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Complex Sorption Treatment of Industrial Waste and Production of Plastic Lubricants

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ABSTRACT

The article deals with the studies on complex sorption treatment of industrial waste of various industries to obtain new C, S, N-containing plastic lubricants, which provide antiwear, antifriction, high load-bearing and heat-resistant properties. The conditions for obtaining diethylammonium salt from the obsolete pesticide Banvel D and its sorption on a mixed sorbent, which consist of activated carbon (AC) and kieselguhr (K), have been established. The conditions for obtaining potassium diethyldithiocarbamate and its adsorption on the surface of the mixed sorbent (AC + K), followed by treatment with copper(II) sulfate of corresponding bis-(diethyldithiocarbamato) copper(II) sorbed on a solid surface, have been examined. The obtained substances of general composition [sorbent (AC + K)]·$[(C_2H_5)_2NS(=S)S]_2Cu$ were studied as active components of plastic lubricants, which provide their thickening, antiwear and antifriction properties. Industrial tribological research was carried out for friction pairs of four-row roller bearings of roller equipment used at private enterprise (PE) "Exim" (Kherson, Ukraine).

Keywords: industrial waste, sorption, complex treatment, bis-(diethyldithiocarbamato)copper(II), plastic lubricants.

INTRODUCTION

Polluted water, soil and air, which are the result of human activities, can be considered as artificial man-made formations. At the same time, their magnitude allows us to consider a huge amount of waste as a valuable secondary raw material. Its rational use can significantly reduce the amount of natural resources and energy resources (oil, gas and coal) extracted from the subsoil. One of the options for such complex treatment of wastes from various industries may be the creation of regional industrial complexes. The basis of their effective operation should be complex, cyclical technological processes of recycling in order to obtain a wide range of required products. Thus, we have previously studied the regeneration of mixed sorbents (AC + K) of the production of soft drinks [Ranskiy et al., 2019]; removal of active substances of 2-methoxy-3,6-dichlorobenzoic acid and dialkylammonium salts of obsolete pesticide Banvel D [Ranskiy et al., 2010]; copper(II) ions from industrial washing waters of the copper-plating process [Khudoyavora et al., 2020a; Malovanyy et al., 2019]; high-toxic carbon disulfide from the head fraction of the crude benzene (HFCB) of coke productions [Ranskiy et al., 2013] and regeneration of used industrial oil I-40 A [Khudoyavora et al., 2020b], which formed the basis for obtaining new C, S, N-containing plastic lubricants as the target product of the above-mentioned industrial processes [Khudoyavora et al., 2020c].

The purpose of this work is to study the complex sorption treatment of industrial waste of various industries with an obtaining of new C, S, N-containing plastic lubricants, which provide

antiwear, antifriction, high load-bearing and heat-resistant properties.

To achieve the specified purpose, the following main tasks of scientific research were set:

1. On the example of obtaining new C, S, N-containing plastic lubricants for special purposes to propose the complex technology for processing industrial waste from various industries, which is based on the use of regenerated mixed sorbent (AC + K).
2. To propose and study by IR spectroscopy a number of topochemical reactions occurring on the sorbent surface (AC + K) during stepwise sorption purification of industrial waste from $(C_2H_5)_2NH$, CS_2 and Cu^{2+} cations.
3. To show the prospects of industrial use of the developed new C, S, N-containing plastic lubricants in heavily loaded and high-temperature friction units.

MATERIALS AND METHODS

Materials and methods of research. The sorbent was a mixture of activated carbon (AC) of Dekolar A brand and kieselguhr (K) of Bekogur 200 and Bekogur 3500 brands (produced by E. Begerow GmbH & Co, Deutschland) used in the production of soft drinks (PE "Panda", Vinnytsia) and regenerated according to the procedure described in [Ranskiy et al., 2019].

As a source of carbon disulfide was used HFCB of coke production with a CS_2 content of 32.0-32.8 wt.% (PJSC "Yasynivka Coke Plant", Makeyevka, Ukraine). The main regularities of carbon disulfide reagent extraction are given in [Ranskiy et al., 2013].

