Petroleum and Coal

Article Open Access

THE POSSIBILITY OF REDUCING THE CARCINOGENICITY OF COAL TAR ELECTRODE PITCHES

Fedor F. Cheshko, Alexandr L. Borisenko, Alla Yu. Martynova, Vladimir M. Shmalko, Oleg I. Zelenskii

Ukrainian State Coal-Chemistry Institute, 61023, Kharkov, 7 Vesnina Str., Ukraine

Received March 13, 2018; Accepted April 27, 2018

Abstract

The technological value of the coal tar electrode pitch is largely determined by the high content of condensed polyaromatic compounds in its composition. An attempt to change the chemical composition of the coal tar electrode pitch in order to reduce the content of carcinogenic polyaromatical hydrocarbons (PAH) will bring it closer to oil binders that are significantly inferior in their technological properties, or inform them of the new properties that are not desirable from the consumer's point of view. Involving carcinogenic PAH in the process of chemical transformations the products of which are not determined by analytical methods as indicators of cancer risk, will not necessarily lead to a decrease in the carcinogenic risk of coal tar pitch as a physicochemical system.

Keywords: *coal tar pitch; carcinogenity; polyaromatical hydrocarbons; benz(a)pyrene.*

1. Introduction

As known, the coal-tar electrode pitches namely the product of coal tar processing, are used in the production of a wide range of conductive materials as well as structural elements. For example, these are anodes and anode masses for the production of aluminum, graphitized electrodes for the electrowelding of steel, materials for sliding contacts, *etc.* The main purpose of the pitch in such industries is to act as a binder for carbon fillers which are mainly electrode cokes based on the same coal tar pitch, as well as oil and shale tar. The indispensable processing stages, which are mixtures of filler and binder, are high, and in some cases–very-high-temperature processing (up to 1500-2500°C) [1]. As a result, a fairly uniform material with high carbon content, a low electrical resistivity, and a number of other specific properties are formed. When making electrodes, the pressed blank is subjected to preliminary heating, then the resulting porous solid body of the future product is impregnated with a special pitch for filling the pores, increasing the density and mechanical strength on further thermal and mechanical treatment.

The normative properties of electrode binders and impregnating pitches are determined by the requirements for qualitative parameters of the final electrode product and the features of the technology of its production at specific enterprises. The pitch, used as an electrode binder, should have optimal binding properties and cake well with carbonaceous fillers, firmly binding their grains and providing a high yield of the coke residue. The main requirements for impregnating electrode pitches are low viscosity at the impregnation temperature and the ability to penetrate into the pores of the impregnating material. In addition, impregnating pitches, as well as electrode binders, should create a strong adhesion contact with the surface of the work material, and while carbonizing, they should ensure the highest possible yield of the coke residue. To improve the technological properties of electrode binders (mainly) and impregnating materials, the initial pitches obtained directly at the rectification stage of the coal tar as a non-boiling residue are subjected to the subsequent treatment at temperatures from 250 to 400°C with the use of special technological methods intensifying the polymerization and polycondensation reactions in the pitch melt. As such methods in different countries, different manufacturers produce thermooxidation with air oxygen, vacuum heat treatment, thermal soak under upacting pressure, modifying chemical-active additives, *etc.* [1-3].

Another property of the coal pitch that does not relate to specific technological indicators, but which is of great importance for the staff's health and life of manufacturing and processing enterprises, is carcinogenic activity. The biological index of carcinogenicity of various coal tar pitches (Aibolla index)[1] ranges from 20 to 45. It is massively higher than that of similar petroleum products. There are also numerous medical and statistical data that irrefutably prove the causal relationship of the systematic (professional) impact of the coal tar pitches and resins with the contraction of an oncology disease of a number of human organs [4-7].

The carcinogenicity of the coal tar materials that is resins and derived from them is related to the presence of polycyclic aromatic hydrocarbons (PAH) in their composition. However, not all representatives of this class of substances are equally oncologically dangerous.

