Petroleum and Coal

Article **Open Access**

Technology for the Production of Preservation Greases Based on Secondary Polymer Raw Materials

A. Grigorov[1], O. Bryhada[2], S. Bondarenko[2], S. Vavreniuk[2], L. Yurchenko[2], O. Sharovatova[2]

[1] *National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine*

[2] *National University of Civil Defense of Ukraine, 61023, 94 Chernyshevskaya str., Kharkov, Ukraine*

Received December 22, 2023; Accepted February 1, 2024

Abstract

The article considers the possibility of involving in the technological production of commercial greases, secondary polymeric raw materials represented by such polyolefins as high and low density polyethylene (LDPE and HDPE) and polypropylene (PP). The results of laboratory studies of the obtained greases samples are presented. On the basis of the obtained results, a scheme for the production of greases is proposed, in which the stage of dispersion of components is realised by boiling the polymer in the base oil. The proposed scheme makes it possible to reduce the degree of grinding of polymer raw materials, which reduces energy consumption and the duration of preliminary preparation of the polymer thickener.

Keywords: *Recycled raw materials; Polyolefins; Recycling; Greases; Additives; Homogenization; Adhesion.*

1. Introduction

Today, polymer waste is one of the main sources of environmental pollution. They are formed both during production processes (production waste) and during economic activity (consumptive waste) of the earth population. Moreover, this problem has become particularly acute over the last two decades due to the rapid development of the technosphere and the production of goods from cheaper and highly functional materials, which turned out to be polymers: polyethylene, polypropylene, polystyrene, etc. At the same time, polymeric waste accumulated at landfills and dumpsites of various sizes can be considered by industry as a valuable secondary raw material for the production of lubricants, including preservation greases, due to its properties.

2. Analysis of publications

Greases for various functional purposes are among the most expensive materials and, due to their properties (capable of performing their functions under high loads and speeds of movement of vertical friction surfaces), are in great demand in the global oil market [1]. With the modern development of the oil refining and petrochemical industries, research is continuously being conducted to reduce the cost of greases while simultaneous improving their functional properties. For this purpose, various components (thickeners, fillers and additives) are constantly added to their composition, which can significantly improve their stability, water resistance, resistance to aggressive environments and expand the temperature limits of their use [2-4]. One of these components are liquid and solid polymers that are crushed and dispersed in the volume of the greases.

An alternative family of high-quality liquid (HQL) lubricants obtained by the catalytic conversion of polyolefin waste before and after consumption was proposed in [5]. The resulting lubricants were characterised by enhanced lubricating and anti-wear properties, which makes it possible to use them as a dispersion medium for plastic lubricants. Recently, polymer-based materials have been widely used as lubricants for functional hydrate lubrication [6]. The effect of the concentration of recycled low-density polyethylene (LDPE) on the rheology of lithium greases and their relationship with the microstructure of the grease is presented in [7]. Recycled LDPE has been found to be an effective additive for changing grease rheology (increasing the viscoelastic properties of the grease) acting as a filler in the entangled soap microstructure.

Polymers (polyethylene, polypropylene, polyisobutylene, halogenated polyethylene, polymethacrylate, and polyurea) incorporated into the grease structure can be used to improve properties such as consistency, shear resistance, water resistance, adhesion, stickiness, and soap performance. It was found that the type and structure of the polymer (polyisobutylene and polyisoprene) significantly affect the properties of complex lithium grease, including low flow temperature, thickening efficiency and shear resistance [8].

Thus in paper [9] a new microstructure of polymeric grease consisting of amorphous polypropylene nanoparticles evenly distributed in the base oil was discovered. Such a grease demonstrates excellent stability and fluidity. With the absence of crystallisation and a mesh thickener structure, it has the potential to be used at extremely low ambient temperatures.

