Ljiljana Pedišić, Irena Polenus

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METHOD OF METALWORKING EMULSION SPLITTING AS IMPROVEMENT OF TOTAL FLUID MANAGEMENT

Abstract

Selection of a suitable metalworking fluid is not possible without systematically lifecycle considerations that include material production phase, application phase and disposal phase. Metalworking emulsions are used for cooling and lubricating at metalworking operations like rolling, drawing, boring, grinding, milling, sawing, etc. Emulsions are prepared mixing emulsifying concentrate with water at metalworking plant production. Concentrates must be properly optimised in order to obtain the required emulsion working properties. They consist of base oils, emulsifiers, corrosion inhibitors, lubricating additives, biocides, defoamers and other components. During application into working emulsions inflow "tramp" oil, micro-organisms and other contaminants that shorten its working life. Used emulsions can contain up to 10 % of mineral oil, so they should be treated in sense of the separation of oil and other impurities before they are disposed in sewage system. The separation of oil from metalworking emulsions is difficult because they should be stable during whole time of application. Used emulsion can be treated at the site on technical equipment or can transport to the certificated company. The paper shows examination results of used emulsions physical chemical properties and splitting process concerning local and state laws.

Key words: *metalworking fluids; life cycle assessment of metalworking fluid; metalworking emulsions; emulsion splitting; water quality*

1. Introduction

Functions of metalworking emulsions are cooling, lubrication, clearing working zone, and corrosion protection through long period of application [1]. Lifecycle of metalworking fluid include material production phase through selection of optimal components, application phase as maintenance support and disposal phase or splitting process that is presented on Figure 1 [2]. Metalworking emulsions are stable systems of constituent components as are mineral oils, corrosion inhibitors, fatty oils and acids, surface active substances, antifoaming, biostatic agents and other compounds in water. Producers select components that can satisfy all working requirements but should be harmless to the workers and environment.

At application conditions emulsions are being contaminated with metal particles, grinding materials, "tramp oil" (oils from slide-way, hydraulic oils, anticorrosion material), inorganic salts, oxidation products, soaps, organic contamination, micro-organisms, and others [3]. Those contaminants influence to the emulsion stability and quality and cause that emulsion loses its functions. Finally contaminants shorten emulsion working life. During use emulsions can be treated with some chemical or physical methods in order to extend its working life [4]. But when it is not possible repair function properties of emulsion, at that point contaminated emulsion should be changed with fresh emulsion for proper metalworking process operation [5]. 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. In compliance with the requirements of relevant laws, waste emulsions have to be managed properly [6,7].

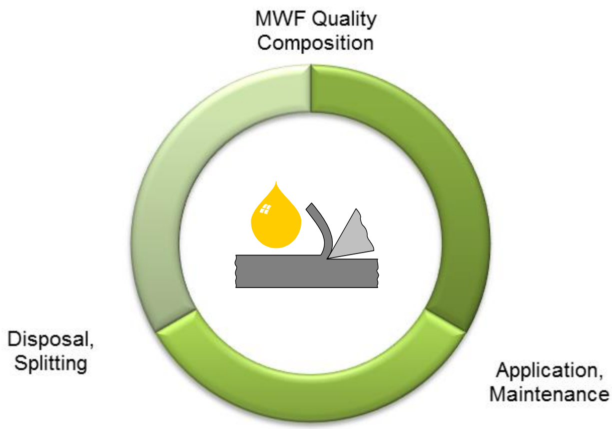

Figure 1: Metalworking fluid lifecycle considerations

2. Classification of waste emulsions

European Commissions Directive 2008/98/EC sets the basic concepts and definitions related to waste management, such as definitions of waste, recycling, and recovery [8]. It explains when waste ceases to be waste and becomes a secondary raw material and how to distinguish between waste and by-products. The Directive lays down some basic waste management principles: it requires that waste be managed without endangering human health and harming the environment, and in particular without risk to water, air, soil, plants or animals, without causing a nuisance through noise or odours, and without adversely affecting the countryside or places of special interest. Waste legislation and policy of the EU Member States shall apply as a priority order the following waste management hierarchy, Figure 2.

The Directive introduces the "polluter pays principle" and the "extended producer responsibility". It incorporates provisions on hazardous waste and waste oils. This Regulation defines the categories, types and classification of waste depending on the characteristics and location of waste, as well as determining waste catalog, the list of hazardous waste and a list of waste in transboundary movement. Waste metalworking fluids are classified in the group 12 according to the European Waste Catalogue and represent hazardous waste:

12 00 00 - Wastes from shaping and physical and mechanical surface treatment of metals and plastics
12 01 08 - Waste emulsion containing halogens
12 01 09 - Waste emulsion halogen free [9].

