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ECONOMIC EFFICIENCY AND ANTHROPOGENIC RISKS OF REGENERATION OF INDUSTRIAL OILS

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Abstract. *In this article a principal scheme of a modification of the regenerated industrial oil by additives derived by reagent recycling of the obsolete pesticides and shown the decrease in anthropogenic risks of their reagent processing was developed. The economic effect of usage of the studied additives in the regenerated industrial oils was calculated.*

Keywords: additives; anthropogenic risks; obsolete pesticides; reagent processing; regenerated industrial oils.

1. Introduction

The lack of proper implementation of the clean-tech industries in the major industrial branches of Ukraine (metallurgy, chemical, coke and oil industries) leads to a significant accumulation of industrial waste, as well as increasing energy and materials capacious of finished products. Meanwhile, processing of such waste and herewith obtaining the secondary products allows considering them as valuable recyclables, among which the organic component is significant. It should be noted that the use of chemically modified active compounds of organic waste as additives to hydrocarbon materials (gasoline, diesel fuel, motor oil, lubricants) allows to significantly reduce material and energy outgoings to overcome resistance at the work of many engines, machines and mechanisms. Thus, the number of studies observes that for overcoming resistance in all engines, machines and mechanisms consumes 30–40 % of the energy generated during the year, and losses from wear of machine parts reach 4–5 % of the national income of developed countries of the world [Handbook…1989; Composite…2012].

Therefore, research and implementation in various areas of new additives that reduce friction is an important and actual task. Herewith those additives for oils and lubricants, which are products of secondary processing of organic waste, can significantly change the material and energy costs in most industrial production associated with the exploitation of machine engines and mechanisms, as shown in Fig. 1.

It should be noted that the use of additives for fuels and lubricants in order to improve their performance is important both for mineral (oil and gas) [Composite…2012], and for renewable (biodiesel, bioethanol) [Devyanin et al. 2007] types of fuels (Fig. 1).

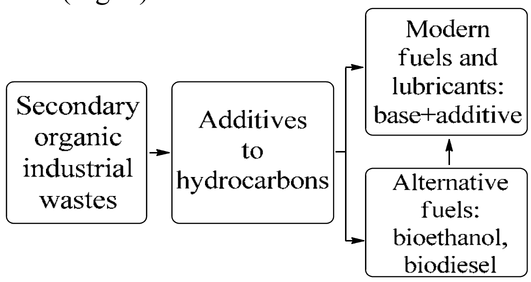


Fig. 1. Logical scheme of saving material and energy resources through the use of alternative fuels and applications to fuels and lubricants

As additives can be used the products of chemical modification of the obsolete pesticides based on chlorine [Haididei 2003], sulfur [Composite…2012] and phosphorus-containing [Ranskiy et al. 2012] organic compounds.

The **purpose** of this work is definition of anthropogenic risks at obtaining benzoates and dithiocarbamates of metals – products of reagent processing of the obsolete pesticides as additives to regenerated industrial oils and establishing economic efficiency of the process.

2. Experimental Section

The object of research of the reagent processing on purpose to obtain additives (modifiers) to the regenerated industrial oil was the obsolete pesticide Banvel, the active substance of which is dimethylammonium salt of 2-methoxy-3,6-dichlorobenzoic acid [Melnikov et al. 1980]. The reagent recycling of the obsolete pesticide Banvel was performed according to the method given in [Gordienko et al. 2011].

Antiwear and frictional properties of "pure", regenerated and modified oil I-40A were studied by traditional methods on a friction machine of SMC-2 type with friction pairs "shoe - roll" under the conditions given in [Composite…2012].

The regeneration of used industrial oil was performed by technology which schematic diagram is shown in Fig. 2.

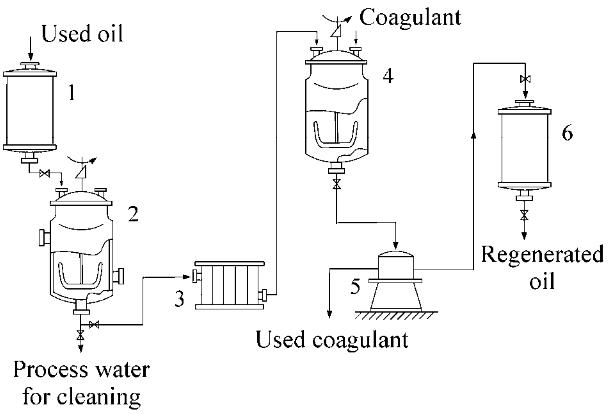


Fig. 2. Scheme of the regeneration of industrial oil I-40A:
1 – tank for used (waste) industrial oil;
2 – reactor for separation of water and oil;
3 – belt filter press;
4 – coagulator;
5 – centrifuge;
6 – tank for regenerated oil

