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NEW CLASS OF LUBRICANTS FOR GREEN TRIBOLOGY

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Abstract: The possibility of obtaining a new class of lubricating oil bodies (PET-acylglycerol) with the help of modification of the natural fat molecule by a fragment of a link of a synthetic polymer-polyethylene terephthalate is considered. The distribution of electrostatic charge in molecules of beef fat and synthesized PET-acylglycerol is shown. A relationship between the structural hierarchy of the synthesized lubricating oil bodies and the tribotechnical indexes has been established.

Keywords: “green tribology”, natural fat, PET-acylglycerol, dipole moment, tribotechnical properties.

INTRODUCTION

For today, the dominant of the development of a civilized society [1] is striking stable balance of the society with the environment, which is impossible without solving complex issues, including further reducing energy, material costs, radical improvement of environmental protection, improving the quality of life. This led to the emergence of an extremely popular trend of improving technologies, materials, energy sources under the names of "green technologies", "green engineering", "green chemistry", "green power production", "green products" etc. The term "green" means a new round of scientific thinking, which includes views on the ecological balance and principles of environmental protection. The industry of lubricants in the perspective of new thinking – "green tribology" provides among many tasks: – ecological aspects of manufacturing new lubricants with the use of renewable raw materials and their biodegradation after the end of their life cycle. Potential raw materials for the creation of environmentally friendly lubricants are vegetable oils, animal fats and synthetic alcohol esters [2]. Their positive properties: the polarity of molecules, low volatility, fire resistance, relative stability of viscosity for temperature. Negative aspects of fats: low frost resistance, low resistance to oxidation.

In developing the technology of chemical recycling of waste polyethylene terephthalate (PET bottles) by glycerolysis, Professor Mandzyuk I.A proposed a mechanism of the process with the formation of oligomeric products – recyclables of different molecular weights [3]. The process of chemical recycling of PET, in the framework of the presented model, was considered as consisting of a sequence of reactions: the destruction of the main chain of polyethylene terephthalate under the action of degradation agent – glycerol; synthesis – polyesterification; intermolecular exchange [4, 5].

The field of technical application of vegetable oils continues to expand, the volume of production of products based on vegetable oils significantly increases –tractor oils, oils for the food industry, industrial hydraulic oils, oils for chainsaws, gear oils, various oils for metalworking, oils for metal forming processes, cooling oils in transformers; as well as staple oils, oils for foundry molds, engine oils for two-stroke engines: in the field of plastic lubricants – industrial and for the food industry with the use of various thickeners – from organo-bentonite, in complex aluminum, lithium and complex lithium [2]. At the same time, attention should be focused on the fact that oil and synthetic lubricants and their components are toxic products. Some polycyclic aromatic hydrocarbons are carcinogenic. Laboratory studies have shown that waste lubricants are quite toxic to animals, especially for embryos and newborn animals. Thus, the eggs of the bobwhite and wild duck appeared to be very vulnerable to the effects of waste lubricants, even a low concentration (to 0.015 ml) can lead to the death of 88% of bobwhite embryos and 84% of wild duck embryos [6]. Other harmful effects are manifested in the appearance of birth defects and increased level of mortality [6].

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Analyzing new, modern trends in the development of tribotechnics, one should note that one of the effective directions for implementing the concept of "green tribology" is the development of new lubricant compositions based on natural ecologically safe fats capable of biodegradation. A special weightage to such scientific research is given be the use of recycling technologies of secondary raw materials [6–8].

EXPERIMENTAL PART

The aim of the work was to study the structure and tribotechnical characteristic of modified natural fats by grafting polyester oligomer (polyethylene terephthalate).

