Thermolysis Technology and Technical Means for Processing Organic Technogenic Materials

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Abstract Scientific and technical developments were carried out to create resource-saving technology and patent-protected devices for low-temperature thermolysis processing of municipal solid waste (MSW) with various physical and mechanical characteristics. Pilot tests of a thermolysis reactor with a spiral conveying body of combined action were carried out and design, technological and thermal engineering parameters of low-temperature processing of organic MSW, as well as rubber waste (RW) were obtained. Samples of recovered carbon black (rCB) were obtained, corresponding to industrial products in terms of their physicochemical characteristics and properties. The possibility of using carbon black obtained by low-temperature thermolysis in the paint and varnish industry has been confirmed. Presented are the test results of paint and varnish compositions made on the basis of three types of polymer binders (alkyd, epoxy, acrylic) carbon black grades P-803, K-354 and rCB, obtained by low-temperature thermolysis technology. It has been established that these compositions, as well as coatings based on them, in terms of their performance, meet the requirements for carbon black grades P-803 and K-354.

Keywords Ecology · Low-temperature thermolysis · Solid municipal waste · Carbon black · Recovered carbon black · Paint and varnish industry

1 Introduction

Carbon black (CB) is a highly dispersed carbonaceous material that is formed during incomplete combustion or thermal decomposition of hydrocarbons contained in natural or industrial gases, as well as in liquid products of petroleum or

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coal origin [1]. The world's carbon black output is currently more than 13 million tons per year. Among the world's manufacturing firms, which produce more than 40% of the world's CB volume, two companies predominate—Cabot (USA) and Evonik (formerly Degussa, Germany) [2]. In Russia and the CIS countries, the largest manufacturer of CB—Omsk Carbon Group, is one of the world's top ten producers of carbon black.

Carbon black is widely used in various industries. The main share (more than 80%) of the produced CB is used in the tire industry, as well as in the preparation of rubber mixtures as filler for their reinforcement. In the electrical industry, a mixture of graphite, carbon black, and a binder (coal peck) is used to produce DC motor brushes [3]. For painting electrical insulation materials, gas channel carbon is used, which has a relatively high content of volatile substances (oxygen-containing groups—lactane, quinone, phenolic and carboxyl), which contributes to low electrical conductivity [4]. In the electrical industry, a mixture of graphite is used for the production of brushes of DC electric motors, which is a technical component in metallurgy, and is a mandatory component of most steel grades. By changing the ratio between the amount of ferrite and perlite in the structure of a solid metal, carbon makes it possible to obtain a metal with a wide range of mechanical properties [5]. Carbon black is also included in the composition of polymer materials for color change, and is also a stabilizer when used in polyolefines and other thermoplastic polymers to increase their resistance to the influence of the atmosphere, as this substance has the ability to protect polymers from the action of ultraviolet radiation on them [6]. In addition, CB is used in the production of abrasives, in printing, as well as an adsorbent in wastewater treatment. CB is not unimportant in the construction industry as a dye in the production of cement, concrete, self-leveling floors, asbestos cement, paving slabs and silicate bricks [7]. Carbon black plays a significant role in the paint industry as a pigment in the production of black and gray weather-resistant paints and enamels. Having high temperature resistance, resistance to light and many chemical compounds, the ability to absorb ultraviolet, infrared radiation and light of the visible part of the spectrum, CB gives paint and varnish materials significant performance qualities [8].

The above-mentioned areas of use of technical equipment, its wide application for the production of various types of technical products indicates the relevance of the development of this scientific and technical direction and the search for unused technological reserves, design and technological improvement of equipment.

2 Materials and Methods

In the industry, CB is obtained in various ways: furnace, channel thermal, lamp, acetylene. The feedstock can be liquid or gaseous. Carbon black is distinguished by its dispersion (high-, medium-, low-dispersed), by its activity in the rubber mixture (high-, medium-, semi-, low-active), and by its structure (high-, medium-, low-structure). Other methods of obtaining recovered carbon black (rCB) from organic raw materials are also possible, for example, from solid municipal waste (MSW), in particular - from rubber waste (RW), with low-temperature thermolysis of the feedstock [9]. The main advantages of the proposed method:

- effective solution of environmental problems in the complex processing of MSW;
- creation of resource-saving technologies and implementation of recycling of secondary (technogenic) materials;
- solving state problems of import substitution and obtaining innovative materials;
- implementation of national projects of the Russian Federation aimed at the rational use and processing of MSW to produce various types of marketable products, etc.

