

NON-LUBRICANT RELATED COMPOUNDS IN USED MINERAL OILS

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Abstract

Used mineral oils (UMO) represent an important commodity, which is interesting from the viewpoint of both their energy-production utilization and material valorisation via their recovery. Being a hazardous waste, they are of environmental concern too. The quality and yield of the reclaimed oil are determined by the UMO quality. UMO which were selectively collected are of a substantially higher utility value. In the present contribution, possible contaminants of the separate collection of UMO in garages, depots, vehicle parks, service stations etc. are identified. They are brake fluids (polyethylene glycols and their ethers) and cooling mixtures (glycols) as anti-freeze agent. As a third possible contaminant, fatty acid methyl esters (FAME) are recognized. FAME appear in UMO during engine running with this alternative fuel. The results given in this contribution manifest that glycol and polyglycol-based admixtures are only incompletely miscible with engine oil and, in addition, they can be separated from UMO at recovery operation simply as overhead distillate at vacuum distillation using a film-type evaporator. FAME, if present, are collected also in the light fraction. The presence of these contaminants at the UMO recovery based on vacuum distillation does not represent any fundamental issue. The separation process can be monitored with the use of IR spectroscopy, utilizing the intensity of selected bands, characteristic for the respective contaminant.

Keywords: used mineral oil; infrared spectroscopy; anti-freeze agent; brake fluid; fatty acid methyl esters.

1. Introduction

Used mineral oils (UMO) represent an extremely complex and gradually changing material containing an exceptionally wide spectrum of ingredients which are currently not fully classified. According to European legislation, UMO are a hazardous waste. In the reviewed period of the 1990s, the share of collected oils reached about 50% of the sold oils of which about 30% were used for energy production (combusted), about 30% were transformed to base lubricating oils, about 25% were transformed to industrial fuels, and about 10% underwent cleaning to yield special industrial oils (hydraulic, transformer, etc.). The data are extracted from EU 1993 sources [1]; in the following years the data have varied and depended on several factors, mainly of market and legislative nature (crude oil price, demand/supply, tax policy, subsidies). In 2000, about 220 kt of base oils were obtained in EU via UMO recovery, which is less than 5% of consumption.

UMO are always formed where mineral oils are used as lubricants in machines, engines, vehicles, etc. They are formed also at manipulation with storage tanks, containers and oil-involving systems such as transformers, hydraulic equipment, etc. Their secure collection and at the same time their strict separation by the oil type are an important starting point to prevent their undesirable environmental impact. Used oils processing is desirable and necessary at the time being. The crude oil sources are limited, its price shows a permanently increasing tendency, and petroleum-based products and lubricants saving in particular is becoming a vital issue. Lubricants consumption is reduced through introduction of high-performance lubricating compositions in vehicles and industry. There is, however, also other effective mode of saving this natural source, i.e. UMO recycling and regeneration. While a content of crude oil components exploitable for lubrication purposes (5–7 %) is rather low, their content in UMO ranges from 70 to 90 %. In addition, UMO are a domestic raw material.

There are two basic approaches to UMO processing. One of them is focused on preparation of the material usable as fuel, or used otherwise (absorbent, flotation oil, separation oil). Within this mode, procedures such as UMO purification, cracking, gasification are applied.

The essence of the other mode lies in UMO profound purification and their adaptation to a material usable as base oil for lubricants manufacture, i.e. its regeneration and/or re-refining. The key steps in this procedure consist of distillation or extraction, combined with an appropriate chemical treatment such as hydrogenation.

A loss in the functionality of lubricating compositions is a consequence mainly of additives depletion and the presence of polluting components from external sources (dust, metal particles from abrasion, carbon from incomplete combustion, fuel residues, water, metal oxides from corrosion, etc.) and from lubricant itself (products of additives decomposition, oxidized oil products, sludge, varnishes, etc.). From 90 to 95% of hydrocarbon components remain still unchanged and are at the disposal to recovery operations eliminating the contaminants, improving the reclaimed oil odour and colour. In the ideal recovery, the undesirable substances are eliminated from UMO without changing their hydrocarbon composition. Such recovery must be economically sound and must not lead to devastating wastes.