In the first stage the used oil I-40A from tank 1 was supplied to the reactor *2* for separation of water and oil. Depending on the season decanter was heated (~55–60 °C) and had an electromechanical controller for mixing waste oil. After separation of water the oil was delivered to the belt filter press 3 to remove mechanical impurities using belting and cardboard as filter materials. Purified from water and solids oil was directed to the coagulator *4* to light from oil-soluble oxidation products. Herewith it was used as a coagulant ammonium persulfate, sodium or potassium orthophosphate, sodium metasilicate and other combined coagulants. Introduced coagulants not only lit the oil, but also normalized its acid value. To improve the process of coagulation the coagulator was equipped with an electromechanical controller for mixing.

After settling the oil was supplied to centrifugation *5*, and then - in a tank *6* for regenerated oil I-40A.

Further modification of regenerated industrial oil I-40A was carried out by introducing inside the received additives, which provided better tribotechnical properties. The scheme of modification of the regenerated industrial oil I-40A is shown in Fig. 3.

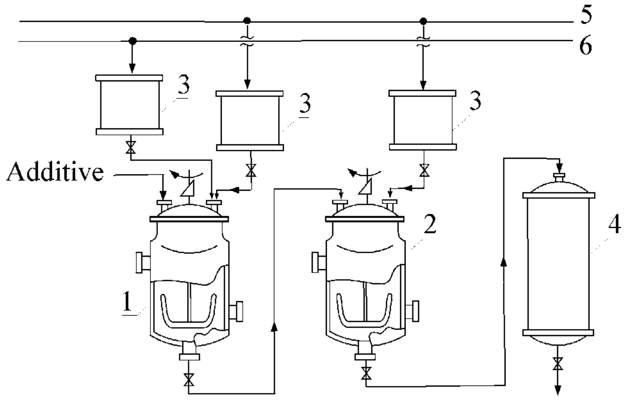
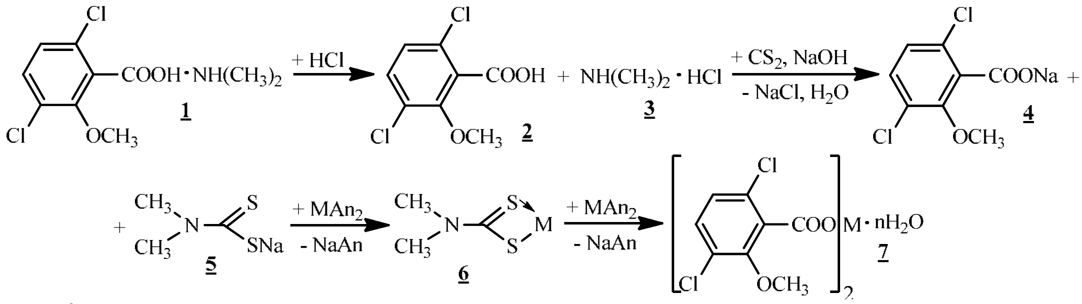


Fig. 3. Scheme of the modification of industrial oils by synthesized additives:
1 – reactor for the preparation of modified concentrate;
2 – reactor for the modification of industrial oil;
3 – batcher;
4 – tank for modified industrial oil;
5 – line of the regenerated oil;
6 – line of dimethylformamide (DMF)

According to the scheme (Fig. 3) dosed amount of DMF and additives as a solid agent was delivered into the reactor *1*, equipped with electromechanical controller for mechanical stirring of the mixture. In the reactor *1* a mixture based on regenerated oil I-40A to enhance solubility of introduced additives can be warmed if necessary. The resulting concentrated lubricant composition in dosed amount was introduced into the reactor *2* and mixed with regenerated oil. Then the modified oil was supplied in a tank *4* for storage and later use.

