Ecological and Toxicological Characteristics of Metalworking Fluids Used in Finishing Processing in Russian Federation

S N Grigoriev\(^{1,a}\), N M Bobrovskij\(^{2,b}\), P A Melnikov\(^{2,c}\), I N Bobrovskij\(^{2,d}\), O O Levitskih\(^{2,e}\)

\(^{1}\)Moscow State Technological University Stankin, Vadkovskij per. 1, Moscow, Russian Federation
\(^{2}\)Togliatti State University, Belorusskaya st. 14, Togliatti, Russian Federation

E-mail: \(^{a}\)Rector@stankin.ru, \(^{b}\)bobrm@yandex.ru, \(^{c}\)topavel@mail.ru, \(^{d}\)bobri@yandex.ru, \(^{e}\)loo-05@mail.ru

**Abstract.** Nowadays, metalworking fluids (MWF) in the design of technological processes in most cases are considered as mandatory persistent components despite the constant improvement of the technology of machining, tools and equipment. Three main functions of MWF: cooling, lubrication, waste chips removal – seems to be the essential condition for stable process. In most cases, cooling reduces wear of tool and improves the quality of the processed surface. The cooling characteristics of the MWF affect not only the heat capacity and thermal conductivity, but metal surfaces wettability and vaporization. If processing speed and temperature of the fluid are high then it may not be in direct contact with the surface of the tool due to low wettability or vapor blankets. Improvement of machining process with applying the MWF is accompanied with negative factors. Due to the high temperatures in the treatment area it is exposed to MWF vaporization. This article presents estimation of the applicable in Russian Federation MWF: fire risk, toxicological and environmental hazards.

### 1. MWF fire risk

Modern MWF contains components that have a limit of inflammability. For example, the mechanical production assembly of JSC AvtoVAZ contains 356 units of metalworking machinery, which use about 2 thousand tons of emulsive MWF where 60% are irrecoverable loss (Table 1). MWF vapors accumulate and increase fire risk due to inadequate ventilation and air filtration (Fig. 1).

In this way fire occurred in engine plant "KAMAZ" in April 14, 1993. The fire engulfed the whole enterprise in minutes, completely destroyed not only the production facility, but also almost all of the equipment. Firemen managed to eliminate fire only five days later, the latest were extinguished the burning oil pockets in the basement of the plant. According to experts, spontaneous ignition of MWF used in machining equipment was one of the most probable causes of fire.

Automatic machining line of main brake cylinder casing mechanical in assembly production of JSC AvtoVAZ caught fire in July 20, 2002. Due to the strong fire plant was given the increased number of the fire complexity, the evacuation of workers was carried out. The fire was located and extinguished
two hours later by efforts of 200 people and 23 fire units. According to experts, the cause of the fire was also coolant spontaneous ignition.

Table 1 – Annual need MWF mechanical assembly production of JSC AvtoVAZ

| №  | Brand name                              | Limit of inflammability, °C | Modulus of flow (kg) |
|----|-----------------------------------------|-----------------------------|----------------------|
| 1  | BASIS OF LOW VISCOSITY MWF TU 38.401 188-98 | 80°C                        | 66767.000            |
| 2  | MWF LIQUID MP-10K TU 0253-015-27833685-2001 | 175 °C                      | 149028.570           |
| 3  | BASIS OF WORK LIQUID RJ-8U TU 0258-01-70015191 1-99 | 125 °C                      | 1034117.600          |
| 4  | LUBRICOCOOLANT LZ MWF1T TU 38.101.85      | 180 °C                      | 14252.500            |
| 5  | ROSSOIL MP TU 0258-012-06377289-98       | 158 °C                      | 152117.970           |
| 6  | ROSSOIL-1MIO GREASE TU 0258-013-06377289-98 | 160 °C                      | 252076.300           |
| 7  | ROSSOIL 23M ADDITIVE TU 0257-015-06377289-99 | 160 °C                      | 25693.100            |
| 8  | ROSSOIL-26MO ADDITIVE TU 0258-014-06377289-98 | 156 °C                      | 140641.770           |
| 9  | GREASE ROSSOIL-SHOK TU 0258-001-06377289-94 | 169 °C                      | 3902.439             |
| 10 | GREASE ROSSOIL-305 TU 0258-006-06377289-96 | 90 °C                       | 38311.000            |
| 11 | TECHNOLOGICAL GREASE ROSSOIL-503 TU 0258-018-06377289-2000 | 135 °C                      | 1160.200             |
| 12 | INDUSTRIAL OIL I-12A GOST 20799         | 105 °C                      | 180529.000           |
| 13 | MWF MP-7 TU 0258-154-06377289-01       | 180 °C                      | 83970.000            |

