1. Introduction

During the rapid development of science and technology, there is a need for continuous improvement of mechanical equipment. Therefore, optimizing and improving processes are constantly carried out to reduce the wear value of machine parts. Improvement of the process quality of the technical equipment depends on high-quality characteristics of lubricants. It is known that engines and parts of the main and auxiliary equipment elements of power plants are exposed to different types of wear and, eventually, breakdown. The wear of parts leads to worsened operation modes, reduced efficiency, energy loss by power units as well as increased noise and vibration that reduce the product quality and lead to premature industrial failure. Replacement of equipment and parts requires significant costs; therefore, research to improve the durability and longevity of the equipment is a very important technical and economic task [1].

The intense development of technical devices requires the use of lubricants with new performance properties. The quality of the lubricants, particularly of the motor oil, can be improved by adding to the oil some special chemical substances – additives [2, 3]. The additives must meet certain requirements: namely, be soluble in oil or form stable systems; keep solubility and stability throughout the operating temperature range during transportation, storage, and use; produce no sediment on the filter; withstand water; and sustain other operational properties of the lubricant. Besides, the additives should not cause any deterioration and negative interaction with metal, rubber or polymer products; they must be compatible with the other additives that are introduced into the lubricating composition and must be technologically and economically feasible and affordable.

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OBTAINING OF POLYMETHACRYLATE ADDITIVES AND STUDYING OF OPERATIONAL PROPERTIES OF AN ALLOYED INDUSTRIAL OIL

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These requirements limit the range of compounds that can be used as additives to lubricants; therefore, a very limited range of products is used. Polymethacrylate multifunctional additives occupy one of the main places among the whole variety. They meet all requirements put forward to them. Therefore, the urgent tasks are to obtain such additives and to study their influence on the operational properties of an alloyed industrial lubricant.

2. Analysis of previous studies and statement of the problem

The most rational way of improving friction units in different climates is to develop new lubricant compositions with effective viscosity-and-temperature, depressing, lubricating, and antiwear properties [4, 5]. The complex of these properties can be provided only by oils with additives because the basic oils do not comply with all the requirements put forward to them.

The multiple classes of organic compounds with different functional groups and elements [6] are used as additives to provide the necessary operational parameters of the oil. Therefore, an additives classification and their division on the basis of their functionality are conditional because the organic compound can influence some operational characteristics of the oil and, to some extent, improve or worsen certain indices. Most manufacturers of oils prefer to use a single multifunctional additive in all spectra of the lubricant oils.

There are additives with various chemical compositions on the market: polyolefins [7], poly(alkyl methacrylates) [8–10], copolymers of hydrogenated styrene-butadiene [11], terpolymers [12], etc. Each chemical composition of the polymer provides a balance between cost and performance characteristics that make them more or less suitable for using in certain compounds of lubricating oils.

The most effective among additives that possess viscosity and depressor properties are the copolymers based on higher alkyl methacrylates. Ghosh and Das synthesized polymethacrylate additives based on esters of methacrylic acid with fatty alcohols fractions C_{14}–C_{26} that can effectively limit the reverse crystallization of paraffins, which also facilitates the oil mobility and vastly extends the range of operations at low temperatures [13]. This type of additives allows production of mineral oils without the expensive dewaxing process.

It should also be noted that Neveu et al. identified that polymers of a linear structure have a better thickening ability compared to similar branched polymers due to the presence of a larger number of possible conformations of chain macromolecules [14]. Poly (alkyl methacrylate) copolymers with different molecular weight and consisting of monomers with various functional groups have an antifriction effect owing to adsorption on the surface and forming a thin film in the boundary friction [8, 15].

To date, despite the large number of studies in the field of oils and lubricants, there are no reliable criteria for selecting a lubricant additive for gear pairs that work in some specific conditions. Attempts to justify the use of additives in industrial oils are mentioned in Lazutina’s PhD work [10]. However, the recommendations contained therein are either very general or are intended for very narrow application. Therefore, studies aimed at synthesizing new polymers with enhanced functionality and testing them as multifunctional additives are very important from scientific and applied perspectives. Such a study can provide a solution to the problem of producing competitive and high quality lubricants in Ukraine.

