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ECOLOGICAL CHARACTERISTICS OF NEW FEW-COMPONENT ANTICORROSION CONSERVATION MATERIALS BASED ON OIL

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Abstract
The toxicological characteristics of the components of the anticorrosive conservation materials based on oil, including a series of the mineral oils, polyaminoamide TVK-1, amides of the carboxylic acids, a mixture of synthetic fat acids of C_{10}-C_{16} fraction, the synthetic fat acid bottoms, some individual amines, normal fractions of primary amines C_7-C_9, C_{16}-C_{20} and C_{10}-C_{16}, have been studied. Conservation materials dispersion from the place of their application in the square with 600 m side has been studied.

Introduction

The oil conservation materials (CMs) are used for the metal protection against atmospheric corrosion [1]. The conception of the creation of the few-component CMs has been suggested [2]. These CMs are characterized by high technological efficiency of their preparation and the practical use, a low cost price, a wide raw material base. Simultaneously they must not have more low efficiency than the traditional multifunctional compositions. It is more easy to prepare the few-component CMs as ecological safe. The last demand determines a necessity of the integral estimation of the toxicological properties of such compositions and their components.

Toxicological and physical-chemical meaning of the criterion quantities

LAC_{wz} - the limiting admitted concentration of a working zone – characterizes a maximum admitted real concentration of the given individual substance or the product at the working place (on data of the State Standard of Russian Federation).
LAC_{md} - the limiting admitted middle day (24 hours) concentration - characterizes a maximum admitted real concentration of the given individual substance or the product in the atmospheric air of the constant places where people live.

$$LAC_{wz} / LAC_{md} \geq 10 \qquad (1)$$

LAC_{ms} - the maximum single once limiting admitted concentration - characterizes a maximum admitted real concentration of the individual substance or the product in the atmospheric air where the workers are present during 30 minutes (no more).
LAC_w - the limiting admitted concentration in water of the natural or the artificial springs.

$$LAC_{ms} >> LAC_{wz}$$

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BCO_5 - the biochemical consumption of oxygen in conditions of self-cleaning water in a basin during 5 days – is expressed with mg O_2 consumed from 1 ml of a solution. If the substances are slightly soluble BCO_5 is measured with mg O_2 consumed from 1 ml of a saturated aqueous solution or from the diluted saturated solution.
CCO - the chemical consumption of oxygen in conditions of self-cleaning water in a basin – is measured with the same units as BCO_5. The LAC is famous for BCO_5 and CCO too. LAC (BCO_5) is equal to 0,006 mgO_2/ml and 0,002 mgO_2/ml for the waste water and the fish economic water basin respectively. LAC (CCO) is equal 0,003 mgO_2/ml for first and is not set for last.

Experimental

The estimation of CCO and BCO_5 values has been made according to [3]. A calculation of the quantities of the middle year and the maximum single once throwing away pollutants into the environment during the period of the anticorrosion protection of equipment has been carried out according to [4-7]. Conservation materials dispersion from the place of their application in the center of the square with 600 m side has been studied by the universal program «Ecologist» [8]. The criterion values have been received for number multifunctional additives to the oils: the amides of the carboxylic acids [9], the synthetic fat acids (SFA) and the synthetic fat acid bottoms (BSFA) [10], TVK-1 [11], mineral unused and waste oils [12] and others. Sometimes the calculation of the LAC_{md} has been made according to approximate equation (1).

Results

The values of LAC_{wz} have been determined for the simplest aliphatic amines (AA) and the fractions of primary saturated AA (Table 1). LAC_{ms} for the synthetic fat acids of the C_{10}-C_{16} fraction, TVK-1, mineral oil, saturated hydrocarbons of the C_{12}-C_{19} fraction are equal to (mg/m^3) 0,6; 100; 25 and 900 respectively. The active part of some few-component anticorrosion CMs on oil base and themselves mineral oils and waist ones are slightly soluble in water and neutral aqueous solutions. Therefore CCO and BCO_5 values have been estimated for their saturated solutions (SS) and the media received by a dilution of last 2, 4 and 8 times.

