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Innovative Trends in Expanding Carbon Black Types in Russia

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Abstract

Analysis of the evolution of carbon black grades manufactured in Russia was given on the example of the Russia largest enterprise that is OMSK CARBON GROUP. Development trends innovative technologies of the enterprise in expanding varieties of carbon black grades were demonstrated. Innovative products including those manufactured under the brand OMCARB for various designations were presented in detail. Some results of scientific research carried out by the Scientific and Technological Center of Carbon Materials and Institute of Hydrocarbon Processing (IHP SB RAS) in the development trends of carbon black types were presented. Recommendations on rational choice and use of innovative varieties of black carbon were proposed in the first place to tire and industrial rubber goods, as well to as other polymer products manufacturers.

Key words: carbon black, various types, preparation technology, morphology, rubber, elasticity, hysteresis, rolling resistance, electrical conductivity, pigment

INTRODUCTION

Sales volumes in accordance with consumption growth by industries systematically grow at the global carbon black market. Thus, the actual global carbon black market in 2015 exceeded 12 mln t, which amounted to a five percent increase in comparison with the previous period [1]. Lately, countries of the Asia-Pacific Region have significantly increased production growth rates. In this regard, the major leaders in the production of carbon black consolidated its position on the on the world scene are China, the USA, Russia, India, Japan, South Korea, Brazil, and Thailand. In 2015, Russia ranked third in the world with the volume of manufactured production of over 0.8 mln t. By capacity of enterprises, three active brand manufacturers (Omsk, Nizhnekamsk, and Yaroslavl plants) and three low active brand manufacturers (Tuymazy, Ivanovo, and Sosnogorsk plants) represent the carbon black market in our country [2].

The Omsktekhuglerod JSC has been a part of the Omsk Carbon Group since 2011. Currently, the holding is a dynamically develop-

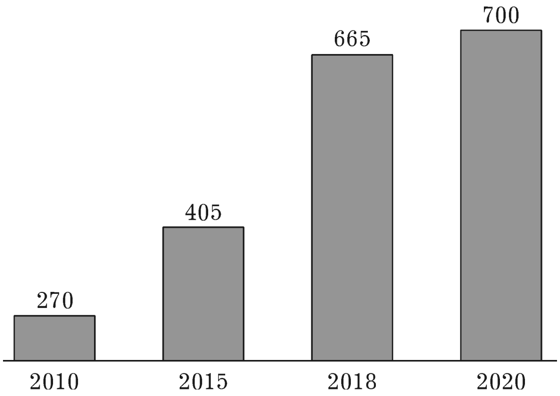

Fig. 1. Development dynamics of production capacities of Omsk Carbon Group, thousand t.

ing enterprise on the production of carbon black with two operating production sites in the cities of Omsk and Volgograd and the one under construction in Mogilev (Republic of Belarus), as well as the Scientific and Technological Center of Carbon Materials and a developed network of International Trade Representations. According to production volumes, the holding is an industry leader in Russia and enters the top ten world largest manufacturers. Plans for further development of the enterprise provide for an increase in productive capacities (Fig. 1) and growth of the product range, including innovative brands in carbon black. One of the promising areas of innovative developing the holding is the production of new carbon black varieties corresponding to both the ASTM