3. The aim and objectives of the study

The study is aimed at obtaining new polymethacrylate additives with enhanced functionality and studying the influence of their concentration and composition on the operational properties of the alloyed industrial lubricant I-20A.

To achieve this aim, it is necessary to solve the following tasks:
- to establish optimal conditions for obtaining polymethacrylate additives through kinetic research on the homopolymerization lauryl methacrylate in benzene;
- to obtain polymethacrylate additives by copolymerization of lauryl methacrylate with methyl acrylate in benzene; and
- to study the operational properties of the alloyed lubricant I-20A.

4. Materials and methods

4.1. Research materials

Lauryl methacrylate CH_{2}–C(CH_{3})–COO(CH_{2})_{11}–CH_{3} (LMA) is a colorless liquid with a strong smell, graded as “chemically pure”. Its molecular weight is 254.41 g·mol^{-1}, the T_{b(boiling point)} (under a pressure of 720 mmHg)=167 °C, ρ_{4}^{20}=0.868, and n_{D}^{20}=1.4452.

Methyl acrylate CH_{3}–CH–COOCH_{3} (MA) is a colorless liquid with a strong smell, graded as “chemically pure”, purified with distillation at the atmospheric pressure; the content of the basic substance is 99.9 %. Its molecular weight is 86.09 g·mol^{-1}, T_{b} (under a pressure of 720 mmHg)=80 °C, ρ_{4}^{20}=0.953, and n_{D}^{20}=1.489.

Benzene C_{6}H_{6} is a colorless liquid with a strong smell, of a “pure analytical grade”. Its molecular weight is 78.11 g·mol^{-1}, T_{b}=80.1 °C, T_{M} (melting point)=5.3 °C, ρ_{4}^{20}=0.879, and n_{D}^{20}=1.5017.

Benzoyl peroxide (С_{8}H_{11}CO_{2}O_{2} (BP) is a powder of white colour. Water from benzoyl peroxide was removed by a double dissolution in acetone. Benzoyl peroxide was also filtered, and then it evaporated at room temperature and under atmospheric pressure. It was additionally dried in a vacuum at room temperature. The content of the main substance was at least 76.2 %. Its molecular weight was 242.23 g·mol^{-1}, T_{b}=100 °C, and T_{M}=102 °C.

The industrial oil I-20A was produced by AZMOL, psc. (Berdiansk, Zaporizhzhia Oblast, Ukraine). Kinematic viscosity: ν_{50}=16.7 mm^{2}s^{-1} (at Т =50 °C) and ν_{100}=4.28 mm^{2}s^{-1} (at T=100 °C), viscosity index (VI) 97, T_{Ft} (freezing point)=−15 °C, T_{Ff} (flash point) =196 °C. Paraffin naphthenes content − 83.8 %, aromatic hydrocarbon content − 15.6 %, and resins content − 0.6 %.

4.2. Research methods

The kinetics of the radical LMA homopolymerization in benzene was studied by using a dilatometer method, which is based on measuring the reduction of the monomers’ reaction mixture volume during polymerization as the reaction mixture density increases in the process of the monomer changing into a polymer.

Polymethacrylate additives were synthesized in the medium of an inert gas (argon) in a two-neck flask equipped with a reflux condenser and a thermometer. Lauryl methacrylate and methyl acrylate were dissolved in benzene (3.6 mL); the amount of the monomers depended on the required polymer composition. The volume ratio of the
monomer to the solvent was equal to 1:1. Benzoyl peroxide was used as an initiator of the polymerization process in an amount of 0.5 wt. % against the total weight of the monomers. The polymerization process was conducted during 3 to 4 hours at 80±1 °C. After polymerization, the reaction mixture was precipitated with ethanol. The obtained polymer was several times reprecipitated with ethanol from benzene solution. The final polymer was dried in a vacuum (at P=1,330–3,990 Pa and T=60–70 °C).

