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The Use of Coke-Chemical Materials to the Regulation of the Electrode Coal Tar Pitch Quality

Evgeniy T. Kovalev [1], Fedor F. Cheshko [1], Natalia V. Ponomarenko [2]

[1] Ukrainian State Coal-Chemistry Institute (SE "UKHIN"), 61023, Kharkov, 7 Vesnina Str., Ukraine
[2] Ukrainian State University of Railway Transport (UkrSURT), 61050, Kharkov, 7 Feyerbakh Str., Ukraine

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Abstract

The article is devoted to the feasibility of using chemical (including secondary) tar products of coal coking from the point of view of the possibility of using them as additives to the coal tar pitch in order to modify their properties. On the basis of the laboratory and production experiments, it has been shown that due to the mixing of various additives of coke-chemical origin into the initial medium-temperature pitch, it is possible to promote both the accumulation of high-molecular components of the group composition (in the production of electrode pitch based on low-pyrolized tars) and the decrease of their content in the final product (during the processing of the initial pitch based on coal tar with a high degree of pyrolysis). The targeted production of additives to electrode pitches from materials of coal origin, characterized by a more pronounced constancy of properties than by-products is promising.

Keywords: *Coal tar pitch; Electrode binder; High molecular weight components; Coal tar; Degree of pyrolysis; Additives.*

1. Introduction

Coal tar–non-boiling products of coal tar rectification are currently the main raw material for the production of carbon electrodes. The largest consumer of electrode binder pitches is the aluminum industry. Therefore, it is the primary aluminum market that is traditionally an indicator of the demand for this type of raw material [1]. It is characteristic that, according to the International Aluminum Institute [2], the world production of aluminum for the period from August 2019 to August 2020, despite the general negative trends in the global economy associated with the coronavirus pandemic, not only did not decrease, but even showed some upward trend (mainly due to North America and China).

Currently, coal electrode pitches, which have a number of valuable technological properties, are in short supply, and the tendencies of world markets promise, at least in the short and medium term, the continuation of this shortage. One of the directions of expanding the raw material base of electrode binders over a number of years has been the development of additives to coal tar pitch based on heavy oil residues, pyrolysis resins, cracked residues, and other products of petroleum origin. However, the listed materials are characterized by a significantly lower content of high molecular weight aromatic components, a lower C/H ratio and, therefore, a significantly lower yield of coke residue compared to coal-tar counterparts [2-3].

It should be added that the shortage of coal tar pitch is aggravated by periodic fluctuations in the quality of coal tar. The latter is a by-product of the production of metallurgical coke, and therefore the control of its properties at the stage of formation and condensation in the gas collector is extremely difficult due to the need to comply with the technological regime for obtaining a high-quality main product. This is especially true when changing the raw material base of coking, aging of the furnace stock, etc. The result can be the prevalence in the overall balance of production of resins of low or high degree of pyrolysis, unsuitable for the production of high-quality electrode binders due to, respectively, too low or too high content of high molecular weight components [4]. As one of the possible examples: it is known that a high amount of pulverized fractions in the initial coal blends for cokemaking process reduces the bulk density of the blend in the coking chamber, thereby reducing its productivity, worsens the loading conditions and leads to a deterioration in the quality of coal tar [5].

Considering that coal-based substances have a more significant chemical affinity for coal tar pitch than petroleum products, all of the above causes interest in chemical (including secondary) resinous products of coal coking from the point of view of the possibility of using them as additives to coal tar pitch to increase the yield of the electrode binder and modify its properties.

In this regard, the attention of researchers has long been attracted by the anthracene fraction of coal tar as a component that can not only play the role of a pitch diluent during joint heat treatment, but also take part in thermochemical transformations of its components [6].