TABLE 1

New carbon black grades

Carbon black grades	*J*, g/kg (ASTM D 1510)	OAN, cm^3/100 g (ASTM D 2414)	COAN, cm^3/100 g (ASTM D 2414, ASTM D 3494)	STSA, m^2/g (ASTM D 6556)	NSA, m^2/g (ASTM D 6556)	Tint, % (ASTM D 3265), no less than	Sieve residue, % (ASTM D 1514), no more than; Sieve size, μm: 500	45
Superfine								
N115	160±8	113±7	–	124±8	–	–	0.001	0.1
N121	121±6	132±6	–	116±6	–	–	0.001	0.1
N134	142±6	127±6	–	133±7	–	–	0.001	0.1
High structure								
OMCARB CH85	80±6	140±6	–	–	69±6	–	0.000	0.005
Electroconductive								
OMCARB C40	43±5	123±5	–	–	38±5	–	0.000	0.004*
OMCARB C140	355±35	130±10	–	–	300±30	–	0.000	0.005
OMCARB CH200	180±15	168±10	–	–	165±15	–	–	0.01
OMCARB CH210	255±25	181±15**	–	–	235±25	–	0.000	0.01
High purity								
OMCARB S500	43±5	121±5	85±5	37±5	–	53	0.000	0.01
OMCARB S700	30±6	65±6	–	–	–	–	0.000	0.01
OMCARB S800	20±5	92±5	68±5	22±5	–	33	0.000	0.01
OMCARB S810	20±5	102±5	73±5	20±5	–	33	0.000	0.01
OMCARB S820	28±5	123±5	81±5	25±5	–	42	0.000	0.005
Pigment								
OMCARB P80	–	72±5	–	–	78±6	104	0.000	0.02
OMCARB P110	–	114±5	–	–	113±6	110	0.000	0.005
OMCARB P140	–	118±5	–	–	137±6	118	0.000	0.005

Notes. 1. *J* is iodine adsorption, OAN is oil absorption number, COAN is compressed oil absorption number, NSA is specific surface by multipoint nitrogen adsorption, STSA is the external surface by the static thick thickness of the layer, and Tint is the colouring power. 2. The dash indicates not regulated.

* The sieve of 25 μm.