The molecular weight (MW) of the resulting polymers was specified by a cryoscopic method of molecular weight determination. The polymer solutions in benzene (20–25 mL of 0.1–0.2 mol) and benzene as the solvent (20–25 mL) were cooled in a Peltier refrigerator. The freezing temperature was determined by using a Beckmann thermometer. An analytical balance was used for all weighings with a precision of 0.0002 g.

The molecular weight of the polymers was calculated by using the following formula (1):

\[
MW = \frac{1000 \times K_{Fr} \times g_2}{g_1 \times AT_{Fr}},
\]

where \( K_{Fr} \) is the solvent freezing constant (5.07), \( g_1 \) and \( g_2 \) are the weights of the solvent and the substance g, respectively, and \( AT_{Fr} \) is the reducing freezing point of the solution, °C.

The infrared (IR) spectra were recorded with the Specord IR-75 spectrometer, and KBr wafers were used with the wavenumber in the range of 4,000–1,400 cm\(^{-1}\).

Thermal stability of the samples was studied with using the derivatograph Q-1500D (the Paulik-Paulik-Erdey system) at a dynamic mode of the heating rate of 10 °C/min in the air medium. The weight of each sample was 200 mg. The sensitivity on a scale of a differential thermal analysis (DTA) was 250 mV, on a scale of thermogravimetric analysis (TG) – 200 mg, and on a scale of differential thermogravimetric analysis (DTG) – 500 mV. Alumina was used as the standard.

The main indicators of the operational properties of the alloyed industrial lubricant, which were determinant in the experiment, were chosen as follows: kinematic viscosity (\( \nu_0 \) and \( \nu_{0,90} \)), a viscosity index (VI), a freezing point (\( T_{Fr} \)), and antikear properties.

The model lubricant compositions were prepared to determine the functional influence of the synthesized additives. The polymer was weighed on the analytical balance with a precision of 0.0002 g, and the estimated amount of the oil was weighed on a technical balance. Besides, both substances were mixed for 40 to 60 minutes at 60 °C to 120 °C. The prepared solution was cooled to and left at room temperature for 6 to 12 hours.

The viscometer VPIZh-2 with the capillary diameter of 0.56 mm (the viscometer constant of 9.67×10\(^{-3}\) mm\(^2\)s\(^{-1}\)) was used to determine the kinematic viscosity of petroleum oils.

The study was repeated three times. The efflux time during each experiment differed from the arithmetic mean by no more than 0.5%.

The kinematic viscosity of the oil was calculated by the following formula (2):

\[
\nu_i = C \cdot \tau_i,
\]

where \( C \) is the viscometer constant as the passport value of the corresponding viscometer, mm\(^2\)s\(^{-1}\); \( \tau \) is the arithmetic mean of the oil efflux time, s\(^{-1}\).

The VI was determined according to the measured viscosity values at 50 °C and 100 °C. The obtained results were compared with the standard requirements for the corresponding brand of oil, and conclusions on the possibility of its practical use were made [16].

The freezing point was determined by a standardized method according to ASTM D 97 [16], with the aim to evaluate the low temperature properties of the oil.

The antikear properties of the alloyed industrial lubricant were tested in friction on a four-ball machine (FBM). To simulate durability (wear resistance) in this machine, there were used variable balls with a diameter of 12.7 mm, made of steel SHKh15. The study was carried out under the following conditions: the load on the upper ball was 200 N, the upper ball’s cycle frequency was 1,500 min\(^{-1}\), and the research time study was 20 min [16].

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was diluted in benzene, the interaction between the alkyl side-groups were weakened, which resulted in a decrease in the rate of polymerization. Conversion was equal to 98 % at the volume ratio of [benzene]:[LMA]=1:1 (Fig. 2, curve 3), which indicated almost complete conversion of the monomer to the polymer. At the volume ratio of [benzene]:[LMA]=1:2 and 1:3 (Fig. 2, curves 4, 5), the polymerization rate decreased with time (S=83–87 %). As seen from the experimental data, the optimal ratio of [benzene]:[LMA] was 1:1.

