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Designing and characterization of aqueous microemulsions for metalworking operations

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Eco-favorable water-based microemulsion metalworking fluids were designed with application of oleochemical sulfanes, waste glycerol from biodiesel manufacturing and available co-surfactants. Their characterization has shown that use of sulfanes and waste glycerol, in composition with benzoic, salicylic, or boric acids, facilitates preparation of metalworking fluids, improves their stability and tribological characteristics and enables to reduce energy and material spending.

Any kind of metal mechanical alterations are accompanied by the use of metalworking fluids (MF). These fluids are generally multipurpose materials, which provide removal of metal debris from operation zone, cooling of equipment details, prevention of wear and corrosion during the metalworking. Hence, use of MF increases productivity, accuracy and purity of processing and, in many cases, decreases duration and reduces number of manufacturing steps [1, 2].

Regarding to the chemical composition of MF, they are classified as oil-based and water-based fluids [3]. The first class is usually represented by composition of mineral or vegetable oils with various functional additives, in contrast to the second class, which, generally, are emulsions of oil in water or micellar solutions of surfactants and solubilized synthetic materials in them [4-7]. The last is the most perspective for industrial application due to its lesser toxicity and flammability, better cooler properties and material availability [1, 3, 7]. However, aqueous MF (AMF) has poor stability during storage and worse tribological properties that have significantly limited their use [3]. Thus, designing of stable in time AMF with improved qualities is a common and urgent task of modern industry.

Among the most promising AMF are microemulsions. Microemulsions are superdipersed systems, which contain nanoscale droplets in a bulk phase and, in contrast to macroemulsions, have both thermodynamic and kinetic stability, thus, they are steady in time. This stabilization effect is a consequence of extra-low interfacial tension between water and oil phases that usually is provided by the mixture of surfactants. Selection of surfactants, as well as microemulsion composition, is a difficult target and, for the most times, depends from the terms of use and operation type [1].

There were attempts to apply aqueous microemulsion MF in metalworking operations, which shown both their efficiency and technological disadvantages [1-3]. In spite of high colloid stability, cooler ability and resistance to microbial attack, they consist of expensive materials that make them noncompeting in the lubricant market [3]. On the other hand, extreme pressure and anti-friction agents, which are generally included in dispersed phase of microemulsions for improving tribological properties of MF, are toxic and heavily biodegraded that considerably complicats their utilization.

Nowadays, in the field of lubricating materials organic polysulfanes occupied a prominent place. These sulfur-rich compounds are effective tribological additives, which interact with metal surface and prevent wear and scoring during processing. Moreover, in contrast to phosphor- or chlorine-containing analogues, polysulfanes have high degree of biodegradation and do not cause harm to the natural environment [8].

The purpose of proposed work is designing and characterization of eco-favorable microemulsion AMV, with application of sulfur-rich additives and available materials.

Experimental

For preparation of microemulsion AMF we used following components:

− Nonylphenol ethoxylated with 10 moles of ethylene oxide NP-10 (Chemproduct, Ukraine), as a surfactant;

− Triethanolamine TEA (Sigma-Aldrich Chemie GmbH, Germany), as a co-surfactant, corrosion inhibitor and inhibitor of bacteriological processes;

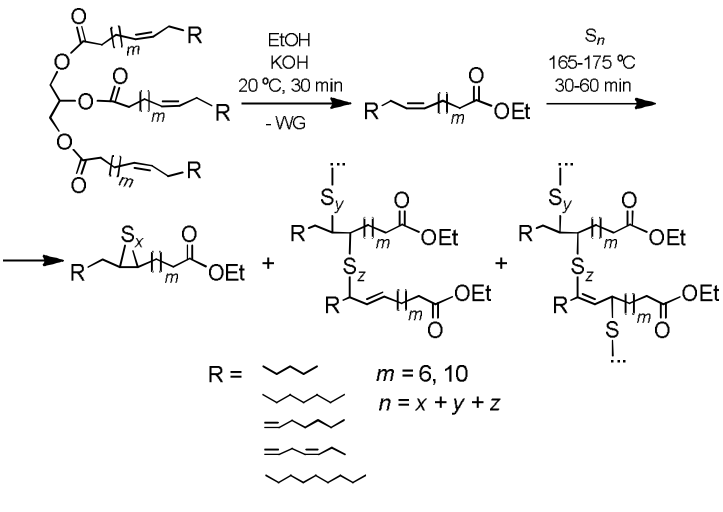
− Benzoic, salicylic, boric acids (Chemlaborreactiv, Ukraine), as a co-surfactant and corrosion inhibitor;

− Sulfur-rich fatty acid ethyl esters with 10, or 29.1 wt.% of S (10S-FAEE and 29.1S-FAEE respectively), as an extreme pressure additive and friction modifier;

− Waste glycerol (WG) from biodiesel manufacturing, as a co-surfactant, stabilizer and cooling agent.

We obtained S-FAEE and WG from unrefined rapeseed oil via procedure described in [9] and depicted in the Scheme.