UMO regeneration has emerged mainly in the second half of the previous century. As the first commercial procedure, a classical acid/clay technology was applied and it is still in operation in spite of increased problems concerning wastes and a regenerated oil low quality. Modifications of this procedure partially eliminate undesirable environmental impact. A survey of the technologies applied in the practice may be found in papers [2-4] and EU document [1].

In the EU, about 25 companies deal with UMO recovery [5] with the total production capacity approaching 500 kt/y, the individual capacities ranging from 35 up to 160 kt/y. Technological procedures are similar to those common in oil industry. On the other hand, primary refineries are not willing to recover UMO [6]. Recovery is in operation in Germany (7 enterprises), Italy (5 facilities), France, Spain, Denmark, Poland and Greece. Currently, a decrease in recovery capacities may be seen in some EU countries (France, Germany, Italy), new capacities are, however, under construction (France, Germany, Italy, Spain). In Slovakia, two companies – DETOX Banská Bystrica and KONZEKO Markušovce – deal with UMO recovery.

Globally, there are about 400 recovering units with a total capacity of 1800 kt/y, e.g. in the USA, Canada, Tunisia and Saudi Arabia. Most of these units are located in East Asia (India, China, Pakistan) and their capacities are small, 2 kt/y in average. The majority of these units utilize the acid/clay procedure and only a few of them produce good-quality reclaimed base oils and pay attention to the environmental protection.

At UMO recovery, the following key steps are applied:

- Raw impurities sedimentation, filtration, water and light hydrocarbon fractions (fuel residues) elimination;
- Vacuum distillation and/or extraction using solvents able to remove heavy decomposition products, additives and resins;
- Final treatment consisting of final hydrofinishing or hot contact (adsorption on clay) to improve colour and increase stability against oxidation.

Recovery procedures differ mainly in the used pretreatment operations, purification, fractionation and final treatment.

A main important factor of the UMO yield and recovery efficiency is selection of the UMO suitable for recovery. It concerns the following types of UMO:

- (Dark) engine oils representing more than 70% of all UMO. This source of the highest potential, relating to the operation of motor vehicles, is substantially homogeneous and searched for recovery purposes. As such, it has a great chance to be collected separately;
- Dark industrial oils representing about 5% of UMO. They are potentially suitable for recovery, due to the content of specific additives, they are not, however, preferred;
- Light industrial oils with a 25% share of UMO – turbine, hydraulic, compressor and others. Transformer oils represent a special case. All these oils are relatively pure and their market price is high. Their utilization is frequently of specific nature and independent of collection for classical recovery. They can be subjected to recovery *in situ* or used directly for less demanding purposes.

The UMO composition gradually becomes still more complex, mainly due to the following reasons:

- Dispersing agents, esters and polyolefins are used in an increased extent with the aim to prolong the oil lifetime. The resulting UMO are then complex mixtures with a higher content of impurities;
- Intensive replacement of conventional mineral lubricants for synthetic ones with better performance characteristics. While some of the synthetic products may be recovered together with mineral oils, others (e.g. ester-based) are less suitable to common recovery, less stable at alkaline pretreatment and hydrofinishing.

An increase in UMO recovery quality both significantly improves ecological parameters of recovery unit and reclaimed oil quality. Selectively collected UMO have much higher applicability potential than a simple combustion for energy-production purposes. Development in the automobile sector is oriented to exchange of engine and gear oils in vehicle service stations, closed motor parks, garages etc., and DIY self-service is becoming the past. At large-scale centres served to oil replacement there is no principal problem to execute separate UMO collection and to prevent unqualified addition of undesirable and devastating wastes to UMO. Thus, sound conditions for separated UMO collection are created, which is a quality background of reclaimed oils in the future.

