Advances in Engineering Research, volume 158
International Conference on Aviamechanical Engineering and Transport (AviaENT 2018)

Novel Technology For Production Of Petroleum Pitches For Non-Ferrous Metallurgy

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***Abstract*— The most important raw material component in the production of most types of carbon products is binding materials, the quality of which largely determines the physical and mechanical properties of the product. A favorable combination of high coke-forming ability and low viscosity in the molten state distinguishes pitch from other types of binding materials for various carbonaceous compositions subjected to subsequent carbonization. For this reason, pitch worldwide is a priority binder for many types of carbon products (anode masses, electrodes, structural materials, electrical products, etc.).**

The advantages and shortcoming of available binding materials for the production of anode mass were discussed in detail. The known and novel methods for obtaining oil binders were analyzed. The obtained binders were compared with coal tar pitch. An alternative method for production of the binders via the compounding technique was proposed. Implementation of this technology will allow replacing the coal tar pitch containing a significant amount of 3,4 benz [a] pyrene by a carcinogen-free petroleum pitch.

Coal pitches have a high carcinogenic activity due to the high content of 3,4-benz [a] pyrenes and other (up to 4%) polyaromatic hydrocarbons, impurities (F, Fe, Co, V, W, etc.) and ash. In addition, such pitches have different technological characteristics (from different manufacturers) and high cost. The imperfection of production technology, the considerable remoteness of production from consumers and, as a consequence, high transportation costs allow considering the coal pitches as off-market materials

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***Keywords*— binder materials, petroleum pitch, anodes of aluminum electrolyzers, coal-tar pitch, benz [a] pyrene**

I. Introduction

Binder substances represent the materials providing under certain conditions (temperature, pressure, etc.) binding of fine materials (oil and gas fines, coal waste, etc.) into a conglomerate. There are three large groups of binding materials: organic (petroleum bitumen, coal tar pitches, etc.), inorganic (cement, clay, soluble glass, cast iron borings, etc.) and combined (bitumen and clay, lime and sulfite liquor, bitumen and sulfite-alcohol liquor, etc.). Let us discuss the organic binders in detail.

There are several classifications of organic binders. Thus, depending on the application, they are classified into the following groups [1]:

- pitch binders used in the manufacture of self-burning or burnt anodes, graphite electrodes, etc.
- impregnating pitches;
- briquetting pitch binders (for partial briquetting of the coal before cooking, foundry coked briquettes, the coked briquettes for nonferrous metallurgy);
- fiber-forming pitches (for producing graphitized carbon fibers);
- special pitches (for production of nanomaterials);
- pitches as raw material for coking.

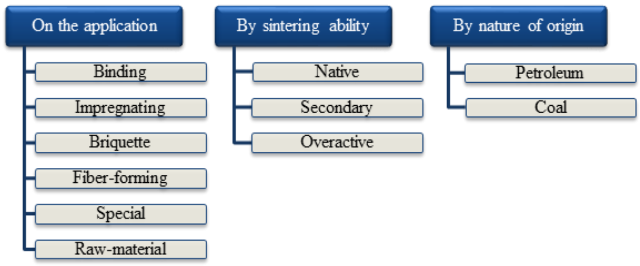

Fig. 1. Classification of pitches

II. Problem Statement

In terms of caking capacity, the pitches are divided into the following groups.

- The first group includes oil products obtained by non-destructive processing of oil, such as bitumen, asphalt. The testing of bitumen has shown their high swelling capacity upon coking, which leads to decrease in the structural strength of the carbon materials obtained on their basis. Contradictory results have been received for the deasphalting products of the oil residues. The addition of asphaltites to the binders allows improving the properties of carbon materials. However, investigations of asphaltite isolated from tar of sulphurous oil at the Kharkov experimental coke plant have shown low caking properties of this product.

- The second group of caking additives comprises the products of oil destructive processing, which are partially used in the manufacture of carbon materials. These are products of visbreaking, thermal cracking, coal hydrogenation as well as oxidized cracking residues.