** According to GOST 25699.5–90.

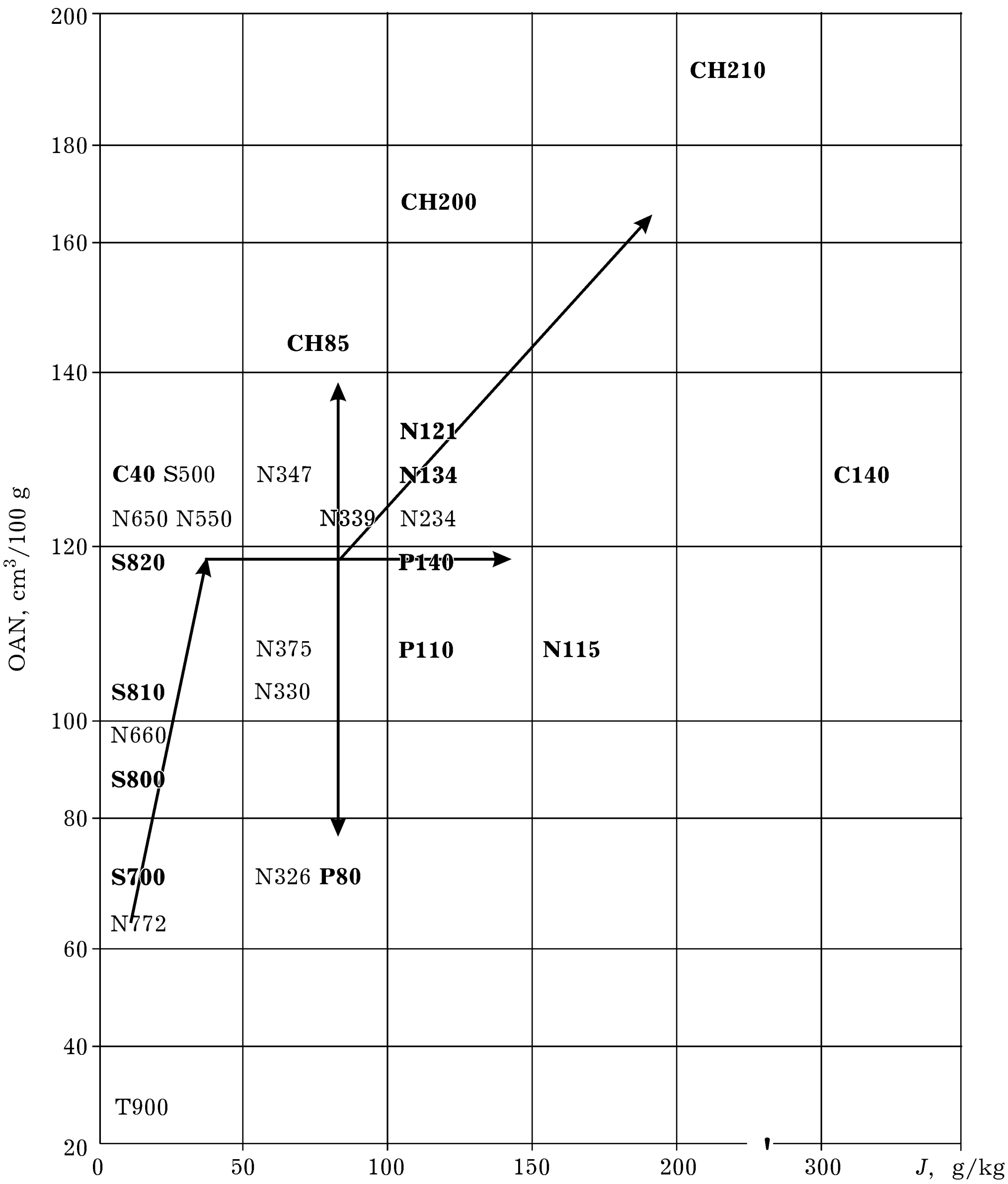

Fig. 2. Map of development of carbon black types. Bold lines indicate some serial and new grades, arrows – modern development trends of its varieties.

D1765-10 nomenclature (American Society for Testing and Materials) and other, special purpose ones [3]. Special purpose carbon black brands are produced under the trademark OMCARB registered in some countries [4].

EVOLUTION OF VARIETIES OF CARBON BLACK

Industrial development of carbon black was always determined by requirements of its major consumer that is tire industry and possessed a different orientation at different stages. Filler is one of the major rubber ingredients giving way only to rubber according to content in its composition, therefore, the development of special grades is of great interest. Only low-dispersion and low-structure grades of carbon black were produced by the thermal method early last century in the historical aspect, and priorities shifted to the side of the product dispersity growth, since insuring tread wear represented the basic requirement of tire producers. Currently, regulatory requirements acting in Europe on issues of ecology, energy efficiency, safe operation and tire noise reduction