Based on analyzing possibilities of UMO contamination in vehicle service stations, garages etc., it follows that there is a narrow set of contaminants which can potentially become part of engine and gear oils. These are brake fluids and cooling mixtures. FAME as residues of alternative fuels may act as a further contaminant.

Engine oils belong to highly contaminated and thermally degraded oils with a high content of additives such as detergents/dispersants, viscosity index improvers, antioxidants, depressants, antiwear and anticorrosion additives representing from 15 to 20% of base oil. Their content in UMO reaches from 10 to 12%, they are usually less volatile than the components of base oil.

The aim of presented study is to monitor the mentioned contaminants in the UMO, to trace their movement through the fraction during regeneration and confirm their absence in regenerate. To prove if presence in the input UMO does not bring some problems for regeneration such contaminated UMO using the distillation step as a key purification operation.

2. Experimental

2.1. Materials

Original (fresh) mineral oil MADIT M6AD (Slovnaft Bratislava, SR) was used as the standard of an additivated mineral oil. ALYCOL (MOL-LUB, Hungary) was used as the standard of engine coolant/antifreeze. The standard of brake fluid was EVOX DOT 4+ (MOL, Hungary). FAME were prepared by alkali-catalyzed transesterification of cold pressed rapeseed oil with methanol^[7], finally treated by washing with water and drying. The used FAME meet the standard EN 14 214. As a UMO sample the used lubricating oil from separated collection from the service department was used.

2.2. Equipment

A laboratory molecular evaporator MO 15 with wiped film has been used for fractioning of model contaminated motor oil^[8]. The main parameters of the evaporator: evaporation area 75 cm², condensation area 280 cm², distance evaporator – condenser ca 15 mm, usual working pressure 1 – 100 Pa, working temperature up to 260°C, optimum feed 80 – 120 ml/h, capacity of feed reservoir ca 500 ml.

Fourier transform – infrared spectra (FTIR) were recorded in a Nicolet model NEXUS 470 spectrometer in the energy range of 4000 – 650 cm⁻¹. Each spectra was averaged over 256 scans.

2.3. Process

The blended specimens of original motor oil MADIT M6AD were prepared by adding 10 wt. % of the respective model contaminant. The specimens were thoroughly mixed, and the IR spectra have been measured together with the spectrum of the reference motor oil MADIT M6AD and reference spectra of model contaminants. It was found that the system MADIT-MEG was not stable, and relatively quickly sets apart: the spectrum therefore

most likely does not represent the average composition. The mixed specimens were gradually distilled with the use of molecular evaporator, and the IR spectra of the obtained fractions were measured again.

The STU process [6] for UMO regeneration utilises successively chemical pre-treatment of sedimented and filtered UMO, stripping of water and light components, especially hydrocarbons, further two-stage vacuum distillation in molecular evaporators, and finally hydrogenation as the final treatment for improving the quality of raw regenerate. Chemical pre-treatment is based on the contact of UMO with alkali lye at elevated temperature. A light-oil fraction in the amount of 5 - 10 % from dried and stripped UMO is separated as a distillate in the first stage of vacuum distillation in a short-path evaporator. A distillate - raw regenerate - with the yield of 70 - 75 % from dried UMO is produced in the second stage. Distillation residue with the ratio of about 20 % contains especially polymers, additive residua, solid impurities and other contaminating components. Final refinement by hydrogenation (so called hydrofinishing) is not necessarily required, and it is usually used for improvement of the quality of basic oil, improvement of colour, removal of characteristic odour, and decreasing the content of nitrogen, oxygen, and sulphur compounds in UMO. The quality of the regenerate after distillation is good; after hydrogenation it is excellent. In presented article, the above mentioned process procedure except hydrofinishing was used.