As the objects of research, the raw material: natural fats of vegetable origin – rapeseed oil and of animal origin – beef fat were considered. According to the developed technology [3], synthesized intermediate compounds of acylglycerols of natural fats, from which PET-acylglycerols of fats are synthesized. The latter were considered as the basic body of greases. To assess the structural characteristics of synthesized materials, rheometry and IR spectroscopy were used. The geometric image of the molecules and the calculation of the electrostatic potential are realized using the HyperChem programme package. The tribotechnical characteristics of the synthesized lubricants were determined on four-ball friction machine in accordance with the procedure [9].

RESULTS AND DISCUSSION

From the standpoint of the chemical structure, natural fats are compounds that are obtained as a result of the reaction between glycerol and aliphatic carboxylic acids with the formation of esters – acylglycerol (Fig. 1). By developed technologies for recycling waste PET bottles, we have obtained intermediate compounds – recyclables (PET oligesters) the combination of which with natural fats produces PET-acylglycerols (Fig. 2).

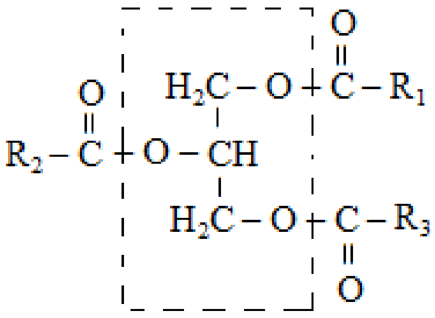


Figure 1. Structural formula of the composition of natural fats.

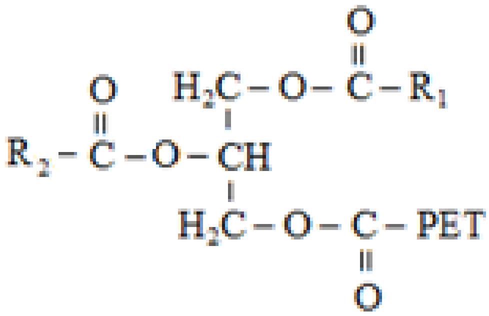


Figure 2. Schematic form of synthesized PET-acylglycerol.

On the output spectrum of rapeseed oil (Fig. 3) characteristic transmission peaks are observed, an intense band with maxima at 2966 cm^{-1}, 2887 cm^{-1}, 2843 cm^{-1}. These peaks can be attributed to stretching vibrations of (ν) ≡C–H bond in the CH_3 groups (2962±10 cm^{-1}) and =CH_2 (2926 cm^{-1} and 2853±10 cm^{-1}). The deformation vibrations (δ) = CH_2 correspond to peaks at (1465±10 cm^{-1}) and 1380 cm^{-1} for –CH_3 and = CH_2. The intense band in the region of 1744±10 cm^{-1} is characteristic for valence vibrations of =C=O bond. The stretching vibrations of the ≡C–O bond are manifested for the triacylglycerols of the three peaks of 1238 cm^{-1}, 1242 cm^{-1}, 1170±80 cm^{-1}.

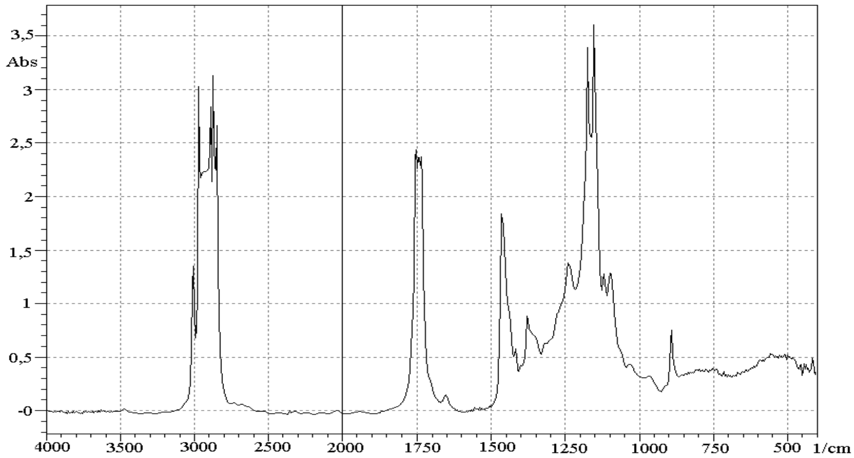


Figure 3. IR spectrogram of rapeseed oil.

