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TECHNOLOGY OF METALWORKING EMULSIONS SPLITTING BY INA-METHOD

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ABSTRACT
Metalworking emulsions, during service life, should be stable systems of mineral oil, water, emulsifier and other additives. After working time, used emulsions should not be drained into sewage systems because of harmful compounds' content. Wasted emulsions can contain up to 10 % of mineral oil. According to very strong water legislative, wasted emulsions should be cleaned. The separation of mineral oil and surfactants from metalworking emulsions creates certain difficulties since emulsions are stable systems and technical equipment for used emulsions-waste treatment needs additional expenses. Emulsion separation to water and oil phase is known as emulsion splitting. In this work we used INA-method for metalworking emulsion's splitting. INA-Method for wasted emulsions splitting is physical-chemical method that uses organically compound for reaction. Compared to other methods, the advantages of splitting with INA-method is that no need for expensive treatment facilities, no need for heating and high energy consumption. There is no sedimentation, pH-value of water phase is neutral and oil separation is excellent - even 99.99 %.
Here is shown examination of micro and milky emulsions' splitting. The results show that these emulsions can be splitted by this technology.
Keywords: metalworking emulsions, disposal of waste emulsions, emulsions' splitting, wastewater

1. INTRODUCTION
Metalworking emulsions are stable systems of constituent components as are mineral oil, corrosion inhibitors, fatty oils and acids, surface active substances, antifoaming, biostatic agents and other compounds in water. Functions of metalworking emulsions are cooling, lubrication, clearing working zone, and corrosion protection through long period. During application emulsions are being contaminated with metal particles, grinding materials, "tramp oil" (oils from slide-way, hydraulic oils), inorganic salts, oxidation products, soaps, organic contamination, microorganisms, etc. [1]. Those contaminants influence on emulsion working life and cause that emulsion loose its functions. At that point contaminated emulsion should be changed with new emulsion for proper metalworking process operation. Contaminated or used emulsion now becomes waste emulsion that can not be drained into sewage system without cleaning because of high quantity organic and inorganic component that are harmful for the environment.

2. METHODS FOR DISPOSAL OF USED METALWORKING EMULSIONS
There are many methods for used emulsion clearing in purpose waste reduction. Primary treatment methods are removing free floating oil and mechanical particles by skimmers, separators, filtration and similar devices. Secondary treatment methods involve separation of emulsified oil from the used emulsion or separation water from oily components. Tertiary treatments include improvements of phase's quality by reverse osmosis, nanofiltration, carbon adsorption, electrofiltration, etc.

In compliance with the requirements of relevant laws, waste emulsions have to be managed properly [2]. Metalworking fluid users have several options in disposal methods. The most expensive method is to have the fluid hauled away for treatment by a waste treatment company. Treating the waste metalworking fluid prior to disposal to the sewers is the most common choice. The sludge from the treatment is the volume, which must be disposed, not the total coolant volume. Many plants have treatment facilities that are set up to handle emulsions or waste waters [3]. After pre-treatment the emulsion itself has to be split into water and oil phase. A whole series of methods has been developed, whereas Table 1 shows the ones most frequently encountered in practice.

Table 1. Comparative Properties of some Emulsion Splitting Methods

PROPERTIES	MEMBRANE FILTRATION	EVAPORATION	ACID SPLITTING	ORGANIC SPLITTING
Investment costs	Medium	High	Low	Low
Operating costs	Medium	Medium to high	Low	Low
COD reduction	Low	High	High	High
Oil reduction	High	High	High	High
WATER QUALITY	High emulsifier content	High purity	Highly acid	Pure
Re-use	Possible	Possible	No	Possible
OIL QUALITY	High water content	Low water content	Highly acid	Low water content
Re-use	Possible	Possible	Partially	Possible

Based on that comparison it may be observed that organic splitting has a certain advantage over other splitting methods. The quality and management of secondary waste matters influence the choice of the most suitable method also [4]. The purpose of all the methods is considering the possibility of re-use, either for the same purpose or as a useful feed [5]. After emulsion splitting oil phase cannot be reused as emulsifying metalworking fluid because equilibrium stability lost. It may be refined or applied usefully for some other purpose or as a fuel. It should be pointed out that here chlorine–containing oils and emulsions is under high risk or regulation. That means that attention must be paid when selecting lubricants, whereas this also renders the management of such oil phases more complicated.