There is no consensus on the carcinogenic hazards of the various components of the coal tar pitches. Few of them are produced in pure form on a scale that is sufficient for representative statistical generalizations concerning the oncological impact on production personnel. At the same time, it is well known that the same substances with respect to different biological organisms can exhibit different carcinogenic activity – from very strong to zero. Although nowadays the lines of laboratory animals that are genetically close to a person have been produced, it is undoubtedly impossible to achieve a one hundred percent identity. This is the reason for some discrepancies in the literary sources regarding the classification of substances that are cancerous for people.

Thus, according to the authors [8-9], among the high-molecular PAH, the most dangerous one is benzo(a)pyrene (BaP, $C_{20}H_{12}$, five conjugated rings in the molecule). In addition to BaP, a number of PAH are also classified as carcinogens. Among them, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene and indeno (1,2,3-cd)pyrene. PAH, known for its carcinogenic and mutagenic properties, also includes benz(j)fluoranthene, benz(ghi)perylene, coronene, ovalene, *etc.*

Currently, more than 500 carcinogenic PAH have been identified. Since it is not feasible to carry out individual sanitary monitoring of the content of such substances quantities in different environments, for this purpose various national and international environmental organizations identify a number of priority groups.

For example, 16 PAH, including BAP, is designated by the US Environmental Protection Agency to represent the results of test measurements; 4 PAH-BaP, benz(c)fluoranthene, benz(k)fluoranthene, indeno(123-cd)pyrene are used as indicators for emission inventories under UNECE Protocol[2]. In order to analyze the carcinogenicity of the exhaust gases of internal combustion engines, a priority group has been singled out. This group includes BaP and 11 PAH: benz(v)fluoranthene, benz(a)anthracene, chrysene, benz(g,h,i)perylene, fluoranthene, pyrene, benz(e)pyrene, perylene, indenoprene, diben(a,h)anthracene and coronene [10].

It should be noted that the level of BaP content (which is included in all the above and many other categories) has been used for a long time as a universal indicator of the carcinogenicity of the material. Thus, according to the Document of EC Commission No. 208/2005 / EEC[3], the content of benzo (a) pyrene can be used as an indicator of the presence and danger of carcinogenic polycyclic aromatic hydrocarbons, even in food products.

---

[1] The index of carcinogenicity (Aibolla) Ikants is determined by the results of biological tests on living organisms. Ikants = (A / L) × 100; where A is the number (%) of the test specimens in which malignant tumors were detected as a result of the tests; L - duration (days) of the latent period [4].

[2] The Protocol on Persistent Organic Pollutants to the 1979 Convention on Long-range Transboundary Air Pollution of the United Nations Economic Commission for Europe.

[3] COMMISSION REGULATION (EC) No 208/2005 of 4 February 2005 No 466/2001 as regards polycyclic aromatic hydrocarbons.

Thus, the BaP to the present time is a kind of indicator of the presence in materials, atmospheric emissions, sewage and other media of carcinogenic PAH.

2. Experimental

Below (Tables 1-3) we give the obtained data on the content in the various coal tar peaks of the BaP (1995, Table 1), as well as carcinogenic PAH (2016, Tables 2, 3).

Table 1. The content of BaP in various coal tar pitches of industrial origin (1995)

Indicators	Initial pitches			Medium temperature pitches			High temperature pitches	
	1	2	3	4	5	6	7	8
Softening point according to K&S, %	50.5	56.0	60.0	67.5	68.0	86.5	149.0	250.0
The content of the BaP, %	1.60	2.25	2.30	2.15	1.48	2.10	1.83	1.52

The results obtained by us are well correlated with the literature data of the corresponding periods, for example, Table. 1 – with the data of the works [7, 11], and the data of Table 2 – with the data [12].