The influence of polyisobutylene (PIB), ethylene-propylene copolymers (OCP), styrene-hydrogenated butadiene (SBR), styrene-hydrogenated isoprene (SI), radial hydrogenated polyisoprene (Star), acid-treated polymer (FP), polymethacrylate (PMA), styrene ester copolymers (SE) and styrene-ethylene-butylene copolymer (SEBCP) on the properties of aluminium greases was investigated. It was found that polymers in the form of liquid, gel, powder and granules increased the shear resistance and water resistance of greases, and also contributed to an increase in grease yield of up to 17% [10].

Plastic lubricants obtained by mixing (within 1-3 hours) ethylene/propylene copolymer treated with acid anhydride (OCP-A) and OCP-P at 90 °C in the base lubricant had high water resistance and adhesive properties and low penetration values [11].

There are a number of works in which it is proposed to use polyethylene as an additional component of plastic lubricants. So, for example, the authors of the paper [12] suggest using low-molecular-weight polyethylene (waste from the production of high-pressure polyethylene) as a dispersed phase in the production of plastic lubricants.

In paper [13] it was proposed to add various waste and pure polymers (polyethylene, polypropylene, and EVA copolymer) to lithium grease to modify its viscosity. It has been found that recycled polymers improve the rheological properties of grease more significantly than the original materials. However, in cases where the grease containing such polymers was subjected to significant mechanical stress, a slight deterioration in its stability was observed.

Research was conducted in the direction of the production of plastic lubricant by adding a mixture of polypropylene and high-density polyethylene (PP+HDPE) to a mixture of basic paraffinic mineral oils of group I and group II (kinematic viscosity at 40 ºC is 160 mm2/s), which are produced by the company Indian Oil Corporation Ltd. (Faridabad, India). In the result a plastic lubricant with high rheological properties was obtained [14].

Based on the mixing of two components, molten polypropylene or low-density polyethylene in a base oil and a base oil thickened with sodium stearate, a plastic lubricant is obtained that is 80-85% more resistant to the action of water than a conventional sodium lubricant [15].

But a significant drawback of these studies is that the addition of polymers was carried out in distillate fractions or in commercial greases, and the issues related to the use of these additives in used lubricating oils without deep cleaning of the latter were practically not considered.

Taking this into account, the authors of papers [16-18] proposed the production of plastic lubricants for various functional purposes on the basis of used lubricating oils (process, hydraulic, motor and transmission) and prepared (washed, dried and crushed) recycled high and low density polyethylene (LDPE and HDPE) and polypropylene (PP). This area is very promising and can be implemented using various technologies with further integration into existing production.

3. The objective of the research

It is known that one of the main directions that characterizes the technical and economic efficiency of production (including the production of plastic lubricants) is the reduction of the harmful impact on the environment caused by raw materials, the production process itself and the waste generated during the production. Considering this, the goal of this research is the development of a waste-free technology that uses solid crushed polymeric materials as raw materials - production and consumption waste, and the target product is preservation greases with a high level of performance properties. In accordance with the objective, the materials and methods of the research were further defined.

4. Materials and methods of the research

To achieve the research goal, used products made of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) and polypropylene (PP) were selected as a secondary polymeric material - a thickener for plastic lubricants. These products were washed from impurities, dried and crushed to a particle size of 1×1 mm. The dispersion medium to which the polymeric thickener was added was used semi-synthetic motor oil SAE 10W-40 API SL and SAE 5W-30 API SN. The identified materials were mixed in a ratio of 1:1-3:1, placed in a laboratory apparatus (a glass flask (V=1 dm^3) with a connected reverse water cooler for cooling, condensation, and returning of low-boiling oil vapours to the reaction volume) and kept at a temperature of 260-270°C (boiling point of motor oil) for 2 hours. Subsequently, the obtained mixture was cooled and studied using a high-speed laboratory centrifuge (rotation speed of the centrifuge rotor up to 8000 rpm) to determine the adhesive properties of plastic lubricants [19] and standard research methods: method for determining penetration (ASTM D 1403-10(E)), method for determining water resistance (DIN 51 807/1), method for determining corrosion on metal (ASTM D4048), method for determining melting point (ASTM D 127), colloidal stability (ASTM D 1742), flash point (ASTM D 92).

