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DEVELOPMENT OF NEW C, S, N-CONTAINING PLASTIC LUBRICANTS BASED ON PRODUCTS FROM INDUSTRIAL WASTE INTEGRATED PROCESSING

The object of this research is the integrated processing of industrial waste from various industries, which makes it possible to reduce the use of material and energy resources and improve the ecological state of the environment. Waste from the chemical, petrochemical, and machine-building industries was subject to integrated technological processing.

The common link that united the investigated complex technological cycles was the use of a regenerated mixed sorbent (activated carbon+kieselguhr), on the surface of which topochemical transformations of chemicals that were part of industrial waste took place. Using a regenerated mixed sorbent, exhausted industrial oil which was the mineral basis of the developed new C, S, N-containing plastic lubricants was purified. In particular, we have established the conditions for obtaining diethyl ammonium chloride from unusable pesticides of the formula $R^1R^2R^3R^4C_6HCOOH{\cdot}HN(C_2H_5)_2$, whose topochemical interaction on the surface of the mixed sorbent leads to the formation of a sorbed fragment [sorbent (activated carbon+kieselguhr)]$\cdot$[$(C_2H_5)_2NC(=S)SK$]. Subsequent interaction of aqueous solutions containing copper(II) ions with such a fragment leads to the formation of bis–(diethyldithiocarbamate)copper(II) on the surface of mixed sorbent. The resulting substances of the general composition [sorbent (activated carbon + kieselguhr)]$\cdot${$[(C_2H_5)_2NC(=S)S]_2Cu$} were studied as thickeners and active polyfunctional components of the obtained plastic lubricants. Research into the tribological properties of new C, S, N-containing plastic lubricants showed their high anti-wear and heat-resistant properties and the possibility of effective use in highly loaded friction nodes

Keywords: integrated technologies, industrial waste, plastic lubricants, bis-(diethyldithiocarbamate)copper(II), sorption, modified surface

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1. Introduction

The current world use of non-renewable energy resources (coal, oil, gas), and minerals is accompanied by the formation of a huge amount of industrial waste, which ends up at landfills or accumulates at special landfills for their processing. The use of renewable energy sources (solar, wind, and hydropower) does not provide the necessary global energy consumption, which leads to an even greater use of fossil non-renewable energy resources and deterioration of the ecology of the environment. So, for example, the production of oils is the most valuable product of oil processing. It is necessary to spend 1 barrel (159 dm^3) of crude oil to produce 1 dm^3 of oil by vacuum distillation of oil. Therefore, in order to rationally use this important natural resource for Ukraine, used oils should be considered a valuable secondary industrial raw material. However, according to statistical data, Ukraine collects about 25 % of used oils from the total volume of their use, and only 15 % is regenerated, which is approximately 3 % of the total volume of their consumption. In addition to the general, mostly environmental damages from the inefficient use of used oils, it is advisable to mention its energy loss component. According to the general assessment of specialists regarding friction as a phenomenon in human life: 30–40 % of all energy produced on the planet during the year is spent on overcoming frictional resistance [1, 2], and 3 % on the restoration of worn parts and equipment [3]. Thus, it seems quite logical to develop the latest theoretical and experimental knowledge about wear, friction, plastic lubricants, and the study of the properties of contacting surfaces in friction pairs. It is also worth noting that the production of modern plastic lubricants is connected not only with technological issues of their production but also with the market value of their components (MoS_2, ultradispersed diamonds, fullerenes). Such functional applications provide high multifaceted functional properties of plastic lubricants within the framework of the circular economy. Thus, the currently dominant global model of a linear economy does not ensure a reduction in the use of natural resources. It is the cause of huge environmental pollution. In this regard, the circular economy is considered to be a new economic model capable of limiting the use of natural and energy resources and reducing the negative impact of industrial production on the environment [4]. Within the framework of the circular economy, the reuse and recycling of secondary resources is considered using the main provisions of the "3R" concept: reduce, reuse, and recycle.

Thus, it can be stated that in the development, research, and production of new plastic lubricants, it is necessary to solve not only the task to improve their operational properties but also the issue of resource, technological, financial, and environmental support.

Therefore, it is a relevant task to investigate the development of new C, S, N-containing plastic lubricants using secondary raw materials.

2. Literature review and problem statement

Work [1] reports a large body of fundamental and applied research into plastic lubricants. The latter included various components of the dispersion medium, dispersed phase/thickeners, and functional applications. However, the authors did not consider friction as a process of self-organization at the nano-level. Study [2] gives data on the synthesis of thioamides and their complex compounds and investigates the resulting compounds as part of oils and lubricating compositions. However, the low availability of compounds of this class significantly limits the possibilities of their practical use. In work [3] and in a number of other papers, it is noted that the introduction of advanced tribological technologies significantly reduces wear and friction. But at the same time, there is no data regarding the possible use of secondary raw materials in the production of plastic lubricants of general or special purpose. So, for example, in [5], research was carried out on lubricating compositions that included a complex MoS_2/graphene thickener. Such a thickener is quite expensive. In addition, there is no industrial technology for its production, and its use is possible only in lightly loaded friction pairs.