- The third group, the superactive caking additives consists of coal tar pitches, as well as pitches obtained via pyrolysis and thermal polycondensation of petroleum feefstock. Unlike other binders, these ones are employed in the production of carbon materials completely. Depending on the nature of the origin, pitches are divided into petroleum and coal ones.

In any field of application, petroleum pitches compete with those from other natural raw materials, first of all, with coal tar pitches. Unlike the latter, petroleum pitches possess a higher reactivity in thermochemical processes, lower carcinogenicity and other advantages. Coal tar pitch is referred to as a residue obtained by the fractionation of coal tar. It is a black product, homogeneous in appearance. Pitch transfers (at certain temperatures range) to a sold state and has a conchoidal fracture. It has no definite melting and solidification points.

According to the data of the World Health Organization, cancer rate depends by 70-80% on the effects of environmental object, chemical carcinogens including polycyclic aromatic hydrocarbons (PAHs).

III. RESEARCH PROBLEM

The main sources of environmental pollution by carcinogenic substances are the smokes of various heating systems, heat power plants, emissions of coke-pitch plants, graphite, asbestos, soot production; oil refining, coke, metallurgical, aluminum plants; automotive and aircraft engines. The level of harmful emissions depends strongly on the processing or production high molecular products of fuel pyrolysis (coal, oil).

According to the Russian National Standard (GOST, 12.1.005-88) resinous sublimates of coal tars and pitches belong to the first class of danger. Their maximum permissible concentration, MPC, (with the content of benz [a] pyrene, BP, of less than 0.075) is 0.2 mg/m^3. When the concentration of BP ranges 0.075-0.15 and 0.15-0.3%, the values of MAC are 0.1 and 0.05 mg/m^3. For BP, generally accepted Carcinogenicity indicator, MPC value is 0.0015 μg / m^3.

In the air of production facilities producing and processing coal tar and pitch, the content of harmful substances is much higher than MPC. In products of electrode manufacture, BP is detected in the following amounts: pitch-14,1 g / kg; forms of cold pressing-1,3 g/ kg, forms of hot pressing-1,6 g / kg; after firing-0,003 g/kg, after graphitation - 0,002 g / kg.

Various studies have shown that the formation of PAHs occurs at 600-850 °C upon combined pyrolysis of aliphatic and aromatic hydrocarbons. According to other data, PAHs are formed during dry distillation and incomplete fuel combustion at 300-400 °C.

The production of electrodes involves the processing of medium-temperature coal pitch at temperatures: preparation and storage of pitch - up to 180°C, mixing of electrode masses - 125 - 140°C, pressing cooled to 85-105 °C mass - at the temperature of the mouthpiece caliber 140-165 °C. While firing products, the temperature in the workpiece body reaches 850-900 °C. Thus, during the processing of coal medium-temperature pitch, not only emission of BP takes place, but also its synthesis occurs [3].

Imperfection and depreciation of the equipment of the electrode plants of the favor the increase of harmful emissions. Improvement and complete pressurization of the equipment is a way to reduce harmful emissions. Another way is to eliminate the source of pollution, i.e. coal pitch.

Despite the technological methods for reducing carcinogenicity of coal tar pitch are known, they have not found industrial application. Carcinogenicity of coal tar pitches remains high. Concequently, the risk of cancer occurrence is also high. Therefore, the search for carcinogenicity-free alternatives to coal tar remains an urgent challenge. In the opinion of many researchers, the optimal variant to reduce cancer danger of the electrode production may be the replacement of coal tar pitch by petroleum pitch.

Besides, the use of coal tar pitch is complicated by the problem of economic and logistical nature. Under pressure from environmental legislation and human rights organizations, the production of coal tar, the main raw material for the production of coal tar pitch, is steadily reducing for a long time.