Table 2. The content of priority PAH, %, in industrial samples of the coal tar electrode pitch (2016)

Component name	Electrode pitches						High temperature pitches		
	Model number								
	1	2	3	4	5	6	1	2	3
Naphthalene	0.05	0.227	0.493	0.256	n.a.	0.229	1.509	0.099	0.147
2-Methylnaphthalene	0.03	0.065	0.121	0.072	n.a.	0.006	0.400	0.002	0.036
2,3 Dimethylnaphthalene	n.a.	0.026	0.029	0.025	n.a.	0.005	0.054	0.008	0.018
Ascenaphthylene	n.a.	0.004	0.008	0.004	n.a.	0.002	0.026	0.001	0.002
Acenaphthene	0.27	0.335	0.544	0.336	0.12	0.032	0.809	0.010	0.180
Fluorene	0.13	0.191	0.349	0.211	0.03	0.066	0.572	0.057	0.136
Fenatren	1.17	1.025	1.750	1.078	0.63	1.562	1.676	0.076	0.865
Anthracene	0.36	0.206	0.507	0.293	0.26	0.464	0.518	0.022	0.167
Fluoranthene	1.86	1.581	2.213	1.674	1.27	2.110	2.044	0.638	1.609
Pyrene	1.81	1.562	2.023	1.575	1.31	2.001	1.880	0.703	1.561
Benz (a) fluorene	0.50	0.495	0.424	0.419	0.35	0.444	0.409	0.280	0.524
Benz (b) fluorene	0.40	0.340	0.386	0.336	0.25	0.500	0.387	0.249	0.348
Benz (a) anthracene	1.18	0.886	1.191	1.073	0.74	1.175	1.194	0.738	0.919
Chrysene	1.42	1.177	1.305	1.192	1.32	1.325	1.170	1.063	1.274
Benz (b) fluoranthene	1.67	1.452	1.416	1.367	1.33	0.518	1.357	1.013	1.528
Benz (k) fluoranthene	0.73	0.501	0.526	0.501	0.71	1.334	0.508	0.296	0.497
Benz (e) pyrene	1.05	0.797	0.818	0.791	0.86	0.757	0.757	0.697	0.800
Benz (a) pyrene	**1.62**	**1.001**	**1.166**	**1.114**	**1.30**	**1.146**	**1.122**	**0.976**	**1.019**
Perilen	0.81	0.360	0.388	0.365	0.70	0.375	0.377	0.323	0.371
Indeno (1,2,3-c, d) pyrene	1.93	0.512	0.495	0.505	1.47	0.217	0.445	0.207	0.496
Dibenz (a, h) anthracene	0.47	0.264	0.260	0.271	0.23	0.920	0.231	0.816	0.260
Benz (g.h.i) perylene	1.75	0.727	0.572	0.728	1.27	0.763	0.487	0.659	0.698

n.a.-not available

A certain decrease in the content of the electrode coal tar pitches of BaP, noted over the past twenty years, is probably due to the general trends in the change of the raw material base and technological equipment for coking coal. Thus, a decrease in the content of coal gas in coal batches and the increase in the share of heavy-duty furnaces (including new ones or those that have undergone rearrangement) in the total volume of coke production led to a decrease in the degree of pyrolysis of the coal tar.

Nevertheless, despite the marked tendency, the level of carcinogenic activity of the pitches produced from the coal tar continues to be very high. This forces producers and consumers of raw materials for electrode products to look for the alternative types of binding and impregnating materials. However, the main driving force of such searches is the ratio of production and consumption of the coal tar pitches in the world.

Thus, the authors of the work [13] noted that in the pre-crisis period in most regions of the world, the production of coal-bearing electrode pitches was significantly lower than the demand. The greatest deficit was observed in the countries with a developed aluminum industry, which is the dominant consumer of coal tar pitches. The production of this kind of electrode raw materials is limited by the level of coke production.

It can be concluded that the tendencies of the world markets for pitch, aluminum, and metallurgical coke promise, at least in the near and medium term, the preservation of the deficit of electrode pitches. One way of making good this deficit can be the production of electrode binding and impregnating materials on an alternative basis. Taking into account the number of resources, the development consumption of such raw materials in related sectors (manufacture of electrode fillers, carbon fibers, carbon black, *etc.*), as well as the relative proximity to the coal tar according to the physico-chemical properties,oil stock attracts the most attention in this regard.