On the IR spectrogram (Fig. 4) of the synthesized base bodies of lubricants base on rapeseed oil and PET waste, it should be noted the appearance of bands in the region of 1577 cm^{-1} – stretching vibrations of the C–C = benzene ring groups, deformation vibrations of the benzene ring in the plane at 1540 cm^{-1} and 1020 cm^{-1}, which indicates the presence of fragments of the PET link in the composition of acylglycerol of rapeseed oil.

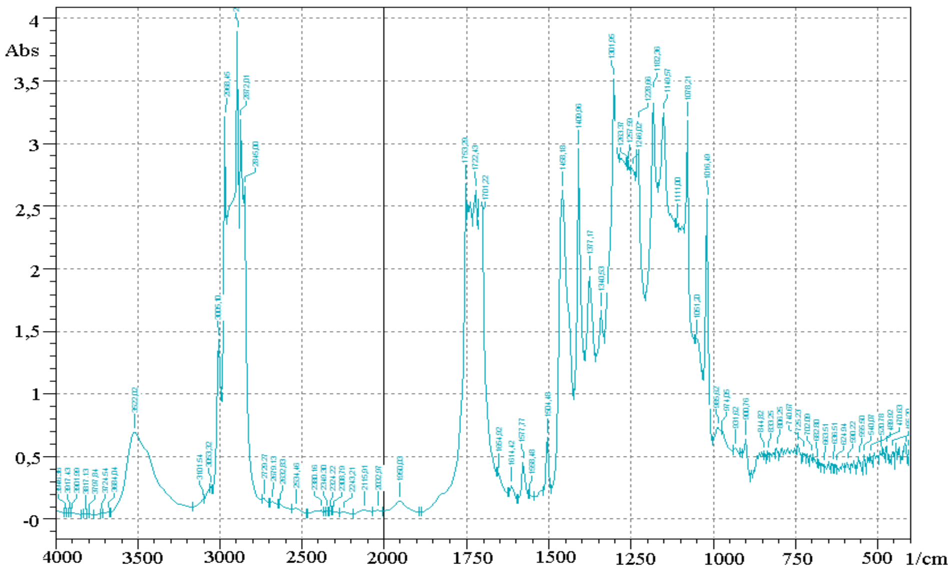


Figure 4. IR spectrogram of PET-acylglycerol based on rapeseed oil.

With the help of computer simulation using empirical calculation methods (molecular mechanics method), a geometrical image of synthesized compounds was obtained. The above images (Fig. 5, Fig. 6) indicate a difference between the structure of PET-acylglycerol and the structure of the initial fats with the geometric form of macromolecules and their placement in space. Calculations of the value of the dipole moment for output beef fat and PET-acylglycerol from beef fat showed a significant difference, for the fat molecule – 4,22D; For PET-acylglycerol – 9,43D. The distribution of electrostatic charge in molecules of beef fat and synthesized PET-acylglycerol is shown in Fig. 7–8.

The direction of the total dipole moment as regard to the horizontal plane, which can be considered a friction plane, and the distribution of the electrostatic potential clearly show the orientation of the molecules of lubricants in the adsorbed layer on the metal surface. It is the specific structure of synthesized compounds – PET-acylglycerol which allows them to be adsorbed parallel to the surface of the metal.

Attention is drawn to the fact that for the PET-acylglycerol molecule, in contrast to fat, a large number of dipoles distributed along the length of the grafted oligomeric PET molecule are observed with respect to the horizontal plane.