The importance of the practical use of plastic lubricants in numerous modern machines and mechanisms requires the provision of high anti-wear, anti-corrosion, anti-oxidation, viscosity-temperature, dispersing, and other operational properties in friction pairs. New technologies for the production of base oils, new thickeners and new operational additives are being developed to create plastic lubricants that meet the above-listed indicators. At the same time, mainly two directions of obtaining new plastic lubricants are being researched and developed. The first is related to the synthesis of fundamentally new listed components: fugerenes; nanoscale thickeners of an inorganic nature; oleophilic graphite; synthetic polymers, as a rule, are expensive, do not have developed technologies for obtaining final products and are far from practical implementation. The second direction is the use of industrial waste as secondary raw materials to obtain, first of all, fundamentally new multifunctional thickeners. This approach is most appropriate for the unbalanced economy of Ukraine, in the absence of the necessary financial and natural resources. However, it should be noted that similar research and technological developments are practically absent in global practice. In addition, it should be noted that conducting a critical analysis of the obtained results based on the data of published scientific articles in the field of tribochemistry faces objective difficulties. This is due to the fact that the comparison and analysis of the results obtained from different sources is possible only in the case of conducting research using a single methodology, under the same conditions and on similar friction machines. Taking into account the above, the analysis involved, first of all, components included in the formulation of lubricating compositions, the technology of their production, which currently determined their practical value.

Modern plastic lubricants contain lubricating fluids (petroleum, synthetic, vegetable oils), inorganic and organic thickeners (Li, Na, K, Ca-soap, highly dispersed modified SiO_2, oleophilic graphite, MoS_2, etc.) and functional additives for various purposes [1, 2, 5]. The listed main components ensure reliable operation of plastic lubricants in friction pairs of machines and mechanisms, for example, under conditions of high temperatures and loads.

It should be noted that such plastic lubricants must be considered as a highly structured dispersed phase, which, due to adsorption, capillary, and other physical connections, holds the dispersion medium/lubricating liquid in its three-dimensional framework. Especially effective are modified nano-sized thickeners, which are formed directly on a solid surface due to the flow of topochemical reactions [6]. In the development of such modern plastic lubricants, solid dispersed phases (SiO_2, graphite, MoS_2, CuS_x, and other compounds) with an ordered surface structure are used [7].

The operational properties of plastic lubricants are determined mainly by the type of thickener used. Thus, the load-bearing and high-temperature properties are ensured by the presence of the most common components in their composition – graphite and molybdenum disulfide [1, 8–10]. The latter has a high cost, therefore, in a number of works [11–13], studies were conducted to replace it with cheaper copper polysulfide. The modification of the surface of a mixed sorbent consisting of activated carbon and kieselguhr with sulfide ions was investigated in [14]. The modified sorbent was used to purify galvanic industrial waters from copper(II) ions with the formation of sorbed nanosized particles of copper(II) sulfide and elemental sulfur. The obtained ordered carbon-sulfur-containing surface was considered by the authors of [14] as a promising dispersed phase of new high-temperature and high-load plastic lubricants. It was assumed that the probable topochemical formation of copper polysulfide CuS_x (x=2–5) on the solid surface of the mixed sorbent can effectively replace the expensive molybdenum disulfide MoS_2. Basic lubricating fluids are also important components of plastic lubricants. Usually, these are common solidols, which consist of a mixture of petroleum oils of medium viscosity, thickened with calcium soaps of synthetic fatty acids. At the same time, it is important to use regenerated oils rather than primary resources [13]. In a number of works, the processing of waste/secondary raw materials of various industrial productions was investigated. Thus, in work [14], a technology was devised for the combined utilization of industrial sulfide-alkaline solutions of petrochemical industries and metal cations of washing waters of electroplating industries with the production of the corresponding poorly soluble metal sulfides or copper(II) CuSx polysulfide. Work [12] developed a complex technology for the processing of industrial waste from various industries. Waste from the food industry was processed – a mixed sorbent consisting of activated carbon and kieselguhr was regenerated and activated. Waste from the petrochemical industry was processed – toxic ions S^{2-}, HS^{-} were removed and disposed of from used sulfide-alkaline solutions. Electrochemical production waste was processed – Cu^{2+} ions were extracted from galvanic washing waters. Waste from the machine-building industry was processed – used industrial oil I-40A was regenerated. The devised integrated technology most fully corresponded to the main provisions of the "3R" concept: reduce, reuse, and recycle [15]. Work [16] reports the results of similar studies on the development of plastic lubricants using natural fats and polyethylene terephthalate (PET bottles) recycling products.

In a number of works [11–14], the results of the effective use of secondary raw materials of various industrial productions for the development of new plastic lubricants are given. The list of such industrial productions, as well as the chemical substances included in their composition and which are the starting compounds for obtaining plastic lubricants, is shown in Fig. 2. However, there are reasons to believe that the list of such secondary raw materials/range can be significantly expanded. In addition, the above reference data indicate the importance of such technological research aimed at effective use of renewable material and energy resources and improvement of environmental ecology. Thus, objective data from our literature review give grounds for asserting the absence of comprehensive studies on the use of secondary raw materials for the production of new C, S, N-containing plastic lubricants, as well as the expediency of conducting them.

3. The aim and objectives of the study

Our research aimed to develop new C, S, N-containing plastic lubricants through complex processing of industrial waste from various industries. This could make it possible to obtain a new technical product – plastic lubricants, and to reduce the negative impact of industrial production on the environment.