A petroleum pitch is produced from heavy oil residues, pyrolysis resins, cracked residues, *etc.* [14]. The use of such raw materials has also ecological and sanitary reasons: as it has already mentioned above, oil pitches are characterized by a much lower content of carcinogenic substances. In particular, the concentration of benzo(a)pyrene, according to the results of the studies, is 0.04-0.15 % in the pitches from cracked residues, and 0.3-0.8 % in pyrolytic pitches [14, 15].

However, the differences in the chemical composition of coal and petroleum pitches are an advantage of the latter only from the point of view of the relative ecological safety. In terms of technological properties, the situation is the opposite. At the same softening temperature, the coal tar pitches are characterized by a much higher content of high molecular components (substances which are insoluble in toluene, TI) than petroleum. For example, for vacuum-distilled cracked pitches, the content of such components is 5-16 times lower than in the coal tar pitch with a similar softening point value. Specifically, because petroleum pitches contain less polycondensed aromatic compounds, they have a lower C/H ratio and, consequently, a much lower yield of the coke residue compared to coal analogues. For even a partial leveling of these negative differences, it is necessary to increase the softening point of the petroleum pitches. However, this leads to an increase in viscosity and a decrease in the wetting power with respect to the filler [14-17].

There are known efforts to improve the properties of oil pitches by adding dust of petroleum coke, soot, and other high-carbon components in them [15, 18]. However, the increase in the coke residue due to only solid disperse additives without the presence of intermediate fusible carbonaceous components in the pitch can not contribute to the improvement of the entire complex of properties of the electrode material, both binding and impregnating ones.

For these above mentioned technological drawbacks, at present oil pitches find an extremely limited industrial application in the USA and Canada (about 10-12 % of the total amount of pitch used), traditionally experiencing a critical deficit of coal electrode binders. At the same time, it is proved that the oil pitch, due to the high yield of volatile substances, the low content of coke-forming components, the increased softening temperature, and high viscosity, is not able to replace coal analogues adequately. Therefore, it is considered expedient to use a petroleum pitch only in a mixture with coal tar. The approximate composition of such a compound is 15 % oil and 85 % the coal tar pitch [14, 19].

All the above mentioned information prompted and encourages various researchers to find the ways to reduce the carcinogenic activity of the coal tar pitch. The most common in this regard are the attempts to reduce the content of carcinogenic PAH, and most notably BaP through the chemical pitch treatment.

For example, it is known, that during the heat treatment of the initial pitch, which is necessary to impart the required technological properties, the addition of various chemically active additives can contribute to both intensification and inhibition of the processes that lead to the formation of additional quantities of BaP; it is also possible to achieve a significant reduction in its concentration in the processed pitch melting in comparison with the raw material. Table 3 shows the conditions and results of our research in this field. The original pitch was subjected to the treatment with the following parameters: softening point – 50.5 °C; the mass fraction of substances that are insoluble in toluene – 25.4 %; the mass fraction of substances that are insoluble in quinoline – 8.8 %; the content of the BaP – 1.6 %. The heat treatment was carried out in a laboratory cube-reactor until electrode pitches with similar softening temperatures were obtained.