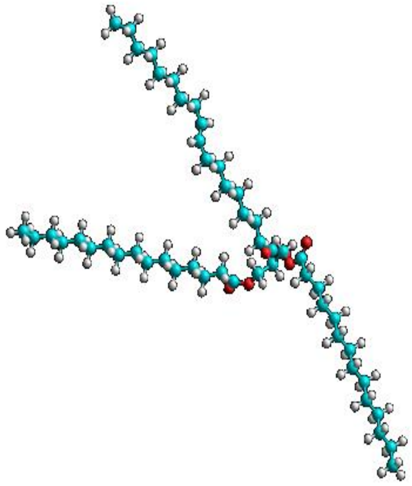


Figure 5. Optimized geometric shape of the beef fat molecule.

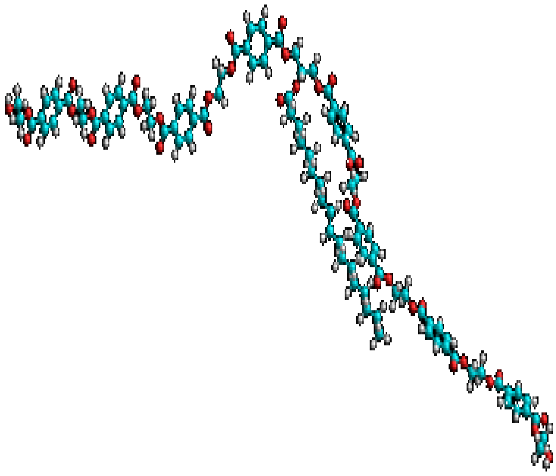


Figure 6. Optimized geometric shape of the PET1,3-acylglycerol molecule based on beef fat.

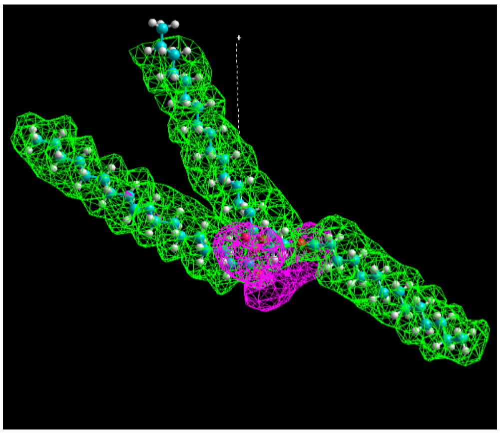


Figure 7. The model of the beef fat molecule and the distribution of the electrostatic potential the dashed vertical line is the direction of the vector of the dipole moment (red is negative potential, green is positive potential).

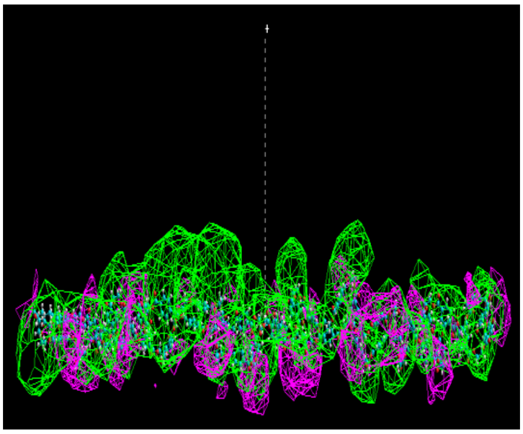


Figure 8. The model of the synthesized PET-acylglycerol on the base of beef fat molecule and the distribution of the electrostatic potential the dashed vertical line is the direction of the vector of the dipole moment (red is negative potential, green is positive potential).

The results of the research cycle to determine the change in tribotechnical properties, depending on the sequential complication of the system under study: natural fat – a synthesized base, with a polymer (PET-acylglycerol) – lubricating oil made from the synthesized base, containing the Irgalube (BASF) additive package are listed in Table 1.