To achieve the goal, the following tasks had to be solved:

– to establish the features of topochemical transformations on the surface of a mixed sorbent consisting of activated carbon and kieselguhr;

– to carry out regeneration of used industrial oil I-40A with its subsequent use as a dispersion medium for new plastic lubricants;

– to establish patterns of technological transformations of industrial waste from various industries and obtaining new C, S, N-containing plastic lubricants.

4. The study materials and methods

The object of our research is integrated processing of industrial waste from various industries, which makes it possible to reduce the use of material and energy resources and improve the ecological state of the environment.

The main hypothesis of the research assumes that purposeful interaction of chemical components of various industrial wastes can be effectively used to obtain popular products, in particular, plastic lubricants.

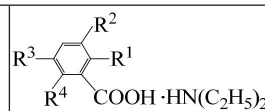
As a sorbent, a regenerated mixture of activated carbon (AC) of brand Dekolar A and kieselguhr (K) of brands Bekogur 200 and Bekogur 3500 (manufactured by E. Begerow GmbH & Co, Deutschland) was used, which was applied in the production of soft drinks at PP "VF "Panda" (Vinnytsia). Regeneration of mixed sorbent (AC+K) was carried out under a hydrodynamic mode using a high-speed magnetic stirrer of brand VELP ARES (VELP Scientifica, Italy). The relative sorption capacity of the regenerated mixed sorbent (AC+K) for iodine was 96.7–100.0 % [17].

The head fraction of crude benzene with a carbon disulfide content of 30.0–32.8 % by weight, selected at PJSC "Yasynivsky Coke Chemical Plant" (Makiivka, Ukraine), was used as a source of carbon disulfide for the matrix synthesis of bis-(diethyldithiocarbamate)copper(II). Reagent extraction of carbon disulfide from the head fraction of coke chemical production was carried out according to the procedures given in [18].

Unusable chlorine-containing pesticides (Table 1) were selected at the agricultural enterprise "Sura" in the Dnipropetrovsk oblast (Ukraine), and the extraction of their active substances was carried out according to the procedures given in [19].

Table 1

Chlorine-containing pesticides used for research

Pesticide name	Chemical name of the active ingredient					CAS number*	LD_{50}**, rats, mg/kg
		R^1	R^2	R^3	R^4		
Chloramben	diethylamonic salt of 3-amino-2,5-dichloro-benzoic acid	Cl	NH_2	Cl	H	133–90–4	3500
Tricamba	diethylamonic salt of 2-methoxy-3, 5, 6-tri-chlorobenzoic acid	OCH_3	Cl	Cl	Cl	2307–49–5	300
Polydym	diethylamonic salt of 2,3,6-trichlorobenzoic acid	Cl	Cl	H	Cl	50–31–7	570

*Notes: * – CAS number for the active substance of the pesticide;*
*** – the dose of the pesticide that causes the death of 50 % of experimental animals*

The modified surface of the sorbents (AC+K) was studied using the diffuse reflectance method on an IR-Fourier spectrometer Nicolet iN 10 FX from Thermo Fisher Scientific (USA) in the range of 4000–525 cm^{-1}. Decoding of the obtained spectra was carried out according to the data of the library of IR spectra from the software package "Omnic Picta 1.5.126" (USA) and the data given in [20–24].

Modification of the surface of the mixed sorbent (AC+K) using Chloramben was carried out in two stages. At the 1st stage, the unusable pesticide Chloramben (diethyl ammonium salt of 3-amino-2.5-dichlorobenzoic acid, Table 1) was treated with hydrochloric acid to obtain the structural fragment [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl}. To 100 ml of a 30.0 wt% aqueous solution of Chloramben, a 30 wt% solution of hydrochloric acid was added to pH=3 while stirring in small portions. The acidity of the reaction mass was monitored using a universal indicator paper. The reaction mass was kept under intense stirring and heated to 65 °C for 45 minutes, and then cooled to room temperature. The precipitate of 3-amino-2,5-dichlorobenzoic acid that was formed was filtered on a Schott filter and washed with cold water (2×25 ml).

To isolate the diethyl ammonium salt, which is part of the pesticide Chloramben, the filtrate was treated with a mixed sorbent (AC+K), intensively stirred at a temperature of 35–40 °C for 60 min. After that, it was filtered on a Schott filter and the sorbed salt of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl} was isolated, washed with cold water, and dried in a chamber at 65 °C.

At the II stage, surface modification of the mixed sorbent (AC+K) was carried out to obtain a structural fragment [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}. The setup for stage II consisted of a three-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and an ice bath. 150 g of modified sorbent (AC+K) containing 10.86 g (0.1 mol) of diethyl ammonium chloride was loaded into a three-necked flask. In addition, 120 ml of benzene, 30 ml of a 40 % (0.3 mol) aqueous solution of potassium hydroxide were added to a three-necked flask. At the final stage, 26 ml of the head fraction with a carbon disulfide content of 31.7 % (0.1 mol) was added through a dropping funnel to a three-necked flask with intensive stirring. The reaction mass was kept under this mode at a temperature of 0–5 °C for 3 hours. After that, the ice bath was removed, and the reaction mass was intensively stirred for 1 hour at a temperature of 20–25 °C.

At the last stage of chemical transformations, a concentrated aqueous solution containing 9.50 g (0.038 mol) of $CuSO_4{\cdot}5H_2O$ was added for 15 min. The formation of an amorphous brown precipitate was observed in the solution and on the surface of the mixed sorbent (AC+K). The reaction mass was filtered on a Schott filter, dried, and a modified sorbent was isolated, which included the structural fragment [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}.

