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Application of the modified heavy dye pyrolysis resin as a binding component for the production of anode mass in the production of aluminum

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Abstract. The main environmental problems of non-ferrous metallurgy in Russia and possible solutions are considered. Summarized and analyzed the results of work aimed at creating a technology for producing the anode mass corresponding to regulatory and technical requirements and with improved environmental properties. The effect of the modified heavy pyrolysis resin on the environmental characteristics and performance of the anode mass was studied. Practical recommendations on the use of modified pyrolysis resin as a modifying additive to oil pitch are made.

1. Introduction

With the ever-closer integration of Russia into the world economy, increasing capacities for the production of primary aluminum, addressing issues of improving environmental safety is becoming increasingly relevant. Therefore, companies and enterprises of the aluminum industry constantly make large investments in measures to reduce such impacts [1,17-21].

The experience of leading foreign aluminum companies using Soderberg technology shows that the best results in the consumption of anodes, electricity and emissions of harmful substances are achieved by those enterprises that use dry anode mass based on pitches with an increased softening temperature (brand B grades according to GOST 10200- 83). The binder content in the anode mass largely determines the quality of the anode and affects its properties such as electrical conductivity, mechanical strength, oxidizability, destructibility and specific consumption of the anode mass for aluminum production. In order to improve the properties of the binder material and ensure the formation of the structure of the pitch-coke composition during sintering, the combination of coal tar pitch with thermosetting resins is widely used.

The raw materials for the production of the anode mass and calcined anodes are electrode coal pitches and electrode cokes. It should be noted that the correct selection of starting materials is the most difficult task of production preparation. The basic properties of coke and pitch substantially depend on which oil products or coke chemistry they are derived from. The main disadvantage of coal tar pitch is its high carcinogenic activity, due to the specific chemical composition and significant content of polycyclic aromatic hydrocarbons and phenols that enhance their effect. In the Russian Register of Potentially Hazardous Chemical and Biological Substances, three types of polyaromatic hydrocarbons are classified as extremely hazardous: benz (a) anthracene, benz (a) pyrene and dibenz



(a, h) anthracene. An indicator of a carcinogenic hazard is benz (a) pyrene, the concentration of which in air should not exceed 10^{-9} g/m³. [2]

It becomes obvious the need to create reasonable formulations of composite raw materials, taking into account the data of environmental and economic analysis.

Thus, one of the ways to improve the properties of the binder for the production of dry anode paste, as well as to obtain a more environmentally friendly binder and to reduce emissions due to this, may be to use mixtures of high-temperature coal tar pitch and modified heavy pyrolysis resin. [3]

Modified Heavy Pyrolysis Resin (MHPR) is a residual product of the pyrolysis process. The yield of heavy resin mainly depends on the fractional composition of the feedstock and the pyrolysis conditions. A heavy pyrolysis resin is released during the stepwise condensation of a vapor-gas mixture of pyrolysis products leaving the furnace with the appropriate modification of the fractionation column.

2. Materials and research methods

In view of the foregoing, in laboratory conditions, an additive of MHPR, which is a waste of ethylene production, to the dry anode mass was tested. In order to evaluate the properties of the compounded binder and determine the effect on the quality of the dry anode mass, 4 batches of the anode mass were prepared and tested, in which the dosage of MHPR in the coke charge (1-10%) was changed over a fairly wide range, with the coke charge dosage and temperature being unchanged mixing.

Representative samples of raw materials, petroleum, calcined coke (grains 1, grains 2, screenings, dust fraction) that underwent routine preparation under industrial conditions (BrAZ) were selected for laboratory research.

Analysis of the quality of the starting components: coke charge, coal binder was determined by methods that meet the conditions of TU 0258-003-00149452-96 in accordance with applicable GOSTs. In addition to the guest indicators, the coke residue was additionally determined according to the international standard ISO 6998 by the method of two crucibles at a temperature of 550 °C, the actual density was determined by the pycnometric method in a mixture of ethyl alcohol and distilled water (1: 1) at a temperature of 20 °C. The sodium content was determined by flame photometry on a flame photometer PFP-7.

As coke-filler used varietal coke materials selected in the workshop of the anode mass of the Bratsk aluminum plant.