TOTAL | 2142567.449

Figure 1 – Trace of fire in industrial ventilation system
2. Toxicological characteristic of MWF

Modern MWF represent complex multicomponent system containing additives for different purposes, some of which may be toxic for workers. Chemical compounds that do not possess toxic characteristics may acquire them as a result of the interaction or synergy of various chemical constituents of MWF, workpiece and tool materials.

Principle routes through which MWF gets into human organism are represented on Fig. 2 [1,2,3].

![Diagram of MWF impact on workers](image)

**Figure 2** – Principle ways of harmful substances in the human body and their occupational diseases

Several studies show that the average lifetime of MWF varies from two weeks to a month and a half. The MWF which consist of industrial oil, alkali, glycol, asidol, and a number of other substances presents significant danger. Moreover, the used MWF in 15-30 times more toxic than new, it is shown in [4].

Fragment of a generalized classification of MWF on toxicological characteristics which most commonly used in Russian enterprises presented in Table 2.

MWF can expose with prolonged contact with the skin and the flow of vapor (fog) through the respiratory tract. It depends on the extent and nature of cleaning MWF and various protective and ventilation devices, as well as human environment (temperature, humidity etc.).

Smoke emission and oil mist occur during processing with mineral oils and oil MWF at elevated cutting modes (in the processing of hard-machinable materials under intense spraying liquid). Flow of inhaled aerosol and volatile oil products of MWF with thermo-destruction (carbon monoxide, hydrogen chloride, hydrocarbons, sulfurous anhydride, aldehydes) may exceed the norm in 2…3 times (maximum permissible concentration (MPC) oil MWF aerosol in the air of the working area is 5 mg/m$^3$, hydrocarbon vapors – 300 mg/m$^3$). List of chemicals subject to hygiene supervision in the work area when operating the MWF may be found in sanitary regulations of Russian Federation [5].
Long work in such conditions leads to irritation of the mucous membranes of the upper respiratory tract and even the development of lipoid pneumonia, reduced total immunobiological reactivity, the change of the nervous system [6].

Table 2 – Classification of MWF on toxicological characteristics, danger class 4

| №  | Brand name | Limit of inflammability, °C | Toxico-hygienic characteristic                                                                 |
|----|------------|----------------------------|--------------------------------------------------------------------------------------------------|
| 1  | AVITOL-1   | -                          | provides irritating action on the skin, has cumulative properties                                |
| 2  | AKVOL-18   | -                          | slight effect on skin and mucous membranes of the eyes, causing sensitizing action and has no cumulative properties |
| 3  | AKVOL-6    | -                          | No irritating action on the mucous membranes of the eyes.                                       |
| 4  | AKVOL-15   | -                          | Has no skin resorbtive and cumulative effect, slight effect on skin and mucous membranes of the eyes |
| 5  | AKVOL-18   | -                          | Has no action on the mucous membranes of eyes and no sensitizing effect, has skin resorbtive effect.|
| 6  | SINTAL-2   | -                          | Has no effect on skin and mucous membranes of the eyes, has no skin resorbtive effect, no sensitizing effect. |
| 7  | SINHO-2M   | -                          | slight effect on skin and mucous membranes of the eyes                                           |
| 8  | SN-C       | 170                        | slight effect on skin and mucous membranes of the eyes                                           |
| 9  | UVEROL     | 139                        | slight effect on skin and mucous membranes of the eyes                                           |
| 10 | UKRINOL-5/5| 150                        | no effect on mucous membranes of the eyes, no sensitizing effect                                |
| 11 | UKRINOL-5OU| -                          | slight effect on skin and mucous membranes of the eyes, no cumulative and sensitizing effect     |
| 12 | UKRINOL-202| 75                         | Has no skin resorbtive and sensitizing effect                                                   |

With prolonged contact with oil MWF workers can get professional skin lesions (dermatosis): folliculitis decalvans, occupational hyperkeratosis, papillary tumor, pigmentation, xeroderma and desquamation [7]. Occurrence and progression of disease are determined by individual predisposition and presence of skin micro trauma (scratch, abrasion, irritation overalls). The most frequent localization of dermatosis is on the hands, especially on the right.