Modification of the surface of the mixed sorbent (AC+K) during the processing of the pesticides Trikamba and Polydim with obtaining sorbed structural fragments [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl} (I stage) and [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$} (II stage) was carried out similarly.

A regenerated mixed sorbent (AC+K) was used to regenerate used industrial oil. Used industrial oil I-40A was previously purified from mechanical impurities by filtering through a paper filter and from water by adding 1.5 g of anhydrous Na_2SO_4 for every 100 ml of oil with subsequent filtering. 100–200 ml of used industrial oil was added to 10 g of mixed sorbent (AC+K), the mixture was stirred on a high-speed magnetic stirrer for 30–40 min at a temperature of 20–25 °C. After vacuum filtering, the regenerated industrial oil is ready for the study of its physical and chemical characteristics.

Preparation of lubricating compositions of the PM series (general procedure). Lubricant composition PM-2 (Table 2) was prepared using a high-speed magnetic stirrer VELP AREC (VELP Scientifica, Italy) while heating the consistent mass to 70–90 °C. 15.0 g of an organoboron compound was added to a mixture of 25.0 g of Konstalin grease 1–13 and 10.0 g of regenerated industrial oil I-40A, a magnetic stirrer was turned on, and the mixture was stirred at 40–45 °C for 30 min. After that, 20.0 g of a mixed sorbent (AC+K) with a modified surface [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$} was added gradually. Further high-speed mixing was carried out for 30–40 min, gradually increasing the temperature of the reaction mass to 70–75 °C. At the final stage, 20.0 g of graphite and 10.0 g of oleic acid were added in portions. The reaction mass was kept until complete homogenization, and then cooled.

Table 2

Composition of lubricants of the PM series

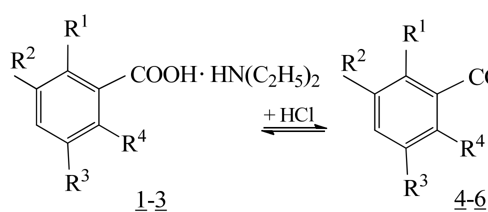
Composition, % wt	Lubricant				
	PM-1	PM-2	PM-3	PM-4	PM-5
Konstalin 1-13	100	25	25	30	30
Industrial oil I-40A	–	10	10	10	10
Modified sorbent [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}	–	20	25	30	40
Organoboron compound	–	15	15	10	10
Oleic acid	–	10	10	10	10
Graphite	–	20	15	10	–

The resulting new C,S,N-containing consistent lubricants were ready for tribotechnical studies. Laboratory studies of the developed lubricant compositions PM-2 – PM-5 (Table 2) were carried out at the Department of Mechanical Engineering of the Vinnytsia National Technical University (Ukraine) in a friction pair of steel St-40X - aluminum alloy AL9.

5. Results of research on obtaining new C, S, N-containing plastic lubricants

5. 1. Study of topochemical transformations on the surface of a mixed sorbent (AC+K) using IR spectroscopy

To increase their solubility in water, chloroderivatives of benzoic acid (herbicides) are used in the form of diethyl ammonium salts 1–3, which were regenerated according to the general scheme (Fig. 1) [19].



+ [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl}, (1)
7

1: $R^1 = R^3 = Cl$, $R^2 = NH_2$, $R^4 = H$;
2: $R^1 = OCH_3$, $R^2 = R^3 = R^4 = Cl$;
3: $R^1 = R^2 = R^4 = Cl$, $R^3 = H$;

4: $R^1 = R^3 = Cl$, $R^2 = NH_2$, $R^4 = H$;
5: $R^1 = OCH_3$, $R^2 = R^3 = R^4 = Cl$;
6: $R^1 = R^2 = R^4 = Cl$, $R^3 = H$.

Fig. 1. General scheme for the extraction of chemicals from unusable pesticides of the general formula $R^1R^2R^3R^4C_6HCOOH{\cdot}HN(C_2H_5)_2$

Benzoic acid derivatives 4–6 were isolated by filtering the reaction mass on a Schott filter and recrystallized from benzene. The obtained crystalline compounds 4–6 were used for IR spectral studies. An aqueous solution of diethyl ammonium chloride was treated with a regenerated mixed sorbent (AC+K) and the sorbed fragment 7 was obtained.

The topochemical reactions of obtaining potassium diethyldithiocarbamate 8 and then bis-(diethyldithiocarbamate)copper(II) 9 were carried out, respectively, according to schemes (2) and (3):

$$\underset{\underline{7}}{[\text{sorbent (AC+K)}]\cdot\{[(C_2H_5)_2NH_2]Cl\}} \xrightarrow[0\text{-}6\ ^{\circ}C]{+\,KOH,\ +\,CS_2} \underset{\underline{8}}{[\text{sorbent (AC+K)}]\cdot[(C_2H_5)_2NC({=}S)SK]}, \quad (2)$$

$$\underset{\underline{8}}{[\text{sorbent (AC+K)}]\cdot[(C_2H_5)_2NC({=}S)SK]} \xrightarrow[20\text{-}25\ ^{\circ}C]{+\,CuSO_4} \underset{\underline{9}}{[\text{sorbent (AC+K)}]\cdot\{[(C_2H_5)_2NC({=}S)S]_2Cu\}}, \quad (3)$$

$$\underset{\underline{7}}{[\text{sorbent (AC+K)}]\cdot\{[(C_2H_5)_2NH_2]Cl\}} + KOH + CS_2 + CuSO_4 \longrightarrow$$

$$\longrightarrow \underset{\underline{9}}{[\text{sorbent (AC+K)}]\cdot\{[(C_2H_5)_2NC({=}S)S]_2Cu\}}. \quad (4)$$

Reaction (2) proceeds when the reaction mass is cooled due to the volatility of diethylamine, which is formed during chemical transformations. The overall reaction (4) indicates that compound 8 is an intermediate of the given transformations, therefore, IR spectral studies were performed only for the final bis-(diethyldithiocarbamate)copper(II) 9, which is sorbed on the surface of the mixed sorbent (AC+K).