There are four main steps of genesis and flow of waste oils or emulsions:

- Producer / importer of fresh fluid-production
- Owner of waste emulsion-by metalworking process result of waste emulsion
- Collector of waste oils and emulsions-authorized firm
- Recovery and /or disposal of wasted oil/emulsion- authorized firm [10].

According to all laws, European and Croatian, waste oils or emulsions should be collected separately, transported, treated and analyzed at laboratories that are authorized and all steps should be followed by proper documentation.

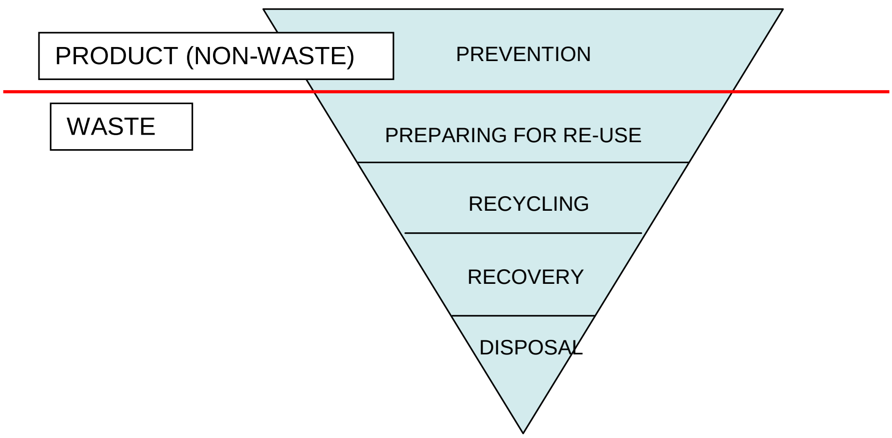

Figure 2. The priority order of waste management hierarchy

Waters sampling and testing of indicator values and allowable concentration of hazardous and other substances in waste water can be performed only by authorized laboratories, and tests are conducted in accordance with standards and Water rights permits [11]. Regulation on Limit Values of indices, hazardous and other substances in waste water, defines limit values for indicators and allowed concentrations of hazardous and other substances: for the industrial wastewater before discharging into the public sewage system, or to another receiver [12].

3. Methods for disposal of used metalworking emulsions

There are many methods for used emulsion treatment in purpose waste reduction that are divided into three groups [13,14]. 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 water. Tertiary treatments include improvements of separated phase's quality by reverse osmosis, nanofiltration, carbon adsorption, electrofiltration, by UV (ultra-violet) light or microorganism's treatment, etc. Metalworking fluid users generally have two options in disposal methods. Many plants have treatment facilities that are set up to handle emulsions or waste waters. More expensive method is to have the fluid transported away for treatment by a waste treatment company. After pre-treatment the emulsion itself has to be split into water and oil phase [15]. Table 1 shows comparison properties of the most frequently methods used in practice. The quality and possibility of re-use of separated waste matters influence the choice of the most suitable method also.

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	Not without additional treatment	Possible
OIL QUALITY	High water content	Low water content	Highly acid	Low water content
Re-use	Possible	Possible	Partially	Possible

It should be pointed out that here chlorine-containing oils and emulsions are under high risk of regulation. That means that attention must be paid when selecting lubricants for use, whereas this also renders the management of such oil phases more complicated. When selecting method for emulsion splitting it should be consider a lot of data:

- type of emulsion
- type of oil contained in the emulsion
- content of floating oil in the emulsion
- pH of the emulsion
- content of solid particles or other contaminants

- additional surface active compounds
  (detergents from cleaning machines or parts)
- the type of mechanical treatment of waste emulsion before it was collected
- plant availability system
- energy balance and others.

The process of used emulsion treatment and splitting with deemulsifier is presented in Figure 3.