Some by-products of by-product coke production are also capable of influencing the process of heat treatment of pitch due to the components that intensify the physicochemical processes of increasing the average molecular weight of the alloy. From this point of view, of particular interest are, for example, acidic resins of by-product coke production, containing high-molecular-weight organic sulfonic acids. Such materials are capable not only of actively polymerizing upon heating, but also initiating the processes of thermo-polymerization and polycondensation in materials containing aromatic, aliphatic, unsaturated, and other organic compounds. However, the introduction of by-product resinous sulfo-containing products of coke production into pitch is complicated by their low pH level and other features. Preliminary heat treatment can provide their qualified technological application with retention of chemical activity. As a result of such processing, it is desirable to obtain a fusible material with rheological properties close to coal tar pitch.

Based on the foregoing, it seemed appropriate to assess, including in production conditions, the possibility of obtaining additives based on products of the coke-chemical origin, capable of adjusting the properties of coal tar pitch, depending on the degree of pyrolysis of the original coal tar.

2. Experimental

2.1. Intensification of the accumulation of high-molecular fractions of group composition in the pitch during its heat treatment (relevant for the processing of the initial pitch based on low-pyrolyzed coal tar).

We have carried out pilot studies of the production of pitch-like material from sulfur-containing resinous by-products (acid resins) of the by-product coke production. Based on what was said earlier, it is permissible to assume that the addition of such a material to the original pitch during heat treatment will contribute to the intensification of the increase in the mass fractions of TI and QI. Based on the preliminary laboratory studies, compounds of the following composition, % by weight, were selected as feedstock:

- compound No. 1: a mixture of acid resins of the crude benzene rectification workshop and sulphate department – 25; benzene compartment polymers (by-product of absorption oil regeneration) – 25; anthracene fraction of coal tar (total) – 50;
- compound No. 2: a mixture of acid resins of the crude benzene rectification workshop and sulphate department – 50; benzene polymers – 25; anthracene fraction (total) – 25.

The anthracene fraction and the polymers of the benzene compartment play the role of diluents and retarders of polymerization processes in the compounds, which proceed too actively in non-neutralized sulphonated resins when they are heated. The properties of the initial components of the compounds are presented in Table. 1.

The heat treatment of the mixture was carried out under the conditions of an operating by-product coke plant on a semi-industrial cube reactor with fired heating. The mixing of the liquid phase was carried out by periodically supplying small portions of air (0.075 m^3/h) through a bubbler into the bottom zone of the cube. The temperature of the liquid phase was 310-320°C; vapor phase – 270-280°C.

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Table 1. The properties of the compounds initial components

Quality indicators	Anthracene fraction	Benzene polymers	Acid resins mixture
Density, kg/m ^{3}	1133	1116	ND
Mass fraction of sulfur, %	0.62	1.55	6.43
Volatile matter yield, %	97.7	90.6	76.6
Ash content, %	–	0.12	0.78
Initial boiling point, °C	246	240	-
Final boiling point 90 %, °C	412	346	-

During the tests, two representative batches of solid fusible materials were produced, the properties of which are presented in Table. 2. The properties of both obtained materials allow to mix them with coal tar pitch in melted form.

Table 2. Characteristics of solid fusible materials

Quality indicators	Product obtained from: compound No. 1	compound No. 2
The yield of the target product from the initial mixture, %	58.0	77.0
Melting point, °C	59.0	119
Volatile matter yield, %	75.0	67.4
Mass fraction of sulfur, %	1.56	2.98
Ash content, %	0.50	1.26
Mass fraction of water-soluble components, %	traces	traces

Attention is drawn to the fact that under industrial conditions an increase in the proportion of acidic resins in the initial compound made it possible to increase both the softening temperature and the yield of the target material. This made it possible to assume that the material obtained from compound No. 2 has a more direct chemical potential.

2.2. Suppression of the accumulation of high-molecular fractions of group composition in the pitch during its heat treatment (relevant for the processing of the original pitch based on highly pyrolyzed coal tar).