Table 3. The conditions and results of heat treatment of the pitch including chemically active additives

Processing parameters and pitch quality indicators	Additive		
	Benzoyl peroxide	Sulfanilic acid	
Experiment Number	1	2	3
The content of the additive,% of the mass of pitch loading	1	5	5
Liquid phase temperature, °C	330	290	330
Steam phase temperature, °C	300	250	300
Pitch quality indicators			
Softening point accordint to K&S, %	91	90	92
Mass fraction of substances insoluble in quinoline (QI), %	18.9	9.3	16.2
Mass fraction of substances insoluble in toluene (TI), %	37.0	41.9	42.1
Mass fraction of substances insoluble in toluene, but soluble in quinoline (β-resins), %	18.1	32.6	25.9
Mass fraction of substances soluble in toluene (TS), %	63.0	58.1	57.9
Volatile matter yield at 850 °C, %	53.9	52.0	52.7
The content of BaP, %	2.55	0.44	2.50

3. Result and discussion

According to the results of our earlier studies [20], benzoyl peroxide ($H_2N–C_6H_4–SO_3H$) under experiment No. 1, and sulfanilic acid ($(C_6H_5CO_2)_2$) under experiment No. 3 intensify the course of the radical polymerization processes, which, judging from the data in Table 3, lead to a significant (more than one and a half times) increase of the content BaP in the pitch. In contrast, sulfanilic acid under the conditions of experiment No. 2 intensifies the course of the reactions of increasing the molecular weight by the ionic mechanism, in which, apparently, BaP is not a product but a reagent, that leads to a decrease in its concentration in the final pitch 3.6 times compared with the initial one. In this case, the initiation of the primary course of ionic polymerization during the heat treatment of the initial pitch does not lead to a deterioration in the technological properties of the electrode pitch (see Table 3). If the BaP content was indeed a sufficient indicator of carcinogenic activity, the problem could be considered solved.

The same applies to another method of decreasing the carcinogenicity of coal tar pitch, which has been attracting researchers' attention for a long time [7, 12] – to the oxidation of coal raw materials.

Thus, according to the author of the paper [21], thermal oxidation with oxygen, ozone, and other oxidizing agents is an effective way to reduce the carcinogenic activity of coal tar pitches. For example, the low-temperature (up to 300 °C) thermal oxidation of the raw feedstock (especially the air with an additive 0.3-1.6 % ozone) makes it possible to reduce the content BaP in the electrode coal tar pitch to a level of 0.2-0.3 %, which is 10-15 times lower than in the ordinary industrial samples. It is commensurate with the content of BaP in petroleum pitches. A similar result was obtained by other investigators [22] during the thermal oxidation of a low-temperature pitch with the air at 265 °C for 1.5-2.0 hours. BaP level in such a pitch was 0.24 %. Similarly, the analysis of industrial samples of coal tar pitches [23] showed that vacuum-distilled pitch contains 1.5 times more carcinogenic PAH than those obtained under the thermal oxidation with air oxygen.

From the point of view of the technological (consumer) properties of the thermooxidized pitches, it is appropriate to recall that the thermooxidative treatment of coal tar initial pitches did not become widespread due to a rather narrow range of raw material quality indicators (coal tar, initial pitch), suitable for obtaining high quality electrode binders for this technology [3]. In addition, according to the available data, some consumers put forward a requirement that the pitch cannot be oxidized by oxygen (including the air) during heat treatment. The most common opinion is that oxidation worsens graphitization because, during oxidation, strong cross-links are formed between the condensed layers in the form of oxygen bridges. In this connection, it is believed that the presence of more than 7 % oxygen in the feed leads to complete suppression of the mesophase processes and to the production of non-graphitized coke [3, 24]. However, the very fact of a decrease in the concentration of BaP and other specific carcinogenic PAH in the pitch as a result of chemical (especially oxidative) treatment is by no means evidence of a decrease in the overall oncological danger of the pitch as a physicochemical system.

PAH and their derivatives (except for epoxides), like some other chemical compounds (for example, aromatic amines), refer to genotoxic carcinogens of indirect action. Such substances are not carcinogenic in the original form, but, having relatively low reactivity, accumulate in the body, where in the process of metabolism they undergo enzymatic activation with the formation of highly active electrophilic metabolites. The latter interacts with nucleophilic DNA groups, causing malignancy[4] of cells [25-26].

