2), \nu_{\text{s}}(\text{CH}_3)$ of hydrocarbon radical |
| – | 1742 | $\nu(\text{C=O})$ in esters |
| 1647 | 1661 | $\nu(\text{C=O})$ in amides (Amide I band) |
| 1564 | 1567 | $\delta(\text{N-H}), \nu(\text{C-H})$ component frequencies (Amide II band) |
| 1469 | 1469 | $\delta_{\text{as}}(\text{CH}_3)$ of hydrocarbon radical |
| – | 1185 | $\nu_{\text{as}}(\text{C-O-C})$ in esters |
| 725 | 725 | pendular fluctuations $(\text{CH}_2)_n$ of hydrocarbon radical |

It was interesting to compare the emulsifying properties of the received products with the studied emulsifiers. The technique was as follows. The distilled water, tinted by methylene blue, and 20 % solutions of SAS in diesel fuel was poured in measuring cylinder with ground stopper in mass ratio 2:1. The stopper was closed, and the cylinder intensively stirred up within one minute. The cylinder was thermostated at temperature of 25 °C for 24 hours, noting the dynamics of emulsion breakdown. Time of half-decay and percent of emulsion breakdown for 24 hours was considered as indicator of emulsifying ability. The measurement results are given in table 3. The product of PIBSA-MEA was obtained in laboratory using reaction (2) from PIBSA (“Chemical”, China), $M = 1000 \text{ g/mol}$.

As it seen of Table 3, AFA possesses the maximum emulsifying action. It is explained by its high interphase activity at the phases interfacial “water/diesel fuel” ($\gamma = 6,2 \text{ mJ/m}^2$). It is essential, that in

IR spectrum of AFA the absorption band corresponding to valent fluctuations of group -NH- ($\nu = 3300 \text{ cm}^{-1}$) is observed. It is close to characteristic frequencies of ammonium nitrate and NH_4^+ absorption. It allows to assume that AFA will show specific adsorption on ammonium nitrate nucleus, preventing the crystal growth, just as LZX and PIBSA-MEA.

Table 3

Half-decay time ($\tau_{1/2}$) and decay rate (%) of “ $\text{H}_2\text{O}/\text{solution SAS in diesel fuel}$ ” emulsions for 24 hours

| SAS name | $\tau_{1/2}$, hours | Decay rate for 24 hours, % |
|------------------------------------|----------------------|----------------------------|
| PIBSA (“Chemical”, China) | 0.025 | 87.5 |
| PIBSA-MEA | 4.83 | 52.7 |
| Lonzest SMO EG 215279 (Lonza, USA) | > 24 | 39.9 |
| Amide of fatty acids AFA (Ukraine) | > 24 | 1.7 |

Results and Discussion. The main lack of polymeric PIBSA emulsifiers and products based on it is the emulsification complexity (Table 3). Process is fully implemented only in dynamic mixers with high speeds of mixer rotation. This lack complicates use of PIBSA based emulsifiers and its derivatives in high-performance static type mixers because of low speeds of mass transfer.

Unlike PIBSA derivatives, use of AFA emulsifier provides obtaining the stable reverse emulsions in mixing devices of both dynamic and static type. That is proved by multiple experiments in different devices modes.

Based on the received amide of fatty acids the complex emulsifier of reverse emulsions is developed. It has got the name “Amolyn” (TC U 24.6-19436711-003) which has found wide application in the industry.

The mechanism of SMO action as emulsifiers of reverse emulsion consists in high interphase activity at the HLB optimum value. The presence of impurities of oleic acid, di- and trioleates in SMO leads to increasing of interfacial tension, increasing of oil solubility of emulsifier and decreasing of emulsions resistance to crystallization.

Specific interaction on the mechanism of “spectral resonance” is possible between emulsifiers of the PIBSA-MEA, LZX type and crystals nuclei of ammonium nitrate in dispersed phase of emulsion which leads to stopping of emulsion crystallization processes.

Amidation of vegetable oils is implemented by monoethanol amine at the lowered temperatures (90...100 °C), and the method of IR-spectroscopy has proved availability in product mainly of fatty acids amides. The received amides of fatty acids possess good emulsifying ability and, allegedly, show specific adsorption on ammonium nitrate nucleus similar to LZX and PIBSA-MEA.

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