Modification of the surface of the mixed sorbent (AC+K) during the processing of the unusable pesticide Chloramben.

Stage I. The yield of 3-amino-2,5-dichlorobenzoic acid was 17.5 g (85 %). m.p.=199.5–200.0 °C. Found, %: C 40.43; H 2.14. For $C_7H_5Cl_2NO_2$, the following were calculated: C 40.81; H 2.45. IR spectrum, ν, cm^{-1}: 3470 sl., 3375 sr. (NH_2); 1780 s. (=C=O); 1680 s. (COOH, dimer); 1475 sr. (C–H_{Ar}); 790 s. (C–Cl). The sorbed salt of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl}: yield 9.3 g (in terms of diethyl ammonium chloride). IR spectrum, cm^{-1}: ν 3360 sl. (N–H); ν 2850 s. (C_2H_5N); ν 2700 s. ([$H_2N(C_2H_5)_2$]Cl); δ 1475 (N–H).

Stage II. Modified sorbent, which included the structural fragment [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}: yield 12.6 g (in terms of bis-(diethyldithiocarbamate)copper(II))). IR spectrum, cm^{-1}: ν 2935 sl. (C–H); δ_1 1380 sl. (CH_3); δ_2 1360 sl. (CH_3); ν_1 1525 d.s. (C–N); ν_2 1155 sr. (C–N); n 1280 s. (C–S); ν 1095 sr. (C=S).

Modification of the surface of the mixed sorbent (AC+K) during the processing of the unusable pesticide Trikamba.

Stage I. The yield of 2-methoxy-3,5,6-trichlorobenzoic acid was 21.2 g (83 %). m.p.=138–138.5 °C. Found, %: C 37.36; H 1.45. For $C_8H_5Cl_3O_3$, the following were calculated: C 37.61; H 1.97. IR spectrum, cm^{-1}: 1780 s. (C=O), 1680 s. (COOH, dimer); 1460 sr. (C–H_{Ar}), 1230 sr. (OCH_3), 785 s. (C–Cl). Sorbed salt of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl}. Yield 9.1 g (in terms of diethyl ammonium chloride). IR spectrum, cm^{-1}: ν 3355 sl. (N–H); ν 2845 s. (C_2H_5–N); ν 2700 s. ([$H_2N(C_2H_5)_2$]Cl); δ 1475 sl. (N–H).

Stage II. Structural fragment of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}. Yield 12.5 g (in terms of bis-(diethyldithiocarbamate)copper(II)). IR spectrum, cm^{-1}: ν 2930 sl. (C–H); δ_1 1375 sl. (CH_3), δ_2 1355 sl. (CH_3); ν_1 1520 d.s. (C–N), ν_2 1150 sr. (C–N); ν 1275 s. (C–S), ν 1090 sr. (C=S).

Modification of the surface of the mixed sorbent (AC+K) during the processing of the unusable pesticide Polidym.

Stage I. The yield of 2,3,6-trichlorobenzoic acid was 19.4 g (86 %). m.p.=124–124.5 °C. Found, %: C 37.03; H 1.17. For $C_7H_3Cl_3O_2$, the following were calculated: C 37.29; H 1.34. IR spectrum, cm^{-1}:1785 s. (C=O), 1685 s. (COOH, dimer); 1465 sr. (C–H_{Ar}). Sorbed salt of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NH_2$]Cl}. Yield 9.2 g (in terms of diethyl ammonium salt chloride). IR spectrum, cm^{-1}: ν 3360 sl. (N–H); ν 2850 s. (C_2H_5–N); ν 2700 s. ([$H_2N(C_2H_5)_2$Cl]; δ 1475 sl. (N–H).

Stage II. Structural fragment of the composition [sorbent (AC+K)]·{[$(C_2H_5)_2NC(=S)S]_2Cu$}. Yield 12.6 g (in terms of bis-(diethyldithiocarbamate)copper(II)). IR spectrum, cm^{-1}: ν 2935 sl. (C–H); δ_1 1382 (CH_3), δ_2 1358 sl. (CH_3); ν_1 1525 d.s. (C–N), ν_2 1155 sr. (C–N); ν 1282 s. (C–S), ν 1095 sr. (C=S).

5. 2. Regeneration of used industrial oil I-40A and obtaining interchangeable lubricating fluid

Sorptive cleaning of used industrial oil I-40A was carried out using a sorbent (AC+K). Preliminary regeneration and activation of the latter was carried out with a 1.25 % NaOH solution [17]. The resulting purified industrial oil I-40A was used as a dispersion medium in the production of new C, S, N-containing plastic lubricants. The physical-chemical characteristics of industrial I-40A SN 300 oil, used oil (UO), and regenerated oil (Table 3) were determined in accordance with the current regulatory documents.

