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SELECTIVE TRANSFER MECHANISM IN TERMS OF RESONANCE POTENTIAL ACCORDING TO NECHAEV

The paper studies the selective transfer phenomenon in terms of selective adsorption of organic compounds on metal surfaces according to Nechaev. Resonance potentials of such metals are presented that realize the selective transfer (Cu, Co, Fe, Sn, Ni) and could be used in different friction pairs. An attempt is made to explain the selective transfer phenomenon by comparing the obtained high antifriction and antiwear properties of waste oils in the block-roller ("bronze-steel") friction pair with calculated resonance potentials of the investigated filler materials (thioamids, dithiocarbamates and their copper(II) metal chelates).

Key words: *friction, selective transfer, resonance potential, thioamids, copper (II) dithiocarbamates.*

Selective transfer (ST), discovered as a natural phenomenon in 1956, is still a subject of hot argument and numerous publications [1 – 3]. ST is a complex self-regulating process that is accompanied by physicochemical, chemical, electromechanical and mechanical phenomena in friction pairs. During this process a plastic film with the width of 1 – 2 μm is spontaneously created in the contact zone, the film having a constant number of dislocations and a large number of vacancies [4]. A characteristic feature of ST process is metal transfer from one surface of the friction pair to the other without growth of the friction force and friction coefficient. ST is characterized by a sharp reduction of friction and wear. The value of relative wear reaches 10^{-10}-10^{-12} and friction coefficient – 0,01…0,005. In this work we used a "bronze-steel" friction pair that is practically the most convenient one for ST investigation. Creation of the metallic dronze film on the steel surface was fixed visually (qualitative analysis) and wear itself was determined by the gravimetric method (quantitative analysis).

Transfer of copper cations from the bronze to the steel surface of the "bronze-steel" friction pair with their further restoration and copper film creation assumes selective adsorption (chemisorption) of the organic ligand on metal surface. According to Nechaev [5], in order to predict organic compounds adsorption (chemisorption) it is necessary to determine resonance potential $\dot{I}_r$ of these compounds. In later works a theory of selective adsorption in nonaqueous media was developed by V. Kuprin, which has made it possible to characterize this phenomenon quantitatively and to determine $\dot{I}_r$ of metals by the formula [6]:

$$\dot{I}_r = 2\left(\Phi_M + e \cdot M \cdot \psi_{H_2O}\right),$$

where Φ_M is the work function of $\bar{e}$ from the metal; $M \cdot \psi_{H_2O}$ – volt potential on the corresponding interface of phases with zero charge potential ($E_M^g = 0$).

In the same work [6] the researcher has determined practically and calculated theoretically the values of "resonance potential" $\dot{I}_r$ for metals that realize ST effect. The obtained data are presented in table 1.

Table 1

Experimental and calculated values of "resonance potential" $\dot{I}_r$ of metals that realize ST effect

Metal	Φ_M, eB	$M\psi_{H_2O}$, eB	Values of $\dot{I}_r$, eB	
			calculated	experimental
Sn	4,30	0,35	7,30	7,35
Pb	4,06	0,27	7,58	7,80
Cu	4,55	0,95	7,20	7,20*
Ag	4,30	0,40	7,80	8,90
Au	5,10	1,40	7,40	7,30
Cr	4,45	0,45	8,00	7,90*
Fe	4,80	0,85	7,90	7,90
Co	5,00	0,98	8,04	–
Ni	5,10	1,02	8,16	7,90

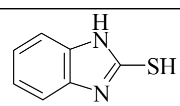
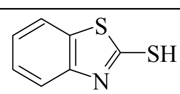
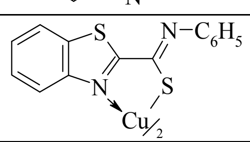
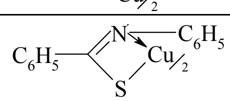
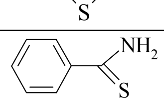
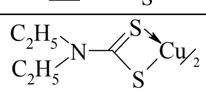
Notes:* – experimental values of $\dot{I}_r$ with oxide film creation on the metal surface taken into account. Y. Nechaev determined additional $\dot{I}_r$ for Cu^0 – 7,90 eB; for steel – 7,20 eB and 9,45 eB.

In order to study selective adsorption of N-, S-containing organic ligands and their complex compounds, their "resonance potentials" (presented in table 2) were determined.

It was assumed that if $\dot{I}_r$ of metallic copper of the bronze friction pair and of the additive introduced into industrial oil И-40 coincide, adsorption (chemisorption) will be maximal, which, in its turn, will improve tribochemical characteristics of the friction pair in the investigated oil medium.

Table 2

Calculated values of $\dot{I}_r$ and data on antiwear and antifriction properties of S, N-containing organic compounds as well as their metal chelates used as additives in oil И-40

№ п/п	Structural formula	$\dot{I}_r$, eB	Wear $\dot{I}$, g	f_{TP}
1		7,80 –	0,0015	0,03
2		– 8,1	0,0012	0,03
3		7,95 8,85	0,0006	0,019
4		7,85 9,25	0,0007	0,029
5		7,80 –	0,0009	0,020
6		– 8,50 9,25	0,0019	0,01
7	Oil И-40	– –	0,0015	0,05

Notes: Investigations were performed in the block-roller friction pair for the speed of 1,5 m/sec, friction path of $5 \cdot 10^3$ m and limit load of P_{max} = 36 MPa; concentration of the introduced additives was equal to 0,1 – 0,05 wt %.