Obsolete pesticide preparate (OPP) Banvel D was taken from the agricultural enterprise "Bilopillya" in Vinnytsia region and regenerated according to the method described in [Ranskiy et al., 2010].

Used industrial oil I-40A SN 300 (manufactured by LLC "Dolphin Industry", Ukraine) was taken from PE "Exim" (Kherson, Ukraine) and studied as a mineral basis for the production of new C, S, N-containing plastic lubricants. The main regularities of industrial oil I-40A SN 300 purification are given in [Khudoyavora et al., 2020b].

Model solutions with Cu^{2+}concentration of 1.5–150 mg/dm^3 were used as galvanic wash water of the copper plating process.

The modified surface of the sorbents (AC + K) was investigated using the diffuse reflection method on an IR-Fourier spectrometer Nicolet iN 10 FX (Thermo Fisher Scientific, USA) in the range of 4000-525 cm^{-1}. The decoding of the obtained spectra was performed according to IR spectrum libraries from the software package "Omnic Picta 1.5.126".

New C, S, N-containing lubricants were tested in the Department of Secondary Polymer Raw Materials Processing of PE "Exim" (Kherson, Ukraine), using the rollers SM-PD 1500 660/660 LM1, manufactured by the Yaroslavl Plant of Polymer Engineering. The load (P_{max}) and temperature characteristics of the friction unit were compared to the recommended standard operating conditions of solid oil under real operating conditions using the developed C, S, N-containing lubricants, the composition of which is shown in the Table 1.

Preparation of PM-2 lubricant composition (general method). Lubricants of the PM series were prepared using a high-speed magnetic stirrer VELP AREC (VELP Scientifica, Italy) when the consistency mass was heated to 70–90 °C.

15.0 g of organoboron were added to a mixture of konstalin 1-13 (20.0 g) and I-40A SN 300regenerated industrial oil (10.0 g). Then a mixture was stirred at 40–45 °C for 30 minutes using a magnetic stirrer. After this 20.0 g of mixed sorbent (AC + K) having a modified surface [sorbent

Table 1. Compositions of lubricants of the PM series

Composition, wt.%	Lubricant				
	PM-1	PM-2	PM-3	PM-4	PM-5
1. Konstalin 1-13	100	25	25	30	30
2. Industrial oil I-40A SN 300	–	10	10	10	10
3. Modified sorbent [sorbent (AC + K)]·$[(C_2H_5)_2NS(=S)S]_2Cu$	–	20	25	30	40
4. Organoboron additive	–	15	15	10	10
5. Oleic acid	–	10	10	10	10
6. Graphite	–	20	15	10	–

(AC + K)]·[$(C_2H_5)_2NS(=S)S]_2Cu$ was gradually added. Further rapid stirring was performed for 30–40 min, gradually raising the temperature of the reaction mass to 70–90 °C. In the final stage, 20.0 g of graphite was added first, followed by 10.0 g of oleic acid. The reaction mass was kept until complete homogenization, and then cooled to room temperature.

Stage 1. Modification of the surface of activated carbon (AC) and kieselguhr (K) mixture during the processing of obsolete pesticide Banvel D to obtain a structural fragment [sorbent (AC + K)]·$[(C_2H_5)_2NH_2]NO_3$

200 ml (15.5 wt.%) of OPP Banvel D solution, which is used in the form of diethylammonium salt of 2-methoxy-3,6-dichlorobenzoic acid, were loaded into the reactor.A solution of nitric acid (60 wt.%) was added in small portions under vigorous stirring. The acidity of the reaction mass was controlled by a universal indicator paper to pH = 3. The reaction mass was kept under vigorous stirring and heating to 65 °C for 45 min, and then cooled to room temperature. The formed light brown precipitate of 2-methoxy-3,6-dichlorobenzoic acid was filtered off on a Schott filter and washed with cold water (2 x 25 mL). Yield 15.1 g (75%). mp = 114.0–115.5 °C. Found: C, 43.22; H 2.39. For $C_8H_6Cl_2O_3$ calcd.: C 43.47; H 2.74. IR spectrum, ν, cm^{-1}: 1740 (SCl–C(=O)); 1673 (COOH, dimer); 1470 (CH_{ar}); 1230 (OCH_3).