The kinetic curves of the LMA homopolymerization at different temperatures are shown in Fig. 3.

The molecular weight of the synthesized copolymers was determined by a cryoscopic method. An increase of the MA content from 10 to 30 mol % in the monomeric mixture increased the molecular weight of the copolymer from 10,200 to 16,000 (±0.2 %). Therefore, the solubility of the synthesized copolymers in lubricants can be worsened with the MA content in the monomer mixture above 30 mol %.

The research results of the thermal stability analysis of poly(LMA) and copolymer of poly(LMA-co-MA) with the molar ratio [LMA]:[MA]~70:30 % are shown in Fig. 4.

According to the thermogravimetric analysis, at the thermo-oxidative degradation in the entire temperature range poly(LMA-co-MA) loses weight less intensively compared to poly(LMA). This further demonstrates a higher thermal stability of the composition at low temperatures.
to 350 °C. At this temperature, the weight loss of poly(LMA) was equal to 53.5 %, and for poly(LMA-co-MA) it was less than and equal to 47 %, which also indicates a higher heat resistance of the latter.

The research of viscosity-and-temperature properties of the alloyed industrial lubricants was performed by determining the following:

1) the dependence of viscosity on the concentration of the additive in the oil;
2) the dependence of viscosity on the composition of the additive.

The concentration of polymethacrylate additives (PMAs) in the oil was respectively 1, 2, 3 and 4 wt. %.

The dependence of viscosity-and-temperature properties of the oil I-20A on the content of (co)monomer in the additive and on the concentration of the additive in the oil are shown in Fig. 5.

![Dependence of kinematic viscosity on the PMA additive concentration in the oil I-20A](image)

As can be seen in Table 1, the viscosity index of the oil I-20A increases from 97 (for base oil) to 99–145 (I-20A with the PMA additive) with an increase of the additive concentration from 1 % to 2 %. Such a viscosity index change can be explained by the fact that in dilute solutions the macromolecules are less dependent on each other in their heat flows, and under the influence of Brownian forces they can take many forms in oil. A further increase of the additives’ concentration in the oil from 3 % to 4 % does not significantly influence the viscosity index of the oil because of significant structural changes of the macromolecules in the solution, which makes the samples less mobile.

![Dependence of viscosity on the composition of the PMA additives](image)

Based on the above listed data and research description, the study of the depressor properties of the lubricant was carried out at the optimum concentration of 2 wt. % of the PMA additive in the oil I-20A. The depressor property of the oil, thickened with additives, was studied by determining the freezing temperature.

The oil I-20A thickened with the PMA20 additive was tested for its antioleak properties. The high viscosity index of the oil with the PMA20 additive (2 wt. %) was found to reduce mechanical friction losses at low temperatures. The antioleak properties of the base oil are significantly improved with the addition of the PMA20 additive, with the wear index (Di) for the base oil I-20A Di=0.41 mm and for the I-20A with 2 wt. % of the PMA20 Di=0.32 mm. The lowering of the wear index to 0.32 mm occurs due to formation of a stable boundary film at high contact loadings during the FBM testing.

## 6. Discussion of the research results of obtaining polymethacrylate additives and the operational properties of the alloyed oil I-20A

The reaction sequence with respect to the initiator and the monomer was calculated according to the experimental points (Fig. 1, 2) of the first fixed area of polymerization (S≤10 %) [17]. The calculated sequence of the reaction with respect to the initiator (1.38±0.07) and the monomer (1.69±0.02) is high due to the high structuring of the LMA and the high viscosity of the system.

The LMA homopolymerization was studied at different temperatures (Fig. 3), which made it possible to calculate the activation energy E_a=96.4±0.506 kJ/mol, as was previously confirmed by published data on radical polymerization of vinyl monomers [18].

The results of the kinetic research have made it possible to justify the optimal parameters of obtaining PMA additives. The PMA additives were received by radical copolymerization of the LMA and the MA in benzene while using predetermined regimes.