3. Result and discussion

3.1. Infrared spectroscopy characterization of non-lubricant compounds in model samples

Fig. 1 shows the part of IR spectrum, which demonstrates separation of MEG from oily environment. The figure compares the spectra of original motor oil, MEG-based anti-freeze liquid ALYCOL, motor oil with contaminant, and finally the motor oil after removal of the contaminant into front fraction. Virtually identical spectra of contaminated oil, the regenerate, and also of the original oil are most likely observed due to admixture of the MEG contaminant in the course of spectrum measurement.

In Fig. 1 strong peaks in the region $3000 - 3650 \text{ cm}^{-1}$, characteristic for O-H vibration in diol are present. This typical peak is, however, absent in the model mixture engine oil - antifreezing agent, which is a consequence of immiscibility of glycols and mineral oil. From the viewpoint of recovery and/or separation of such mixture, this is a positive factor enabling at least partial separation of these contaminants via simple centrifugation or decantation. A peak in the region $1030 \text{ to } 1090 \text{ cm}^{-1}$ is attributed to antisymmetric vibrations of the C-O-C moiety, which indicates the presence of DEG or other ethers partially miscible with engine oil. This characteristic peak was present also in a sample of contaminated oil.

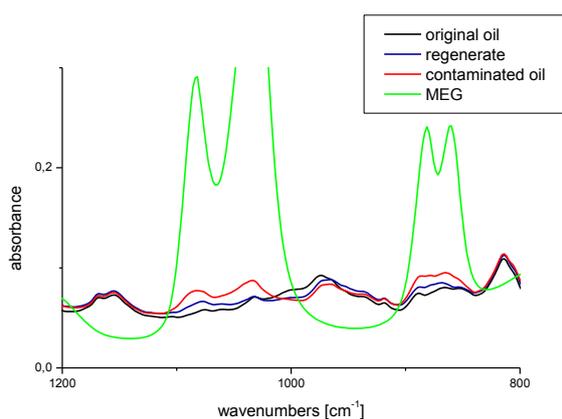


Fig.1 IR spectrum of the original motor oil, contaminant (MEG), contaminated oil, and oil after contaminant removal. Model contaminant is engine coolant/ antifreeze (MEG), 10 wt. %.

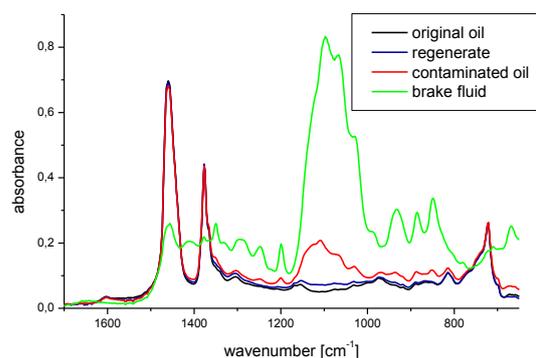


Fig. 2 IR spectrum of the original motor oil, contaminated oil, and oil after contaminant removal. Model contaminant is brake fluid, 10 wt. %.

As shown in the IR spectra for this tested system in Fig. 2, this contaminant is also reliably separated into the front fraction, which represents about 13 wt. % of the feed. Alkali pre-treatment of UMO with the content of brake liquid does not represent a problem. Peaks characteristic for antisymmetric vibrations C-O-C, measured in the region $1060\text{-}1130 \text{ cm}^{-1}$

in samples of brake fluid and also contaminated oil, may be attributed to DEG or TEG-based ethers.

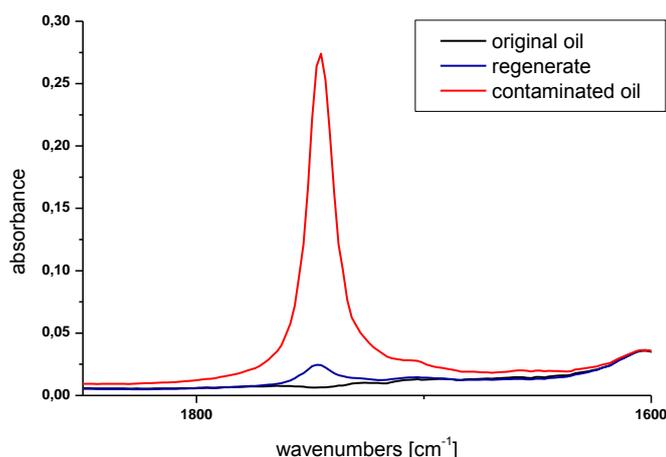


Fig. 3 IR spectrum of the original motor oil, contaminated oil, and oil after contaminant removal. Model contaminant is FAME, 10 wt. %.