To extract the diethylammonium salt, which was part of the OPP Banvel D, the filtrate was treated with a mixed sorbent (AC + K), stirred vigorously at a temperature of 35-40 °C for 60 minutes and filtered on a Schott filter. Then the sorbed salt of the composition [sorbent (AC + K)]·$[(C_2H_5)_2NH_2]NO_3$ was dried in an oven at 60 °C. Yield 9.18 g (based on diethylammonium nitrate). IR spectrum, ν, cm^{-1}: 3355w (N–H); 2845s (CH_3–N); 2700s ($[H_2N(C_2H_5)_2]NO_3$); δ, 1470 w (N–H); 1365v.s (NO_3).

Stage 2. Modification of the mixed sorbent (AC + K) surface to obtain a structural fragment [sorbent (AC + K)]·$[(C_2H_5)_2NS(=S)S]_2Cu$

A three-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer and ice bath to cool the reaction mass was loaded with 200 g of modified sorbent (AC + K) containing 13.7 g (0.1 mol) of diethylammonium nitrate, 150 ml of benzene and 30 ml (0.3 mol) of 40% aqueous potassium hydroxide solution. 26 ml of HFCB (0.1 mol) with a CS_2 content of 31.7% were added dropwise under vigorous stirring. The reaction mass was kept in this mode at a temperature of 0–5 °C for 3.0 hours. Next, the ice bath was removed and the reaction mass was kept for another 1.0 h at a temperature of 20–25 °C under vigorous stirring.

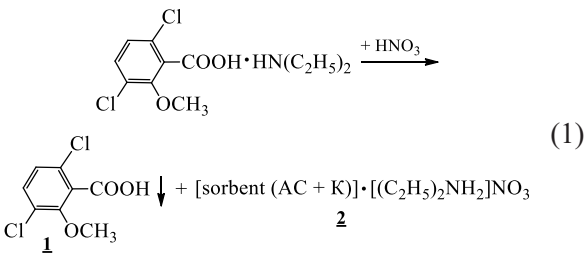
In the last stage of chemical transformations, 15.58 g (0.038 mol) of a concentrated aqueous solution of copper(II) sulfate were added during 15 minutes. The amorphous black precipitate was formed in the solution and on the surface of the mixed sorbent (AC + K). The reaction mass was filtered on a Schott filter, dried and a modified sorbent with a structural fragment [sorbent (AC + K)]·$[(C_2H_5)_2NS(=S)S]_2Cu$ was extracted. Yield 10.66 g (in terms of bis-(diethyldithiocarbamato)copper(II)). IR spectra, cm^{-1}: ν, 2930 (C–H); δ, 1375, 1355 (CH_3); ν_1, 1520 (C–N); ν_2, 1150 (C–N); ν, 1275 (C–S); ν, 1070 (C=S).

RESULTS

The peculiarity of this research is that all chemical components, except copper(II) sulfate, were obtained by sorption treatment of industrial waste, including mixed sorbent (AC + K). Figure 1 shows the logistic scheme of complex studies on different industrial wastes to obtain special-purpose plastic lubricants necessary in various industries (mechanical engineering, metallurgy, mining and chemical industries).

The integrated approach to the treatment of various industrial wastes using regenerated mixed sorbent (AC + K) of the soft drinks production includes the following technological operations:

- processing of OPP Banvel D with reagents using the regenerated sorbent (AC + K) at the final stage according to the general scheme (cycle I):



(1)

Reaction (1) leads to the formation of weak 2-methoxy-3,6-dichlorobenzoic acid 1 and diethylammonium salt 2 sorbed on a solid surface;