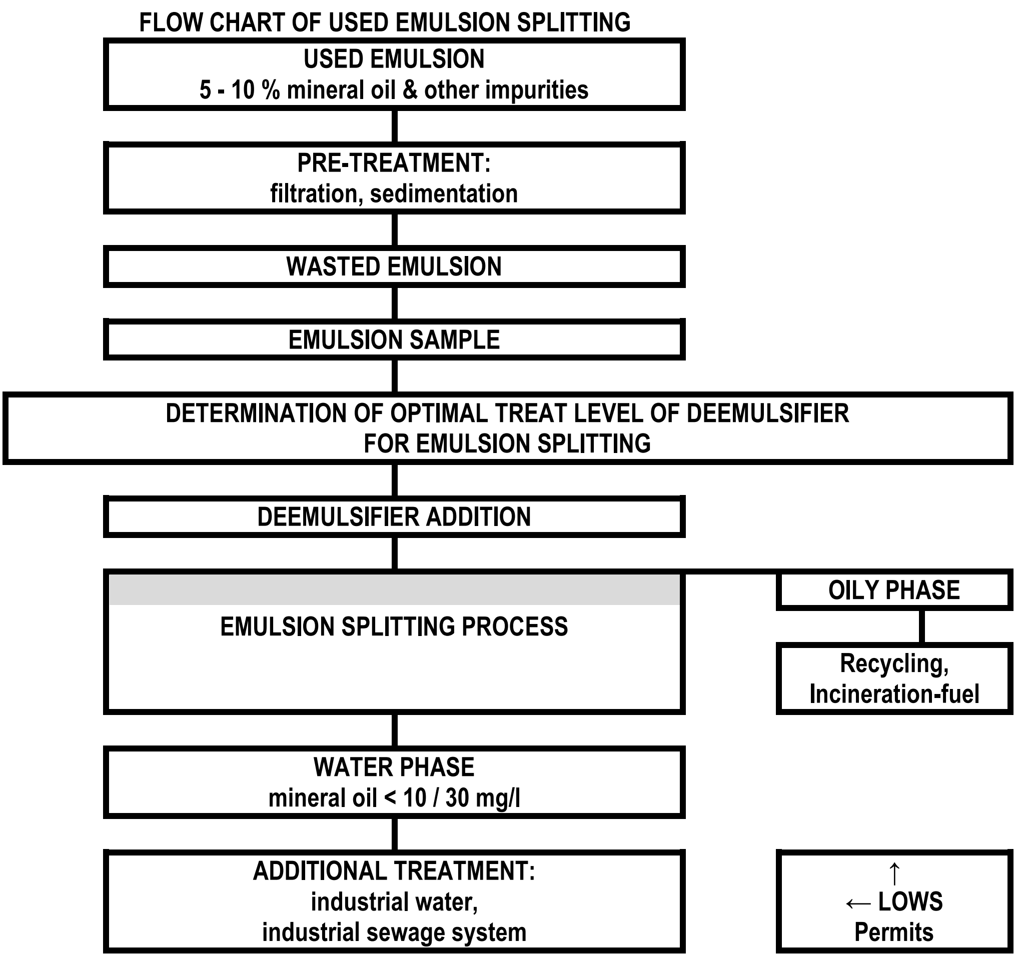

Figure 3: Flow chart of used emulsion splitting

4. Experimental part

4.1 Test fluids

Test metalworking emulsions collected from two metalworking workshops. Those are two types of emulsions: E1 conventional and E2 semisynthetic that are mixed from two metalworking concentrate fluids with water. Both concentrates are produced in accordance to ecological and safety regulation. Emulsion E1 is used emulsion of conventional concentrate that contains 70 % mineral oil, alkyl succinic acid derivative, polyglycol ether and natural carboxylic acid, Cl free. Mixing with water forms white milky emulsions. Concentrate of semisynthetic fluid contains 30 % oil, fatty carboxylic acids mixture, ether carboxylate, ethoxylated fatty alcohols, and do not contain chlorinated compounds. When mixed into water, semisynthetic metalworking fluid forms semitransparent yellowish stable microemulsion. Properties of test deemulsifier are presented in Table 2.

Table 2: Properties of deemulsifier

PROPERTIES	DEEMULSIFIER	METHOD
Appearance and color	Clear, pale yellow liquid	Visual
Density at 20 ^oC, g / cm³	1.167	ASTM D 4052
Kinematic viscosity at 40 ^oC, mm² / s	86	ISO 3104
pH Value (1 % wt. in D.W.)	6.9	ASTM D 1287
Appearance (1% wt. in D.W.)	Clear, colorless liquid	Visual

D.W. = Demineralized Water

4.2. Deemulsifier emulsion splitting

Required quantity of deemulsifier for the successful separation of the emulsion to be treated is determined on small samples. The process of emulsion splitting by deemulsifier conducted at normal temperature preferably from 18 to 22 ^oC. In several 150 mL glass beakers pour 50 g of the test emulsion and then in each beaker add a certain amount of deemulsifier. Place the test beakers on Variomag Telesystem Stirrer, mix at moderate speed for 10 minutes and then leave to stand until it starts separating no longer than one hour. If separation does not occur prepare new mixtures with higher or lesser proportion of the deeemulsifier, depending on the characteristics of the tested emulsions. The properties being monitored and evaluated at emulsion splitting are transparency of water phase and separated oil and declared by the grades from 0-4 shown in Table 3.

