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POSSIBILITY SOLUTIONS FOR DISPOSAL OF WASTED METALWORKING

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Abstract. Emulsions used should be treated in the sense of minimising waste. The treatment can be carried out in the same place where the waste is produced or the waste could be delivered to the service companies. In this paper the comparative results of delamination of emulsion waste with physical and chemical methods are presented, with particular emphasis on the breaking from ecological polyelectrolyte. The results of fission tests in this way show excellent separation in mineral oil, good quality of the water phase and oil phase, which can be used as an alternative fuel.

Keywords: wasted metalworking emulsions, physicochemical treatment of used emulsions, water pollution and protection.

AIMS AND BACKGROUND

Used emulsions after machining process of metal become waste. Waste emulsions contain a high concentration of the compounds that are considered to be polluting the environment[1]. In addition to the constituent components such as a mineral oil, a surface active substance, EP additives based on chlorine compounds, sulphur, boron, phosphorus and the like worn emulsion may contain metal particles, the lubricant from the sliding surfaces, inorganic salts, compounds that are developed during processing as well as various organic pollutants. Some countries have regulations in the area of emulsions and among them the most significant impact has a limit of oil and grease in the effluents of 100 mg/l according the regulations of the composition of wastewater discharged into the public sewerage system[2].

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The development trend of world law is in the direction of reducing the limits of pollution so that in some countries it is 10 mg/l. Therefore, the emulsion must be purified before discharge[3].

When the emulsion is added in the watercourse, it is not noticed immediately that mineral oil was discharged because the emulsion is a fine dispersion composition of the oil in water. However, the action of microorganisms on the emulsifier in the emulsion mineral oil begins to stand out on the surface of water. The rapid increase in the consumption of oxygen present in the microbiological degradation of large amounts of organic matter significantly changes the life of natural waters[4]. In addition to biodegradation, it leads to the evaporation of harmful compounds and creation of aerosols. The action of the sun creates conditions for the photo-oxidation of the oil to tar deposited on the bottom and banks of rivers, lakes or the sea and it is very difficult to be removed[5]. The separated oil stains may be at a considerable distance from the city to engage so that it is difficult to find the culprit irresponsible. Mineral oil discharged into watercourses can cause many unpleasant effects such as covering the surface of water which prevents the natural aeration of the water and causing a risk of fire, toxic affect some life forms in the water, thus making the water and the fish tasteless.

Particular attention should be paid to groundwater contamination with mineral oil because it provides water for drinking disgusting taste even in the dilution of $1:10^6$ and remained for several decades degradable by microorganisms. Due to the difficult biodegradability of mineral oil, it is increasingly being replaced by synthetic esters which are believed to be biodegradable[6]. In this case, it will reduce the need for separation of emulsions but not completely eliminated because the emulsion is discharged into the fresh state then polluted.

In the industrial plants the problem with waste emulsion disposal is solved in two ways: by taking into specialised company engaged in processing effluent emulsion or building its own plants[7].

EMULSION SEPARATION MECHANISM

Emulsions for cooling and lubrication in metal processing are those compositions dispersing oil in the water and are electronically regulated by the action of surface-active substances – emulsifiers. They can destabilise an electrical disturbance force outwards. During the application, layering of the emulsions occurs by changing the pH, changing the composition of the emulsion due to microbial degradation, the action of metal particles entering the oil with sliding surfaces, etc. Search destabilised emulsion can be made by applying active substances, high temperatures or filter micron pore size.

There are three types of emulsion instability and these are: the creation of 'milky layer', inversion and demulsifying. All three types of instabilities are, each for itself, a state of the emulsion composition. Often, however, they are connected to one another and to complete the emulsion demulsifying passes through all three stages[7].

At the beginning the stabilisation of the emulsion was made by coagulation into larger particles of oil. This process is still reversible. In the second instance, it leads to the formation of even greater deposition of particles or, which are under the influence of gravitational forces allocated to the surface. It is the creation of the so-called milky layer or scum where actually there are two types of emulsions. The top layer is concentrated emulsions, with a larger proportion of the oil, while the rest – of the poorer mineral oil. After creating a thicker layer process runs until the end – the separation of emulsions and there are clear water and oil layers[7].

One of the important characteristics of the emulsion instability is inversion when emulsion, oil-in-water O/W is transferred to the second form water-in-oil emulsion W/O. In the emulsion W/O, oil dispersant and water dispersion phase and by the look this is much denser than the classical emulsion O/W. In addition to the aforementioned causes of instability, inversion can occur when excessive mixing due to the random motion of molecules breaks monomolecular layer and comes up with regrouping. In the emulsion O/W oil particles are combined passing through the so-called intermediate step, when it comes to the appearance of the water remains 'trapped' in the oil and get the type emulsion W/O.

