UDC 504.064.4.002.8

ECOLOGICAL PROBLEMS OF INDUSTRIAL DONBASS AND UTILIZATION OF COKING BY-PRODUCTS IN ANTIRUST MATERIALS

Yu. B. Vysotsky[1], V. P. Korolyov[2], S. I. Sohina[3], Yu. V. Selyutin[2], O. N. Shevchenko[3]

[1]Donetsk National Technical University
[2]Technological Safety Centre of Donbas
[3]Donbas National Academy of Civil Engineering and Architecture

Abstract

The paper deals with the problems of utilizing industrial by-products in the production of antirust materials. The test results have shown that the use of coal-processing by-products enhances protective properties of antirust metal coatings. The best results have been recorded for antirust compositions containing pitch and polymers of benzol separation. Besides, the utilization of coking industry by-products will help to improve the environment in great industrial regions.

Keywords: ecological problems, coking by-products, antirust composition, protective properties, rust modifier, film-forming base

The analysis of the situation in Donbass industrial megapolis shows that the processing of coal tar pitch at coke plants results in great amounts of by-products which are not utilized. The growth of industrial wastes leads to unfavorable environmental conditions in Donbass region and all over Ukraine. Thus, about a third of such products are produced in Donetsk region (Figure 1).

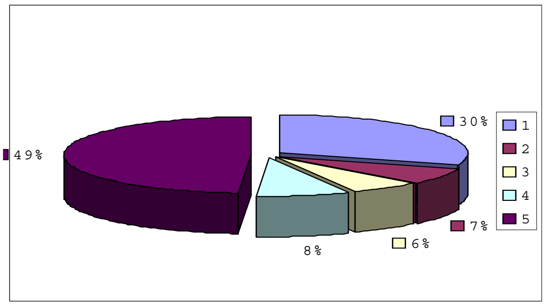

Figure 1. By-products production in Ukraine: 1 – Donetsk region, 2 – Zaporizhzhya region, 3 – Lugansk region, 4 – the rest of regions, 5 – Dnepropetrovsk region

Such products are classified as by-products and some of them as wastes. In our opinion they are a great reserve which can be used to create the industrial basis for producing some new materials by means of up-to-date processing techniques.

We have analyzed the products of Makeyevskiy and Yasinovskiy by-product coke plants and found out that some by-products of coal processing have a high-molecular structure and other contain low-molecular monomers (tar-yielding components). This fact can help to solve the problem of providing paint and varnish industry with film-forming materials of sufficient quality. When selecting the components for antirust raw materials base we took into account both economic and environmental situation in Donbass region and Ukraine in general.

At a certain stage indene-coumarone fraction is used as fuel (that is just burnt), and this process pollutes the air. The study of tar-yielding components polymerization has shown that both heavy benzol fraction and a narrower indene-coumarone fraction (ICF) can be used as row materials for film-forming base.

The presence of tar-yielding components (according to chromatograms they are mainly indene, sterol, their homologs and coumarone) in such a fraction (up to 52% in first grade ICF and up to 42 % in second grade ICF, see figures 2 and 3) makes possible the production of polymerization materials, namely indene-sterol copolymers.

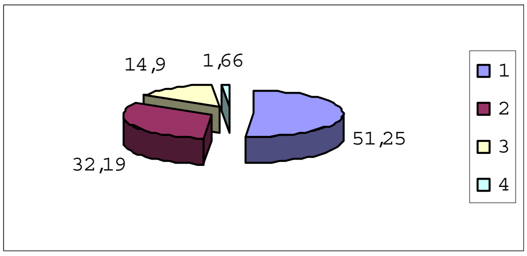

Figure 2. The composition of the first grade indene-coumarone fraction
1 – tar-yielding components (51,25%); 2 – low-boiling (32,19%); 3 –volatile (14,9%); 4 – naphthalene (1,66%)