5. Results and discussion

In accordance with the selected materials and research methods, as a result of experimental studies of the obtained product samples, the results were obtained and presented in Table 1.

Table 1. Properties of the products obtained.

№	Name of the indicator	Units	Actual value of the indicator
1.	Colour	-	From light yellow to brown
2.	Appearance	-	Homogeneous paste
3.	Compliance with classification NLGI	Class	00/1/2/3/5
4.	Melting point, ºC	°C	89-127
5.	Colloidal stability	%	5-7
6	Flash point	°C	215-225
7.	Water resistance	-	Resistant
8.	Corrosive effect on metals	-	Withstands (copper, steel)
9.	Penetration at 25°C, within	mm×10^{-1}	149-438
10.	Adhesive properties, rpm	rpm	2850-6000

The information presented in Table 1 shows that using the selected materials and their processing technology, it is possible to obtain a product that meets the requirements for preservation greases by its properties. Comparing the obtained products with NYCO 65 VASELINE (TECHNICAL PETROLATUM (GREASE)) [20], which is often used as a grease and is a part of some anticorrosive protective mixtures, we note that their melting point is 39-77°C higher than its value, which significantly expands the temperature range of their use. By adding anti-

corrosion additives to the obtained products, it is possible to obtain greases, which in terms of their protective properties will approach the greases of the Mobilarma 700 series [21].
In addition to the indicators presented above, the adhesive properties of the obtained greases, which are among the most important operational properties, were also determined. Adhesive properties of greases were determined for the obtained samples of greases with a range of concentrations of polymer thickener content at the level of 50% to 75% (see Fig. 1).