It is especially important to note that the main way to activate the carcinogenic activity of a number of substances is enzymatic oxidation. For example, chloroethylene oxide proved to be a carcinogenic metabolite of vinyl chloride. In this case, for each carcinogen, there may be, apparently, not one, but several ways of metabolic activation [27].

Thus, if as a result of any (especially oxidative) effect on the pitch, analytical studies show a decrease in the content of specific PAH recognized as indicators of carcinogenic activity, this does not mean a reduction in the oncological danger of the pitch. As an illustration of this, Table 4 shows the data on the content of BAP and Aiboll index obtained for electrode pitches subjected to various special processing techniques [3, 7, 22]. Among the agents of such processing in the literature very exotic ones, for example, γ-irradiation can come across.

Table 4. The study results of carcinogenic activity of modified pitches

Pitch Name	Softening point accordint to K&S, %	Mass fraction of BaP, %	Aiboll index
Industrial, initial	69,4	1,1	44,2
Industrial, electrode, grade B	86,0	2,1	39,5
No. 1, subjected to γ-irradiation	71,0	0,7	33,1
No. 2, thermoaired with ozone	73,0	1,2	39,3
No. 2, reated with gaseous chlorine	84,3	0,8	9,5

As can be seen from the data presented, even a significant decrease in BaP content is accompanied only by a slight improvement in the biological index of Aibolla. With the thermal aeration of the pitch (i.e., when it is oxidized by ozone), the biological index does not change at all, although the mass fraction of BaP decreases by almost half.

The only exception is the chlorinated pitch. However, both the technology of processing coal tar pitch with gaseous chlorine and the use of a chlorinated binder in the electrode production, do not appear to be technological.

[4] Malignization (from Latin malignus) - the acquisition by cells of normal or pathologically altered tissue of the body (including benign tumors) of the properties of a malignant tumor.

The same can be said about a decrease in the carcinogenicity of the pitch by its sulfonation. According to the data of the work [13], such a pitch contains no BaP and has Aiboll index equal to zero. At the same time, according to the data of the work [7], sulfonation gives the coal pitch very uncharacteristic properties for it, for example, water solubility.

4. Conclusion

Thus, from the above mentioned, we can draw the following conclusions:

1. The technological value of the coal tar electrode pitch is largely determined by the high content of condensed polyaromatic compounds in its composition.
2. An attempt to change the chemical composition of the coal tar electrode pitch in order to reduce the content of carcinogenic PAH will bring it closer to oil binders that are significantly inferior in their technological properties, or inform them of the new properties that are not desirable from the consumer's point of view.
3. Involving carcinogenic PAH in the process of chemical transformations, whose products are not determined by analytical methods as indicators of cancer risk, will not necessarily lead to a decrease in the carcinogenic risk of coal tar pitch as a physicochemical system.
4. Efforts to reduce the carcinogenic hazards of coal tar pitches should be focused on improving the production technology and application of these materials in order to minimize their contacts on personnel.

References

[1] Pityulin IN. Scientific and technological foundations of production of coal tar carbon-containing materials for large electrodes; Monograph; Contrast: Kharkov, 2004; p. 480.

[2] Privalov VE, Stepanenko MA. Coal tar pitch: production, processing, application; Metallurgy: Moscow, 1981; p. 208.

[3] Kleshnya GG, Cheshko FF, Pityulin IN. Problems of modern domestic production of electrode coal tar pitch. J. Coal Chem. 2006; 5-6: 63-67.

[4] Zuss R, Kintsel V, Skribner D. Cancer: experiments and hypotheses; Mir: Moscow, 1977; p. 360.

[5] Yanyisheva NYa, Kireeva IS. Protection of the environment from carcinogens at ferrous metallurgy enterprises; Znanie: Kiev, 1988, p. 16.

[6] Yanyisheva NYa, Chernichenko IA, Balenko NB. On methodological issues of rationing the chemical carcinogenic substances in the environment. Hygiene and sanitation. 2003; 1: 54-57.