To obtain pure coke fractions, all material was dispersed into classes. Representative samples of the initial charge materials, petroleum, calcined coke (grains 1, grains 2, screenings, dust fraction) that underwent the usual preparation in industrial conditions were selected.

The properties of the main fractions of the coke charge are given in table. 1 and 2. As a binder, “B” brand coal tar pitch was used (Table 3).

Table 1. Properties of the investigated coke materials.

The name of indicators	Grain 1	Grain 2	Screening	Dust
Ash content, %	0.11	0.14	0.19	0.34
Actual density, g/cm ³	2.04	2.04	2.05	2.04
Electrical resistivity, μOhm-m	536	539	530	-
Sulfur content, %	1.56	1.55	1.45	1.46
Sodium content, %	0.016	0.016	0.017	0.015
Impurity content:				
iron	0.01	0.02	0.02	0.04
silicon	0.07	0.01	0.004	0.02
vanadium	0.03	0.02	0.02	0.03

Table 2. The sieve composition of the investigated coke materials.

The name of indicators	Grain 1	Grain 2	Screening	Dust
Sieve composition, %				
+ 6 mm	0.5			
- 6 + 4 mm	85.0	0.3		
- 4 + 2 mm	14.0	87.5	1.0	
- 2 + 0.08 mm	0.5	12.2	98.5	
- 0.08 mm		0.2	0.5	
+ 0.16 mm				5.0
- 0.16 + 0.08 mm				20.0
- 0.08 mm				75.0
including - 0.05 mm				53.0

The viscosity of the pitch was determined on a BROOKFELD THERMOSEL viscometer brand DV-II + PRO according to the method of ASTM D-4402.

Table 3. Physical and chemical properties of pitch "B".

The name of indicators	Brand pitch "B"
Softening point, °C	90.5
Volatile yield, %	51.56
Ash content, %	0.15
Group composition, %: a - fraction	36.6
a ₁ - fraction	11.5
c - fraction	31.0
Y - fraction	32.4
Coke residue, %	59.1
Actual density, g/cm ³	1.3304
Sodium content, %	0.0041
Sulfur content, %	0.58
Viscosity, cP: 140 °C	41017
160 °C	5178
180 °C	967
200 °C	276
220 °C	74.0

3. Results and Discussion

The properties of the modified heavy pyrolysis resin produced by JSC "Angarsk Polymer Plant" are given in table 4.

The relatively high content of aromatic hydrocarbons, especially polycyclic, and a rather high value of the iodine number, indicating a significant content of unsaturated hydrocarbons, indicate the tendency of heavy pyrolysis resins to densification reactions with the formation of products with high binding and sintering properties.

A great advantage for the widespread use of MHPR is a very low sulfur content (0.001%). This makes it possible to obtain low-sulfur composite carbon-containing materials from pyrolysis resins,

which is very important from a technological point of view (increasing the turnaround path of the installation) and the environmental situation in the aluminum electrolytic production shop. [4]

Table 4. Characterization of modified heavy brand A pyrolysis resin.

Name of indicator	Brand A
Density at 20 °C, g/cm ³ , not less	1.04
Kinematic viscosity at 100 °C, mm ² /s, no more	26
Distillation temperature of 3% volume, °C, not less	180
Coking ability, %, not less	25
Mass fraction of sulfur, %, no more	0.25
Mass fraction of water, %, no more	0.25
Mass fraction of mechanical impurities, %, no more	0.01
Correlation index, not less	126
Mass fraction of sodium ions, %, no more	0.003
Mass fraction of potassium ions, %	0.0002

All test samples were prepared in a laboratory, heated mixer with Z-shaped blades at a mass mixing temperature of 180 ° C. The dosage of the binder was chosen on the basis of obtaining a dry anode mass with a fluidity of 1.2-1.3 relative units. In batches with the addition of pyrolysis resin, the content of the binder was reduced in proportion to the dosage of the pyrolysis resin. The prepared sample of the coke charge was heated in a mixer, and the pitch in an oven to a mixing temperature. After that, the required amount of modified heavy pyrolysis resin was poured into the mixer and averaged for two minutes, then the pitch was added in a predetermined amount. Stirring was carried out for 40 minutes. Firing and technological testing of the anode mass was performed according to TU 48-5-8-86.

The experimental conditions were chosen in such a way as to neutralize the effect of the properties of the coke filler, the granulate composition of the coke charge and the technology for preparing the anode mass on the research results.