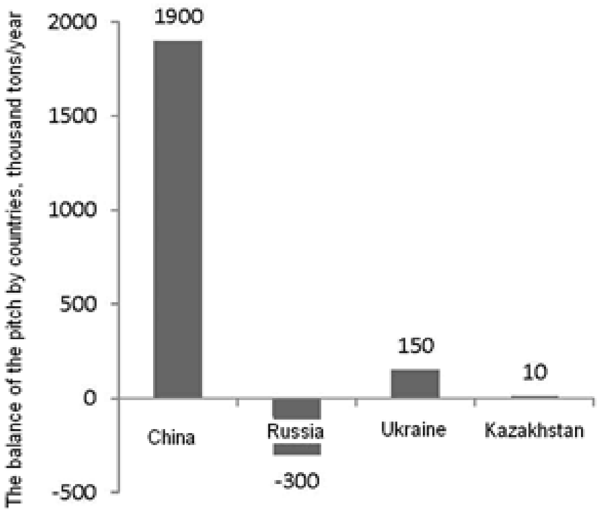

Fig. 2. The distribution of pitch over countries [4].

This leads to the deficit of coal tar pitch and, consequently, to the rise of its selling price that eventually affects the price of primary aluminum. As seen from Figure 2, the distribution of pitch over countries is very different. In Russia, the deficit of pitch is about 300 thousand tons and aluminum producers have to purchase it abroad.

Also, this leads to the fact that one manufacturer is not able to provide even one medium-sized aluminum plant with a sufficient amount of the necessary binder. Therefore, the plants have to buy coal tar pitch from six or seven suppliers to cover their needs in this material. The problem is that different manufacturers use different coals to produce pitch. Hence this means slightly different performance characteristics. In practice, this leads to non-compliance of physic-chemical and performance characteristics of pitches from different manufacturers and, as a consequence, to spending the time and resources for the selection of the right proportions and mixing of the pitches themselves.

IV. Purpose of the Study

Petroleum pitch is a product of high-temperature processing of carbohydrates. Similar to coal tar pitch, the petroleum one contains PAHs in its composition, but the concentration of harmful substances in the air of oil refineries does not exceed the maximum permissible. Comparative assessment of carcinogenic properties of coal tar and petroleum pitches shows a significantly lower carcinogenic activity of the latter. It is found that pyrolysis petroleum pitch contains 99.4 % of resinous substances. This is by aproximately 11 and 23 % higher than for medium temperature (MT) and high-temperature (HT) coal tar pitches, respectively. The experiments on white mousses have evidenced that malignant neoplasms of the skin are 87-96 % for coal tar pitch; 63% - for petroleum pyrolysis pitch; and 6% - for cracking medium-temperature pitch.

The data on isolation of resinous substances during termal processing also speak in favour of replacing the coal tar pitch by petroleum one. The content of resinous substances and BP in the exhaust gases (distillation of pitches to 180 °C) is as follows: 173,0 mg/m^3 and 0.95 mg/m^3 (petroleum pitch); 1649,0 mg/m^3 and 28.3 ág/m^3 (MP coal-tar pitch); 5538,0 mg/m^3 and 250 ág/m^3 (HT coa; tar pitch) [5]. The anode mass prepared from petroleum pitches releases significantly lesser amound of BP that is usual. It is shown [5] that the use of petroleum binder allows reducing the content of BP in the electrolysis shops more than 60 times.

It is known that the amount of resinous substances, released during firing the coke compositions from petroleum cracking pitch is 2.5-3 times lower in comparison with coal-tarl pitch, and the release of BP is 30 times lower. Thus, the use of petroleum pitch as a binder in the electrode production will significantly decrease air pollution in the working area and reduce emissions of harmful substances into the environment.

The works on the development of feasible methods for the production of petroleum pitch as an effective alternative to coal tar pitch were started in the USSR in the seventies of the last century. Many-year experience of investigations of various types of raw materials and qualitative characteristics of the obtained petroleum pitches show that highly aromatic compounds are most suitable for this purpose: pyrolysis resins of ethylene production and cracking residuess.