Knowledge of the mechanism of the emulsion instability is very important because from it can be inferred about the possibilities of separation of waste emulsion.

PROCESSING METHODS FOR WASTE EMULSION

It has been developed a variety of different methods for processing the waste emulsion[8,9]. The spent emulsion can be made by primary, secondary and tertiary methods.

The primary methods include mechanical separation of floating oil and grease with sawdust or other particles collected during processing. For this purpose can be used different separators and filters[10].

Secondary treatment procedures include all actions that achieve separation of oil from the aqueous phase. The procedure is named a separation of the emulsion. Separation can be achieved by physical and chemical (separation by acids, emulsifiers, adsorption) or thermal mechanical processing methods (evaporation, extraction, ultra-filtration)[11,12]. The best oily layer from the surface can be easily removed with the so-called skimmers.

The physicochemical separation methods do not require expensive installations and are suitable for smaller volumes of emulsion or for a small business or workshop[13]. From the physical and chemical separation procedures of a emulsion can be separated into two: inorganic electrolytes (acid and multivalent metal salts) or organic electrolytes (high-molecular-electrolytes de-emulsifiers).

The mechanism of action of the electrolyte consists in the neutralisation or destruction of emulsifier. Separation of inorganic electrolytes achieves good separation of oil but it has more disadvantages. These are: the need of a large amount of electrolyte, a secondary precipitation occurs and the pH-value of the aqueous phase is very low, which requires even more additional neutralisation. Separation of the organic electrolyte has a considerable advantage in relation to the separation of inorganic electrolytes, such as with an excellent separation of oil, a small amount required of the electrolyte, the pH-value of the aqueous phase is neutral and does not require additional neutralisation and no subsequent precipitation of the salts[14].

After the separation of the individual phases of the emulsion it must be further processed by the tertiary methods. The oily layer can be removed by any method of burning: as an alternative fuel in existing power plants or in specially designed incinerator[15]. The aqueous layer is desirable, if necessary, to be processed by electrochemical or biological processes[16].

The selection of processing procedure of the emulsion depends on the composition of the emulsion (emulsifier, mineral oil, etc.), the level of impurities, the amount of emulsion, investment costs, costs of the proceedings (chemicals, energy) and on the removal of secondary waste materials[17].

EXPERIMENTAL

Emulsion separation was done using two physicochemical methods:

- Separation with acid – the used electrolyte was 30% sulphuric acid. The emulsion with 30% acid was heated at a temperature of 100°C for a period of 2 h to complete separation of the oil and aqueous phases.
- Separation procedures of emulsion by de-emulsifiers[18], i.e separation of a 2% aqueous solution of organic polyelectrolyte. This method of separation comprises the use of de-emulsifier emulsion of cationic type since the emulsion for metalworking is stabilised mainly by anionic and nonionic emulsifiers[19]. Formed thereby a salt without an electric charge is collected in the larger agglomerates. The scheme of action with de-emulsifier is given in Fig. 1.

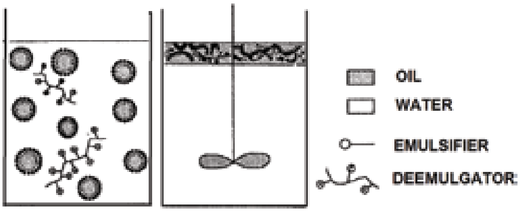

Fig. 1. Scheme of action with de-emulsifier

Working emulsions. To test the separation process three different species emulsions were used E1, E2 and E3, the label W refers to used emulsion whose values are compared with the corresponding fresh emulsions (Table 1).

Table 1. Characteristics of test emulsions

Emulsion	Emulsion appearance	Application	Time of work	pH value	Coverage of de-emulsifiers
E 1	opalescent	–	0	9.2	1.12
E 1W	blue and green floating oil	copper	7 month	9.12	0.3
E 2	transparent		0	9	0.66
E 2W	lactic floating oil	steel, aluminum copper	1 month	9.13	0.84
E 3	transparent	–	0	9	0.56
E 3W	yellow-lactic floating oil	steel	3 month	8.45	0.85

Properties of tested emulsions. The properties of the tested emulsions were determined by standard methods for testing cooling and lubrication liquids in metal machining. The quality of water layers was determined by testing the water and it has a label: VSK – aqueous layer after separation with acid, VSD – aqueous layer after separation with de-emulsifiers.