The author’s team of researchers of BSTU named after V.G. Shukhov and engineering and technical employees of Ecotrans TC LLC, conducts scientific and technical developments and the introduction of resource-saving technology and special equipment for low-temperature thermolysis of organic waste into real production.

The method allows the use of recyclable organic MSW of various morphological and physical composition: small-scale polymer, wood, pulp and paper, rubber and other waste in a loose or compacted state during their heat moisture treatment. The proposed method of low-temperature processing of organic MSW at a temperature of up to 500 °C makes it possible to obtain high-quality products: recovered carbon black, liquid hydrocarbon fuel and synthetic hydrocarbon gas.

In the presented study, we used various patent-protected technological solutions: sealed material loading and unloading units, structural and technological solutions for the working elements of a thermolysis reactor, aspiration systems, rectification, etc., patent RU 2744225 C1.

A spiral thermal reactor is a combined-action transport body made in the form of a cylindrical body with spiral (or helical) elements placed inside [10]. The housing is equipped with pipes for the input and output, respectively, of the initial raw materials and the resulting products—gaseous reagents, followed by the production of liquid hydrocarbon fuel, carbon black. The spiral-shaped conveying body ensures the movement of the heat-treated material. The developed resource-saving technology and special equipment are currently undergoing pilot testing and implementation at the company “Ecotrans TC” LLC.

The estimated capacity of the low-temperature thermolysis process line for incoming raw materials is 400–500 kg/h. Resource- and energy-saving and design-technological solutions of the implemented developments are based on many years of experience in modeling technological processes in production conditions, testing thermolysis technologies for processing various MSW: rubber waste, wood and pulp and paper waste, polymer technogenic materials, etc.

One of the final products obtained by the developed technology for processing MSW, in particular RW, is carbon black. According to its characteristics, it is a combined meso-macro powder with a predominance of macropores, its specific surface area is 37.9 m^2/g, pore volume is 0. 23 cm^3/g, and the average pore size is 23.9 nm.

3 Results and Discussions

Due to the scale of the scientific and technical tasks to be solved, a wide range of processed MSW, we present the results of research on pilot tests of the technology for obtaining and using CB in the production of paint and varnish materials. At the same time, rubber crumb obtained from MRG waste and decommissioned tires were used as a raw material. Carbon of P-803 and K-354 grades was adopted as the reference recovered carbon black. Table 1 shows the physical and chemical characteristics of rCB.

To test the powder of rCB obtained by low-temperature thermolysis technology and used in paint materials, paint compositions were made based on the most common binders: alkyd (varnish PF-053), epoxy (resin solution E-41r) and acrylic (acrylic resin AR). The composition of the compounds is shown in Table 2.

Paint and varnish compositions were made by dispersing pigments and fillers in a film-forming solution on a laboratory bead mill. The technological parameters of the prepared paint and varnish compositions, as well as the properties of coatings based on them, are presented in Table 3. All the resulting paint and varnish compositions were black in color and after drying formed a homogeneous, even, free of extraneous inclusions surface.

The conditional viscosity, the mass fraction of non-volatile substances, and the degree of grinding were determined in undiluted compositions. To determine the remaining indicators, the paint and varnish material was applied with a paint

Table 1 Physical and chemical characteristics of the rCB sample obtained in the process of low-temperature thermolysis of rubber crumb from RW and decommissioned tires

Parameters	ASTM	Result
Surface area according to BET (m^2/g)	D6556	84.3
Surface area according to STSA (m^2/g)	D6556	55.1
Iodine number (mg/g)	D1510	124.5
pH-Volume (UZ suspension)		5.96
Moisture loss at ignition (125 °C, 1 h) (%)	D1509	1.01
Ash content at ignition (550 °C, 16 h) (%)	D1506	14.74
Sulphur content (%)	D1619	2.69
Fine particle content (%)	D1508	7.5
Toluene light transmission (%)	D1618	98.9