Table 3: Emulsion splitting grades

SPLITTING GRADE	EMULSION CONDITION	
0	unseparated	unchanged emulsion
1	slightly separated	still emulsion
2	separation as good	water phase still obvious turbid
3	separation good	water phase low turbid
4	separation complete	water phase clear

After determined optimal dosage of deemulsifier at small emulsion samples it is prepared needed quantity for emulsion splitting in reaction container of two liters. If examined properties of separated water phase satisfy approved water permit limits process of emulsion splitting is applied on whole waste emulsion quantity (10 and 15 t). This blend mixed mechanically during one hour. After 24 hours of reaction water phase is analyzed. Scheme of deemulsifier addition action and destabilization mechanisms responsible for emulsion splitting is presented in Figure 4.

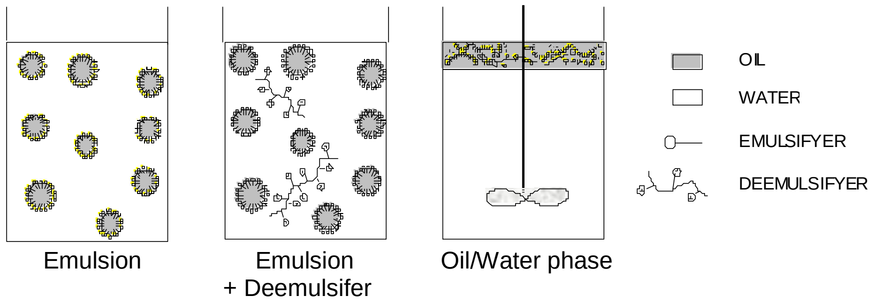

Figure 4: Scheme of emulsion mechanism splitting by deemulsifier

4.3. 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 [16], chemical oxygen demand (COD) and lyophilic compounds content by DIN 38409 and others by standard methods ASTM [17]. Chemical Oxygen Demand (COD), expressed in mg O_2 / L, determined by the method DIN 38409-H41. A method for determining the COD is based on the principle of organic substances in the sample oxidation with potassium dichromate in a sulfuric acidic medium with silver sulfate as a catalyst. After the process of oxidation amount of spent dichromate is determined by titration.

The content of lipophilic substances is determined by the DIN 38409-H18 includes a determination of the total oils and fats and then the content of mineral oil. The method consists in extracting a certain amount of sample by organic solvent (CCl4) and then measuring the intensity of the specific wavelength of the spectrograph obtained on FTIR spectrometer (Perkin Elmer Spectrum One). For the determination of mineral oil extract is passed over aluminum oxide and repeated determination spectrograph. After that the content of lipophilic substances and the mineral oil are calculated and the result is expressed in mg / L.

The metal content is determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF) according to ASTM D6052 at Oxford Instrument X-Supreme. It is measured the resultant excitation energy of the test sample from the X-ray source and the intensity is compared with calibration curves for each element. For the determination of the concentrate ration in emulsion is used optical refractometer type 0-32, with adjusted scale for direct reading in % wt. pH value is determined potentiometrically by a combined electrode ASTM D 1287.

5. Results and discussion

Some characteristics of used emulsions are presented in Table 4. Emulsions for testing are free from floating oils, metal particles, and others mechanical impurities what is achieved by laboratory method of sampling. In Figure 5 determination of deemulsifier dosage for equilibrium emulsions disorder E1 and E2 is presented.

Table 4: Properties of metalworking waste emulsions for testing

PROPERTIES	EMULSION E1	EMULSION E2
Appearance and color, visually	Milky, dark beige	Semi milky, grey
Concentration, refractometer reading, % wt.	3.4	3.1
pH value, ASTM D 1287	8.9	9.0
Metalworking operation, worked materials	Turning, Steel, brass, aluminium	Grinding, milling, Steel, cast iron
Working life, months	6	8
Waste emulsion quantity, t	10	15