Although petroleum pitches noticeably differ from coal tar pitches (with the same softening temperature), in terms of chemical composition, density, yield of volatile substances, they do not deteriorate the quality of carbon materials. Temperature ranges of the mesophase formation for the petroleum pitches (410-470°C) are significantly lower that those for coal tar pitches (450-500°C). The size of spherolithes in the carbonization of petroleum pitches increases more intensively owing to a lower content of α1-fraction. The application of petroleum pitches coke-pitch compositions significantly modifies their properties, imparts greater flexibility, and reduces viscosity [6]. Petroleum pitches are important binding components of the electrode and anode masses, providing fluidity, plasticity, homogeneity when mixed with coke and ensuring strength, electrical resistance and reactivity in subsequent operations of articles firing. Therefore, various technological methods for processing of petroleum feedstock were tested: vacuum processing, thermo-polycondensation, and oxidation.

As a raw material for producing petroleum pitches, residual oil products, possessing high density, aromaticity and low sulphur content, are highly desirable. However, due to the high demand for raw materials of such quality for coking, resources of low-sulphur petroleum residues remain limited. Therefore, sulphur-containing distillate cracking residues, which are by-product in the production of raw materials for carbon black, should be involved into the technology.

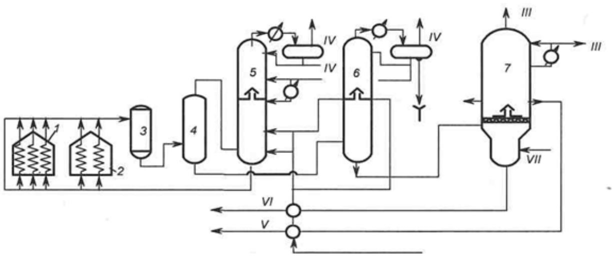

Fig. 3. A technological scheme of pitch production by vacuum concentration

1,2-furnaces; 3-reaction chamber; 4-high pressure evaporator; 5-column; 6-low pressure evaporator; 7-vacuum column; I-raw materials; II-gasoline; III-light gas oil; IV-gases; V-heavy gas oil; VI-pitch; VII-vapor;

Vacuum distillation of cracking residue occurs at 385-390°C under residual pressure of 0.011-0.013 MPa to afford petroleum pitches with a softening point of 82-90 °C, yields of volatile compounds being 60-64%. These pitches have a low density and contain an insignificant amount of α-fraction (no more than 8-10%). Low density and insufficient content of α-fraction does not allow such pitches to compete with coal tar pitches, even taking into account the environmental friendliness of this former [7].

V. Research Methods

Production of petroleum pitches by a thermal polycondensation method.

Thermal polycondensation allows obtaining pitches with a softening point of 65-100°C, and density of 1250-1300 kg/m^3 at 420-430°C for 3-5 h. The increase in the process temperature (460-510 °C) and decrease of its duration (1-5 min) followed by exposure to the reactor at 380-440°C for 1-3 h also lead to formation of petroleum pitch for the aluminium industry.

Petroleum pitches obtained by thermal polycondensation of pyrolysis resin in the two reactors (operating in series) and having a softening temperature of 65 and 100°C, respectively, can be further mixed in various proportions.

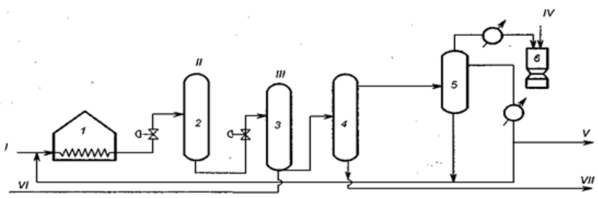

Fig. 4. Technological scheme of producing high temperature pitches by therrmal polycondensation

1-furnace; 2-reactor; 3-atmospheric column; 4-vacuum column; 5-scrubber; 6-ejector; Flows: I-raw materials; II-gases; III-distillate; IV-vapor; V-vacuum distillation; VI-medium- temperature pitch; VII-high-temperature pitch;

The petroleum pitches thus obtained show unsatisfactory results in the manufacture of anode mass due to the following shortcomings [8]:

- due to application of sulphur distillate cracking-residues as the starting materials, the petroleum pitches have an increased sulphur content, the presence of which is undesirable in the preparation of anode mass in the aluminium industry;
- The resulting petroleum pitches contain a insufficient amount of clearly controlled α-fraction, which plays a crucial role in the production of self-baking electrodes in the aluminium industry.
- The burnt anodes and electrodes based on the petroluem pitches do not meet the requirements for strength characteristics.