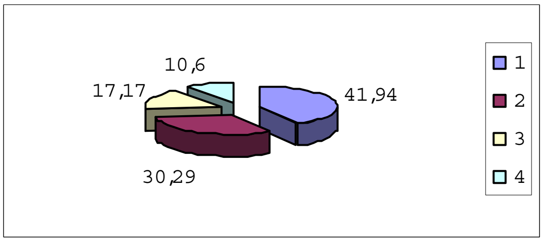

Figure 3. The composition of the second grade indene-coumarone fraction.
1 – tar-yielding components (41,94%); 2 – low-boiling (30,29%); 3 – volatile (17,17%); 4 – naphthalene (10,6%)

Heavy benzol fraction is referred to tonnage products, it can be used to obtain film-forming base for many antirust materials. It will help to increase the amount of resources for producing a great variety of antirust substances which are so scarce today.

The research into the use of indene-sterol copolymers (obtained by means of heavy benzol fraction film-forming components polymerization) as a film-forming base in antirust materials proved the possibility of producing compositions (AM-1 and AM-2) for metal protection in low-aggressive environment.

Further modification of the polymerizate on ICC basis resulted in obtaining antirust compositions “Ikar” with reinforced protective and physical-mechanical properties which can be applied in middle- and high-aggressive environments. For this purpose at the final stage of polymerization at temperature 165-180 C a plasticizing agent should be added (up to 40%). In this case there is no necessity of low-boiling components distillation which took place in the process of producing AM. The possibility of using antirust materials obtained on the basis of modified ICC is also of a certain interest. These materials contain rust modifiers (RM) which allow to color a rusty metal surface (in fact metal surface treatment is often improper, and there remains a certain layer of rust on it). So we suggest the use of powder rust modifier RM “Ferrokor” on lignin base as an admixture for “Ikar” composition. “Ferrokor” contains high-molecular powder rust modifier which can dissolve the corrosion with rust thickness up to 100 micrometers.

The study of the protective properties of “Ikar”-based compositions has shown that optimal content of RM “Ferrokor” is 5 to 9%. The research was made on a cleaned metal surface and on a surface with rust thickness up to 100 micrometers. Protective properties of the obtained coatings were studied by means of potentiostatic methods on steel St.3 on the potentiostat P-5827M in 0,1N solution of potassium chloride. Durability of coatings was also estimated by means of defining a summarized index of coating quality (Aз) according to the quick test method within the program “Industrial Atmosphere”. Table 1 presents the parameters of mathematical treatment of the data from Tafel pieces of polarization curves (AM-0 – pure polymerizate; AM-1 – a composition containing polymerizate and amino-nitro-tar wastes; the composition “Ikar” with 5%, 7%, 9% of rust modifier “Ferrokor”).

Table 1. The parameters of mathematical treatment of tafel pieces of polarization curves

System	*Anodic process*				
	a	b_a	*n*	S_e	R
Without coating	-0,443±0,005	0,069±0,006	15	0,02	0,94
AM-0	-0,457±0,005	0,072±0,06	17	0,02	0,94
AM-1	-0,234±0,010	0,106±0,009	7	0,02	0,94
Ikar	-3,810±0,020	1,413±0,08	21	0,03	0,97
Ikar+5%RM	-2,74±0,014	2,220±0,058	17	0,013	0,966
Ikar+7%RM	-1,510±0,02	2,295±0,05	21	0,014	0,995
Ikar +9%RM	-3,400±0,02	2,667±0,05	16	0,009	0,998
System	*Cathodic process*				
	a	b_c	*n*	S_e	*R*
Without coating	-0,671±0,020	0,070±0,010	10	0,02	0,86
AM-0	-0,704±0,020	0,080±0,010	8	0,01	0,90
AM-1	-0,751±0,030	0,199±0,020	15	0,02	0,90
Ikar	-5,99±0,05	1,010±0,07	17	0,013	0,967
Ikar+5%RM	-6,24±0,056	1,820±0,06	9	0,005	0,996
Ikar+7%RM	-5,82±0,037	2,280±0,046	20	0,012	0,996
Ikar +9%RM	-7,067±0,04	2,272±0,06	15	0,01	0,995

Where: b_a and b_c are the slopes of Tafel pieces of the polarization curves which express the degree of complicatedness of the process of electrode reactions (anode and cathode polarizabilities),
n – the number of points, R – correlation coefficient, S_e – statistical error.