The calorific value of the oil layer was determined by ASTM D 2382 method. The metal content was determined by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

The emulsion for aluminum machining E1 is made up of mineral oil, natural oil, synthetic esters, boric acid derivatives and emulsifiers. To separate this emulsion was required relatively high concentration of de-emulsifier because the emulsion is very stable. Waste emulsion E 1W has been in operation for 7 months. Due to the degradation of the quality of the emulsion it is necessary smaller amount of de-emulsifier for separation. Performance of separation is shown in Table 2.

Table 2. Test results of the emulsion E 1W and water phases after separation

Properties	Emulsion 5%	VSK	VSK efficiency (%)	VSD	VSD efficiency (%)
COD (mg O_2/l)	142890	7260	95	9190	93.60
BOD_5 (mg O_2/l)	31350	460	98.6	270	99.10
Mineral oil (mg/l)	3942	1.25	99.97	0.42	99.99
Detergents					
anionic (mg TBS/l)	0.61	3.70	60.4	1.71	27.90
nonionic (mg Tx/l)	742.2	16.70	97.8	17.61	97.70

*COD – Chemical oxygen demand; BOD_5 – Biochemical oxygen demand; TBS – tetrabutyldimethylsilyl.

The emulsion E 2W is composed, in addition to water, of mineral oils, natural oils, amine, boron acid derivative and emulsifier. The emulsion was applied for cooling and lubrication during machining of ferrous materials. Test results of the emulsion E 2W and water phase after separation are shown in Table 3.

Table 3. Test results of the emulsion E 2W and water phase after separation

Properties	Emulsion 5%	VSK	VSK efficiency (%)	VSD	VSD efficiency (%)
COD (mg O_2/l)	77122	13500	82.5	16400	79.1
BOD_5 (mg O_2/l)	27772	1115	96.0	2620	90.6
Mineral oil (mg/l)	20460	0.92	99.996	0.93	99.996
Detergents					
anionic (mg TBS/l)	6.486	1.44	77.8	3.74	42.3
nonionic (mg Tx/l)	839	2.72	99.7	5.23	99.4

Also the separation of emulsions that are less harmful to the environment and humans, among them are emulsions without dye-ethanolamine, without chlorine compounds and without compounds containing aromatic nucleus. Used emulsion E 3W was used with machines for steel screws based on three months period. Due to the large influx of oil from the sliding surface it has a higher content of mineral oil which reduces its lifetime. The result of the emulsion separation is shown in Table 4.

Table 4. Test results of the emulsion E 3W and water phase after separation

Properties	Emulsion 5%	VSK	VSK efficiency (%)	VSD	VSD efficiency (%)
COD (mg O_2/l)	65730	6150	90.7	6990	89.4
BOD_5 (mg O_2/l)	19000	433	97.7	3400	82.11
Mineral oil (mg/l)	16200	25.92	99.94	29.96	99.9
Detergents					
anionic (mg TBS/l)	62.35	0.66	99.0	1.91	97.0
nonionic (mg Tx/l)	551.5	2.68	99.5	7.06	98.7

Table 5 shows the results of the mixture of oil layers with fuel oil. Mixtures are well prepared by ultrasonic mixer and remained stable for more than 6 h. According to the calorific value of oil layers obtained it can be used as an alternative fuel.

Table 5. Results burning of testing of the oil phase after separation of the emulsion

Mixture	Appearance of the mixture	Content S (%)	Water content (%)	Calorific value (MJ/kg)
Fuel oil	clear, red-brown	0.451	0.00	40–41
+14% oil layer after separation E 1W	gray, emulsified	0.356	4.65	38.53
+14% oil layer after separation E 2W	clear, orange-brown	0.426	0.53	41.19
+14% oil layer after separation E 3W	blurry brown	0.412	1.32	40.47

CONCLUSIONS

The separation of the emulsion by physicochemical methods, acid and de-emulsifier was successfully implemented. The resulting layers of water and oil are completely separated.

The concentration of de-emulsifier for each emulsion is different and depends on the type of emulsion: milk, semi-synthetic, bio stable, emulsion concentration, age, or the contamination of the emulsion.

The quality of water layers appraisement of COD, BOD, oil content and detergents are similar. Chemical and biological oxygen consumption was reduced by more than 80 or 90%. It was achieved by reducing the oil content of more than 99%. Content of detergents is decreased. The values were lower than the limit values of the Ordinance on the composition of the wastewater discharged into the public sewer system. Taking into account the content of oils and fats to book a mineral oil, water layers can be discharged into drains. However, after separation of the aqueous layer which has a pH acid value of 1, should be further processed in the neutralisation.