Table 3

Physicochemical characteristics of I-40A oil

Indicator name	Lubricant I-40A SN 300*	Used lubricant I40-A	Regenerated lubricant		
			Mass ratio (AC+K):(UO)		
			1:10	1:15	1:20
Kinematic viscosity at 40 °C, mm^2/s	61–75	70	73	72	71
Mass fraction of water, % mass	traces	0.15	traces	traces	0.05
Acid value, mg KOH/g	0.05	0.81	0.09	0.22	0.37
Optical density, A470	0.082	0.362	0.093	0.210	0.298
Flash point in an open crucible, °C	220	210	220	218	212
Mechanical impurities, wt%	absent	0.23	absent		
Density, g/cm^3	0.886	0.900	0.890	0.895	0.897

*Note: * – manufacturer DOLPHIN INDUSTRY UKRAINE LLC*

Laboratory studies have shown that the developed lubricant compositions PM-6 – PM-9 are superior to industrial plastic lubricant Konstalin 1-13 (PM-1, Table 2) in terms of antifriction properties.

5. 3. Technological features of using industrial waste to obtain C, S, N-containing plastic lubricants

In addition to sorption purification and reagent separation of active substances of industrial objects, the technological aspects of integration of selected chemical components into the demanded final product – into new C, S, N-containing plastic lubricants are being studied.

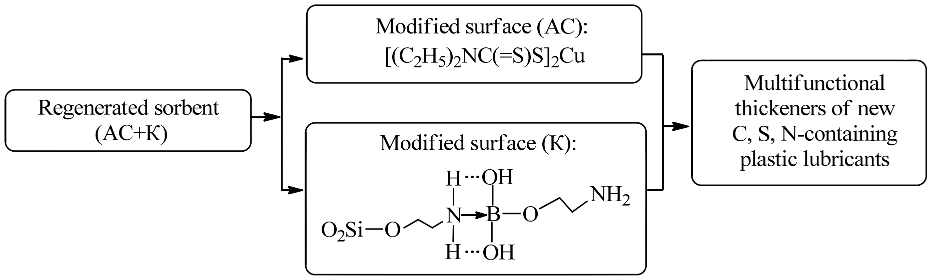


Fig. 3. Scheme of formation of structural framework fragments of new C, S, N-containing plastic lubricants

Fig. 2 shows the basic technological scheme for obtaining new C, S, N-containing plastic lubricants using industrial waste from various industries.

Plastic lubricants based on sodium, sodium-calcium, complex calcium and lithium components no longer meet the increased operating conditions of modern equipment. New, highly effective, and multi-purpose plastic lubricants should ensure the operation of machines and mechanisms in a wide range of temperatures, working loads, and aggressive environments [1]. The necessary level of volumetric and mechanical properties of such lubricants is achieved by introducing new thickeners and corresponding functional applications that form their structural framework. For the developed C, S, N-containing plastic lubricants, the necessary structural frame is formed due to the modified surfaces of activated carbon and kieselguhr (Fig. 3).

The introduction of such multifunctional thickeners of the frame type into the composition of plastic lubricants provides a number of operational properties.

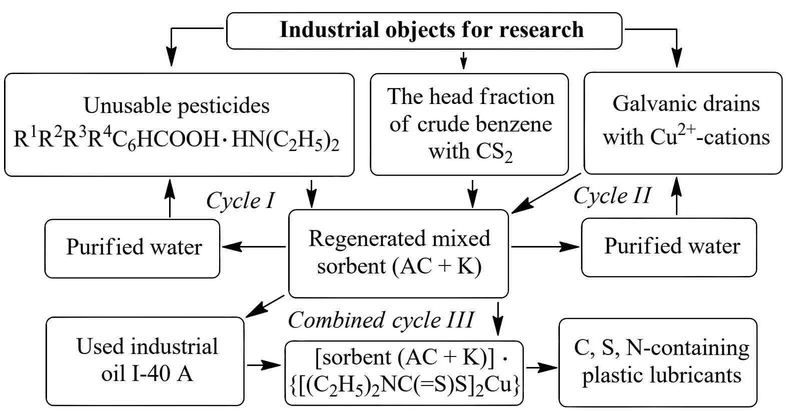
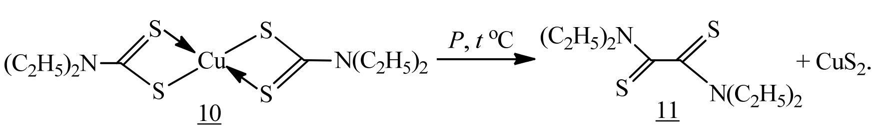


Fig. 2. Basic technological scheme for obtaining C, S, N-containing plastic lubricants using industrial waste from various industries

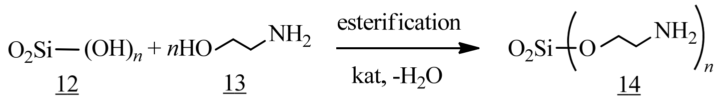
Modification of the surface of activated carbon (AC) (Fig. 3) is ensured by the final adsorption of bis-(diethyldithiocarbamate)copper(II), which at high contact temperatures and loads in friction pairs can be partially desulfurized according to the scheme:



(5)