Fig. 3 shows the IR spectrum from the study of removal of FAME as the contaminant of motor oil. The respective band at 1750 cm^{-1} can be assigned to the vibration of C=O bonds of carbonyl group, which is presence in molecule of esters. Methyl metacrylate oligomer-based viscosity improver also exhibits IR absorption in this area.

3.2. Regeneration of model samples

Anti-freeze agent, as expected, the presence of mono ethylene glycol (MEG) in the motor oil does not represent any problem for oil regeneration. The oil used as a basis for production of medium viscosity motor oils is obtained by vacuum distillation at the temperature of $250 - 350^{\circ}\text{C}$ and pressure $6 - 13\text{ kPa}$ [9], while according to the EN STN 56 1302 the distillation range for MEG (0 – 95%) at the atmospheric pressure is between 190 and 202°C . The volatility of both components is thus sufficiently different. The temperature of MEG elimination in vacuum evaporator with wiped film with respect to the mentioned range corresponds at the pressure around of 1 kPa to values between 70 and 80°C . At the used temperature of heating cylinder of evaporator 140°C practically all present MEG is transferred into the front fraction, which represents about 10 wt. % of the feed in the case of this model blend. However, the system motor oil + MEG is not stable, and despite the presence of an emulsifier in motor oil it sets apart spontaneously. This fact does not represent any problem, and can be used with advantage: separated heavier polar phase is not fed into the process. The situation is similar also in the case when the present antifreeze agent is based on ecologic and non-toxic propylene glycol. Normal boiling point of 1,3-propanediol is only slightly higher than that of MEG (215°C in comparison to 197°C); boiling point of 1,2-propanediol is even lower than that of MEG. This provides sufficient space for efficient evaporation of these components without significant loss of mineral oil. Non-diluted ALYCOL was used for the measurements. The presence of MEG, or other glycols, does not represent a problem for potential alkali-based UMO pre-treatment.

Brake fluid taking into account the presence of poly glycols and poly glycol ethers with higher molar weight and expected decreased volatility, the off-take of the front fraction was carried out at low pressure around 50 Pa .

As mentioned above, the properties of FAME are close to the properties of fossil oil. The fuel residua (petrol, diesel) are routinely removed from UMO by vacuum, but also atmospheric distillation (stripping). This assumption has been confirmed also when removing FAME as model contaminant from motor oil at the temperature and pressure range usual for our technology of regeneration at the off-take of volatile front fraction. The off-take of the front fraction was 13 wt. % of the feed. Alkali pre-treatment of FAME-containing UMO could result in hydrolysis of FAME and to formation of alkali soaps, which could result in gel-like consistence of treated UMO. However, this problem can be solved by adjustment of regeneration process, or the alkali pre-treatment can be skipped. Conditions of fractionation are summarized in Tab. 1.

Tab. 1 The operating conditions of fractionation of the blends original motor oil + contaminant, 10 wt. %

<i>contaminant</i>	<i>pressure, Pa</i>	<i>temperature, °C</i>	<i>front fraction, wt %</i>
anti-freeze agent	1200	140	8
brake fluid	50	130	13
FAME	50	130	13

While the presence of studied contaminants MEG (anti-freeze agent), poly glycols and their ethers (brake liquid) and FAME (fuel for diesel engines) in UMO represent virtually unsolvable problems for other regeneration technologies, the regeneration process with vacuum distillation as the main purification step allows their efficient and simple removal.