3. Results and Discussion

For obtaining an individual salts of 2-methoxy-3,6-dichlorobenzoic acid 7 and metal chelates of dimethyldithiocarbamic acid 6 a "cascade" method of successive addition to the initial Banvel solution 1 an equivalent amount of HCl was studied, then carbon disulfide in the presence of alkali, and at the end – a saturated aqueous solution of the appropriate metal salt [Gordienko et al. 2011]:



(1)

where M^{2+} = Cu, Co, Ni, Zn; An^{-} = Cl, NO_3, $1/2SO_4$; n = 1-3.

Obtained by scheme (1) dimethyldithiocarbamates of metals 6 and benzoates 7 were used as additives to the regenerated industrial oil I-40A.

For comparison in Table 1 physical and chemical characteristics of "pure", waste and regenerated oil I-40A, indicating the efficiency of regeneration, which was carried out according to the scheme: separation - filtration - coagulation - centrifugation are shown.

Table 1. Physical and chemical properties of industrial oil I-40A

Characteristics	Oil I-40A		
	Pure	Waste	Regenerated
Viscosity at 50 °C	18,9	20,9	19,8
Acid value, mg KOH/g	0,03	0,35	0,07
Ash content, wt%	0,004	0,065	0,015
Content, wt%:			
water	No	Up to 0,5	No
mechanical impurities	No	1,05	No
water-soluble alkalis and acids	No	Acids	No

To improve the performance of regenerated oil I-40A in its composition we introduced additives received under the scheme (1). Antiwear and frictional properties of oil I-40A, which were explored under the conditions [Composite…2012], are shown in Table 2.

Listed in the Table 2 data indicate that the introduction of a modifier-concentrate in an amount of 3 wt% relative to the total volume of the studied lubricant compositions improves tribotechnical properties of regenerated oil. Thus, using a modified oil decreases wear of friction pair in 2,13-3,05 times and the coefficient of friction – in 1,34-1,45 times in comparison with regenerated oil.

Thus, our studies indicate the feasibility and theoretical possibility of technological developments as follows: reagent processing of the obsolete pesticides based on alkyl (aryl)-hetarylcarboxylic acids → chemical modification of active substances with obtaining additives to industrial oils → obtaining a modifier-concentrate of additives based on industrial oil → modification of the regenerated industrial oils.

Table 2. Tribotechnical characteristics of industrial oil I-40A

Characteristic	Oil I-40A			
	Pure	Waste	Regenerated	
			ZnBA + ZnDTC	CuBA + CuDTC
$I \cdot 10^{-4}$, g	6,2	6,4	2,1	3,0
I/I_0	–	–	0,33	0,47
$f \cdot 10^{-2}$	5,4	5,5	3,8	4,1
f/f_0	–	–	0,69	0,75

Footnotes. Ratio I/I0 and f/f0 were calculated relatively to regenerated oil. ZnBA, CuBA – 2-methoxy-3,6-dichlorobenzotes of Zinc and Copper(II) respectively. ZnDTC, CuDTC – dimethyldithiocarbamates of Zinc and Copper(II) respectively.

Anthropogenic risks of reagent processing of the obsolete pesticides can be conditionally estimated as the difference between static and dynamic risk indicators of treatment of the obsolete pesticides. Static risk indicators include: the risks of water pollution, soil and air pollution by chemicals, the risks associated with increasing content of the obsolete pesticides and their degradation products in the flora and fauna; the risks of population disease, the risks of accidents at storage facilities. Dynamic risk indicators include: risks associated with the transportation of the obsolete pesticides to a place of their reagent processing, risks associated with the technology of their processing and the possible formation of secondary hazardous waste.

Note that static risk of treatment of the obsolete pesticides are kept during indefinite term, the obsolete pesticides totally pollute the water, soil and air, while a dynamic risks associated only with the time of their technological processing, and in accordance with the regulatory framework the contents of the obsolete pesticides and products of their processing in the environment must not exceed the current threshold of limit values.

Analysis of anthropogenic risk of the processing technologies of hazardous substances indicates that in many modern models of risk assessment it is defined as the degree of probability of a negative impact that may occur at certain time or under certain circumstances in high-risk facilities and/or outside [Ukraine…2001], namely risk is reduced to the estimation of the probability of an accident at the facility for a definite period of time, usually a year [Khmil, Lycychenko 2011]:

$$R(A) = P(A),$$

where $R(A)$ – risk of an event A;

$P(A)$ – probability of an unwanted event A.