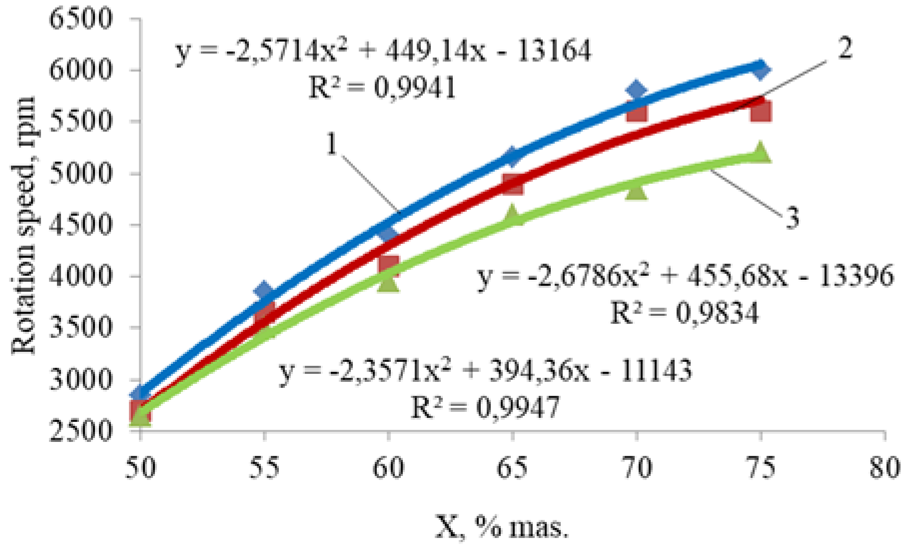

Figure 1. Dependence of adhesive properties on X: 1 – HDPE; 2 – LDPE; 3 – PP

Within the studied concentrations of the polymer thickener, all grease samples showed fairly high adhesive properties, ranging from 2550 rpm for samples with 50 % thickener to 6000 rpm for samples with 75 % thickener. The best adhesive properties among the tested samples are those containing 75% polymer, which is explained by the ability of the polymer to retain liquid base oil in the grease volume. Among the polymers, HDPE has the best adhesive properties while PP has the worst due to the structure of the polymer and its properties, in particular, the ability to swell when interacting with a liquid medium. It is known that in a grease, without the presence of special adhesive additives, the adhesive properties are determined by the liquid base oil, which forms an absorption layer on the metal surface [22]. In case the polymer has a high degree of swelling, the amount of oil is no longer enough to create a strong layer on the metal surface, which leads to the deterioration of the adhesive properties (detachment of the grease from the metal surface, for example, under the influence of centrifugal forces).

On the basis of our research, we propose a technology for the production of greases that is implemented according to the scheme shown in Fig. 2. This scheme is more simplified than the scheme presented in paper [23]. The main difference between these schemes is that the stage of dispersion of the components using a mechanical stirring device was replaced by the stage of boiling the polymer in the base oil. With this approach, it is possible to reduce the degree of grinding of polymer raw materials, which reduces the energy costs and the duration of preliminary preparation of the polymer thickener, as well as increase the safety of production due to the absence of elements that have a significant mass and rotate at high speeds.

According to the given scheme, after preliminary coarse grinding, the polymer (flow I) was loaded into the reactor (2), where the prepared dispersion medium (flow II) from the container (1) is supplied by the pump (12). In the reactor (2) for 1800-3600 seconds the dispersion medium in which the dispersed phase (polymer) is dispersed, is boiled at a temperature of 240-270 °C with the removal of vapors that pass through the heat exchangers (4, 5) and enter the separator (6), where the destruction gases (flow IV) are separated from the solvent, which is returned to the reactor (2) by the pump (12). Gases of destruction, represented by C_2-C_3 hydrocarbons, which are produced in the amount of 1.0-3.0% of the row material, are combusted and the resulting heat energy is used to power the plant's electrical equipment.