Table 2 presents polarizabilities in anode and cathode areas of the corrosion process and inhibition effect of the obtained antirust materials.

Table 2. Protectiove properties of the antirust materials (AM) with indene-sterol copolymers base

Systems	Polarizabilities		I_{cor}.	Inhibition coefficient (γ)	
	b_a	b_c		$i_{\kappa cor}$(without coat)/ i_{cor}	I_{cor}(Ikar)/ I_{cor}(Ikar+RM)
Without coating	0,069±0,006	0,07±0,01	$12,0\cdot10^{-3}$	-	-
AM-0	0,072±0,006	0,08±0,01	$5,0\cdot10^{-3}$	2,4±0,2	-
AM-1	0,106±0,009	0,12±0,02	$2,0\cdot10^{-3}$	6,0±0,5	-
Ikar	1,430±0,08	1,010±0,07	$3,0\cdot10^{-6}$	-	-
Ikar+5%RM	2,220±0,058	1,820±0,06	$2,0\cdot10^{-6}$	-	1,5±0,2
Ikar+7%RM	2,295±0,05	2,280±0,046	$1,0\cdot10^{-6}$	-	3,0±0,2
Ikar+9%RM	2,667±0,05	2,272±0,06	$1,0\cdot10^{-6}$	-	3,0±0,2

The results of polarization research (table 1) have shown that plasticizing agent enhances protective properties of the coatings based on pure polymerizate AM-1 and of the coatings based on the composition which contains amino-nitro-tar wastes acting as inhibiting agent (AM-1). The inhibition takes place both in anode and cathode areas of corrosion.

Rust modifier “Ferrokor” used in the plasticized composition “Ikar” enhances protective properties of the coatings. However, the best results are obtained for the composition with 7% of RM “Ferrokor”. The increase of RM “Ferrokor” share has no significant influence on the polarizabilities (within the error) on anode and cathode pieces of polarization curves.

The obtained results were confirmed by the method of quick comparative testing “Industrial Atmosphere” (State Standard 9.401-91 method 5) on standard samples with one-layer coating.

Test cycle “Industrial Atmosphere” includes the following stages:

- 4 hours in the humidity chamber with relative humidity 97±3% and temperature 40±2C;
- 2 hours in the humidity chamber without heating;
- 2 hours in the sulfurous gas chamber with SO_2 concentration 5 ± 1 mg/m^3;
- 3 hours in freezing chamber at the temperature -45±3°C;
- 7 hours in the artificial weather chamber;
- 6 hours at the temperature 15-30°C and relative humidity not more than 80%.

One cycle lasts for 24 hours. According to State Standard 9.401-91 after 15 testing cycles the coating must retain its protective properties (A_{pr}). Overall estimation of protective properties (A_{pr}) (table 3) includes relative estimates of the damage (such as blisters, cracking, corrosion, flaking) and relative estimates of linear sizes of the damage after 15 and 25 cycles. Physical and mechanical properties of the coatings (table 3) were determined according to protective film impact strength and adhesion (the strength of cohesion of the coating with the metal). The frequency of testing remained the same.