Microemulsion AMF was achieved by sequential preparation and mixing of solutions or dispersions of the above described components. Firstly, we dissolved 1.0 g of NP-10 in 6.5 g of demineralized water, followed by addi-



Scheme Synthesis of S-FAEE and WG from rapeseed oil

10S-FAEE, Yield ~100%. IR (liquid film, cm^{-1}): 2,923 (ν CH$_3$), 2,853 (ν CH$_2$), 1,736 (ν C=O), 1,461 (ν C–O), 1,372 and 1,301 (δ_s CH$_3$), 1,243 (γ CH$_3$), 1,177 and 1,117 (ν_s C–O), 1,034 (ν_{as} C–O), 967 (δ =CH), 723 (ρ CH$_2$), 550-450 (broad ν S–S). ^{1}H NMR (400 MHz, CDCl$_3$/TMS, ppm): 5.36-5.31 (m, –CH=CH–), 4.11 (q, J = 7.00 Hz, –O–CH_2–CH$_3$), 2.27 (t, J = 7.40 Hz, –O–CH$_2$–CH_3), 2.00-1.94 (m, –CH=CH–CH_2–), 1.68-1.57 (m, –CH_2–CH$_2$–CO–), 1.37–1.20 (m, –CH$_2$–), 0.87 (t, J = 6.40 Hz, –CH$_3$). Found: S 9.99%.

29.1S-FAEE, Yield 97%. IR (liquid film, cm^{-1}): 2,923 (ν CH$_3$), 2,853 (ν CH$_2$), 1,735 (ν C=O), 1,460 (ν C–O), 1,372 and 1,301 (δ_s CH$_3$), 1,243 (γ CH$_3$), 1,177 and 1,117 (ν_s C–O), 1,034 (ν_{as} C–O), 800 (δ =CH), 724 (ρ CH$_2$), 550-450 (broad ν S–S). ^{1}H NMR (400 MHz, CDCl$_3$/TMS, ppm): 6.85 and 6.54 (s, –S–C=CH–), 4.12 (q, J = 7.00 Hz, –O–CH_2–CH$_3$), 3.66-3.50 (m, –S–CH–CH=CH–), 3.00-2.93 and 2.85-2.80 (m, –S–CH–), 2.72 (t, J = 7.20 Hz, –S–CH–CH=CH–), 2.28 (t, J = 7.40 Hz, –O–CH$_2$–CH_3), 1.68-1.57 (m, –CH_2–CH$_2$–CO–), 1.37-1.20 (m, –CH$_2$–), 0.87 (t, J = 6.40 Hz, –CH$_3$). Found: S 29.1%.

tion of 1.4 g of TEA, 0.7 g of 10S-FAEE and 0.4 g of WG. This dispersion was mixed at the room temperature for 2 min, until formation of reddish emulsion. At the second step, four solutions were prepared by dissolving of 0.04 g of benzoic, salicylic, or boric acids in 90 g of distilled water. Finally, we received AWF via agitating of initial emulsion and acid solutions during 2–3 min. Besides, we designed microemulsions with addition of 29.1S-FAEE by the similar technique. However, in this case we decreased mass fraction of NP-10 and sulfurized fatty esters in two times.

For comparison and evaluation of quality of developed microemulsions, we prepared a model AWF, according to the patent [10], using sulfurized lard oil with 16 wt. % of S (16S-LO), as a tribological additive, and neodecanoic acid, as a co-surfactant.

Corrosion on steel in media of designed microemulsion AMW was evaluated via technique given in [11]; the tribological properties, such as weld and critical load (*Pw* and *Pc* appropriately), were tested using four-ball tester as per GOST 9490. All of the other characteristics (density, viscosity, pH) were measured by 25 °C and standard procedures.

Composition and characterization of all designed AMW are summarized in Table.

Results and Discussion

Designed microemuslions (Samples 2-5, Table) are transparent liquids, stable in time even after heating at temperature 80-90 °C. In contrast, the analogue with sulfurized lard oil and neodecanoic acid (Sample 1) is an opaque marcoemulsion that could exist, as a stable heterogeneous system within several days only. This difference in stability is a consequence of composition and nature of the main components. Originally, it depends on the sulfur-rich additive which is obviously a part of dispersed phase, due to high hydrophobicity of 16S-LO. Sulfurized lard oil is a solid substance with a melting point over 35 °C. Therefore, solubilization of sulfurized fat is complicated, demands intensive mechanical stirring (8,000-10,000 rpm) or previous melting that in both cases causes energy loss, surfactants surcharge and formation of unstable emulsion. Replacement of sulfurized fat on liquid S-FAEE, however, excludes this drawback, and enables to easily emulsify it under moderate agitation (2,000–4,000 rpm). On the other hand, microemulsions prepared with S-FAEE have comparable or higher triblogical properties than emulsions based on 16S-LO. This fact, apparently, associates with difficulties of additive chemisorption on metal surface from the bulk phase due to high polarity of water, increased interfacial tension and viscosity. Instead, microemulsions with extra-low interfacial tension and moderate viscosity do not prevent contacting between dispersed phase and metal surface and even support it.