In the production of electrode pitch based on heavy resins of a high degree of pyrolysis, the urgent task is not only to limit the content in the product of substances insoluble in quinoline, but also, if possible, to reduce the value of this indicator.

The processes leading to the formation and accumulation in the pitch of both components of the quinoline-insoluble fraction (primary and secondary) under the conditions of thermofractionation of the resin and the production of electrode binder are practically irreversible. Therefore, as methods that reduce the mass fraction of these substances, it seemed appropriate to test a partial dilution of the initial medium-temperature coal tar pitch with a material that meets the following basic requirements:

- affinity for coal tar and the ability, when heated, to form a material similar in properties to coal tar pitch;
- the absence in the composition of substances insoluble in quinoline and a reduced tendency, in comparison with pitch, to form a secondary fraction QI;
- the ability to form stable mixtures with coal tar pitch during its heat treatment.

The anthracene fraction of coal tar most fully meets the listed requirements. The authors of the work [5] investigated the possibility of heat treatment of the anthracene fraction in a separate reactor, followed by feeding the obtained fusible material into the electrode or the initial pitch. From our point of view, a more promising direction is the combined heat treatment of medium-temperature pitch and the original anthracene fraction.

In order to verify this assumption, an experiment was carried out on the heat treatment of pitch in the presence of an anthracene fraction at an operating continuous industrial plant for the production of electrode pitch. In this case, the fraction playing the role of a reactive diluent was introduced in an amount of 10 % of the mass of the initial pitch, supplied for processing, into the bottom zone of the heat-treatment cube-reactor.

In the course of the experiment, the following indicators of the technological regime were maintained: the consumption of the initial medium-temperature pitch per cube-reactor – 5.0 tons per hour; air consumption per cube-reactor – 130 m^3/h; the temperature of the air supplied for bubbling into the cube-reactor – 243-268°C; the temperature of the anthracene fraction fed into the cube-reactor – 100°C; the temperature of the liquid phase in the cube-reactor – 326-346°C.

The initial pitch during the experiment was characterized by the following parameters: softening temperature, – 65.0-68.5 °C; a mass content of substances insoluble in toluene (TI), – 19.6-20.3%; a mass content of substances insoluble in quinoline (QI), – 5.0-5.5%.

3. Result and discussion

3.1. Intensification of the accumulation of high-molecular fractions of group composition in the pitch during its heat treatment (relevant for the processing of the initial pitch based on low-pyrolyzed coal tar).

We have evaluated the effect of the additive obtained from compound No. 2 on the heat treatment of the coal tar pitch. A medium-temperature pitch with the following indicators was used as a raw material for research: - a softening temperature 64.5 °C; a mass fraction of substances insoluble in toluene (TI) 17.8%; a mass fraction of substances insoluble in quinoline (QI) 3.3%; volatile matter yield 65.2%; ash content 0.1%.

This pitch, obtained under the industrial conditions during the rectification of resin with a low degree of pyrolysis, was chosen for this research, since the processes of thermal compaction in such pitches are the least intense. In the course of the research, representative samples of this pitch were heat treated in three ways:

- without the use of intensifying techniques;
- by thermo-oxidative method with bubbling air through the processed melt (air consumption simulated this indicator of an industrial installation for the production of electrode pitch);
- in the presence of 5 % fusible additive obtained from compound No. 2.

The heat treatment was carried out in a laboratory cube-reactor. One-time loading of the feedstock was 0.6 kg; isothermal holding temperature – 360°C. Table 3 presents the qualitative indicators of some pitches obtained as a result of these comparative studies of heat treatment techniques.

