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Integration of Technological Cycles of Industrial Waste Processing

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ABSTRACT

Within the framework of the concept of "green chemistry" and cyclic economy (economy of closed technological cycles) the extraction of chemical pollutants Cu^{2+}, S^{2-}, HS^{-}–ions from wastewater of various industrial productions was investigated. The research was integrated into a single technological cycle of obtaining new carbon-sulfur-containing lubricants for special purposes. The loading and antifriction properties of the developed plastic lubricants were investigated. It was established that the antifriction properties (f_{fr}) of the developed plastic lubricants are 1.25–1.45 times higher those of the Konstantin-1 industrial lubricant Konstantin-1 and can be used in the work of friction units of various machines and mechanisms. The tribotechnical results of the developed plastic oils in the "steel-aluminum" friction pair are justified, first of all, by the presence, of technical graphite brand LG-1 plastic oils, its modified forms of "pseudographite" and pyrocarbon, as well as sulfur-containing components CuS_x and thiobenzaniline (TBA) in the composition.

Keywords: integrated technological cycles, industrial waste, carbon-sulfur-containing plastic oils, antifriction properties.

INTRODUCTION

The linear development of the world economy involves only the reduction of industrial waste through the partial recycling and does not solve the global problem of its accumulation in the environment. This is a significant disadvantage of such a model of economic development of society, because it does not fundamentally solve the most important problem of today, i.e. reducing the use of natural and energy resources.

The closed-loop economy (cyclic economy) is an alternative, which includes closed waste/recycling technologies, similar to natural closed-loop, such as the world's water cycle. It is obvious that the cyclical transformation of a huge amount of man-modified matter into another environmentally safe or popular form, due to their scale, must correspond to the existing cyclical natural phenomena and processes. Similar waste recycling mechanisms implementing the Zero Waste concept have been introduced at the state level in a number of the most developed countries: Japan, Germany, Austria, Switzerland, and the United States. At the same time, the use of new waste processing technologies makes it possible to obtain biogas, synthesis oil, as well as other types of energy and new materials. However, the progressive accumulation of waste in the world requires the improvement of the existing technologies for their processing and the development of new approaches to solve this important problem.

In the work [Kozlov et al. 2012], the processing of industrial (solid waste contaminated with creosote, petroleum products) and household (food waste, oil) waste to obtain biodiesel was investigated within the closed technological cycle. Previously, the authors of this paper investigated the regeneration of mixed sorbents for the production of soft drinks, consisting of activated carbon (AC) and diatomaceous earth (K) [Ranskiy et al. 2019]; extraction of sulfide and hydrosulfide ions from industrial waters [Khudoyarova O. et al. 2020a; Khudoyarova O. et al. 2020b]; copper(II) ions from industrial waters of galvanic productions [Khudoyavora O. et al. 2020c] and regeneration of spent industrial oils [Khudoyarova O. et al. 2020d] in order to obtain plastic oils as a final product of the above-mentioned industrial processes [Khudoyarova O. et al. 2020e].

Previous separate studies [Ranskiy et al. 2019; Khudoyarova O. et al. 2020a; Khudoyarova O. et al. 2020b; Khudoyavora O. et al. 2020c; Khudoyavora O. et al. 2020d] were integrated in this work into a unified technological cycle (Fig. 1), which included the elements of the cyclical economy and ended with the receipt of the required technical products.

MATERIALS AND METHODS

Mixed sorbent (AC + K), consisting of activated carbon (AC) brand Dekolar A and kieselguhr (K) brands Bekogur 200 and Bekogur 3500, was obtained by regeneration of spent sorbent for the production of PC "Panda" soft drinks (Vinnytsia) [Ranskiy et al. 2019]. Extraction of Cu^{2+}-ions (83.2%) from industrial waters of electrochemical copper plating was performed using modified sulfide and hydrosulfide ions of a mixed sorbent (AC + K) [Khudoyavora O. et al. 2020c]. Desulfurization of the sulfide-alkaline solutions from S^{2-}, HS^{-}- ions (96.6%) was carried out using a regenerated mixed sorbent (AC + K) [Khudoyarova O. et al. 2020a; Khudoyarova O. et al. 2020b]. The spent I-40A SN 300 industrial oil, which was used to obtain plastic oils, was regenerated with a mixed sorbent (AC + K) according to the method described in work [Khudoyarova O. et al. 2020d].

Pyrocarbon (p. 9, Table 1) was obtained through low-temperature pyrolysis carbonization of the mixture (LDPE + HDPE) at a temperature of 350–400 °C for 6 hours.