Water phase after emulsion splitting depending on its purity and in according to local lows can be drained into sewage systems or need to be cleaned by tertiary methods [6]. There are electro-chemical treatments for metal ions' removal, biological treatment facilities for organically substances decreasing and others. The water can be cleaned through a joint treatment of all wastewater at a given plant. The limits are very rigorous for discharging directly into waters [7].

3. EXPERIMENTAL
4.

3.1. Test emulsions

In order to perform the splitting procedure we have treated used metalworking emulsions collected from two metalworking workshops. Those are two types of emulsions: E1 conventional and E2 semisynthetic produced from paraffinic mineral oil and with components less harmful to the human and environment. Concentrate of milky emulsion E1 contains 70 % mineral oil, alkyl succinic acid derivative, polyglycol ether and natural carboxylic acid. Semisynthetic emulsion E2 concentrate contains 30 % oil, fatty carboxylic acids mixture, ether carboxylate, etoxylated fatty alcohols and forms semitransparent-yellowish microemulsion. Some characteristics of used emulsions are presented in Table 2. Emulsions for testing are free from floating oils, metal particles, and others mechanical impurities what is achieved by laboratory method of sampling.

Table 2. Properties of metalworking waste emulsions for testing

PROPERTIES	EMULSION 1	EMULSION 2
Appearance of waste emulsion	Milky, dark beige	Semimilky, grey-yellowish
Concentration, refractometer , %	3.5	3
pH-value, ASTM D 1287	8.9	8.8
Metalworking operation materials	Turning, steel, brass, aluminium	Grinding, milling, steel, cast iron
Working life, months	3	6

3.2. Test methods for water and emulsion examination

The properties of emulsions and water phases are determined by standard test methods: for water and wastewater examination [8], chemical oxygen demand (COD) and liophilic compounds content by DIN 38409 and others by standard methods DIN and ASTM [9]. Metal contents are measured by X-ray methods. Concentration of emulsions is measured by optical refractometer.

3.3. INA-Method for waste emulsion splitting

Waste emulsions we treated by INA-Method for emulsions' splitting. INA-Method is based on application of Deemulzin, the organically polyelectrolyte. Deemulzin added at the determined concentration into emulsion disorders emulsion's stability balance and forming oil and water phases. Mechanisms of emulsion splitting presented at Figure 1.

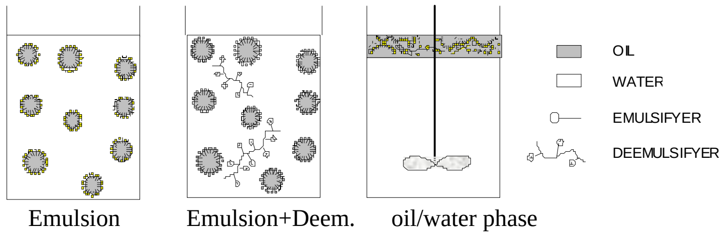

Figure 1. Mechanisms of emulsion splitting by INA-Deemulzin

Dosage quantity of Deemulzin needs to be determined on small samples of emulsion that should be treated. The quantity of 50 ml of the emulsion is prepared in several vessels and certain quantity of Deemulzin is added. The mixtures are mixed at moderate speed for 10 minutes and the results could be seen right away or after certain time. The quality being monitored and evaluated is clearness of water layer and separated oil phase and is declared by the grades 0 – 4, Table 3. If the concentration is well chosen, the splitting of emulsion starts immediately and it is the advantage of this method.