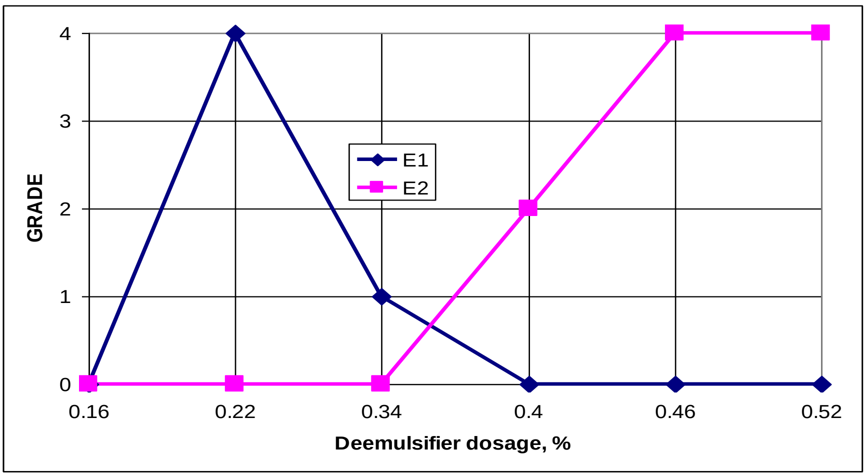

Figure 5: Results of optimum deemulsifier dosage determination for E1 and E2 splitting (% wt.)

INA-Method for emulsions' splitting is based on application of deemulsifier, the organically polyelectrolyte [18]. Deemulsifier added into emulsion disorders emulsion's stability balance according to Stockes' law [19]. Metalworking emulsions should be stable systems during whole period of application. Oil and water are not miscible so they can not make a stable emulsion. Therefore surface active substances, emulsifiers – should be used for stabilization. But, by adding poly-electrolyte emulsion becomes unstable so process of splitting starts with creaming, continued with sedimentation, flocculation, coagulation, coalescence and finally breaking [20].

Efficiency of emulsions splitting is estimated through water phase (WP) quality. The results of physical chemical properties of water phases are presented in Table 5 and 6. In comparison to start values in used emulsions' efficiency of COD decreasing is over 90 %. Value of pH stays in neutral range. Decrease of mineral oil content in water phase is over 99 %. It may be observed that metal content in water phase is dependent on machined materials types. The results of water phases' properties examination show that all parameters satisfy limits of actual water permit and laws.

Table 5: Examination results of emulsion (E1) and water phase (WP1) after splitting with deemulsifier dosage of 0.22 % wt.

PROPERTIES	E1	WP1	DECREASE	LIMITS*
Color	dark-beige milky	clear, colorless	-	-
pH Value	8.9	8.4	0.5	6.5 - 9.5
COD, mg O_2 / L	54 100	4 130	92.36 %	700
Lyophilic, mg / L	-	15.2	-	100
Mineral oil, mg / L	15 540	0.09	99.99 %	30
Fe content, mg / L Al content, mg / L Ni content, mg / L Cu content, mg / L		3.8 3.0 0.1 1.9		10 4 200 20

**Limits according local water laws and water permit (max.)* [13]

Table 6: Examination results of emulsion (E2) and water phase (WP2) after splitting with deemulsifier dosage of 0.46 % wt.

PROPERTIES	E2	WP2	DECREASE	LIMITS*
Color	semimilky, grey	clear, colorless	-	-
pH Value	8.8	8.5	0.3	6.5 - 9.5
COD, mg O_2 / L	158 340	5 795	96.34 %	700
Lyophilic, mg / L	-	17.6	-	100
Mineral oil, mg / L	4 343	0.1	99.99 %	30
Fe content, mg / L Al content, mg / L Ni content, mg / L Cu content, mg / L		9.3 0.0 0.2 0.0		10 4 200 20

**Limits according local ecological and water laws and Water permit (max.)*

Oil phases that floating on surface of water phases are compact, dark yellow color and can be treated without additional costs because both metalworking fluids are new types of metalworking fluid, chlorine free.

6. Conclusion

In the contest of fluid management the producers of metalworking fluids do more than produce new modern products. They also give advice for lubricant selection, participate in maintenance and protection of emulsion and give suggests for the best method of used emulsions decomposition.

To improve fluid management we developed special method for emulsions splitting as support to customer service. Compared to other methods, the advantages of INA-Method for used emulsion splitting are those no needs for expensive treatment facilities, heating and high energy consumption.

There is no additional sedimentation, pH value of water phase is neutral and oil separation exceeds 99 %. By INA-Method waste emulsion can be treated at the customer's site or transport to metalworking fluid producer to production plant for treatment. The method completes total fluid management that contributes to the protection of workers, improves industrial hygiene, reduces waste quantity, environmental pollution, decrease total costs and improve extended producers responsibility.

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Authors
Ljiljana Pedišić, mag. ing. cheming.; e-mail: ljiljana.pedisic@ina.hr
Irena Polenus
INA MAZIVA Ltd, MEMBER OF INA GROUP, Zagreb, Croatia

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