The PL-2, PL-3, PL-4 and PL-5 lubricant compositions, were prepared in hydrodynamic mode using a VELP AREC high-speed magnetic stirrer (VELP Scientifica, Italy), which provided the necessary homogeneity and rheology of the final product [Khudoyarova O. et al. 2020e]. The compositions of the obtained lubricating compositions are given in Table 1.

Investigations of the antifriction and loading properties of the developed lubricating compositions were held on an SMC-2 friction type machine, which consisted of a St–40X steel roller, AL 9 aluminum pad as well as P, and H load systems [Khudoyarova O.S. 2021]. The obtained tribotechnical characteristics of the "ST–40X steel–AL 9 aluminum" friction pair are given in Table 2 and Figure 3.

RESULTS

It should be noted that the sorption studies of industrial waste treatment [Ranskiy et al. 2019; Khudoyarova O. et al. 2020a; Khudoyarova O. et al. 2020b; Khudoyavora O. et al. 2020c; Khudoyavora O. et al. 2020d; Khudoyavora O. et al. 2020e] were based on the effective use of regenerated mixed sorbent (AC + K), as well as obtaining the final product of cyclic transformations, i.e. plastic lubricants for special purposes [Khudoyarova O.S. 2021].

Thus, Figure 1 shows the logistics of the studied industrial facilities as secondary industrial raw materials, including wastewater treatment,

Table 1. Compositions of the obtained lubricating compounds

No.	Composition,%	Compound				
		PL-1	PL-2	PL-3	PL-4	PL-5
1	Constaline -1	100.0	20.0	30.0	30.0	30.0
2	Industrial oil I-40A	–	10.0	10.0	10.0	10.0
3	I-40A + BTA, 0.1%	–	–	10.0	–	5.0
4	CuS_x	–	10.0	–	–	10.0
5	Boron Organic Supplement	–	20.0	10.0	10.0	10.0
6	Oleic acid	–	10.0	10.0	10.0	10.0
7	Graphite	–	30.0	–	–	–
8	Pseudographite	–	–	30.0	40.0	–
9	Pyrocarbon	–	–	–	–	30.0

Table 2. The influence of loading on antifriction properties of lubricating compositions

Loading P, N	Coefficient of friction, f_{fr}				
	PL-1	PL-2	PL-3	PL-4	PL-5
3	0.055	0.040	0.053	0.044	0.042
4	0.048	0.033	0.045	0.037	0.035
5	0.041	0.026	0.036	0.029	0.028
6	0.035	0.021	0.029	0.023	0.022
7	0.030	0.018	0.024	0.020	0.019
8	0.024	0.017	0.021	0.018	0.017
9	0.020	0.016	0.019	0.017	0.017

in particular the topochemical extraction of Cu^{2+}, S^{2-}, HS^{-}- ions on the matrix surface (AC + K) using the principles of "green chemistry", the study of cyclic processes (cycles I-III), the possible use of purified water in the reversible technological cycles of individual industries, as well as the production of plastic oils as the final product of integrated technological cycles.

A comprehensive approach to the utilization of spent sorbent, adsorption treatment of wastewater from individual industries and the removal of substances (pollutants) includes:

- purification of water solutions and the use of purified water in the technological cycle of production of soft drinks (cycle I);
- purification of galvanic washing waters from Cu^{2+}–ions and use of purified water in technological cycles (cycle II);
- purification (complete or partial) of sulfide-alkaline solutions of chemical (petrochemical) productions from S^{2-} and HS^{-}- ions as well as obtaining new carbon-sulfur-containing plastic lubricants (combined cycle III).

In this case, the common link uniting these integrated technological cycles is the use of regenerated mixed sorbent (AC + K).

Thus, the implementation of the "green chemistry" principle (US Department of Energy, DOE), processing of waste (secondary industrial raw materials), in addition to traditional sorption treatment of wastewater and its possible reuse in closed production cycles, treatment of industrial oils, also includes the manufacturing of a new technical product: carbon-sulfur-containing plastic lubricants for special purposes. The plastic lubricants of this type are used as an alternative to native oils to reduce the wear of friction surfaces as well as extend the service life of machine parts and mechanisms. However, in some cases, they prevent burrs, jams or jamming of friction surfaces, perform the functions of sealants and a number of other important performance characteristics [Ishchuk 1996]. The performed research was aimed at obtaining such multifunctional plastic lubricants. The following components in the studied plastics (Table 1) provided:

- homogeneity (components of items 2, 6: I-40A oil and oleic acid);
- wear resistance and heat resistance (components of items 4, 7–9: copper(II) polysulfide, graphite or its modified forms);
- components of items 3, 5 performed special functions.