As a witness sample, a batch of dry anode paste prepared from the above hydrocarbon materials with the same particle size distribution was used without adding a modified heavy pyrolysis resin.

To interpret the data obtained on the study of the effect of the addition of a modified heavy pyrolysis resin on the processes of thermochemical transformations of pitch, it is advisable to use the concepts within which the interaction between the dispersed phase and the dispersion medium in colloidal chemistry and physical chemistry of filled polymer systems is currently considered. [five]

The results of technological testing of the anode mass are presented in table 5.

Table 5. Physical and chemical properties of dry anode mass.

Content of modified heavy pyrolysis resin, %	Binder content, %	Coeff, rel. units	Specific electrical resistance, $\mu\text{Ohm}\cdot\text{m}$	Apparent density	Compressive strength, MPa	Reactivity in a current of CO ₂ , mg/cm ² ·h	Porosity, %
-	26	1.40	71.0	1.52	38.4	43.6	24.49
1	25.74	1.59	74.52	1.48	35.6	43.3	26.65
5	24.7	1.39	76.61	1.48	28.7	39.5	26.85
10	23.4	1.66	70.37	1.48	23.0	37.0	26.68

The obtained results of studies of the anode mass indicate that in order to achieve close values of fluidity, the anode mass based on a mixture of pitch and modified heavy pyrolysis resin requires a lower, by 1.0-1.5%, binder dosage. This is due to the lower viscosity of the mixture of coal tar pitch and pyrolysis tar, which entails a natural increase in the flow coefficient.

In general, the porosity of any carbon-filled, carbonized material should include the pore volume of the filler, unfilled with the binder, the pore volume of the carbonized binder, and the pore volume of macro- and microcracks formed at the boundary between the filler and coke from the binder, mainly due to the shrinkage of the latter and thermal expansion of the filler. during the firing process. Since pure pitch has a higher viscosity in comparison with a mixture of pyrolysis resin and pitch, the probability of coke pores not filled with binder is greater. In addition, the dosage of the binder in the anode mass on a mixture of pitch and pyrolysis resin was higher, by 1.0-1.5%, compared to the mass on coal tar pitch, therefore, the proportion of coke from the binder is greater and the pore volume of the carbonized binder is greater in the mass of prepared on the mixture. The lower viscosity of the binder based on coal tar pitch and pyrolysis resin leads to more efficient filling of coke pores. Therefore, one should expect an increase in the porosity of the anode mass with an increase in the addition of pyrolysis resin to coal tar pitch. This is confirmed by the results of these studies. To this we can add that the porosity of the coke from the binder depends on the structuring of the pitch in the near-surface layers of the filler coke, which in turn depends on the group composition of the pitch. [4]

Moreover, it is possible that coal tar pitch, due to the peculiarities of its physicochemical composition, can have a significant effect on the process of mixing and further roasting of the anode mass. The multidirectional effect of pitch parameters on the quality characteristics of the anode mass is explained by a slight decrease in the porosity of the anode mass in the fourth experiment, with a pyrolysis resin dosage of 10%.

According to modern ideas about the formation of the properties of carbon-filled composite materials, their strength is primarily determined by the forces of molecular interaction (adhesion) between the components and their own, or the so-called, cohesive strength. It is also known that with a decrease in the thickness of the adhesive (cementing) component, the strength of the composite material increases. [5]

It can be seen from the research results that the strength of the anode mass based on a mixture of pitch and modified heavy pyrolysis resin is noticeably reduced to a catastrophic level with a straight-line relationship. Moreover, an increase in the proportion of MHPR and a decrease in pitch viscosity reduce the mechanical strength of the mass, which is possibly associated with a deterioration in the wettability of coke with pitch. Based on the foregoing, it should be noted that the decrease in the mechanical strength of the anode mass with an increase in the pyrolysis resin content in the binder is due to the processes of interaction with the coke-filler, which depend on the properties of the pitch.

The chemical composition and structure of petroleum pitch, as already mentioned, determine the complex physicochemical processes of its carbonization and its technological properties as a binder in the production of anode materials. The electrical conductivity, as well as the mechanical strength of the anode mass, is directly dependent on the coke-forming and sintering capacity of the pitch (the content of a-fraction, a2-fraction and coke residue). An increase in their content in coal tar pitch leads to a greater number of chemical bonds in the binder matrix (interphase layer), which ultimately contributes to the strengthening of the structure of the fired material and the improvement of physical and chemical properties, including electrical conductivity.