After a long time of use, some emulsions may contain higher amounts of metals than allowed. Such an aqueous phase, prior to discharge into drains, should be further processed by a suitable method for removing metal containing compounds. The oily layer after separation with worn emulsion metalworking may be useful to apply as an alternative fuel and also in the existing energy or production facilities.

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REFERENCES

1. L. J. PEDISIC, R. MANDAKOVIC, I. LEGISA, D. IVANCEVIC: Splitting of Worn Emulsions for Metal Processing with Reference to the Type of Emulsifier. In: Proceedings of the First Symposium of the Croatian Society for Tensides, Rovinj, Svibanj, 1993 (in Croatian).
2. Ordinance on the Composition of Wastewater Entering the Public Sewage System. Profesional Journal**,** 84 (1977) (in Croatian).
3. N. KOCH, D. WIEDEL: Splitting of Emulsions – Way of Protecltion of the Environment. Tribology and Technology – **35**, 6 (1988)(in Croatian)..
4. P. KOVAC, D. JESIC, S. KIRIN, B. SAVKOVIC: Water Polution Caused by Oils from Cleaners and Segreasers. Contr Agr Eng, **41** (1), 17 (2015).
5. P. KOVAC, D. JESIC, N. GVOZDENOVIC, V. GOSTIMIROVIC, V. PUCOVSKI: Investigation of Tribological Characteristics of Different Oils Used in Tribomehanical System. In: Proceedings of SERBIATRIB 2015, Belgrade, 2015.
6. E. K. MATHIESEN: New Water Dilutable Esters for Biodegradable Metalworking Fluids. In: Proceedings of the 8th Intemationales Kolloquium, Esllingen, 1992.
7. M. L. BRODEN, S. J. ALLENSON: Reverse Emulsion Breaking Method. C.A. **115**, 16 (1991).
8. LJ. PEDISIC, D. IVANCEVIC: Water Quality after Splitting Endured Emulsion with Physicochemical Procedures. In: Proceedings of Symposium 'MAZIVA 93', **34** (3), 193 (1995) (in Serbian).
9. D. WEIDEL: Waterbased Cooling and Lubrication Fluids Removal. In: Proceedings of Symposium 'Jugoma '90', Opatija, 1990.
10. L. DORCIC: Basics of Oil Pollution Cleaning, SKTH. Chemistry and Industry, Zagreb, (1985) (in Serbian).
11. B. SPEI, K. A. HENKEL**:** Processing of Oil/water Emulsions with Organic Fission Products – New Emulsion Splitting Technologies. In: Proceedings of the 9th Intemationales Kolloquium, Esllingen, 1994 (in German).
12. A. KIECHLE: Disposal of Lubricants from the Point of View of the Consumer, Mercedes Benz AG. In: Proceedings of the 9th Internationales Kolloquium, Esllingen, 1994 (in German).
13. B. LEHMAN, U. LITZINGER, A. G. BAYER: From the Cooling Lubricant to the Wastewater Process for the Disposal of Metalworking Fluids. In: Proceedings of the 9th Intemationales Kolloquium, Esllingen, 1994 (in German).
14. S. NAPIER, K. RICH: Waste Treatability of Aqueous – Based Synthetic Metalworking Fluids. Lubr Eng, **41** (6), (1985).
15. M. STOJILJKOVICH, D. GOLUBOVICH, D. JESIC: Ecotribology Aspects in the Tribological Systems. EXPRES 2014, Subotica, 2014.
16. K. HUNDT, W. FABIG, T. F. BUENEMAN: Biodegradability of Synthetic Lubricants' Components. Tribologie und Schmierungstechnik, 2, (1993) (in German).
17. K. H. HEIER, A. G. HOECHST: Economy, Ecology and Safety at Work-Factors in the Use and Disposal of Water-miscible Metalworking Fluids. In: Proceedings of Symposium 'MAZIVA 95', Poree, 1995.
18. L. J. PEDISHICH: Methods of Splitting a Worn Emulsion for Metalworking by De-emulsification. Zagreb, 1994 (in Croatian).
19. J. C. CHILDERS, S. HUANG, M. ROMBA: Metalworking Fluid Additives for Waste Minimization. Lubr Eng, **46** (6), (1990).
20. P. KOVAC: Theory of Metal Processing. FTN Izdavashtvo, 2014 (in Serbian).
21. B. IVKOVIC**:** Liquids for Cooling and Lubricating in Metal Cutting. JDT, Kragujevac, 2011, p. 125 (in Serbian).

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