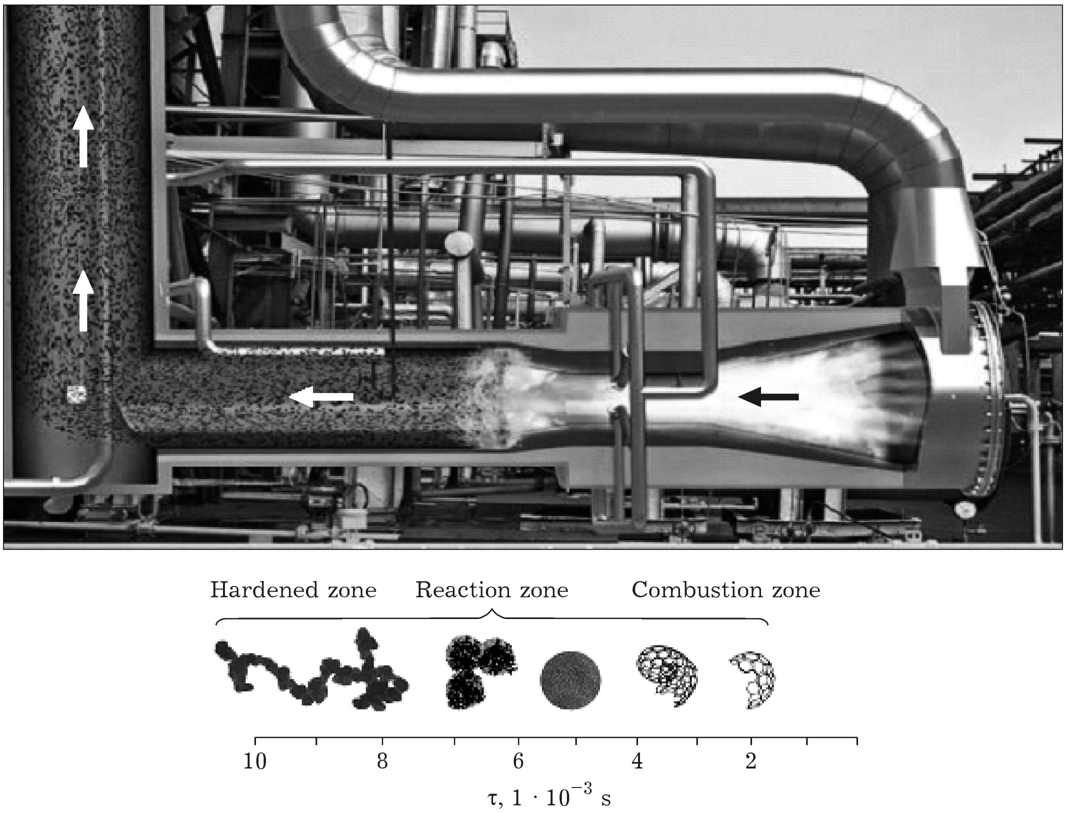

Fig. 3. Photography scheme of the reactor and schematic representation of the stages of the formation and growth of a particle and a carbon black aggregate in the reaction zone in time.

came out on top. This is associated with a decrease of atmospheric emissions due to a decrease in tire rolling resistance and accordingly to a decrease in motor fuel consumption, a relatively reliable grip tread with a dry, wet, and icy road insures driving safety. By changing the formulation of tire rubber mixtures through using new ingredients, especially filler, carbon black, one can affect these critical production characteristics. Requirements to the product for filling other composites depend on the regulatory documentation requirements for specific products.

The total number in the world of carbon black grades with various physicochemical properties and morphology that in turn depend on its preparative method, raw materials used and conditions of technological processes is over 100. Despite the established varieties of grades, they constantly expand. Thus, in recent years, innovative carbon black grades with high dispersity corresponding to ASTM D1765-10 variety, as well as special purpose grades of the OMCARB series have been commercially available: electroconductive, high pure and pigment that often do not have analogs in ASTM D1765 and State Standard GOST 7885–86 classifications (Table 1).

The conditional map of carbon black types that reflects the position of some serial and new grades, as well as modern development trends of its varieties is demonstrated in Fig. 2.

All carbon black grades indicated in Fig. 2 are produced by the oven method in special reactors that have three major areas: combustion zone, where the temperature required for decomposing the original gaseous or liquid raw materials is created, reaction zone and hardened zone, where water cooling the aerosol occurs (Fig. 3). Fuel gas and air are supplied to the axially located reactor burners that when burning allow obtaining high temperatures. The raw material freed from moisture, heated to 200 °C enters to the reaction zone. Spraying of raw materials is performed by high pressure air pre-heated in the air heater to 350–400 °C. At a temperature from 1200 to 1700 °C corresponding to intense sooting, decomposition of hydrocarbon raw materials occurs followed by the formation of carbon black. To end the gasification reaction the aerosol is cooled by water spraying by mechanical nozzles. Cooling the aerosol flow is usually performed in two stages: at first, by water to 900–1000 °C, then in a common collector to a temperature of 650–800 °C. The stages of nucleation and growth of carbon black particle and the formation of the primary particle aggregate in the reaction area are illustrated below schematically in Fig. 3. By regulating synthesis conditions (the structural group composition and degree of dispersion of raw materials, temperature, and other para-meters) one can obtain products with widely differing geometric properties. The preparation of innovative carbon black possessing a set of properties different from existing grades is based on this principle.