Table 1

LAC_i of some individual compounds and mixtures

Product	LAC_{wz}, mg/m^3[13]	LAC_w, mg/l	LAC_{md}, mg/m^3
CH_3NH_2	1	1	-
$C_2H_5NH_2$	18	-	-
$C_3H_7NH_2$	5	0,5	-
$C_4H_9NH_2$	10	4	-
Fractions of AA:			
$C_7 – C_9$	1	0,5*	-
$C_{10} – C_{16}$	1	0,4*	0,1***
$C_{16} – C_{20}$	1	0,03*	0,1***
$C_7 – C_9$	1	0,07**	0,1****
$C_{10} – C_{16}$	1	0,038**	0,1****
$C_{16} – C_{20}$	1	0,028**	0,1****

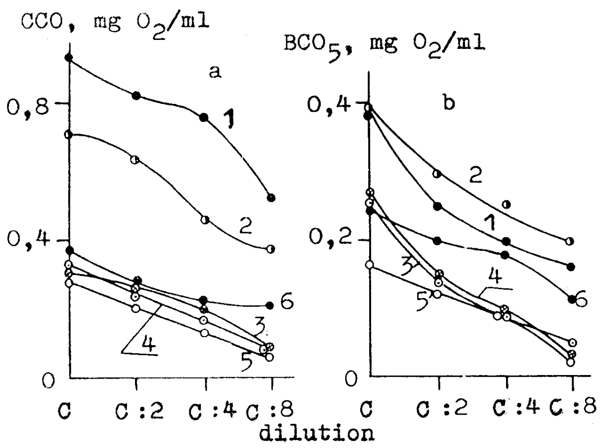
SFA $C_{10} - C_{16}$	5,6***	3,9	0,6****

*the limiting concentration with respect to the processes of a selfcleaning of the basins;
** the limiting concentration according to an influence on the organs of feelings;
*** a recalculation to $CH_3(CH_2)_3COOH$; ****a calculation according to Eq.(1).

A. Mineral oils. The oils are widely used as a labricant and a solvent-support of the different
anticorrosion conservation materials. They catch into the water of the basins together with sewage. They are practically insoluble in water, but it is necessary to take account 2 moments, at least:

1. The oils moisten water well spreading along its surface in the form of the thin (monomolecular, in limit) film. A presence of such films above the water surface must increase CCO and BCO because the oil components may be oxidized by dissolved oxygen, other oxidizers and by the biochemical way. At any case the oils will decrease a dissolved oxygen concentration.
2. The mineral oils contain always the factory additives being surface active substances (SAS), the waste motor oils – in addition the products of the hydrocarbon oxidation being SAS too. At such situation a presence of the oils in the water results a formation of the emulsions of «oil in water» type. Such emulsions become stable in the presence of above SAS as the effective emulsifying agents. This fact, in his turn, causes a large increase of CCO and BCO and an aggravation of water quality.

In Fig.1 it is shown CCO and BCO_5 values of the saturated aqueous solutions of some mineral oils and media received by their dilution with distilled water 2, 4 and 8 times. It is clear that CCO values of the oils SS exceed the corresponding LAC(CCO) many times. The industrial oil I-20A is characterized by the largest CCO (Fig.1a, curve1). The values of CCO and BCO_5 for the transformer oil (TO) SS are less (Fig.1a, curve 2) that may be connected, in certain measure, with smaller number and smaller concentration of the factory additives in it than in the I-20A. Dilution of the saturated solutions decreases their CCO and BCO_5 (Fig.1, curve 1 and 2), but slightly. The oil M 10-G_2 being used for lubrication of the motor and tractor engines in summer is characterized by essentially smaller CCO and therefore it is more ecological. The same picture is observed for TAD-17 I oil (being used for lubrication of the transmissions) and waste motor oil (WMO) and its filtered fraction (Fig.1a, curves 3 – 6).