In fig. 1 shows the dependences of the electrical resistivity of the baked anode mass on the content of the MTSC fraction in the pitch.

As can be seen from the plot of the dependence, the electrical resistivity increases with an increase in the proportion of MTSC in the binder and then sharply decreases. This means that the higher the content of low-boiling fractions in the pitch, the better the wetting ability of the pitch, the more

intensively the coke is impregnated with pitch and, accordingly, the electrical conductivity of the baked anode mass improves.

This is explained, firstly, by an increase in the a1-fraction in pitch with an increase in MTSC content, which, at certain amounts in pitch, negatively affects the ordering of the structure of coke from pitch and, accordingly, worsens its electrical properties. Secondly, as, for example, in this case, an increase in the MHPR dosage leads to an increase in the proportion of more porous and less conductive coke from the binder than the filler coke in the fired mass.

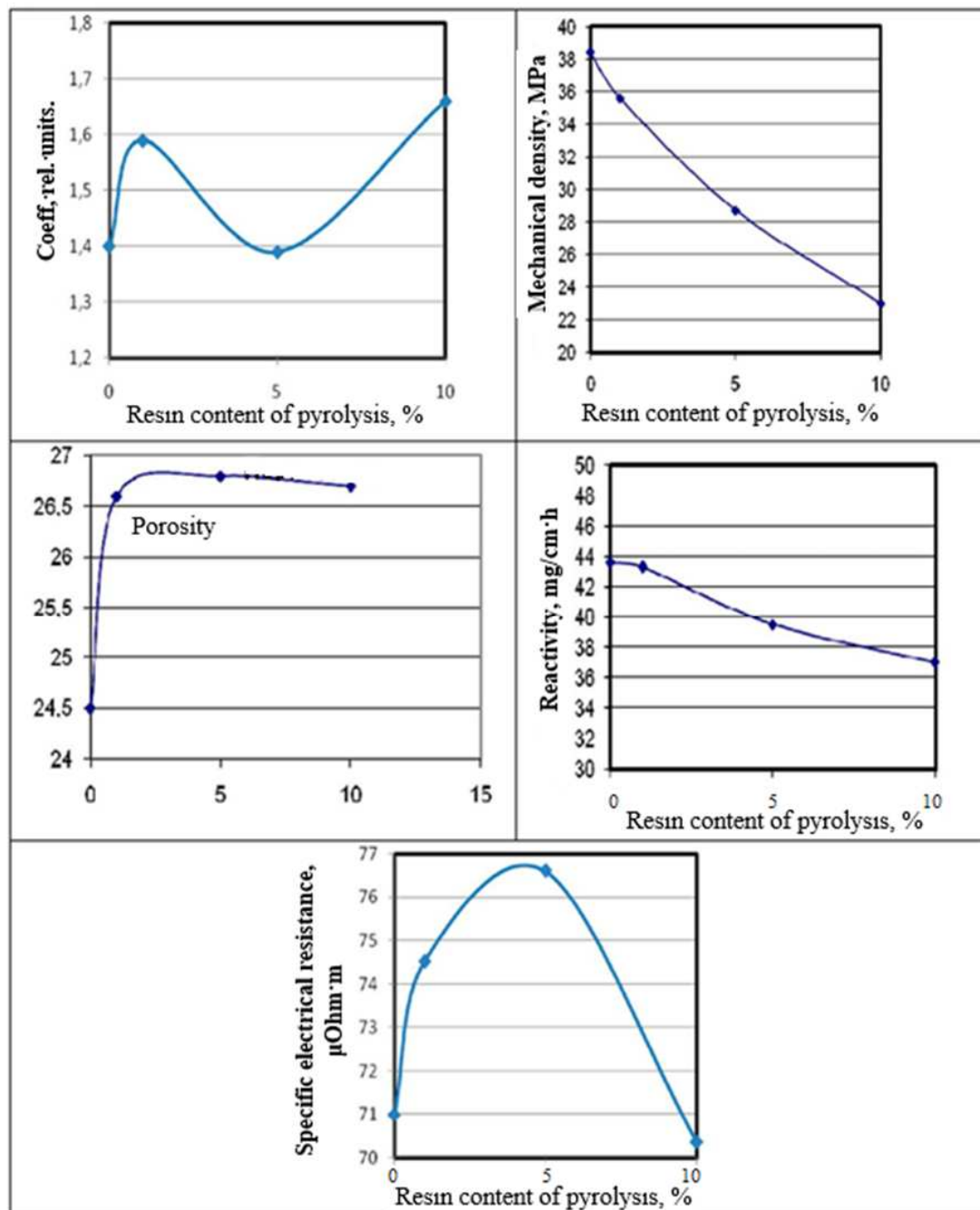


Figure 1. Dependences of the physicochemical properties of the dry anode mass on the MTSC content.

The formation of a larger number of pores in the process of anode baking reduces the specific density of the anode material and, as a consequence, increases its resistance, while the addition of MTSC in large quantities creates areas with inhomogeneous conductivity in the volume of the anode, which also prevents the passage of current. Research data indicate that when the quality indicators of pitch meet the requirements of GOST, the anode mass is obtained with sufficiently high mechanical and electrical characteristics. In this part, we can only talk about the need to stabilize the electrical and strength characteristics of the baked anode mass. At the same time, the chemical activity of the anode mass, assessed by the rate of destruction in CO₂, which largely determines the electrolysis technology and the consumption of the anode, is the main criterion for assessing the quality of the anode mass. Here very often there are problems associated with increased foaming and, as a result, with a breakdown in the electrolysis technology, deterioration of the technical and economic indicators of the process, increased consumption of the anode mass, and environmental degradation. Based on this, in world practice, when choosing electrode raw materials, technological parameters of its preparation and composition of the anode mass, first of all, they are guided by the need to ensure the minimum destructibility of the anode mass in CO₂. [6]

In terms of its chemical activity, the anode is not heterogeneous; therefore, the more reactive coke from the binder burns out first, and coke particles that did not have time to burn fall off the side surface.