Our results show that polymerization occurs at a high degree of conversion of ~96–99 %. The qualitative composition of the additives was confirmed by an IR spectral analysis. The IR spectra of copolymers determined the presence of characteristic bands – an ester bond of the MA carbonyl group (1,730 cm⁻¹ and 2,856 cm⁻¹) and a large paraffin residue of the LMA (2,928 cm⁻¹ and 2,856 cm⁻¹).

Fig. 5 shows that the viscosity of the samples (the oil I-20A with a PMA additive) develops naturally at the temperatures of 50 °C and 100 °C. The viscosity curves indicate

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>[LMA]:[MA] in the initial monomer composition, mol %</th>
<th>The VI of the oil I-20A with the PMA additive</th>
<th>Concentration of the additive in the oil I-20A, wt.%</th>
<th>T_F</th>
<th>Fr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil I-20A</td>
<td>–</td>
<td>97</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>I-20A+PMA10</td>
<td>90:10</td>
<td>99, 100, 103, 105</td>
<td>105–15</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>I-20A+PMA20</td>
<td>80:20</td>
<td>115, 140, 142, 143</td>
<td>143–19</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>I-20A+PMA30</td>
<td>70:30</td>
<td>137, 145, 147, 147</td>
<td>147–16</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
that an increased concentration of additives in the oil results in increased intermolecular interactions between macromolecules and in a combination of their conformational forms.

Lazutina [10] and Potolovskiy et al. [19] found out that adding viscous additives to the oil increases not only its viscosity, but also the VI; however, at an increasing concentration of the additive, the VI increases slower. It is particularly noticeable that viscous additives increase the VI of oils with a low initial viscosity. If the initial VI of the oil is lower, the VI more obviously increases with additives, as evidenced by the experimental data that are summarized in Table 1.

It has been found that a high VI value of the oil with the PMA20 (2 % wt.) additive reduces mechanical friction losses at low temperatures.

The temperature and the speed loss of mobility lubricating oils depend on the nature and degree of crystallization of paraffins and ceresins that are present in the composition of the oil, and also on the viscosity of the movable liquid part of the oil. Dewaxing is usually used for obtaining low-temperature oils, but it is a difficult and expensive technological process. Therefore, to reduce the freezing point of distillate oils containing a small amount of paraffin and ceresin, there can be used more economical methods one of which implies adding of depressors as special additives. Introduction of depressors in oils prevents crystallization of paraffins and ceresins, inhibits the growth of their crystals, and hinders the formation of a crystal slip in the oil. Thus, it is possible to preserve oil mobility [20].

The research results on the operational properties of the alloyed oil I-20A show that the PMA20 additive has the lowest freezing point compared to other samples and can be used with concentration of 2 wt. % in the oil for obtaining an alloyed industrial lubricant as a commodity with desirable operational properties (VI=140 at T_{f}=-19 °C).

The main task of further research in this field is to study the use of the oil I-20A thickened with the multifunctional PMA20 additive whose 2 % concentration in the oil makes it a lubricant for reducing friction in the equipment of power plants.

7. Conclusions

1. The kinetics of lauryl methacrylate homopolymerization in benzene at different concentrations of the initiator and the monomer as well as at different temperatures were studied with using a dilatometer method. The optimal conditions for obtaining polymethacrylate additives were determined on the basis of kinetic studies and the following parameters: the temperature of 80±1 °C, the concentration of benzoyl peroxide of 0.5 wt. % based on the total monomers’ weight, the ratio of lauryl methacrylate:benzene=1:1, and the reaction time of 3 to 4 hours.

2. Polymethacrylate additives were obtained via (co)polymerization of lauryl methacrylate with methyl acrylate in benzene, and their physicochemical properties were studied further. The qualitative composition of the additives was confirmed with the infrared spectrometry. According to a thermogravimetric analysis, it has been found that synthesized (co)polymers are thermally stable up to the temperatures of 255–265 °C.

3. The influence of polymethacrylate additives in the oil I-20A on the rheological, depressor and antiwear properties was also studied. It has been found that the PMA20 additive with a concentration of 2 wt. % in the oil can be used for obtaining an alloyed industrial lubricant as a commodity with desirable operational properties.

References