Subject to consideration of the possible negative consequences of an event A, which depends not only on potential losses, but also on the degree of vulnerability of the object for the event A, we have a model for determination of anthropogenic risk:

$$R(A) = P(A)V(A)U(A), \qquad (2)$$

where $V(A)$ – vulnerability of a facility for event A;

$U(A)$ – conventional full damage as a result of event A.

Expression (2) can be considered as the most common for all types of risks, including anthropogenic. But their practical use in any particular case requires realization of a further research. Therefore, at the reagent processing of the obsolete pesticides the anthropogenic risks, in first approximation, must be considered as a change of ecotoxicological risk (E, ecotox), which is calculated by the formula [Omelchuk et al. 2005]:

$$E = \frac{P\,N}{LD_{50}}, \qquad (3)$$

where P – half-life of a toxic substance;

N – maximum consumption rate of pesticide for the active substance, kg/ha;

LD_{50} – average lethal dose at the oral admission in rats organism, mg/kg.

In this case, for unit ecotoxicological danger of DDT is accepted. Formula (3) was used to compare ecotoxicity of the initial and modified chemical forms by the studied reaction

Thus, the relative ecotoxicity of the studied reaction E_R will be determined by the equation:

$$E_R = \frac{\sum E_{IS}}{\sum E_{PR}}, \qquad (5)$$

where $\sum E_{IS}$ – ecotoxicity of the initial substances;

$\sum E_{PR}$ – ecotoxicity of the reaction products.

In Table 3 the ecotox values of the initial and modified chemical forms (equation 4) are shown.

Listed in the Table 3 data show that in case of direct use (without CS_2) of the formula (5) the ecotoxicity of the products of reagent processing compared to the initial preparation decreased by 8.6 times, and in case of indirect use of formulas (3) and (4), i.e. with a consideration of ecotoxicity of the reagent CS_2, equivalent in this case to the highly toxic obsolete pesticide, ecotoxicity of the final products compared to precursors decreases by 144 times.

Table 3. Ecotoxicity of the organic substances of reagent processing of the obsolete pesticide Banvel

Preparation (substance)	P	N, kg/ha	LD_{50}, mg/kg	E
Banvel	3,5	46,8	2375	$6,9\cdot10^{-2}$
Dicamba	3,5	7,0	4200	$5,8\cdot10^{-3}$
Ziram	1,0	3,0	1340	$2,2\cdot10^{-3}$
Carbon disulfide*	3,5	1,0	3,2	1,09

Footnote. For carbon disulfide the following values: persistence - at the maximum value for the studied obsolete pesticides; allowances - at the threshold limit value of the working area were used.

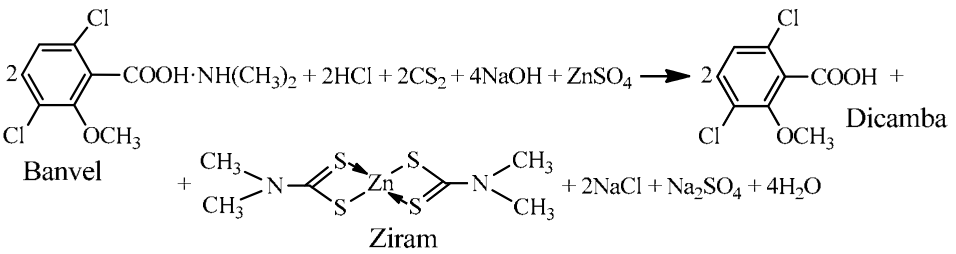
Economic efficiency of 2-methoxy-3,6-dichlorobenzoates and dimethyldithiocarbamates of 3d-metals as modifiers for regenerated industrial oils was determined using the initial data presented in the Table 4.

Price growth (G, UAH/t) by implementing modified oil was calculated using the formula:

$$G = P_1 - R_2,$$

where P_1 – price of the modified oil, UAH/t;

P_2 – price of the regenerated oil, UAH/t.



(4)

Table 4. Data for calculation of economic effect at the obtaining of modified industrial oils

Oil name (oil mixture)	Amount, t/year	Price, UAH/t	Cost of production, UAH/t
Used industrial oils (I-20A, I-40A)	300	3000 – 8000	–
Regenerated industrial oils (clarified fraction after a coagulation)	280	5000 – 7500	800 – 1500
Regenerated industrial oils (fraction after a rectification)	140	7500	1800 – 2500
Modified oils (fraction after introducing an additive-modifier)	70	8000 – 9000	300 – 400

Revenue (R, UAH/year) from the sale of modified oil is:

$$R = GM,$$

where M – amount of modified oil, t/year.