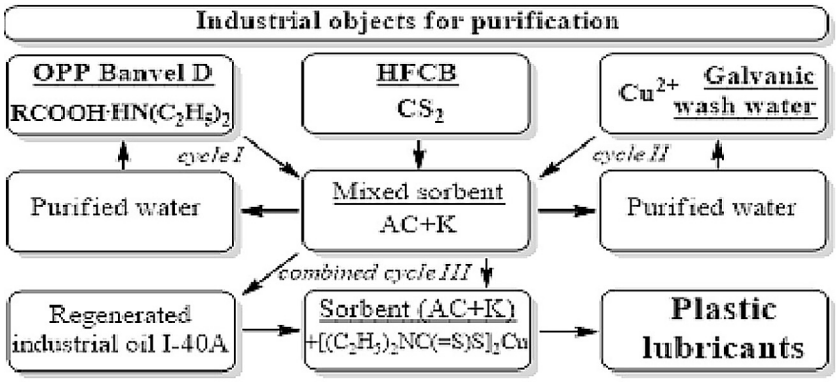


Fig. 1. Logistic scheme of different industrial wastes treatment to obtain final C, S, N-containing plastic lubricants

- purification of HFCB, which includes carbon disulfide, and formation of potassium diethyldithiocarbamate followed by bis-(diethyldithiocarbamato)copper(II) formation on the surface of (AC + K) sorbent according to the scheme (cycle II):

$$\underset{\underline{2}}{[\text{sorbent (AC + K)}]\cdot[(C_2H_5)_2NH_2]NO_3} + KOH \xrightarrow[0\text{ - }5\,^{\circ}C]{+\,CS_2} \underset{\underline{3}}{[\text{sorbent (AC + K)}]\cdot[(C_2H_5)_2NC(=S)SK]} \quad (2)$$

Reaction (2) proceeds on cooling due to the volatility of diethylamine formed during chemical transformations. The final product of the sorbed on the surface (AC + K) compound 3 is bis- (diethyldithiocarbamato)copper(II), formed according to the scheme:

$$\underset{\underline{3}}{[\text{sorbent (AC + K)}]\cdot[(C_2H_5)_2NC(=S)SK]} \xrightarrow[20\text{ - }25\,^{\circ}C]{+\,CuSO_4\cdot 5H_2O} \underset{\underline{4}}{[\text{sorbent (AC + K)}]\cdot\{[(C_2H_5)_2NC(=S)S]_2Cu\}} \quad (3)$$

Reaction (3), which is part of cycle (II), also involves the binding of copper(II) cations in the metal chelate 4, which is sorbed on a solid surface. It should be noted that instead of model aqueous solutions $CuSO_4 \cdot 5H_2O$, the galvanic wash water of copper plating can be successfully used;

- production of new C, S, N-containing plastic lubricants, which include regenerated industrial oil I-40A SN 300 according to the previously described method (combined cycle III).

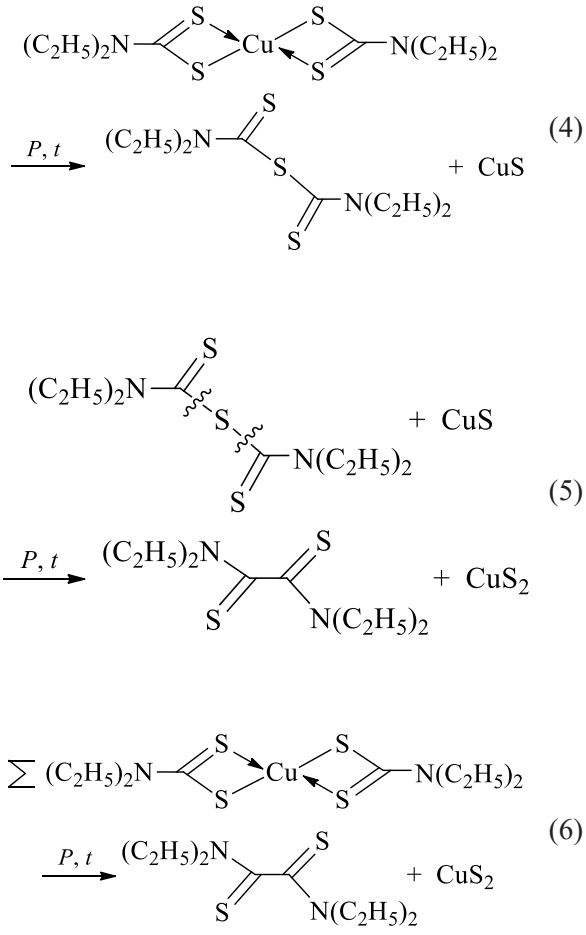
The presence of compounds 2 and 4 on the surface of the sorbent (AC + K) was confirmed by IR spectral studies. Thus, the structural fragment [sorbent (AC + K)]·$[(C_2H_5)_2NH_2]NO_3$ has, first of all, stretching and deformation vibrations of the N–H bond, at 3355 and 1470 cm^{-1}, respectively; stretching vibrations of the N–CH_3 bond at 2845 cm^{-1} and vibrations of the quaternary diethylammonium salt $[H_2N(C_2H_5)_2]$ fragment at 2700 cm^{-1}, as well as vibrations of nitrate anion at 1365 cm^{-1}. Compound 4, which is sorbed on solid surface (AC + K), has respective characteristic stretching and deformation vibrations of ν (C–H) group at 2930 cm^{-1} and δ(CH_3) at 1375, 1355 cm^{-1}; stretching vibrations ν_1 (C–N) at 1520 cm^{-1} and ν_2 (C–N) at 1150 cm^{-1}; stretching vibrations ν (C–C) at 1275 cm^{-1} and ν (C=S) at 1070 cm^{-1}. The obtained IR spectra for compounds 1, 2, 4 correspond to those given in [Tarasevich, 2012; Nakamoto, 1991].