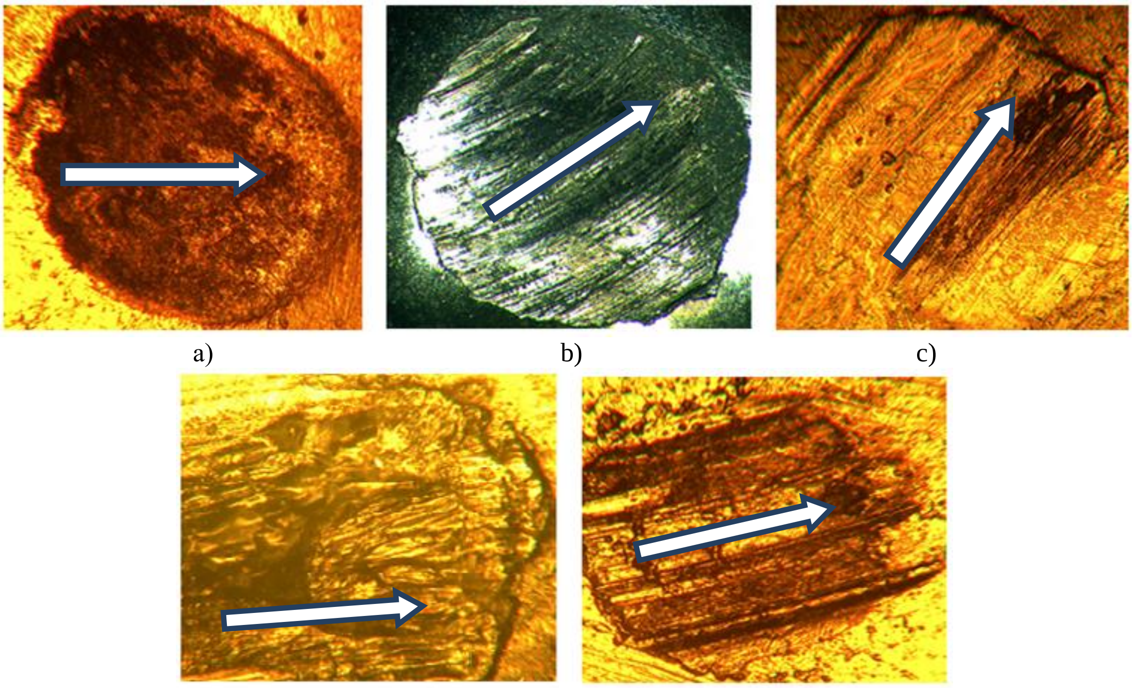
The results of the studies clearly demonstrate the qualitative positive change in the tribotechnical characteristics of the lubricating oils studied with the complication of their structural structure. The transition from the initial fats: beef fat and rapeseed oil to synthesized ones, on their base and PET waste, compounds (PET acylglycerol) provides an improvement in both wear indicators and a decrease in the propensity to weld.

Microphotographs of wear spots of balls investigated on the four-ball friction machine in various lubricating media are shown in Fig. 9.

Table 1. Tribotechnical characteristics of the studied materials

Material	Ultimate load, P_{ult}, (N)	Welding load, P_{weld}, (N)	Scratching index, (SI)	Wear index, (WI), (mm)	Index of friction, k
Beef fat	696	1166	447	1,0	0,15
Rapeseed oil	519	1303	276	1,0	0,15
Beef fat PET-acylglycerol 1/2, 25/75	735	1381	545	0,9	0,10
Beef fat PET-acylglycerol 1/2, 35/65	823	1842	613	0,9	0,11
Rapeseed oil PET-acylglycerol 1/2, 25/75	823	1646	510	0,86	0,08
Rapeseed oil PET-acylglycerol 1/2, 35/65	1098	2067	607	0,84	0,10
Lubricating oil on the base of Beef fat PET-acylglycerol 1/2, 25/75	900	>3400	818	0,53	0,08
Lubricating oil on the base of Beef fat PET-acylglycerol 1/2, 35/65	1235	>3400	720	0,61	0,08
Lubricating oil on the base of Rapeseed oil PET-acylglycerol 1/2, 25/75	980	3087	750	0,45	0,07
Lubricating oil on the base of Rapeseed oil PET-acylglycerol 1/2, 35/65	1166	3283	760	0,57	0,08
Lithol–24	657	1235	301	1	0,17
TSIATIM–201	696	1303	360	0,89	0,2
Divinol Fett R2	519	1235	388	0,87	0,2

where: 1/2 – molar ratio fat:glycerol or oil:glycerol (synthesized acylglycerol),
25/75, 35/65 – mass ratio synthesized acylglycerol:waste PET bottles.