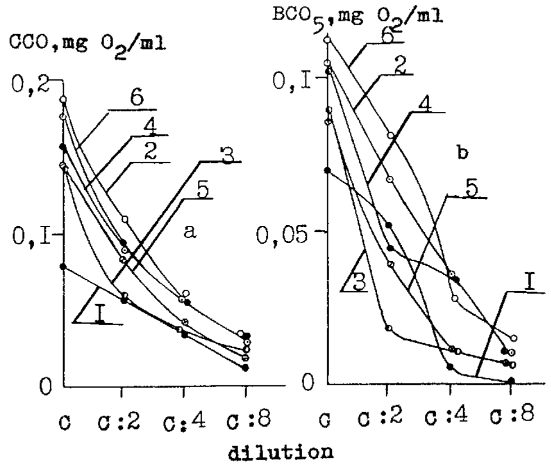


Fig.1 Fig.2

Fig.1. The influence of the oil nature and its concentration in the aqueous solutions on its values of CCO (a) and BCO_5 (b). The oils: 1 – I-20 A; 2- TO; 3 – M 10-G_2; 4- waste motor oil (WMO); 5 – filtered fraction of WMO ; 6 – TAD-17 I. C- a concentration of the saturated solution here and further.

Fig. 2. The influence of the alkane nature and its concentration in the aqueous solutions on its values of CCO (a) and BCO_5 (b). The alkane: 1 – hexane; 2 – heptane; 3 –octane; 4 – nonane;
5 – decane; 6 – pentadecane.

The BCO_5 values of the saturated solutions of the studied oils are less than their CCO. The following row for the BCO_5 values of the saturated solutions is observed:

$$\text{TO} > \text{I-20 A} > \text{TAD-17 I} \approx \text{M 10-G}_2 \approx \text{WMO} > \text{filtered WMO}$$

The peculiarity of the oils is the frequent exceeding of the real values of BCO_5 above LAC(BCO_5) including the diluted media.

B. Alkane hydrocarbons. It is interesting to estimate CCO and BCO_5 values for the saturated aqueous solutions of the C_6 – C_{15} alkanes because they are components of the mineral oils. The corresponding values are shown in Fig.2. Synonymous dependence between a number of carbon atoms in the alkane molecule and the values of CCO in the saturated solutions is absent. In the diluted solutions a character of this dependence is more complicated. In whole the values of CCO in this media is less in comparison with the oil solutions because the oils contain the factory additives and the products of oxidation.

The attempt to estimate an influence of the carbon atoms number n_C in the alkane molecule on its CCO and BCO_5 values is shown in Fig 3. Simultaneously the influence of a dilution of the SS on these values is considered (n_C = const). The tendency of increase of the CCO values with increasing n_C is observed. But one can see a second periodical dependence. The alkanes with the odd number of carbon atoms in the molecule are oxidized more lightly, by bichromate in particular, in comparison with the molecules having the even number of carbon atoms. The same dependence is repeated under the dilution of the saturated solutions two and 8 times (Fig.3, curves 2 and 3). It allows to confirm that the observed dependence is reliable sufficiently. The dilution of the studied solutions results decreasing CCO values. But, of course, a character of CCO dependence from n_C is different for the different concentration solutions. However the differences have a quantitative character, but not qualitative one.

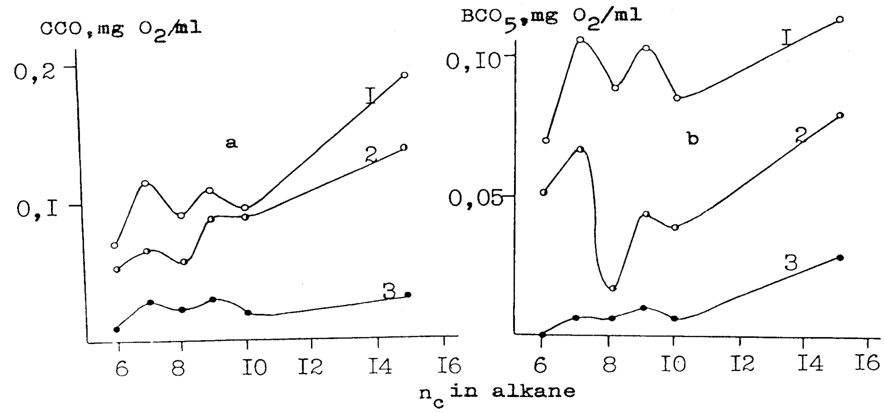


Fig.3. The influence of a carbon atoms number in the alkane molecules and the concentration of their aqueous solutions on CCO (a) and BCO_5 (b) values. 1- a saturated solution; a dilution of SS: 2- twice, 3 – 8 times.

The dependence $BCO_5 = f(n_C)$ is the same qualitatively as the CCO = $f(n_C)$ (Fig.3b).