Plastic lubricants, as the final product of cyclical transformations of industrial waste, have a number of tribotechnical properties which are not characteristic of liquid oils. Apart from antifriction and anti-wear properties, they have high load-bearing properties and thermal stability, which makes them indispensable in some specific friction units. Such lubricants prevent scoring, sticking or jamming of friction surfaces, perform the functions of sealants and have a number of other important performance characteristics [Ishchuk, 1996]. The ultimate goal of the comprehensive research was to obtain multifunctional lubricants, providing them with (Table 1):

- uniformity and homogeneity (components 2 and 5: oil I 40A and oleic acid);
- wear and heat resistance (components 3, 6: bis-(diethyldithiocarbamato)copper(II),

graphite, modified structural fragments of the sorbent (AC + K);
- special functions (component 4: organoboron compound).

It was previously noted that high-temperature and high-load properties for most industrial lubricants are determined by the presence of graphite and molybdenum disulfide in their composition [Ishchuk, 1996]. The use of sorbed surface [sorbent (AC + K)]·$[(C_2H_5)_2NS(=S)S]_2Cu$ as a thickener and active ingredient provides tribotechnical properties similar to MoS_2, and involves the following transformations at high contact temperatures and pressure:



(4)

(5)

(6)

The proceeding of the reactions (4) – (6) is confirmed by the chemical properties of dithiocarbamates of transition metals [Halls, 1969; Ranskiy et al., 2005], as well as the results of tribotechnical studies of similar lubricating compositions, presented in [Khudoyavora et al., 2020c, Khudoyavora et al., 2021].

Laboratory tests of the developed lubricants (PM-2 – PM-5, Table 1) were conducted at the Department of Mechanical Engineering of Vinnytsia National Technical University using the friction pair "ST40H – AL9", and the industrial tests were carried out at PE "Exim" (Kherson). The operational research showed that when using the developed lubricants (Table 1), the temperature in the friction units did not exceed the standard values and the surface of the roller bearings remained clean, smooth, without rolling and cracking during 12 months of preventive observations.

CONCLUSIONS

On the example of obtaining new C, S, N-containing plastic lubricants for special purposes, a complex technology for processing industrial waste from various industries is proposed, which is based on the use of regenerated mixed sorbent (AC + K), consisting of activated carbon (AC) and kieselguhr (K). A number of topochemical reactions occurring on the sorbent surface (AC + K) during stepwise sorption purification of industrial waste from $(C_2H_5)_2NH$, CS_2 and Cu^{2+} cations have been proposed and studied by IR spectroscopy. The prospects of industrial use of the developed new C, S, N-containing plastic lubricants in heavily loaded and high-temperature friction units are shown.

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