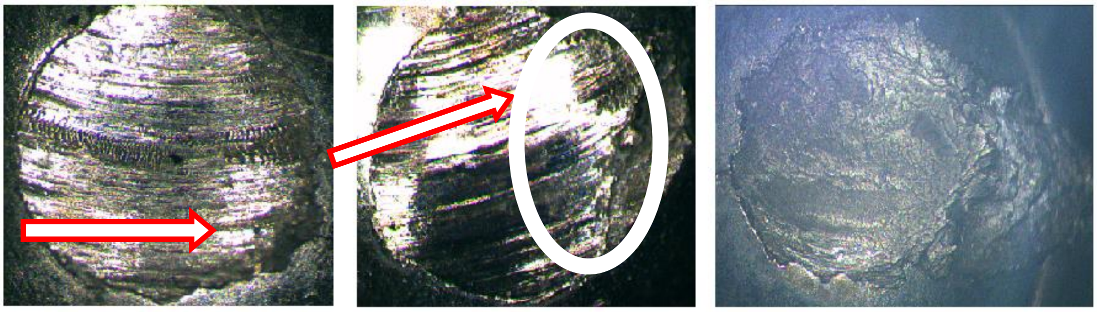
a) b) c) d) e)

Figure 9. The wear spots of the balls at Pult for different lubricating oils, the arrow indicates the direction of motion. (The size of the wear spots is different; consequently the magnification range is different. It will not be correct to compare the microphotographs among themselves mechanically): a) without lubrication; b) beef fat; c) synthesized body of PET-acylglycerol 1/2, 35/65; d) lubricant based on PET-acyl glycerol 1/2, 35/65;
e) Lithol–24.

In the picture (Fig. 9 a), during friction without a lubricating oil (P = 60 N), there are craters due to the adhesion of metal surfaces with signs of cold welding. In case of using beef fat as a lubricant, the limiting friction regime is observed with an equalization of the friction surface due to smoothing of the microroughnesses. On the surface of the spot, two paths of jamming caused by the bonding of metal surfaces can be seen, which can be explained by the falure of the film of the lubricant in the local friction zone at the indicated load value – 696 N (Table 1). The type of wear spot when rubbing with a synthesized body (Figure 9 c) indicates the signs of plastic deformation of a thin layer of metal in the friction zone, which manifests itself in the formation of a mass of metal in front of the ball when it moves. The magnitude of plastic deformations is still insufficient to achieve setting, welding of metal surfaces. Plastic deformation of the metal is evidence of the formation of the intermediate layer in the contact zone, due to the phenomena of adsorption of the lubricating oil on the active centers of the metal surface. Specifically, a large number of dipoles, noted before, explains the extremely high degree of adhesion of PET-acylglycerol to the friction surface, which allows the lubricant film to be retained on the metal surface at high shear stresses and causes a significant improvement in tribological characteristics (Table 1).

When using a lubricating oil obtained from synthesized bodies and additives of a special purpose on the wear spot, it is clearly visible that the metal layer is inflated due to its plastic deformation. As is known [10] due to plastic deformations in the contact zone, the friction surface levels, the contact area grows, causing a decrease in wear and index of friction. In the case of tests of the industrial known lubricant of general purpose Lithol–24, on the area of the wear spot, it is possible to observe the areas of setting of metal surfaces with the formation of craters due to the extraction of the metal. This means that at a given value of the load P_{ult} = 1235 N and the rate, the film of the lubricant Litol–24, namely the hydrocarbon oil, ruins and it does not have time to recover and form an adsorption layer on the contact surface.