C. Amides of the carboxylic acids. The amides of the carboxylic acids are the effective thickening agents of the mineral oils, the oil-soluble corrosion inhibitors and, on whole, the perspective multifunctional additives into the oils. The ecological toxicological characteristics have been studied for the amides of the saturated monobasic carboxylic acids with n_C equal to 5, 10 – 13 (mixture of the synthetic fat acids (SFA)), 11 and the unsaturated $C_{17}H_{33}CONH_2$ and $C_{21}H_{41}CONH_2$. Amid of capric acid ($C_5H_{11}CONH_2$) is soluble in water and we have used its initial concentration equal to 0,5 g/l (0,0058 mole/l). The corresponding experimental results are given in Table 2. For the saturated solutions CCO values decrease in the following line:

$C_{10\text{-}13}H_{21\text{-}27}CONH_2 > C_{11}H_{23}CONH_2 > C_{17}H_{33}CONH_2 > C_5H_{11}CONH_2 > C_{21}H_{41}CONH_2$

A dilution of the SS changes the above tendency and decreases the CCO values. The BCO_5 values of the SS of amides decrease in the following line:

$C_{11}H_{23}CONH_2 > C_{10\text{-}13}H_{21\text{-}27}CONH_2 > C_{17}H_{33}CONH_2 > C_{21}H_{41}CONH_2 > C_5H_{11}CONH_2$

A dilution of the SS draws together the BCO_5 values of the studied solutions of amides.

D. Anticorrosion multifunctional additives.

1) BSFA. BSFA are a mixture of C_{19}-C_{23} saturated carboxylic acids (about 86 mas.% of

SFA), higher paraffins, polymeric acids with n_C = 34 and more. The CCO value of the SS of BSFA is essentially less in comparison with the CCO values of the SS of I-20 A and TO (Fig.1) and other oils. Moreover the CCO value decreases quickly with increasing dilution of the SS but exceeds LAC (CCO) value even at 8 repeated dilution. The same picture is characteristic for the BCO_5 values of the BSFA solutions. Thus BSFA are ecological more pure than the mineral oils. Therefore an introduction of BSFA into the oils increases the ecological purity of the compositions consisting of components of the 4th hazard category.

Table 2.

The CCO and BCO_5 values of the aqueous solutions of the multifunctional additives into the oils.

Product	Concentration of the solution	CCO, mg O_2/ml	BCO_5, mg O_2/ml
$C_{10-13}H_{21-27}CONH_2$	C^*	0,50	0,25
	C/2	0,32	0,11
	C/4	0,17	0,04
	C/8	0,09	0,04
$C_{21}H_{41}CONH_2$	C	0,20	0,16
	C/2	0,13	0,11
	C/4	0,10	0,05
	C/8	0,05	0,02
$C_{11}H_{23}CONH_2$	C	0,22	0,46
	C/2	0,12	0,26
	C/4	0,04	0,12
	C/8	0,02	0,05
$C_{17}H_{33}CONH_2$	C	0,37	0,20
	C/2	0,26	0,13
	C/4	0,14	0,04
	C/8	0,04	0,03
$C_5H_{11}CONH_2$	C^{**}	0,21	0,15
	C/2	0,15	0,13
	C/4	0,08	0,04
	C/8	0,04	0,02
BSFA	C	0,22	0,17
	C/2	0,19	0,15
	C/4	0,14	0,08
	C/8	0,08	0,04
G-89	C	0,11	-
	C/2	0,08	-
	C/4	0,04	-
	C/8	0,02	-
TVK-1	C	0,25	0,14
	C/2	0,19	0,11

	C/4 C/8	0,13 0,08	0,06 0,04

*C – a concentration of the saturation, **C=0,0058 mole/l

2) G-89. This multifunctional additive is a narrow fraction of homologues with the molecule formula

$$[C_nH_{2n+1}NH_2\text{-}N^+H(CH_3)_2]Cl^-,$$

where n = 8 – 9. This substance shows very large thickening and anticorrosion action. It is a product of the interaction of heptyl and SFA narrow fraction.. The CCO value of G-89 saturated solution is less then for BSFA (Table 2) and decreases quickly with increasing dilution of SS mounting to 0,055 mg O_2/ml at 8 repeated dilution (LAC(CCO) = 0,03 mg O_2/ml). Thus the saturated solutions of G-89 are capable to a self-cleaning at 8 repeated dilution. Unfortunately we could not estimate the BCO_5 values of the G-89 solutions. Perhaps this product is not exposed to biochemical oxidation or it proceeds very slowly.