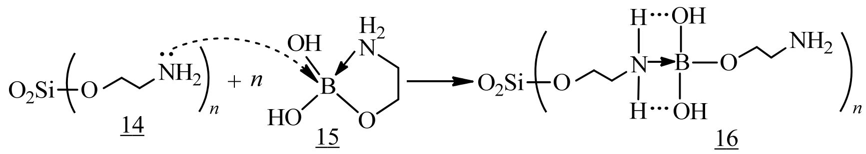
Modification of the kieselguhr (K)/silica gel surface (Fig. 3) is gradual and much more complicated, which is determined by the presence of silanol groups on the silicon surface, monoethanolamine and ethylamine (N→B) borane on the solid surface:

– the first stage is the interaction of surface silanol groups 12 with monoethanolamine 13 with the formation of sorbed fragments 14:



(6)

– the second stage is the interaction of surface monoethanolamine groups with ethylamine (N→B) borane 15 with the formation of surface structures 16:



(7)

It should be noted that, according to work [25], excess monoethanolamine is a catalyst for chemical transformations (6).

6. Discussion of results of the development of new plastic lubricants from the processing products of various industrial wastes

The development of new C, S, N-containing plastic lubricants was based on the possibility of removing chemical pollutants from industrial waste and their possible use as chemical reagents in subsequent technological transformations (Fig. 2). Obtaining the final bis-(diethyldithiocarbamate)copper(II), as a functional additive of plastic lubricants, sorbed on the surface (AC+K), was solved by carrying out successive topochemical reactions shown in schemes (2) to (4). CuS_2, formed in the process of friction according to scheme (5), can be considered as a potential substitute for industrial MoS_2 [1].

Modification of the kieselguhr/silica gel surface (Fig. 3) was carried out by etherification of silanol groups with monoethanolamine according to scheme (6). The first studies of this reaction were carried out at the Surface Institute named after O. O. Chuyko of the National Academy of Sciences of Ukraine [25]; however, the topochemical reactions of etherified ethanolamine groups with ethylamine (N→B) borane were carried out by us for the first time. Ethylamine (N→B) borane (an organoboron compound), which was part of lubricating compositions as a thickener (Table 2), was also obtained for the first time by us.

It should be noted that the peculiarity of the proposed method is that the products of processing (regeneration) of waste from various industries, which have not been used in such a combination before, are used as components of new plastic lubricants. In addition, the extraction of chemicals was carried out using topochemical reactions on the surface of the regenerated sorbent.

Benzoic acid derivatives of compounds 4–6 obtained by reaction (1) (Fig. 1) and diethyl ammonium chloride 7 sorbed on the surface of the mixed sorbent (AC+K) were used for IR spectral studies. Compounds 4–6 are characterized by strong valence vibrations of the C=O carbonyl group in the range of 1780–1785 cm^{-1} and vibrations of the dimeric carboxyl group C(=O)OH in the range of 1680–1685 cm^{-1}. In addition, the valence vibrations of the average intensity of the $C–H_{Ar}$ fragment are 1460–1475 cm^{-1} and the strong valence vibrations of C–Cl are in the interval of 785–790 cm^{-1}. Compound 4 has weak valence vibrations of the NH_2 group at 3470 and 3375 cm^{-1}, and compound 5 has medium intensity valence vibrations of the OCH_3 group at 1230 cm^{-1}.

The sorbed diethyl ammonium chloride 7 is characterized by weak valence vibrations of the N–H bond at 3355–3360 cm^{-1} and deformational vibrations of N–H in the range of 1475 cm^{-1}. In addition, compound 7 has strong valence vibrations of the $C_2H_5–N$ fragment in the interval 2845–2850 cm^{-1} and strong valence vibrations of the structural fragment $[H_2N(C_2H_5)_2]^+Cl^-$ at 2700 cm^{-1}.

The ultimate goal of modifying the mixed sorbent (AC+K) is to obtain bis-(diethyldithiocarbamate)copper(II) 9 on its surface by reactions (2) and (3). Bis-(diethyldithiocarbamate)copper(II) 9 is characterized by valence vibrations ν (C–H) and deformation δ (CH_3) of the ethyl fragment, respectively, in the region of 2935–2930 and 1382–1375 cm^{-1}. In addition, the spectra contain vibrations of the C–N group: ν_1 (C–N) and ν_2 (C–N), respectively, in the region of 1525–1520 and 1155–1150 cm^{-1}, as well as valence vibrations of C(=S)S group: ν (C–S) and ν (C=S), respectively, in the region of 1282–1275 and 1095–1090 cm^{-1}. Thus, compounds 7 (I stage) and 9 (II stage) were obtained during the reagent processing of the pesticides Chloramben, Tricamba, and Polydim (Table 1). In the IR spectra of these compounds, the characteristic oscillations were close or identical and corresponded to the data given in works [18, 24]. The obtained data of IR-spectral studies of the surface of the mixed sorbent (AC+K) confirm the formation of the final bis-(diethyldithiocarbamate)copper(II). In addition, it can be stated that reactions (2) to (4) are classical topochemical reactions that take place on the surface of a solid body.