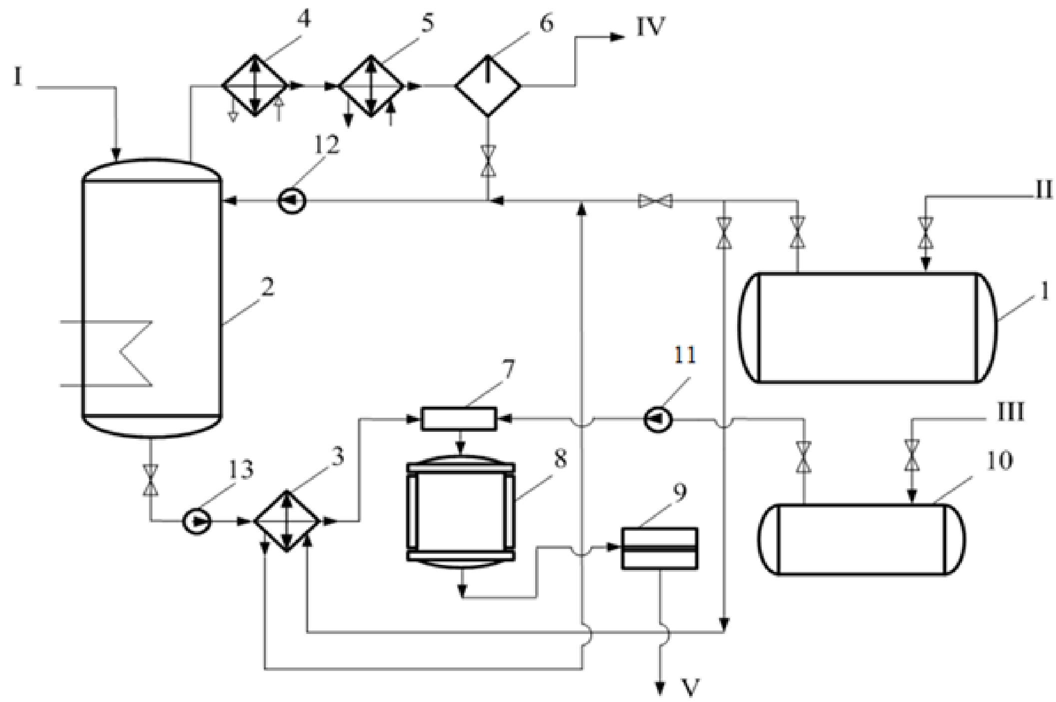

Figure 2. The principle scheme of obtaining greases from secondary raw materials: 1, 10 – containers; 2 – reactor; 3, 4, 5 – heat exchangers; 6 – separator; 7 – mixer; 8 – cooler; 9 – homogenizer; 11, 12, 13 – pumps; I – crushed polymer; II – solvent (dispersion medium); III – anti-corrosion additive; IV – gases of destruction; V – grease

From the bottom of the reactor (2) the pump (13) through the heat exchanger (3) removes the product, which is cooled by pumping the dispersion medium from the container (1) through it. At the same time, the dispersion medium is preheated (to a temperature of 140-160 °C) in the heat exchanger (3). If necessary, the resulting product is mixed with an anti-corrosion additive in the device (7). The anti-corrosion additive is supplied from the container (10) by the pump (11). Next, the mixture enters the cooler (8), where the formation of the structure of the grease begins. The final formation of the grease structure is carried out in the homogenizer (9), where the resulting mixture is pressed under high pressure through holes with a diameter of 80-100 microns. The finished grease comes out of the homogeniser (9) (flow V).

6. Conclusions

Today, the involvement of secondary hydrocarbon raw materials in the technological process of production of fuels and greases, in particular greases, is a very promising area of utilisation of rather hazardous industrial and household waste.

The most promising from the wide variety of secondary raw materials for the production of greases are waste polyolefin products (HDPE, LDPE and PP), which are capable to provide the marketable product with a fairly high potential of properties (water resistance, melting point/drop point, resistance to chemicals, etc.) and are easily processed in a liquid medium - semi-synthetic and synthetic lubricating oils.

The samples of the obtained greases according to melting point (89-127 °C), penetration (149-438 mm × 10^{-1}), colloidal stability (5-7 %), water resistance, and corrosion action on copper and steel, adhesion properties (from 2550 rpm for samples with 50 % thickener to 6000 rpm for samples with 75 % thickener) can be used as an independent grease or to create grease compositions for a wide range of functional purposes (e.g. antifriction, protective, etc.).

References

[1] Modern Technology of Petroleum, Greases, Lubricants & Petro Chemicals (2nd Revised Edition)/NIIR Board of Consultants & Engineers/ NIIR project consultancy services, 2015: 704.

[2] Casserly E, Langlais T, Springer SP, Kumar A. The Effect of Base Oils on Thickening and Physical Properties of Lubricating Greases. E. Casserly. The european lubricants industry magazine –Tech., 2018; 144: 32-37.

[3] Hodapp A, Conrad A, Hochstein B, Jacob K.-H, Willenbacher N. Effect of Base Oil and Thickener on Texture and Flow of Lubricating Greases: Insights from Bulk Rheometry, Optical Microrheology and Electron Microscopy. Lubricants, 2022; 10: 55. https://doi.org/10.3390/lubricants10040055

[4] Rizvi SQA. Lubricant Chemistry, Technology, Selection, and Design. ASTM International: West Conshohocken, PA, USA, 2009 : 443.

[5] Hackler RA, Vyavhare K, Kennedy RM, Celik G. Synthetic Lubricants Derived from Plastic Waste and their Tribological Performance. ChemSusChem., 2021; 14(19): 4181-4189.