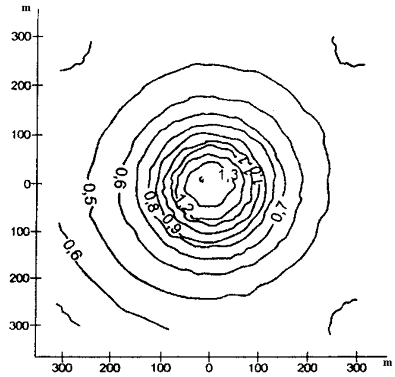
3) TVK-1. It is very effective component for preparation of the few-component conservation materials on the oil base. TVK-1 is a product of the interaction of polyethylenepolyamine and SFA of the C_{21-25} fraction. It is polyaminoamide having following molecule formula

$$RCONH_2(CH_2CH_2NH)_n,$$

where R is C_mH_{2m+1} hydrocarbon radical, m = 20 – 25, n = 2 – 5. It is a substance of the 4th hazard category. The CCO value of the TVK-1 SS is close to that of BSFA. The BCO_5 values of the TVK-1 solutions is even less than that of BSFA and only at 8 repeated dilution of the SS these values become identical.

Pollutant dispersion in atmosphere. Duration of the preparation of the anticorrosion conservation materials on oil base in the place of their use with 300 kg mass is taken equal to 16 hours (chronometer). Duration of the conservation process at the heating of the composition up to 70-80^0 C for pneumatic pulverization is equal to 15 hours. The sum mass of the dispersing material is equal to 30 kg (10%). The dispersion source has no the extract ventilation and other apparatus to take out the pollutants into atmosphere. The throwing out diameter is 0,5 m, a height is equal to 2 m, the throwing out rate is equal to 1,0 m/s. The middle temperature of a flow is equal to 30^0 C. For example the results of the calculation of a dispersion of C_{16-20} aliphatic amines and TVK-1 are shown in Fig.4 and Fig.5. They are pictured as isosters in portions of LAC_{ms}. The value of the background concentration has been taken equal to 0,3 LAC_{ms}. The maximum concentrations of substances are observed in the square with 50 m side in the center of which the throwing out source is situated. Their values:

- a mineral oil 2,67 LAC_{ms}
- the aliphatic amines of C_{10-15} fraction 1,73 LAC_{ms}
- the aliphatic amines of C_{16-20} fraction 1,31 LAC_{ms}
- BSFA 0,5 LAC_{ms}
- TVK-1 0,4 LAC_{ms}
- alkanes 0,36 LAC_{ms}



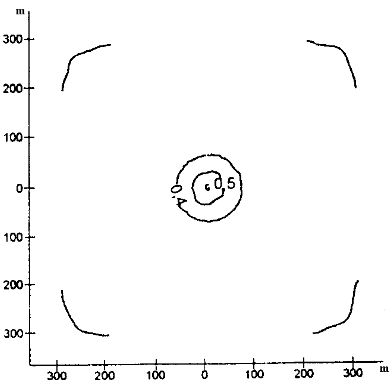


Fig. 4 Fig. 5

Fig. 4. The concentration of air pollution of the machine yard by C_{16-20} aliphatic amines expressed in portions of LAC_{ms} .

Fig.5. The same for TVK-1.

Conclusion

The tendency of increase of the CCO and BCO_5 values with increasing n_C is observed. The alkanes with the odd number of carbon atoms in the molecule are oxidized more lightly, in comparison with the molecules having the even number of carbon atoms. On given criterions BSFA are ecological more pure than the mineral oils because the CCO and BCO values of its SS are essentially less than for the SS of the mineral oils. The saturated solutions of G-89 are capable to a self-cleaning at 8 repeated dilution. The CCO value of the TVK-1 SS is close to that of BSFA. The BCO_5 values of the TVK-1 solutions are even less than that of BSFA.

The conducting operations on the preparation of the few-component conservation materials and the anticorrosion processing of the agricultural machines don't cause above standardized pollution of the environment.

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