More clearly, the difference in the behavior of the lubricating oils studied and the nature of wear of the metal surface is manifested under welding load (Fig. 10).



a) b) c)

Figure 10. Spot wear of the ball with P_{weld} for different lubricating oils: a) beef fat; b) synthesized body of PET-acylglycerol 1/2, 25/75 (the circle highlights the area of brittle failure); c) Lithol–24.

When examining beef fat, a track of wear of the metal surface on the wear spot is observed – wear during seizing. For the wear spot when rubbing with the synthesized PET-acylglycerol body, the surface is smooth, the irregularities were leveled due to plastic deformation and the formation of metal hardening. The increased mobility of the plastic layer of the metal causes the exit of metal from the deep layers to the surface of the dislocations and their concentration in the part of the riveted material. Due to this, the hardness and brittleness of the metal in the hardened layer increase. Figure 10b in the upper right corner shows the metal fracture as a result of brittle ruining.

In the case of studies of Lithol–24, on the spot of wear local areas of welding and significant plastic deformation of the metal surface are visible.

CONCLUSIONS

The conducted studies demonstrate the possibility of a new direction of development of lubricating oil bodies from natural raw materials by implantation of oligomers of different chemical nature in different amounts into fat molecule, thus regulating the rheological, adhesion, tribotechnical properties of lubricants.

REFERENCES

[1] E. Assenova, V. Majstorovic, A. Vencl, M. Kandeva, Green Tribology and Quality of Life, Journal of Advanced Quality, 2012, Vol. 40, No 2, pp. 1–2.
[2] V.V. Ostrikov, S. A. Nagornov, O.A. Klejmenov, V.D. Prohorenkov, I.M. Kurochkin, A.O. Hrennikov, D.V. Dorovskih., Toplivo, smazochnye materialy, tehnicheskie zhidkosti, Tambov: Izd-vo Tamb. gos. tehn. un-ta, 2008, 304 p. (in Russian).
[3] Dekl. patent 60710A Ukrayina, MPK7 S O8 J11/00. Sposib pererobky vidkhodiv polietylentereftalatu / I.A. Mandzyuk, V.M. Holonzhko, T.V. Ivanishena (Ukrayina); zayavnyk i patentovlasnyk Khmel'nyts'kyy derzhavnyy universytet. – № 2003021112 ; zayavl. 07.02.03 ; opubl. 15.10.03, Byul. № 10. – 3 s. (in Ukrainian).
[4] I.A. Mandzyuk, T.V. Ivanishhena, Investigation of chemical recycling – glycolysis of polyethylene terephthalate, Bulletin of Technological University of Podillya, 2002, No 5, pp 186–189.
[5] I. A. Mandzyuk, Questions about handling industrial and household waste, Eco-technology and resource-saving, 2003, No 3, pp. 41–43.
[6] C.J. Byrne, J.A. Calder, Effect of the Water-soluable Fractions of Crude, Refined and Waste Oils on the Embryonic and Larval Stages of the Quahog Clam, Marine Biology, 1977, No 40, pp. 225–231.
[7] M.C. McManus, G.P. Hammond, Life-cycle assessment of mineral and rapeseed oil in mobile hydraulic systems, Journal of Industrial Ecology, 2004, No 7, pp. 163–177.
[8] C. Herrmann, J. Hesselbach, Ecologically benign lubricants – Evaluation from a life cycle perspective, Clean – Soil, Air, Water, 2007, No 35(5), pp. 427–432.
[9] DIN 5135 Testing of lubricants – Testing in the four-ball tester – Parts 1–5. – Publ. 2015–03–01. – Berlin: German National Standard, 2015. – 33 p. (in German).
[10] I.H. Fuks. Dobavky k plastycheskym smazkam, M.: Khymyya, 1982, 248 s. (in Russian).