Similar results were obtained also by processing and IR testing of real UMO samples with the addition of studied contaminants.

3.3. Regeneration of used engine oil

After alkaline pretreatment or without the pretreatment, UMO were processed using a short-path evaporator with wiped film in a two-step operation. To compare the quantitative parameters, both UMO with and without pretreatment were used at distillation. The results in Table 2 show that the application of the alkaline pretreatment has a sound ground. In this step, carbon and resins are separated, coagulated and finally settled, i.e. they do not enter the distillation step. On the other hand, the pretreatment forms a complication for the technological procedure.

Tab. 2 Parameters and yields of materials from regeneration procedures

Parameter	Raw material (UMO)	Regenerate without pre-treatment	Regenerate with pre-treatment	Base oil OHSP 130R Koramo ^[10]
Yield, % wt.	-	73,4	77,9	-
Viscosity, 40 °C, mm ² /s	60.31	37.63	39.9	43.9
Viscosity, 100 °C, mm ² /s	8.797	5.934	6.204	6.89
Viscosity index	121	100	101	113
Water, mg/kg	663.9	55.4	26.6	-
Acid value, mg KOH/g	1.35	1.18	0.045	-
Density, kg/m ³	882.8	875.4	877.3	861
Flash point, °C	224	216	226	235
CCT, % wt	0.53	0.17	0.037	-
TBN, mg KOH/g	4.1	0.45	0.42	-
Sulphur, % wt	0.63	0.6	0.61	2,2 ppm

Alkaline pretreatment influenced mainly the acidity and carbon residue of the regenerated oil. A lower ignition temperature of the regenerated oil prepared without the pretreatment relates to a lower evaporation into recovered fraction, i.e. to a lower yield. Regenerated oil which was subjected to the pretreatment has a lower acidity number and a lower CCT. A higher acidity number is associated mainly with the presence of the antioxidant agent zinc(II) dialkyldithiophosphate (DDTPZn) with the volatility comparable to that of base oil constituents and which distils together with them (see also an increased content of Zn in non-pretreated regenerated oil). In our previous work ^[5] we have documented that during the titration of samples containing DDTPZn at acid value determination, they undergo decomposition by alkali lye, which is manifested by consumption of lye solution and ostensibly higher acid value.

In Table 3, the contents of selected elements in the original UMO, regenerated oil prepared with or without pretreatment are given. The Zn content (its presence in UMO and non-pretreated reclaimed oil was discussed above) and Ca content deserve attention. Ca is present in UMO due to the alkaline reserve and it does not enter regenerated oil.

Tab. 3 Contents of selected elements in the original UMO, regenerated oil prepared with or without pretreatment

Parameter	Raw material	Regenerate without pre-treatment	Regenerate with pre-treatment
Iron, mg/kg	2.5	0.8	0.9
Cooper, mg/kg	7.3	1.6	0.3
Nickel, mg/kg	0.8	< 0.06	< 0.06
Zinc, mg/kg	668	408	105
Sodium, mg/kg	16.1	< 0.01	2
Magnesium, mg/kg	75.3	< 0.01	< 0.01
Lead, mg/kg	4.5	2.5	2.5
Chrome, mg/kg	1.2	< 0.06	< 0.06
Calcium, mg/kg	742	< 0.03	< 0.03
Barium, mg/kg	< 10	< 10	< 10

4. Conclusion

The present study indicates that the contamination of UMO with selected technical fluids, which can come into consideration during separated collection of UMO at the places of large-scale exchange of motor and gear oils in service stations, garages, repair pits etc., does not represent any technical problem for their regeneration which utilizes vacuum distillation. Brake fluid and anti-freeze agent can be efficiently separated from mineral oil as the front distillate fraction. Similarly the residua of alternative fuels for diesel engines – methyl esters – are efficiently removed from UMO, FAME in the front distillate fraction. The separation process can be monitored with the use of IR spectroscopy, utilizing the intensity of selected bands, characteristic for the respective contaminant.

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