CHARACTERISTIC OF INNOVATIVE GRADES OF CARBON BLACK PRODUCED IN RUSSIA

The most important characteristics of constructional materials are properties that ensure long-term operation of products from them. Performance and reliability requirements during the operation, especially under dynamic conditions are relevant in case of rubber. More than half a century of experience in research of strengthening action of carbon black on rubbers led to understanding the need to ensure distribution uniformity as the primary task when its processing. Calculations demonstrate that over 30 % strength of compositional materials, including rubbers has not been implemented yet, which is associated with incomplete filler dispersibility in rubber [5]. The consequence of this is inaccessibility of over 30 % filler surface area for rubber adhesion; the Payne effect due to numerous contacts of carbon black particles and friction between the agglomerates leading to heat emissions under deformation conditions. From the standpoint of physicochemistry, to decrease the number of contacts in particles one must downgrade their surface energy. This is performed through two ways: modifying a part of the surface with substances that reduce the fraction of the dispersive component of the surface energy or decreasing the surface area, *i.e.* dispersity. The active surface decreases in both cases, nevertheless, the second path is more promising provided if a decrease in the surface area is accomplished by a simultaneous increase in structurality of carbon black. Therefore, usually and high structurality (with oil absorption number (OAN) of over 100 cm^3/100 g) is given to superfine grades to produce rubber.

Over the past decade, Russian manufacturers have mastered the production of active grades of carbon black that meet ASTM D1765–10 requirements [6]. In this regard, the domestic tire and rubber industries have obtained resources to improve the quality of manufactured elastomeric products.

Thus, **superfine** carbon black grades N115, N134, N121 according to ASTM D1765–10 nomenclature manufactured in Omsk ensure in rubber not only a high level of strength properties and wear resistance but also high thermogenesis when working under dynamic conditions. Recommended application areas are a protector of passenger high-speed tires, tread section of protector of truck all-metal tires, conveyor belts operating under extreme conditions and other accountable items.

High structure carbon black grades are designed to decrease mechanical losses in rubber (hysteresis). Innovative medium-dispersing carbon black with high structure can ensure a compromise between wear resistance and rolling resistance tire tread [7]. High structure OMCARB CH85 grade meets these criteria. The technology for preparation of high dispersity carbon black with high degree of structure grades requires the application of raw materials with a high correlation index and carrying out the process in reactors of special design. Ensuring these conditions allows reaching a high level of structurality of carbon black on OAN.

Numerous studies carried out on CH85 grade carbon in the formulation of standard (ASTM D3191–14, D3192–14) and operating rubber mixtures at domestic tire enterprises [8] demonstrated that highly structured carbon black is dispersed faster and therefore better distributed in rubber by ensuring rubber compounds with good extrusion properties (high extrusion rating, low shrinkage), and vulcanizates – a greater elasticity under normal conditions and elevated temperatures, better dynamic performance, resistance to tear propagation and a smaller hysteresis, and improve electrophysical properties of composites. The consequence of the latter is a successful application of this grade and for the preparation of electroconductive composites.

Electroconductive, **high-purity** and **pigment** grades belong to carbon black varieties.

Promising varieties of electroconductive carbon black grades were created in accordance with one of the innovative areas of developing Omsk Carbon Group based on research at IHP SB RAS [9]. Variation of parameters of the reagent inputs of the reactor and the time spent by carbon gas mixture in the high temperature area allows reaching the desired level of electrophysical properties of carbon black. Carbon black grades C40, C140, CH85, CH200, CH210 with various morphological characteristics enter in the number of manufactured electroconductive grades of carbon black of the OMCARB series [3].