Table 3. Protective and physical-mechanical properties of coatings based on the compositions “Ikar” and “Ikar”RM “Ferrokor” after 15 and 25 tests

Compositions	“Ikar”			“Ikar”+5%RM “Ferrokor”			“Ikar”+7%RM “Ferrokor”			“Ikar”+9%RM “Ferrokor’”		
Samples	1	2	3	1	2	3	1	2	3	1	2	3
Thickness of coating , mcm	30-40	20-40	90-100	30-40	20-40	80-90	30-40	20-40	80-90	40-42	20-40	90-100
A_{pr} (15 cycle)		0,90	0,60	-	1,0	0,70	-	1,0	0,75	-	1,0	0,76
A_{pr} (25 cycle)	-	0,60	0,45	-	0,68	0,63	-	0,80	0,65	-	0,81	0,65
Adhesion, points (15 cycles)	1	1-2	2-3	1	1-2	2-3	1	1-2	2-3	1	1-2	2-3
Adhesion, points * (25 cycles)	1	1-2	4	1	1-2	4	1	1-2	3	1	1-2	3
impact strength, kgf·cm (25cycles)	10	15	10	15	25	10	15	25	10	15	25	10

1 – check samples,
2 – samples of tests with prepared surface,
3 – samples with rusty surface (up to 100 micrometers of rust).
* For polimerizate (AM-0) these indexes are 2-3 respectively (samples) and 3-4 (after 25 cycles).

The results of the research confirm high protective and physical-mechanical properties of antirust material “Ikar” based on indene-sterol copolymers. If we add lignin-based rust modifier “Ferrokor” into composition “Ikar” it will help to improve its protective and physical-mechanical properties. It should be mentioned that the enhancement of protective and physical-mechanical properties is observed at RM content about 7 %. Further increase of RM content in the composition “Ikar” does not change the protective properties of the coating.

Moreover, the tests have shown that the composition “Ikar” with 7% RM can be used on rusty surfaces with rust thickness up to 100 micrometers and that will allow to exclude thorough antirust treatment of metal surface prior to metal coloring.

In the process of studying the influence of modifying agents on physical-mechanical and protective properties of coatings we also tested by-products of coal-tar pitch processing which contain compounds with high-molecular structure such as acid pitch, pitches from waste water mechanical purification, and polymers of benzol separation which are the residual products of absorbing resin oil.

However, all the above products require a special treatment to be utilized in antirust compositions. Thus, acid pitch contains up to 24% of water and has acidic medium (total acidity reaches 0,75 % in H_2SO_4 equivalent) and that leads to the necessity of its dewatering and neutralization. The results of preliminary tests have shown that such pitch, even if treated, does not improve physical-mechanical and protective properties of the coatings, probably because of the negative effect of sulphate remains. Pitch from wastewater mechanical purification contains up to 37% of water, so it is inhomogeneous and requires preliminary water separation and dewatering. Besides, alkalescent reaction of aqueous extract (alkalinity is 0,17% in sodium hydroxide equivalent) shows that the pitch contains alkali and requires afterpurification. The results of preliminary testing have shown that such pitch is very difficult to extract in dewatered state. That is why its effectiveness in modifying admixtures of indene-sterol copolymers is not sufficient.

The best results were obtained for the polymers of benzol separation (viscous black liquid with 4,0% of moisture and at least 20,0% of pitch).

It has been proved that modification of indene-sterol copolymers with coke industry by-products helps to improve protective properties of antirust coatings. The best protective effect has been recorded for compositions with pitch (produced in the process of naphthalene-containing resin oil rectification) and polymers of benzol separation.

So the utilization of coking by-products in antirust materials makes possible their wide use in the areas with low- and middle-aggressive environment on the one hand and helps to improve ecological situation in industrial regions on the other.

References:

1. Противокорозійна композиція ИКС-1 : патент Украины № 44050А / Горохов Е. В., Королев В. П., Высоцкий Ю. Б., Сохина С. И., Шевченко О. Н., Селютин Ю. В. - Бюл. № 1, 2002.

2. Е. В. Горохов, Ю.Б.Высоцкий, В.П.Королев, С.И.Сохина, О.Н.Шевченко / Фізико-хімічна механіка матеріалів., 2001, с.142-149.

Received on 11.01.2010