[6] Liu G, Feng Y, Zhao N, Chen Z, Shi J, Zhou F. Polymer-based lubricating materials for functional hydration lubrication. Chemical Engineering Journal, 2022; 429: 132324.

[7] Martín-Alfonso JE, Valencia C, Sánchez MC, Franco JM, Gallegos C. Development of new lubricating grease formulations using recycled LDPE as rheology modifier additive. European Polymer Journal, 2007; 43(1): 139-149.

[8] Vargo DM, Lipowski BM. The Effect of Polymer Additives on Grease Flow Properties. NLGI Spokesman, 2016: 15156118.

[9] Muller D, Matta C, Thijssen R, bin Yusof MN, van Eijk MCP, Chatra S. Novel polymer grease microstructure and its proposed lubrication mechanism in rolling/sliding contacts. Tribology International, 2017; 110: 278-290.

[10] Larson BK, Levin V. Benefits of Polymer Additives in Grease. NLGI Spokesman, 2010: 17-25.

[11] Vargo DM. The adhesiveness of grease. Presented at the NLGI 81st Annual Meeting Palm Beach Gardens, Florida, USA June 14-17, 2014.

[12] Diphare MJ, Pilusa J, Muzenda E, Mollagee M. A Review of Waste Lubricating Grease Management. // 2nd International Conference on Environment, Agriculture and Food Sciences (ICEAFS'2013), Kuala Lumpur (Malaysia), 2013: 131-134.

[13] Gozbenko VE, Korchevin NA, Kargapol'tsev SK, Karlina AI, Karlina YuI. Results of Research on Possibility to Use Low-Molecular Polyethylene in Lubricating Compositions. Advances in Engineering Research, 2019; 182 : 120-125.

[14] Martin-Alfonso JE Valencia C, Sánchez MC, Franco J, Catalina G. Rheological modification of lubricating grease with recycled polymers from different plastic waste. Ind. Eng. Chem. Res., 2009; 48: 4136-4144.

[15] Dixena R, Sayanna E, Badoni R. Recycled and Virgin HDPEs as Bleed Inhibitors and Their Rheological Influences on Lubricating Greases Thickened with PP and mPP. Lubricants, 2014; 2: 237-248.

[16] Grigorov A, Zelenskii OI, Sytnik AV. The prospects of obtaining plastic greases from secondary hydrocarbon raw material. Petroleumand Coal, 2018; 60(5): 879-883.

[17] Grigorov A, Tulskaya A, Nahliuk M, Karchakova V. The choice of method of dispersion the thickener for the production of the recycling plastic grease. Petroleum and Coal, 2019; 61(6): 1389-1394.

[18] Grigorov A, Zelenskii O. The use of processed polyethylene products in the manufacture of plastic lubricants. Petroleum and Coal, 2019; 61(1): 21-24.

[19] Grigorov A, Sytnik A, Karchakova V, Ponomarenko V, Rudniev V. Adhesion properties of recycling greases. Petroleum and Coall, 2019; 61(5):918-923.

[20] NYCO 65 VASELINE. URL: https://www.nyco-group.com/product/nyco-65-vaseline

[21] Mobilarma 700 Series. https://www.mobil.com/en/ru-ua/industrial/pds/gl-xx-mobilarma-700-series

[22] Achanta S, Jungk M, Drees D. Characterisation of cohesion, adhesion, and tackiness of lubricating greases using approach–retraction experiments. Tribology International, 2011; 44: 1127-1133.

[23] Grigorov A, Nahliuk I, Zelenskii O, Ponomarenko N. Technology of recycling waste lubricant greases. Petroleum and Coal, 2019; 61(4): 677-681.

To whom correspondence should be addressed: prof. Andrey Grigorov, National Technical University «Kharkov Polytechnic Institute», 61002, 2 Kirpichova str., Kharkov, Ukraine, E-mail: grigorovandrey@ukr.net
ORCID: https://orcid.org/0000-0001-5370-7016