Lubricating liquids, which are included in the composition of plastic lubricants, are their mandatory component, which ensures the necessary operational properties (colloidal stability, penetration, drop temperature, and others). In addition to pure mineral oils, regenerated industrial oils are also used to obtain plastic lubricants. Thus, used industrial oils I-20A, I-40A, I-50A, IHP-18, IHP-30, MGE-46B after their regeneration are applied in the development of new plastic lubricants [11–13]. As a rule, such oils are used in lightly loaded friction nodes, in the absence of high temperatures and an aggressive chemical environment, which allows them to be effectively regenerated [13]. This approach enables more rational use of material and energy resources in Ukraine. According to statistical data, only 25 % of used oils are collected in Ukraine from the total volume of their use, and 15 % are regenerated, which is approximately 3 % of the total volume of their consumption. At the same time, a significant part of, for example, used oil from private vehicles (30–50 %) gets into the environment or sewers, which violates the legislative framework of Ukraine.

It was established that the use of the optimal ratio of sorbent (AC+K): used oil (UO)=1:10 ensures good regeneration of industrial oil I-40A. Such regenerated oil is inferior to “pure” I-40A SN 300 oil in terms of only two indicators: acid number and optical density (Table 3). Further studies proved that the industrial oil I-40A regenerated in this way could be effectively used as a dispersion medium for developed plastic lubricants. Therefore, it can be argued that the use of regenerated I-40A oil as a dispersion medium for plastic lubricants significantly reduces their cost and improves the environmental condition of the environment.

Our research is a continuation of the development of integrated technologies for the processing of secondary raw materials of various industrial productions using selective sorption and reagent methods and obtaining new plastic lubricants. A comprehensive approach to the processing of industrial waste from various industries is based on the effective use of regenerated mixed sorbent (AC+K) from food industries [11–13]. At the same time, the sorbent (AC+K) can be used for its intended purpose for the purification of circulating water of reagent processing of pesticides (cycle I) or for the purification of galvanic washing water (cycle II). In addition, the mixed sorbent (AC+K) also performs an auxiliary function, namely, on its surface, the topochemical formation of the final bis-(diethyldithiocarbamate)copper(II) occurs (combined cycle III). The noted cyclical technological transformations of material flows are shown on the logistic scheme of obtaining C, S, N-containing plastic lubricants (Fig. 2). The resulting solid mixture of the modified sorbent (AC+K) and bis-(diethyldithiocarbamate) copper(II) was not further separated because these components are active components of plastic lubricants. Thus, the modified sorbent (AC+K) is an inorganic thickener that provides high anti-wear, anti-scratch, and thermal properties [1, 2]. Note that bis-(diethyldithiocarbamate)copper(II) is an S,N-containing functional additive that provides high loading, antifriction, and anti-wear properties of plastic lubricants [2].

It is necessary to state that the latest scientific studies into obtaining new nanomaterials with pre-programmed properties are connected with the use of sol-gel technologies (sol-gel processing) [26, 27]. In this case, homogeneous and multi-component gels were obtained by sol-gel technology “from bottom to top” (without converting them into films, powders, or powder products) as components of plastic lubricants. Bekogur 200 mixed kieselguhr and nanosized ethylamine (N→B) borane in monoethanolamine were used as starting compounds. Previously, the use of sol-gel technologies for obtaining plastic lubricants or their individual components was not reported in the special literature. That is, it can be stated that the use of this technology allows obtaining multipurpose organic-inorganic plastic lubricants. Surface structures 16 (scheme (7)) are characterized by donor-acceptor (N→B), intra-fragmentary (HO···H) and macromolecular hydrogen bonds. The formation of organic-inorganic associative systems takes place due to three-dimensional hydrogen bonds [28] between organic (monoethanolamine, ethylamine (N→B) borane) and inorganic (kieselguhr) components. Hydrogen bonds are not enough to prevent phase separation of the components of plastic lubricants, so oleic acid was added to their composition as an additional stabilizer/thickener (Table 2).

In addition, it should be noted that the developed plastic lubricants contain active elements C, S, and N, and are also limited by the presence of only diethyldithiocarbamate and ethanolamine functional groups. However, they provide the necessary operational properties in industrial friction pairs.

Industrial tests of the obtained plastic lubricants at PP "Eksim" (Kherson) proved that when using plastic lubricants of the PM series, the temperature in the friction nodes did not exceed the standard indicators in accordance with GOST 1033-79. At the same time, the surface of the bearing rolls remained clean, smooth, without rolls and cracks after 12 months of preventive observations.

Limitations inherent in this study are the use of certain types of waste. In the case of replacing one of the studied initial components with another, the possibility of changing the functional properties of the final plastic lubricants should be taken into account. The disadvantage of this study is the multifunctionality of the tasks and the need to conduct a large number of relevant experimental studies. The latter predetermines its further development, which is connected with the expansion of both the types of processed waste and the range of technical products obtained.

7. Conclusions

1. Topochemical transformations of individual reagents on the modified surface of activated carbon and kieselguhr were proposed and investigated by IR spectroscopy. The final product of such transformations is bis-(diethyldithiocarbamate)copper(II) as a potential functional additive to plastic lubricants.

2. Regenerated industrial oil I-40A and other extracted chemical components of industrial waste were used as the main components of the resulting plastic lubricants. Thus, homogeneous and multicomponent thickeners of such lubricants were obtained by sol-gel technology ("from bottom to top") based on kieselguhr of brand Bekogur 200 and nanosized ethylamine (N→B) borane.

3. Our research proposes an integrated technological scheme for the processing of industrial waste from various industries with the production of new C,S,N-containing plastic lubricants based on them. A feature of this scheme is the sequential chemical interaction of individual components of industrial waste with the production of final plastic lubricants.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

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