Data presented in table 2 is the evidence that the best results as to the tribochemical characteristics are achieved with the compound of p. 3. In this case the main “resonance potential” of metal chelate of copper (II) – 7,95 eB is very close to the “resonance potential” of the metallic copper (Cu^0) – 7,90 eB, that was determined by Y. Nechaev with the account of copper oxides that are always created on its surface. The obtained high operational characteristics of the “bronze-steel” friction pair show that this approach where the energy of “resonance” potential” of adsorbent and adsorbate (their superimposing or resonance) is taken into account could have effective practical application.

However, it should be noted that according to Nechayev, selective chemisorption of organic compounds is the necessary but not a sufficient condition for full realization of ST effect in “bronze-steel” friction pairs. As a rule, mass fraction of tin in bronze alloys is up to 19% and, therefore, it would be feasible to consider the relationship between free energy of adsorption ΔG_A of organic substances based on tin as well as of their “resonance potentials” of ionization $\dot{I}_r$ and the data on wear in the “bronze-steel” friction pair (oil И-40, $P_{\max}$ = 40 MPa, concentration of organic additives - 1,0 wt %), which are given table 3.

Таблиця 3

Values of free energy of adsorbtion for organic substances ($-\Delta G_A$), their “resonance potentials” of ionization ($\dot{I}_r$), dipole moments (μ) and data on wear ($\dot{I}$) in oil И-40 [6]

№ п/п	Compound	$-\Delta G_A$, kDis/mol	$\dot{I}_r$, eB	μ, D	$\dot{I} \cdot 10^{-5}$, * г
1	Benzidine	28,3	6,88	1,38	15
2	Diphenylamine	31,6	7,25	1,30	33
3	α-naphthylamine	27,6	7,30	1,44	140
4	Rn toluidine	23,4	7,50	1,43	75
5	aniline	17,6	7,70	1,48	10
6	Phloroglucinol	10,0	7,85	0,00	40
7	Phenol	11,5	8,50	1,40	90
8	Pyridine	14,1	9,30	2,20	90
9	Benzamide	24,9	9,40	3,90	100
10	Benzonitrile	21,0	9,71	4,39	50
11	Oil И-40	–	–	–	150

Note: * – data on wear for organic compounds presented in table 3 were obtained by one of the authors of this work.

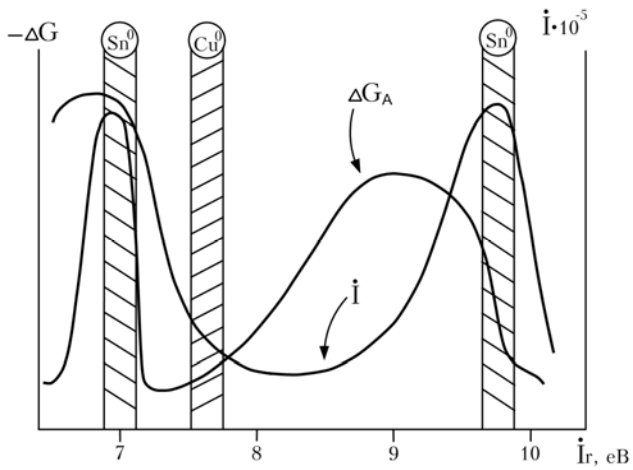


Fig. 1. Influence of the free energy of adsorption ($-\Delta G_A$) and “resonance potentials” ($\dot{I}_r$) on the wear of compounds 1 - 10 in oil И-40 (according to the data of table 3).

Data presented in table 3 and graphic dependences of wear ($\dot{I}$) on free energy of adsorption

($-\Delta G_A$) as well as of wear ($\dot{I}$) on "resonance potential" ($\dot{I}_r$) of oil И-40 for compounds 1 – 10 show that given compounds (mainly aromatic amines or N-containing organic compounds) have different values of – ΔG_A and, therefore, different values of wear of the investigated friction pair based on such soft metal as tin. Along with this, in the value range of the first "resonance potential" $\dot{I}'_r$ = 7,3 eB and the second "resonance potential" $\dot{I}''_r$ = 9,4 – 9,6 eB different compounds are to be found, e.g. diphenilamine (7,25 eB), α-naphthylamine (7,30 eB) and benzamide (9,4 eB) correspondingly. However, it should be noted that closeness or coincidence of "resonance potentials" of organic compounds (introduced additives) and of "resonance potentials" of tin do not provide minimal values of wear but, vice versa, coincide with their maximums, which do not correspond to the main postulates of Nechaey theory. Low values of wear for the investigated friction pair can be explained only by the fact that copper, included into bronze, is a dominant element with "resonance potential" ($\dot{I}''_r$ = 7,9 eB) that corresponds almost to the minimal value of wear.

Therefore, chemisorbtion of organic compounds on the friction surface is the necessary but not a sufficient condition for full realization of ST effect. Our investigation of ST effect in N, S-containing organic compounds (thioamids, thiourea, dithiocarbamates and their copper chelates) in different industrial oils allows to make the following conclusions:

- Additives introduced into oils must have maximal lipophilicity (solubility) in the base oil;
- Additives, introduced into oils, except selective adsorbtion ("resonance potential" on the surface of the friction pair) must also have a distinct chelating effect (the ability to form coordination compounds with metals that realize ST effect);
- Closeness or coincidence of resonance potentials of organic substances (additives) and "resonance potentials" of metals forming friction pairs is the necessary but not a sufficient condition for full realization of the selective transfer effect.

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