Table 3. Emulsion splitting grades

GRADE SPILLITING	EMULSION CONDITION	
0	an-separated	unchanged emulsion
1	slightly separated	still emulsion
2	separation good	water phase still obvious turbid
3	separation good	water phase low turbid
4	separation complete	water phase clear

5. RESULTS AND DISCUSION

On Figure 2 is presented determination of equilibrium quantities or dosage of Deemulzin for emulsions splitting. For E1 emulsion splitting dosage between 0.16 and 0.22 % is optimal. Emulsion separation started at lower and also at higher concentration but it is not compete. We obtained that for splitting E2 emulsion Deemulzin dosage is from 0.46 to 0.52 %. For E2 emulsion splitting bigger dosage is needed than for E1. That is the result of F2 formulation's higher stability because of higher surfactants content. After determined optimal concentration of Deemulzin at small emulsion samples it is prepared needed quantity for emulsion in reaction container. This blend mixed mechanically during one hour. After 24 hours water phase is analyzed. Efficiency of splitting emulsions we estimate through water phase (WP) quality. We measured chemical oxygen demand (COD), pH value, content of liophilic compounds, mineral oil and metals. The results are presented in Table 4. In comparison to start values in used emulsions' efficiency of decrease COD is over 90 %. Decrease of mineral oil content in water phase is over 99 %. Mineral oil content in both water phases is lower than 1 mg/L what is lower than maximum allowed concentration. Value of pH stays in neutral range. Water phases are nearly clear and can be discharged into wastewater system. It may be observed that metal content in water phase is dependent on machined materials types. We obtained that there are same metal quantities but the values are under maximum allowed concentrations by local water's lows. Oil phases can be disposed by burning without additional costs because fluids are new types of metalworking fluid, chlorine free. From the basic formulations oil component is mineral paraffinic type, with low aromatic hydrocarbons content. Emulsifiers are derivatives of natural carboxylic acids and do not contain aromatic ring. Test metalworking fluids are free from chlorine, and others halogenated hydrocarbons, heavy metals, PCB (polychlorinated biphenyl), and other harmful compounds.

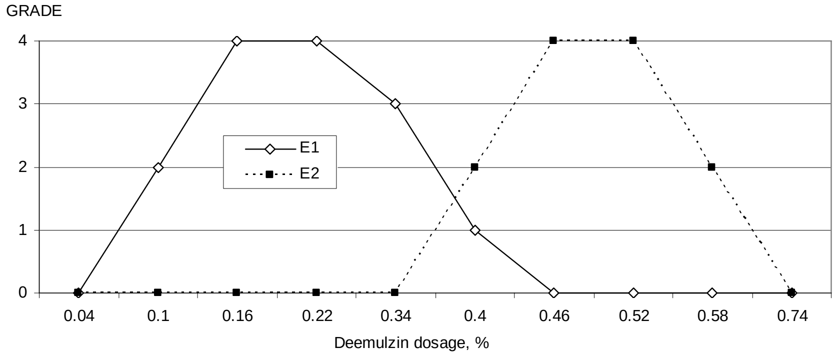

Figure 2. Results of optimum Deemulzin dosage determination for E1 and E2 splitting

Table 4. Examination results of emulsions (E) and water phases (WP) after splitting

PROPERTIES	E1	WP1	DECREASE	E2	WP2	DECREASE
Deemulzin dosage		0.2 %	-		0.46 %	-
Appearance and colour	dark-beige	clear, colourless	-	grey-yellowish	clear, colourless	-
pH-Value	8.9	8.4	0.5	8.8	8.5	0.3
COD, mg O_2/L	54 100	4 130	92.36 %	158 340	5 795	96.34 %
Liophilic, mg/L		15.2	-	-	17.6	-
Mineral oil, mg/L	15 540	0.09	99.99%	4 343	0.1	99.998 %
Fe content, mg/L Al content, mg/L Ni content, mg/L Cu content, mg/L		3.7 3.0 0.1 1.9			11.3 0.0 0.2 0.0	

6. CONCLUSION

After working life waste emulsion have to be splitted because of contaminants and mineral oil content in order to waste minimization. INA-Method has been successfully applied for the conventional E1 and semisynthetic E2 emulsions' splitting. Good quality of water phases after splitting is obtained. Efficiency of oil separation from both emulsions is over 99 % and decrease of COD is over 90 %. Metal contents in water phases depend on metalworking operation. Water phases are further treated by treatment of a given plant's wastewater in compliance with local lows. Oil phases can be mixed into fuel oil because not containing harmful compounds do to new concept of emulsions production and also using INA-Method-splitting with neutral technology.

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