Electroconductive materials are increasingly used in various technology areas that require protection from electrostatic discharges (paints for aircraft, enamel coatings with resistance to spark discharge for equipment, primers, etc.), since the extensive use of polymeric materials leads to the appearance of the static electrisation. One of the major protection methods from static electricity is filling polymers with dispersive conductive materials, among which carbon black occupies an important place. The elevated electrical conductivity of compositional materials is reached because of their properties: fine dispersity, high structurality, low content of volatile products, and applying their dosage exceeding the percolation threshold [10, 11].

Varieties of **high purity** grades consist of several names of the OMCARB series with various morphologies: S500, S700, S800, S810, and S820. Production technology of high purity carbon black envisages the selection of raw mixtures that ensure the exclusion of grit in products and enhanced product quality inspection. The content of foreign inclusions is a major indicator of high-purity grades depending both on properties of the raw materials used and the stability of the reactor operation, injection devices and the availability of micro grinders. Requirements on the lowered content of ash, volatile products and the residue after screening on a sieve are included in specifications for high purity carbon black. One of the important properties of such filler is its chemical purity degree, since heteroatoms, non-carbon inclusions (especially metals and their compounds) can be catalysts of oxidative destructive processes in elastomeric products. The application of high purity grades is efficient for the exclusion of external defects in thin-walled products and semi-finished products from polymers.

High purity carbon black with low dispersion grades are easily dispersed in elastomers, give high specific electrical resistance to composites, which ensures protection of products that contact with metals of variable valency from premature electromechanical destruction (fuel hoses and other items). They are also designed to produce low viscosity porous rubber profiles by ensuring elasticity and smoothness of the surface and various films. The same grades give good technological effectiveness to rubber mixtures with high filling, since ensure the low viscosity growth rate at increasing their dosage.

The research carried out on the application of high-purity carbon black grades in rubbers with gas-barrier properties also demonstrated their efficiency. This is driven by the fact that gas permeability of the polymer itself is significantly higher than that of carbon black particles; therefore, with an increase in the size of filler particles and growth of filling the composite, a decrease in the value of this important parameter is observed [12].

Carbon black **pigment** grades of the OMCARB series having a high demand on the global market are presented by the following names: P80, P110, P140, P80, P110, and P140 that are distinguished by dispersion and structurality levels.

The composition colour for any chemical materials is a result of the interaction of optical properties of the polymer used and pigment. The distinction between pigments consists in the fact how fully they absorb and scatter certain parts of radiation in the optical spectral range. Carbon black efficiently absorbs radiation. In those application areas that require reaching the colour background on reference colours, and light absorption (emissivity factor) and light scattering (tone) have a value. These properties of composites depend on the relative refractive index of the colouring composition, size of particles and primary aggregates, as well as the morphology of carbon black used and its dispersion level in the composite.

Quality criteria of printing inks are colour values, blue hue, shine, covering power, proper rheological properties. This requires a certain compromise, since high saturation of colour tone in compositions for polygraphy is reachable when using fine pigment carbon black, with which a blue hue of printing inks is hard to obtain. The colour tone of printing ink mainly depends on the average size of black carbon particles and a binder dispersion degree. The lower is the particle size, the more saturated paint colour is but with a pronounced brown hue. Coarse carbon black gives a less saturated colour tone to printing inks but with a more intense blue hue. The value of the filler structurality is more meaningful than the particle size in reaching the glitter paint, therefore, the structurality level of a certain grade is given considering the application area of the polymer used [13].

Carbon black is also used in paints to ensure conductivity and protection from UV radiation. Application areas of pigment grades are broad: offset inks, newsprint inks, for magazines, for printing on metal, for decorative packaging and many others.

CONCLUSION

Thus, carbon black various types in Russia have steadily widened in directions of variety of geometric, morphological, optical and electrophysical properties. The major engine of innovative development of carbon black industry is domestic enterprises, among which Omsk Carbon Group takes the first place on innovations. New carbon black grades manufactured by the holding are demanded in the market, meet the state policy of import substitution, the geography of their supply in the country and the world is constantly expanding.

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