Table 3. The qualitative indicators of some pitches obtained as a result of comparative studies of heat treatment techniques

Quality indicators	Without intensifying receptions	Thermal oxidation with atmospheric oxygen	Fusible additive based on compound No. 2
Melting point, °C	86	86	86
Mass fraction of TI, %	32.0	29.5	32.5
Mass fraction of QI, %	8.0	4.2	5.4
Mass fraction of β-resins, %	24.0	25.3	27.1
Volatile matter yield, %	56.5	58.7	56.3
Ash content, %	0.20	0.21	0.25
Mass fraction of sulfur, %	0.56	0.58	0.62

As Table 3 shows, in comparison with a traditional thermal-oxidative treatment (air bubbling), the use of a fusible pitch-like additive based on acid resins provides in the resulting pitch a noticeably higher (by 3 % abs.) content of the fraction α and a lower (by 2.4 % abs.) yield of volatiles substances along with other similar quality indicators. In this case, the pitch obtained in the presence of the tested additive is characterized by the maximum content of the valuable fraction, insoluble in toluene, but soluble in quinoline (β-resins).

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Thus, a fusible additive based on a mixture of acid resins of chemical plants of coke-chemical production had a selective effect on the processes occurring in pitch during its heat treatment, contributing to a decrease in the yield of volatile substances and accumulation of the fraction α (mainly due to its most valuable component – substances, insoluble in toluene, but soluble in quinoline). The disadvantages of using the additive include an increase in the sulfur content in the final product. However, when using less sulfurous raw materials and in the production of the pitch, for which the value of this indicator is normalized at the level of ≤ 0.6 %, this disadvantage does not seem to be crucial.

The results obtained demonstrate the promise of research in the field of production of the pitch modifiers based on resinous sulfoorganic by-products of by-product coke production. At the same time, the acid resins used in this experiment are formed in production in limited quantities and, like all by-products, are characterized by a pronounced variability in quality. Thus, Tables 4 and 5 show the properties of acidic resins, respectively, of sulfate departments and sulfuric acid purification of benzene-toluene-xylene fraction of crude benzene of different enterprises.

Table 4. The properties of acidic resins of sulfate departments of different enterprises

Quality indicators	Acidic resin samples from sulfate compartments			
Mass fraction of water, %	6.6	12.7	15.3	21.3
Mass fraction of substances soluble in toluene, %	81.1	66.8	24.0	54.5
Mass fraction of ammonium sulfate	0.2	7.8	22.9	4.5
pH of the aqueous extract	1.7	1.4	1.7	1.7
Acidity in terms of H_2SO_4, %	1.3	6.7	5.4	6.7
Ash content, %	0.2	0.6	10.8	0.57

Table 5. The properties of acidic resins of sulfuric acid purification of benzene-toluene-xylene fraction of crude benzene of different enterprises

Quality indicators	Acidic resin samples of crude benzene rectification			
Mass fraction of water, %	10.9	11.2	12.5	19.0
Mass fraction of substances soluble in toluene, %	12.2	16.7	55.8	10.8
Mass fraction of sulfonic acids, %	8.9	3.12	46.5	32.7
Mass fraction of sulfates, %	13.0	13.1	12.6	13.4
Mass fraction of H_2SO_4, %	15.1	14.7	12.9	12.6
pH of the aqueous extract	1.5	1.24	0.4	0.1
Ash content, %	2.6	0.5	1.5	0.2

As can be seen from the data presented, the qualitative indicators of by-product resinous sulpho-containing materials of a similar origin of various coke-chemical industries vary within very wide limits. The same inconsistency is characteristic of the properties of these materials, which are formed in different periods of time in the same enterprise. The complex of qualitative indicators of by-products is only indirectly related to the main production tasks of technological processes, as a result of which they are formed.

In consideration of the foregoing, more promising is the purposeful production of modifying additives from coal materials, characterized by a more pronounced constancy of properties than by-products. From this point of view, it is of considerable interest to study the possibility of obtaining a modifying additive by purposeful sulfonation of a commercial product with controlled, standardized properties - for example, anthracene fraction of coal tar [7].