[7] Mochalov VV. Theoretical foundations and technology of production of new carbon-containing materials on the basis of coal tar pitches and high-boiling fractions of coal tar: a thesis for the degree of Doctor in technical science, UKHIN: Kharkov, 1984; p. 435.

[8] Toxicological Profile for Polycyclic Aromatic Hydrocarbons / U.S. Department of Health and Human Services, August 1995; Electronic resource: https://www.atsdr.cdc.gov/toxprofiles/tp69.pdf.

[9] The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons; Under the editorship of Andreas Luch; Imperial College Press: London, 2005; p. 489.

[10] Kanilo PM, Solovey VV, Kostenko KV. Problems of atmospheric pollution of cities with carcinogenic-mutagenic super toxicants. Bulletin of the Kharkov Automobile Road University. 2011; 52: 47-53.

[11] Gogoleva TYa, Shustikov VI. Chemistry and technology of coal tar processing; Metallurgy: Moscow, 1992; p. 256.

[12] Andreykov EI, Amosova IS, Pervova MG. Determining the content of polycyclic aromatic hydrocarbons in industrial samples of coal tar and pitch. Coke Chem. 2008; 8(51): 321-325.

[13] Sidorov OF, Seleznev AN. Prospects of production and improvement of consumer properties of coal tar electrode pithes. Russian Chemical Journal. 2006; 1(50): 16-24.

[14] Vershinina EP, Gildebrandt EM, Selina EA. Trends in the development of binder production for anodes of aluminum electrolyzers. Journal of Siberian Federal University: Engineering & Technologies. 2012; 5: 752-759.

[15] Ugapev AA, Kim IV, Doshlov IO, Lubinskiy MI, Sinshinov PA. Research, development of technology and production of a new composite binder - petroleum pitch HDPE. Polzunovsky almanac. 2010; 2: 314-316.

[16] Perez M, Granda M, Menendez R. Preparation of binder pitches by blending coal-tar and petroleum pitches. Light Metals. 2001; 573-579.
[17] Perez M, Granda M, Garcia R et al. Petroleum derivatives as an alternative to binder coal-tar pitches. Light Metals. 2000; 531-536.
[18] Lazarev VD, Mahalova NP, Tarasevich NI et al. Rus. Patent 2116383 RU, 1998.
[19] Hayrutdinov IR, Ahmetov MM, Telyashev EG. State and prospects of development of coke and pitch production from petroleum raw materials. Russian Chemical Journal. 2006; 1(50): 25-28.
[20] Cheshko FF, Shustikov VI. Catalytic effect on the group and chemical composition of coal tar pitch. Problems of catalysis in coal chemistry (Collection of scientific works); Naukova dumka: Kiev, 1992; p. 289.
[21] Sidorov OF. Carcinogenic activity of pithes depending on the technology of their production. Coke&Chemistry. 2006; 6: 36-40.
[22] Lebedev VA, Branin OB, Dyukanov AG. Reducing the content of benzpyrene in a coal tar binder. Coke&Chemistry. 1988; 8: 36-37.
[23] Anshits AG, Kurteeva LI, Dyukanov AG. Comparative assessment of the emission of carcinogenic substances using medium- and high-temperature pitches. Chemistry for sustainable development. 2001; 9: 345-352.
[24] Rubchevskii VN, Chernyshov YuA, Volokh VM, Kovalev ET, Pityulin IN. Exclusion of oxygen in electrode-pitch production. Coke Chem. 2009; 4(52): 161-167.
[25] Seyts IF, Knyazev PG. Molecular oncology; Medicine: Leningrad, 1986; p. 352.
[26] Belitskiy GA. Chemical carcinogenesis. Problems of Clinical Medicine. 2006; 1(5): 10-15.
[27] Napalkov NP. General Oncology; Medicine: Leningrad, 1989; p. 646.

To whom correspondence should be addressed Dr. Fedor Cheshko, Ukrainian State Coal-Chemistry Institute (UKHIN), 61023, 7 Vesnina str., Kharkov, Ukraine, chishkof@ukr.net