The degradability of the fired anode mass based on the pyrolysis resin under study depends on the proportion of coke from the binder and its reactivity, since the reactivity of the filler coke is the same in all experimental masses. Naturally, and this is confirmed by these studies, with an increase in the content of MTSC and, accordingly, an increase in the proportion of more reactive coke from the binder, an increase in the destructibility of the anode mass does not occur, but a regular decrease is observed. [6]

4. Conclusion

As a result of the laboratory studies, the following conclusions can be drawn:

- the properties of coal tar pitch change significantly when MHPR is added to it. The established patterns of changes in the properties of the compounded binder show that with an increase in the amount of pyrolysis resin in the mixture, rheological properties are significantly improved;
- the use of MHPR in the form of an additive to high-temperature coal tar pitch can reduce the content of 3,4-benz (a) pyrene in the binder, which will have a beneficial effect on improving working conditions at workplaces and increase the environmental friendliness of aluminum production;
- the need for the anode mass in the compounded binder by 1.5% vol. less, in comparison with coal tar pitch "B" to ensure the same plastic properties;
- the addition of MHPR in the amount of 1-10% to high-temperature coal tar pitch (HCP) does not significantly affect the porosity and resistivity of the mass. Their values fit well into the requirements for the AM-0 brand. At the same time, it adversely affects the strength of the fired mass, this limits the addition of pyrolysis resin at the level of 10%;
- MHPR in a mixture with coal tar pitch acts as an inhibiting additive, which is confirmed by experimental data on the reactivity of anode mass samples;
- the use of a compounded binder in the form of a mixture will reduce the dosage of the binder in the anode mass by 2% in comparison with coal ECP to improve the performance characteristics of the dry anode mass;
- based on the results of calculating the expected consumption of anode mass per ton of aluminum and the amount of carcinogenic substances when using high-temperature coal tar pitch mixed with MHPR as a binder, the following indicators were obtained:
 - a decrease in specific consumption of coal tar pitch by 6.7 kg/t of aluminum;

b reduction of harmful emissions by 1.7 times.

Thus, the results of the tests performed show the possibility and feasibility of using high-temperature coal tar pitch in a mixture with MHPR, as well as to reduce the content of carcinogenic substances in the air of the working area, to reduce the output of greenhouse gases, and also to rationally use the non-target oil product - modified heavy pyrolysis resin.

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