Emulsion MWF containing special additives may cause damage to the fat grease skin redness and appearance of nodules, vesicles, crusts (dermatosis). Synthetic MWF containing some kinds of soaps can cause maceration of the skin (stratum corneum, softening the appearance of cracks and abrasions). The water miscible MWF causes sharp skin dryness, peeling, moderate painful cracks.

Intensive evaporation of water during water base MWF operation leads to an increase in the concentration of vapor in the working area, as well as the concentration of additives in the MWF, exceeding the hygienic standards. With prolonged exposure of emulsions with sodium nitrite content over 0.2% workers have headaches, fatigue, loss of appetite, poor sleep, pain in the extremities as a
result of the violation of gas exchange in the body, abnormal hemoglobin in blood. There, ethanolamine have an allergic effect on the organism and causes dermatitis. The emergence of contact dermatitis is also promoted by chromium, nickel, cobalt, which possible in MWF when processing alloyed steels and alloys [8, 9].

An important factor in the sanitary-hygienic condition of the MWF is the degree of microorganisms pollution rate. Microflora of MWF can cause secondary infection of follicles and micro trauma exacerbates skin maceration; as a result of vital activity of microflora in the MWF may occur also toxic substances. Bacterial and fungus microflora develops in all kinds of water mixable MWF when they are stored or used. Bacteria prevail in emulsion MWF, yeast and fungi - in synthetic MWF. Semi-synthetic liquid occupies an intermediate position. Different measures (cleaning, introduction of biocides, etc.) which carried out during the operation can significantly prolong the life of the MWF.

Modern MWF before introduction in industry receive comprehensive laboratory toxicological evaluation and sanitary-hygienic studies in production environments. Therefore, in accordance with the sanitary rules [5] to industrial application are suitable only MWF with permission of the health authorities. However, elimination of MWF adverse effects on the workers can be achieved only through the implementation of preventive measures and measures of individual protection.

3. MWF – ecological risks

Mechanical engineering industry ranked fourth among hydrosphere pollutants after steel, chemical and cellulose-paper industry. Out of the total drain, equal more 7 km³/year, only slightly more than half passes through sewage treatment plants, which usually do not meet modern environmental requirements. Proportion of so-called greasy water (wasted MWF, leakage of lubricating systems and oil storage) is 40...60% of plant total drain. Their characteristics are presented in Table. 1. Spilling, splashing, losses from chips and cleaning material, simply MWF drain to sewage system lead to the contamination of soil, water and air. Thereby, permanently lost portion of the components (including water), which could be extracted and reused for making new batch of MWF or for other purposes.

MWF lead to pollution of surface and subsoil on industrial site of the enterprise and potentially has a number of dangerous and difficult liquidating consequences. MWF in the soil generates multiple types of geological pollution:
- soil;
- zone of suspended water;
- surface of underground water.

Soil pollution is formed primarily in the areas of the MWF opening – the primary contamination. Soil is the most heavily polluted by heavy and viscous oil products of MWF, incapable of deep penetration in subsoil. Secondary pollution occurs in some cases as a result of the rise in groundwater levels [10].

Under the influence of petroleum products increasing number of water-stable soil particles bigger than 10 mm, aggregation of soil particles occurs. Coarse particles content increases, and the content of agronomically valuable small particles decreases. Petroleum-rich soil loses the ability to absorb and retain moisture [5].

Recovery (self restoration) period of soil, polluted by MWF, ranges from 1-2 to 10-15 years.