Having the same softening point, coal tar pitches demonstrate a significantly higher coking capacity and contain much higher amounts of α-fraction as compared to the petroleum pitches. Moreover, in vacuum-distilled cracking pitches, the content of α-fraction is 5-16 times lower (and in pyrolysis pitches by 7-12% lower than the absolute content of α-fraction in coal tar pitches), softening temperatures being the same [9].

Thus, petroleum pitches, in comparison with coal tar ones, contain lower amounts of polycondensated aromatic compounds, have a lower C/H ratio and, consequently, a significantly lower yield of the coke residue. The reduced coke-forming ability hinders their application instead of coal tar pitches, despite the best environmental characteristics (substantially lower content of carcinogenic polycyclic aromatic hydrocarbons). In this regard, development of a new technology for the production of petroleum pitch, free from the above shortcomings, represents a standing challenge.

VI. Results

National research Irkutsk state technical University in cooperation with JSC "Angarsk petrochemical company" (Rosneft) is involved into the development of a technology for obtaining petroleum pitch via the compounding of heavy oil residues with ultra-fine petroleum coke [10].

Fine petroleum coke performs several functions:

- it is a center of microphase generation. As it was mentioned above, the petroleum residues contain insufficient amounts of natural α1-fraction, while ultra-fine petroleum coke is deprived from this shortcoming. The uniform distribution of coke over the whole volume of a binder during baking of the anode ensures anisotropy of properties and allows obtaining a monolithic anode with increased mechanical strength;
- due to its much higher density, the petroleum coke significantly increases the total density of the petroleuml pitch. To increase the efficiency, it is recommended to use calcined petroleum coke with a density of 2.05-2.10 kg / m^3;

- it increases the coke residue. Apart from the increased density, the petroleum coke has a high coke residue, which is beneficial to the total coke residue of the petroleum pitch.

The following characteristics and parameters are important for the compounding process, affecting the quality of the target product:

- particle size and density of the fine petroleum coke. If the coke particles are too large, they are deposited on the bottom during transportation and unloading under the action of gravity. Hence, it will be extremely difficult to remove the coke;

- temperature of mixing the petroleum residues with coke. Often, heavy petroleum residues harden at room temperature or have a high viscosity, which hinders the effective mixing. Therefore, when selecting the mixing temperature, such factors as the initial destruction temperature of the internal structure of petroleum residues and the starting temperature of their physic-chemical transformations should be taken into account;

- efficiency of the mixing. This factor determines the uniformity of the coke particles distribution in the volume of binder and, consequently, the stability of physico-chemical characteristics of the anode.

TABLE I. COMPARISON OF THE MAIN CHARACTERISTICS OF PETROLEUM AND COAL TAR PITCHES.

Characteristics	**Value**	
	Petroleum pitch	**Coal tar pitch (grade A)**
Mass fraction of water in solid pitch, % no more than	absent	4
Softening point, C	95-106	70-80
α-fraction, %	18-25	19-21
Yield of volatile substances, %	60-66	53-63
Ash content, % max	0,08	1,2-4
Content of benz [a] pyrene, %	absents	1,2-4
Density	1.25-1,32	1,285-1,33

The uniform distribution of fine petroleum coke is confirmed by microstructural studies of the samples obtained.