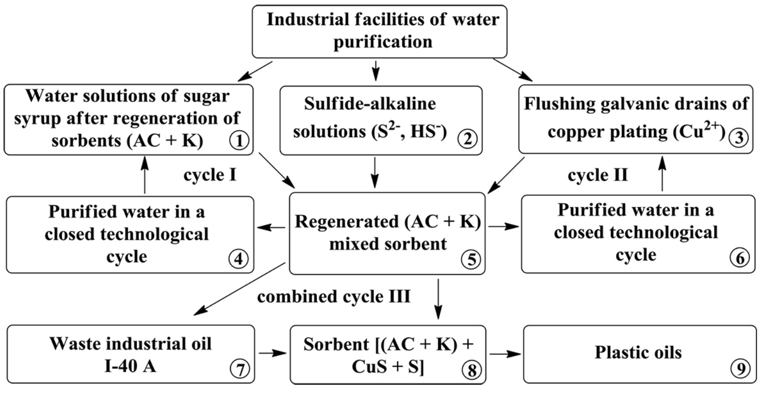
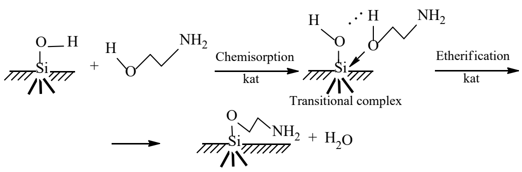


Fig. 1. Logistics of research of industrial objects at complex water purification of chemical pollutants and reception of special purpose plastic lubricants [Khudoyarova O.S. 2021]

Certainly, the specific high-temperature and high-load properties for most industrial plastics are determined by the presence of molybdenum disulfide and graphite in their composition [Ishchuk 1996]. Therefore, it is necessary to carefully examine the surface of the mixed sorbent (AC + K) after its use to treat industrial wastewater [Ranskiy et al. 2019; Khudoyarova O. et al. 2020a; Khudoyarova O. et al. 2020b; Khudoyavora O. et al. 2020c; Khudoyavora O. et al. 2020d; Khudoyavora O. et al. 2020e]. In the work [Khudoyarova O.S. 2021], it was found that after the combined purification of industrial waters from Cu^{2+}, S^{2-}, HS^{-}- ions, the modified surface of the sorbent (AC + K) contains copper(II) sulfide and elemental sulfur. However, given the low value of Gibbs energy for the reaction:

$$CuS + S \rightarrow CuS_2, \Delta G = -37.24\ kJ/mol \quad (1)$$

it is possible to predict the formation of CuS_2 during the operation of different friction pairs. In this case, copper(II) disulfide can be considered as an alternative to expensive and scarce molybdenum disulfide. The surface of another component of the mixed sorbent (AC + K), namely kieselguhr (K), in the manufacturing of lubricating compositions also undergoes significant transformations under the action of organic boron additive (p. 5, Table 1) [Khudoyarova O.S. 2021]:



(2)

The last one consists of an organic boron substance of the general formula $C_2H_8BNO_3$ and monoethanolamine (MEA) in the ratio $C_2H_8BNO_3$: MEA = 1 : 1. MEA, as a bifunctional molecule with strong basic properties, actively interacts with silanol groups of the silicon surface. The conditions for modification/esterification of silanol groups of silicon-containing sorbents with aliphatic amines have been studied in detail in the works [Chuiko 1971]. The etherification reaction takes place by the mechanism of nucleophilic substitution (according to Ingold) [Tertykh et al. 1991] on the matrix surface of kieselguhr. It should be noted that in our case, the reaction (2) takes place at room temperature and an excess of MEA. Obviously, the last one acts in the above-mentioned topochemical transformations not only as a reaction component, but also as a catalyst for the process [Tertykh et al. 1991]. Thus, the mixed sorbent (AC + K), as a component of the developed PL, includes modified surfaces (Fig. 2) and provides the necessary performance properties in the "steel–aluminum" friction pair.

Table 2 and in Figure 3 show the results of research in the "St–40X–AL 9 " friction pair as well as new PL-2, PL-3, PL-4 and PL-5 plastic oils developed by the authors.