In machining process with using MWF under the influence of high temperature in the treatment area may form aerodisperse systems based on aerosols MWF, that further enhances their migration ability [3]. Figure 3 shows the analysis of possible migration ways of MWF aerosols.
The presence of 2 g of petroleum products in 1 kg of soil make it uninhabitable for plants and soil microflora. Petroleum derivatives influence almost all groups of soil invertebrates. The large species (insects, worms) die quickest. Lowering of oxygen concentration in soil contributes to the development of anaerobic microorganisms and aerobic microflora braking. Initially, even the weak soil contamination by petroleum products leads to a decrease the number of soil microorganisms. Restore strength observed a few months after contamination, sometimes even further growth of microorganisms through the use of carbon-mineral oil as a nutrient. However, the intensive growth of microorganisms, with soluble compounds, strongly impoverishes the soil nitrogen and phosphorus compounds. Soil contamination by petroleum products creates a new environment with the appropriate number of organisms in soil. A common feature of all oil-contaminated soils - limited species and ecological diversity pedobionts [4].

4. Conclusions
On the basis of the foregoing, for environmental friendliness and the expected passing of economic effect in the case of "dry" (without traditional MWF) machining many companies are actively engaged in developing the theoretical foundations and practical ways to implement processing without the use of MWF.

The experience of global engineering shows, that increasing legislation and tax sanctions, aimed at protecting the environment, technology’s that minimize the use of MWF, becoming more popular.

Currently used MWF have a negative impact not only on workers health, but also the ecosystem. Research of ways to optimize MWF work is relevant along with minimizing of their use in view of the increasing influence of thermal factors on machining.

One of the modern approaches is to replace the MWF by applying the special coatings or structured workpiece and tool surfaces.

References
[1] Maximum permissible concentration (MPC) of harmful substances in the air of the working area. Hygienic standards. Information on: http://www.gosthelp.ru/text/GN22568698Predelnodopusti.html
[2] N.M. Bobrovskij, I.N. Bobrovskij, A.V. Ezhelev, P.A. Melnikov The surface-plastic deformation technology for parts processing without the use of lubricating and cooling technological means [Tehnologija obrabotki detalej poverhnostno-plasticheskim deformirovaniem bez primenenija smazyvajushhe-ohlazhdajushhih tehnologicheskih sredstv], Samara Scientific Center RAS, Samara, 2012. ISBN: 987-5-93424-598-7.
[3] General hygiene requirements for working zone air. Information on: http://www.generent.ru/files/1216182858.pdf
[4] A.V. Vasiliev, L.R. Hamidullova Analysis of negative influence of lubricating-cooling liquids to the man and to biosphere and of methods of it reduction, Vector of TGU Science. 4 (2011) 45-49.

[5] L.S. Janovskij, A.A. Harin, I.V. Shevchenko, V.P. Dmitrenko Aviation ecology. Impact of aviation fuels and lubricants on environment, INFRA-M Publishing House, Moscow, 2015. ISBN: 978-5-16-010830-8.

[6] P.A. Melnikov, N.M. Bobrovskyi, A.N. Popov, D.V. Gussarova Features education aerodisperse systems when using coolants in machine-building enterprises, Vector of TGU Science. 3 (2011) 87-91.

[7] E. Brinksmeier, D. Meyer, A.G. Huesmann-Cordes, C. Herrmann Metalworking fluids — Mechanisms and performance, CIRP Annals - Manufacturing Technology. 64 (2015) 605–628.

[8] K. Weinert, I. Inasaki, J.W. Sutherland, T. Wakabayashi Dry Machining and Minimum Quantity Lubrication. Annals of the CIRP — Manufacturing Technologies 53 (2004) 511–537.

[9] E. Brinksmeier, C. Heinzel, M. Wittmann Friction, Cooling and Lubrication in Grinding. Annals of the CIRP — Manufacturing Technologies. 48 (1999) 581–598.

[10] N. Bay, A. Azushima, P. Groche, I. Ishibashi, M. Merklein, M. Morishita, T. Nakamura, S. Schmid, M. Yoshida Environmentally Benign Tribo-systems for Metal Forming. Annals of the CIRP — Manufacturing Technologies. 59 (2010) 760–780.