Another factor, which determines AMF efficiency, is a sulfur concentration and chemical structure of sulfur-rich additive. As depicted in the scheme, S-FAEE is a mixture of linear and cyclic organic polysulfanes. However, increase of sulfur content induces growth in length and number of polysulfane chains. In result, these groups facilitate tribochemical interaction and greatly diminish deterioration of metal details. This statement is reflected in values of *Pc*

Table. **Composition and characterization of AMV**

№	Composition, wt.%					Characterization					
	NP-10	TEA	WG	Tribological additive – content	Acid – content	Viscosity, $mm^2 \cdot s^{-1}$	Density, $kg \cdot m^{-3}$	pH	Steel corrosion	*Pc*, N	*Pw*, N
1	10,0	18,0	–	16-LO – 6,8	Neodecanoic – 0,40	52,95	1030	10,2	Non	1098	1235
2	1,0	1,4	0,4	10S-FAEE – 0,7	Benzoic – 0,04	1,18	1041	9,2	Non	1235	1303
3	1,0	1,4	0,4	10S-FAEE – 0,7	Salicylic – 0,04	1,22	1040	9,3	Non	1166	1235
4	1,0	1,4	0,4	10S-FAEE – 0,7	Boric – 0,04	1,47	1044	9,3	Non	1039	1235
5	0,5	1,4	0,4	29.1S-FAEE – 0,35	Salicylic – 0,03	1,31	1048	9,3	Non	1180	1744

and *Pw*. As we can see from the Table, sample 5 prepared with 29.1S-FAEE provides higher anti-wear and extreme pressure characteristics at lower concentration.

Further investigation shows that addition of organic or inorganic acid makes significant impact on dispersions stability and properties. During selection of AMF composition, we established that systems prepared without acids generally are emulsions. Additionally, high basicity of AMF induces sulfur precipitation, because sulfanes are unstable at increased pH [12]. We deduce that acids, or rather their salts, play a role of co-surfactants and pH-regulators, which decrease surface tension, enable microemulsion formation, prevent sulfanes degradation and appearance of free sulfur. On the other hand, it was established that addition of various acids differently influences on tribological properties. Among investigated samples benzoic acid is the most effective due to higher values of *Pc* and *Pw* of resulted microemulsion AMF.

Apart from the described components, we'd like to mention a positive impact of WG on microemulsion formation and stability. Glycerol itself is a cooler agent and stabilizer of different dispersed systems, especially gels [13]. WG from fatty acid esters manufacturing, despite glycerol, also includes contaminants of fatty acid salts and acyl glycerides, which provide emulsifying and stabilizing properties. Hence, WG is a complex additive, which improves conditions of microemulsion preparation and prolongs it storage time.

In summary, we want briefly outline industrial importance of the designed composition. Ethoxylated nonylphenol and TEA are widely used inexpensive components for achieving stable non-corrosive aqueous dispersed systems for metalworking operations [10]. Application of benzoic, salicylic or boric acids that are available in Ukrainian market instead of deficient neodecanoic acid, not only is economically advantageous, but also enables to achieve stable microemulsion AMF with improved properties. Substitution of sulfurized fat on liquid sulfur-rich fatty acid ethyl esters facilitates preparation of microemulsion AMF, makes it more energy-, resource-efficient and provides resulted product with increased tribological characteristics. Finally, addition of WG from biodiesel manufacturing, as emulsifier and stabilizer of microemulsion AMF, is a new avenue of use and utilization of one of the large-scale by-products that is certainly a great movement towards non-waste production of fuels and lubricants and sustainability in the 21st century.

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Розроблення та характеристика водних мікроемульсійних мастильно-холодильних рідин для металообробки

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Із застосуванням олеохімічних сульфанів, відходів гліцерину від виробництва біодизельного палива та доступних співПАР розроблено екологічно сприятливі мікроемульсійні мастильно-холодильні рідини на водній основі. Дослідженням їх властивостей показано, що використання сульфанів у поєднанні з технічним гліцерином, бензойною, саліциловою чи борною кислотами полегшує процес приготування МХР та підвищує їх стійкість і трибологічні характеристики за зниження енергетичних і матеріальних витрат.

Разработка и характеристика водных микроэмульсионных смазочно-охлаждающих жидкостей для металлообработки

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С применением олеохимических сульфанов, отходов глицерина от производства биодизельного топлива и доступных соПАВ разработаны экологически благоприятные микроэмульсионные смазочно-охлаждающие жидкости на водной основе. Исследованием их свойств показано, что использование сульфанов в сочетании с техническим глицерином, бензойной, салициловой или борной кислотами облегчает процесс приготовления СОЖ и повышает их устойчивость и трибологические характеристики при снижении энергетических и материальных затрат.