The data shown in Figure 3 indicate that in the studied range of workloads of 3.0–9.0 N, the lubricating compositions, which include graphite brand LG-1, as an antifriction component (lubricating composition PL-2), modified sorbents [(AC + CuS + S) + (K + MEA)] ("pseudographite", lubricating compositions PL-3, PL-4) or pyrocarbon PL-5, exceeded the antifriction properties of Constantine-1 (PL-1) industrial oil by 1.25–1.45 times. The comparison of the antifriction properties of PL-2 and PL-4 lubricating compositions in the previously defined range of workloads indicates that the PM-2 composition has 1.09–1.13 times better performance properties. In the authors' opinion, this may be due to a twofold excess of very active organic boron supplement in the composition of PL-2, in comparison with PL-4. However, a slight difference

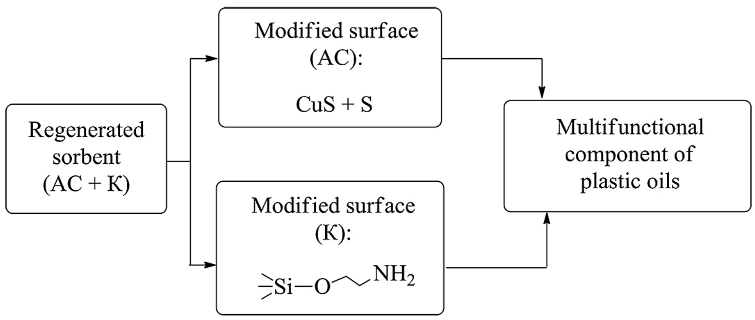


Fig. 2. Scheme of formation of modified surfaces of new carbon-sulfur-containing plastics

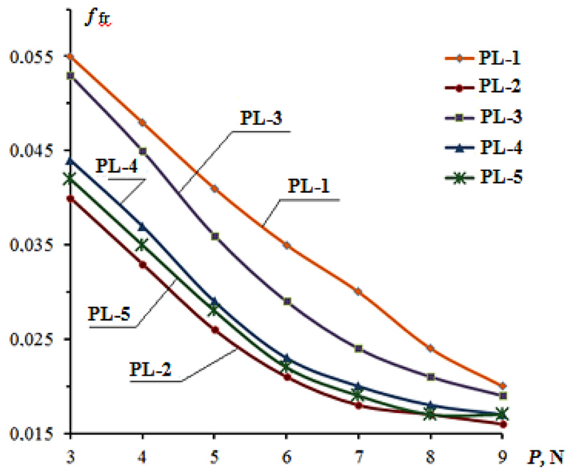


Fig. 3. Dependence of the coefficient of friction on the load in the friction pair "St–40X–AL 9" (υ = 125 rpm)

in the obtained coefficients of friction $\Delta f_{fr} = 0.04$ indicates the efficiency of our "pseudographite" in new carbon-sulfur-containing lubricants, as well as the possibility of its use as a substitute for industrial graphite brand LG-1 in such lubricants.

The comparison of antifriction properties of PL-2 and PL-5 lubricating compositions in the studied load range of 3.0–9.0 N also indicates a slight improvement in the antifriction properties of PL-2 based on industrial graphite brand LG-1 in comparison with PL-5 based on pyrocarbon with the same amount of sulfur-containing component (CuS_x, 10.0% wt.). However, as in the case of the composition of PL-4, the composition of PL-5 included half the amount organic boron additive. The following series of reduction of the antifriction properties (friction coefficient) has been established for the investigated plastic lubricants:

PL-1 > PL-3 > PL-4 > PL-5 > PL-2

Thus, the results of the studies related to the antifriction properties of the developed PL-2, PL-3, PL-4 and PL-5 lubricating compositions, in comparison with Konstalin-1 industrial oil (PL-1) indicate the effectiveness of their use in the "St–40X–AL 9" friction pair and, accordingly, for the possibility of usage in industrial machines and mechanisms.

CONCLUSIONS

1. On the example of obtaining plastic lubricants for special purposes, a general integrated scheme for the processing of industrial waste of various industries, based on the principles of "green chemistry" and cyclical economy has been proposed.
2. The technology of obtaining new carbon-sulfur-containing plastic lubricants for special purposes has been developed; the loading and antifriction properties of the obtained carbon-sulfur-containing plastic lubricants have been studied. It was established that the antifriction properties of the developed plastic lubricants are 1.25–1.45 times higher than those of the Konstalin-1 industrial lubricant and can be used in the work of industrial machines and mechanisms.

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