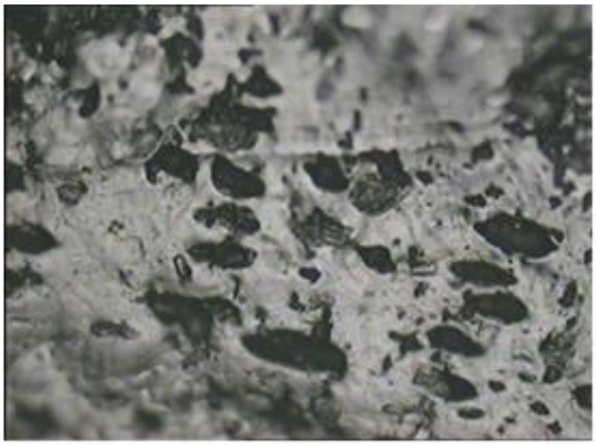

Fig. 5. The microstructure of petroleum pitch. (100HAL ZEISS AXIOTECH Microscope with Leica DC300 Camera).

VII. CONCLUSION

The obtained data clearly indicate a principal possibility of replacing coal tar pitch by petroleum pitch produced by a compounding technique. The application of these materials does not require the modernization and reconstruction of the facilities of aluminium plants working using both pre-baked and Soderberg (self-baking) anode technologies.

The technology for the production of petroleum pitches by compounding has obvious advantages over other technologies for manufacturing of oil binders due to its simplicity and efficiency. In addition, the capacity of modern oil refineries in Russia is more than sufficient to meet all the demands of the Russian aluminium industry relative to petroleum binders with constant physical and chemical composition and stable operation characteristics [11].

References

[1] L. V. Dolmatov. et al, HTTM., No. 1, 1988, p. 4-6.

[2] D. F. Varfolomeev “ Prospects for the production and use of NSD in the preparation of metallurgical coke from charge with a high content of weakly and non-flowing coals”. Moscow: Tsniiteneftekhim, 1990, p. 40

[3] A. D Sokolov, V. G Konstantinov, G. A Podgaiko “On the carcinogenic hazards of working in an electrode workshops in aluminium plants” The issues of occupational health in the electrode industry, Omsk, 2016 p. 55-56.

[4] E. P. Vershinina, E. M. Gildebrandt. E. A. Selina “Tendencies of development of production of binder for anodes of aluminium electrolysers” journal of the Siberian Federal Universit Technique and technology 5 (7) p. 20-24, 2012

[5] V. V Suprunov “Obtaining sintering materials from heavy oil residues. Auto-Ref. dis. kand. Tech. sciences'. Sverdlovsk, 1969, p. 28

[6] I. R. Khairudinov “Use of oil stabilizers and bonding agents in the production of Koks” Coke and chemistry, No. 9, p. 11-12, 1988.

[7] G. G. Teleshev HTTM, No. 4, p. 8-10, 1987.

[8] I. R Khairudinov, A. F. Makhov R. H. Sadykov “Oil Refining and petro chemistry” No. 5, p. 12-13, 1992.

[9] I. R. Khairutdinov “Ways of obtaining pitch from petroleum raw materials”, ChitaNET-Khim, p.48, 1991.

[10] A. A Ugapeev., O. I Doshlov “Prospects for the use of oil of pitch PND, as al alternative binder for the production of anode paste”Proceedings of the IV regional scientific and technical conference of young specialists of JSC "ANKhK", p. 58-62, Irkutsk, 2011.

[11] A. I. Meleshko “Carbon, carbon fiber, carbon composites” science press, p. 192, Moscow, 2011

[12] C Moreno-castilla, F Carrasco-marín, F.J. Maldonado-hódar “Effects of non-oxidant and oxidant acid treatments on the surface properties of an acti-vated carbon with very low ash content” Carbon, № 1-2. p. 145 – 151, 1998

[13] I.O. Doshlov “A promising technology for the production of oil binders for the production of anode paste, proceedings” 72-international youth scientific conference "Oil and gas 2018", Gubkin Russian state University of Oil and Gas , p 110-120, Moscow, 2018 23-26 april.