The resulting additive of sulfonated anthracene fraction is characterized by a flow point of 90-100°C, a mass fraction of sulfur of 14.1 %; ash content 0.8 %; The pH of the aqueous extract is 3.2. The effect of the additive as a modifier in the production of electrode pitch depends on the process temperature. Thus, at temperatures close to the physical temperature of the initial medium-temperature pitch after the second-stage evaporator, the addition of sulfonated anthracene fraction creates conditions for the predominant accumulation in the pitch of substances insoluble in quinoline. At temperatures of heat treatment of pitch at the level of 260-280°C, the product obtained with the addition of sulfonated anthracene fraction, in comparison with the analogue obtained by traditional thermal-oxidative treatment at practically equal softening temperatures and mass fractions of QI, is characterized by a significantly higher content of TI and a much lower yield of volatile substances. Thus, this direction of the research [7] opens up a fundamental possibility of obtaining a modifying additive to the pitch, which has the positive properties of additives based on resinous sulfonated by-products of coke production, but is characterized not only by constant, but also controllable properties.

3.2. Suppression of the accumulation of high-molecular fractions of a group composition in the pitch during its heat treatment (relevant for the processing of the original pitch based on highly pyrolyzed coal tar).

Table 6 shows the results of analyzes of electrode pitch samples taken during the industrial experiment for adding of the anthracene fraction of coal tar to the initial coal tar pitch during it heat-treatment.

Table 6. The properties of electrode pitch samples taken during the industrial experiment for adding of the anthracene fraction of coal tar to the initial coal tar pitch during it heat-treatment

№	Melting point, °C	Volatile matter yield, %	Mass fraction, %,		Ash content, %	NB
			TI	QI		
1	96.0	57.2	30.2	9.9	0.14	Ordinary thermo-oxidative mode
2	96.0	56.8	31.1	9.4	0.14	
3	98.0	55.2	31.4	9.6	0.17	
4	100.0	58.3	31.6	9.9	0.15	
5	98.0	55.7	30.9	10.0	0.13	
6	103.0	55.5	31.7	10.6	0.12	
7	104.0	55.0	31.0	9.7	0.13	
8	103.0	55.2	30.8	10.0	0.11	
9	98.0	55.4	33.0	9.5	0.10	
10	105.0	54.0	32.2	9.8	0.12	
11	93.0	60.0	29.0	5.0	0.12	Feeding the anthracene fraction to the bottom zone of the reactor cube
12	103.0	57.3	29.9	5.2	0.11	
13	93.0	57.6	29.3	5.0	0.12	
14	102.0	58.1	28.9	4.8	0.16	
25	100.0	29.0	28.6	5.3	0.12	
16	82.0	60.0	27.7	4.7	0.11	

In the course of the pilot-industrial experiment, due to the large flow rate of bubbling air and its high temperature, it was possible to obtain pitches with a significant (more than 100°C) softening temperature. Nevertheless, the supply of the anthracene fraction to the bottom zone of the cube reactor made it possible to reduce the content significantly (by 5 % abs.) in the final pitch of substances insoluble in quinoline. The noted effect is very important from the point of view of the production of electrode pitches based on coal tar with a high degree of pyrolysis.

4. Conclusion

The effective additives can be obtained for controlling the quality of electrode pitches during the heat treatment of the initial medium-temperature pitch on the basis of coking chemical products.The purposeful production of additives to electrode pitches from coal materials, characterized by a more pronounced constancy of properties than by-products is most advanced.

By introducing various additives of coke-chemical origin into the initial medium-temperature pitch, it is possible to promote both the accumulation of high-molecular components of the group composition (in the production of electrode pitch based on low-pyrolized resins) and a decrease in their content in the final product (during the processing of the initial pitch based on high-grade coal tar) degree of pyrolysis).

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To whom correspondence should be addressed: Dr. Fedor F. Cheshko, Ukrainian State Coal-Chemistry Institute (SE "UKHIN"), 61023, Kharkov, 7 Vesnina Str., Ukraine, E-mail: chishkof@ukr.net