Expenses (Sp, UAH/year) of the obtaining of modified oil was calculated using the formula:

$$Exp = Exp_1 + Exp_2,$$

where Exp_1 – expenses of additives production, UAH/year;

Exp_2 – expenses of the production of a modifier-concentrate and modified oil, UAH/year.

Costs of additives production include the cost of additional equipment, the cost of chemicals, the cost of water and wastewater, energy costs in the processing, salaries, charges for amortization of equipment, charges for insurance and transport costs. The cost of the production of modifier-concentrate and modified oil was calculated by the formula:

$$Exp_2 = MC,$$

where C – cost of production at the obtaining of modifier-concentrate and modified oil, UAH/t.

Economic effect (Ef, UAH/year) from the introduction of additive-modifier at the manufacture of modified oil is the difference between revenue and expenses:

$$Ef = R – Exp.$$

Calculated economic effect of the use of the obtained compounds in this paper, which improve the antiwear and frictional properties of regenerated industrial oils, was 27,720 UAH/t.

4. Conclusions

1. A scheme of the modification of regenerated industrial oils by using a synthesized benzoates and dithiocarbamates of Copper(II) and Zinc was developed.
2. It was found that introduction of benzoates and dithiocarbamates of Copper(II) and Zinc to regenerated industrial oils improves their tribotechnical characteristics.
3. Using ecotoxicity of the chemicals both initial and products of reagent processing of the obsolete pesticide Banvel showed the reduction of anthropogenic risks of storage of the unusable pesticides.
4. An economic effect of the use of the explored additives in the regenerated industrial oils was calculated.

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Розглянуто НПП Банвел, діючою речовиною якого є диметиламонієва сіль 2-метокси-3,6-дихлорбензойної кислоти. Визначено техногенні ризики при отриманні бензоатів та дитіокарбаматів металів – продуктів реагентної переробки НПП як додатків до регенерованих індустріальних олив. Протиспрацьовувальні та антифрикційні властивості «чистої», регенерованої та модифікованої оливи І-40А досліджено за традиційною методикою на машині тертя типу СМЦ-2. Техногенні ризики реагентної переробки НПП оцінено як різницю між статичними та динамічними показниками ризиків поводження з НПП. Розроблено принципову схему модифікації регенерованих індустріальних олив додатками, отриманими реагентною переробкою непридатних пестицидних препаратів. Із використанням екотоксичності вихідних хімічних речовин та продуктів реагентної переробки НПП Банвел показано зменшення техногенних ризиків зберігання непридатних до застосування пестицидних препаратів. Розраховано економічну ефективність застосування 2-метокси-3,6-дихлорбензоататів і диметилдитіокарбаматів 3d-металів як модифікаторів регенерованих індустріальних олив.

Ключові слова: додатки; непридатні пестицидні препарати; реагентна переробка; регенеровані індустріальні оливи; техногенні ризики.

А.П. Ранский[1], О.А. Гордиенко[2], Т.С. Титов[3], С.И. Ткаченко[4], А.А. Пивоваров[5]. Экономическая эффективность и антропогенные риски при регенерации индустриальных масел

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Рассмотрен НПП Банвел, действующим веществом которого является соль 2-метокси-3,6-дихлорбензойной кислоты. Определены техногенные риски при получении бензоатов и дитиокарбаматов металлов – продуктов реагентной переработки НПП в качестве присадок к регенерированным индустриальным маслам. Противоизносные и антифрикционные свойства «чистого», регенерированного и модифицированного масла И-40А исследованы по традиционной методике на машине трения типа СМЦ-2. Техногенные риски реагентной переработки НПП оценены как разница между статическими и динамическими показателями рисков обращения с НПП. Разработана принципиальная схема модификации регенерированных индустриальных масел присадками, полученными реагентной переработкой некондиционных пестицидных препаратов. С использованием экотоксичности исходных химических веществ и продуктов реагентной переработки НПП Банвел показано уменьшение техногенных рисков хранения непригодных к применению пестицидных препаратов. Рассчитан экономический эффект применения 2-метокси-3,6-дихлорбензоатов и диметилдитиокарбаматов 3d-металлов в качестве модификаторов регенерированных индустриальных масел.

Ключевые слова: некондиционные пестицидные препараты; присадки; реагентная переработка; регенерированные индустриальные масла; техногенные риски.

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