Table 2 Composition of paint and varnish compounds based on polymer binders and carbon black of various brands

Compound, №	1	2	3	4	5	6	7	8
Binder, wt%	89.2	89.2	35.61	35.61	35.61	15.0	15.0	15.0
Pigments and fillers, wt%	–	–	3.5	3.5	3.5	1.5	1.5	1.5
P-803	5.04	–	7.0	–	–	3.7	–	–
K-354	–	–	–	7.0	–	–	3.7	–
rCB (thermolysis)	–	5.04	–	–	7.0	–	–	3.7
Functional additives	2.52	2.52	–	–	–	1.8	1.8	1.8
Hardener	–	–	30.0	30.0	30.0	–	–	–
Solvent	2.52	2.52	23.89	23.89	23.89	78.0	78.0	78.0

Table 3 Properties of paint compositions and coatings based on them

Composition, №	1	2	3	4	5	6	7	8
Conditional viscosity at a temperature of (20.0 ± 0.5) °C according to a viscometer with a nozzle diameter of 4 mm (s)	35.0	27.0	19.0	25.0	18.0	58.0	61.0	64.0
Mass fraction of non-volatile substances (%)	38.9	45.1	46.5	46.0	45.3	27.4	25.3	21.5
Degree of grinding, Microns	60.0	60.0	40.0	40.0	40.0	40.0	40.0	40.0
Drying time to degree 3, at temperature (20 ± 2) °C (h)	24.0	24.0	6.0	6.0	6.0	2.0	2.0	2.0
Coverage of the dried film (g/m^2)	–	–	18.52	12.04	14.81	17.0	16.67	17.0

sprayer to the corresponding plates prepared according to GOST 8832-6 “Paint and varnish materials. Methods for obtaining a paint coating for testing”. Table 4 shows data on the conditional light resistance of coatings. The tests were carried out in accordance with the requirements of GOST 21903-76 “Paint and varnish materials. Methods for determining the conditional light resistance”. The DRT-400 lamp was used for testing. Samples of coatings applied to white drawing paper according to GOST 597-73 with a size of 100 × 200 mm were subjected to UV irradiation and after 2, 6, 12 and 24 h, the brightness coefficient was measured on a OUF device with a correcting absorber. The test results are shown in Table 4.

Table 4 Conditional light resistance of coatings based on polymer binders and carbon black of various brands

Compound, №	1	2	3	4	5	6	7	8
Brightness coefficient before UV irradiation (%)	–	0.10	0.13	0.10	0.10	0.18	0.10	0.17
2 h after UV irradiation (%)	–	0.10	0.13	0.10	0.10	0.19	0.10	0.17
6 h after UV irradiation (%)	–	0.10	0.13	0.10	0.10	0.21	0.10	0.18
12 h after UV irradiation (%)	–	0.10	0.13	0.10	0.10	0.28	0.11	0.18
24 h after UV irradiation (%)	–	0.16	0.13	0.13	0.17	0.29	0.12	0.18

4 Conclusion

1. A complex of scientific and technical developments and research on the creation of resource-saving technology and patent-protected devices for the processing of MSW with various physical and mechanical characteristics was carried out.
2. According to the results of pilot tests, the design, technological and thermal parameters of the thermolysis technology for processing various MSW were worked out. The technical, economic and environmental feasibility of using the completed developments was confirmed.
3. The possibility of using CB samples obtained by low-temperature thermolysis technology in the formulations of paint and varnish materials is investigated.
4. Paint and varnish compositions are made on the basis of polymer binders of three types (alkyd, epoxy, acrylic) of carbon black grades P-803, K-354 and rCB, obtained by low-temperature thermolysis technology.
5. It is established that paint and varnish compositions made using the technical technology of low-temperature thermolysis, as well as coatings based on them, meet the requirements for technical carbon grades P-803 and K-354. The obtained results meet the requirements for obtaining paint and varnish coatings (GOST—9.032-74).
6. Recovered carbon black obtained by low-temperature thermolysis technology can be used in the production of black and gray paint materials.

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