Influence of Nature of Pigments and Dyes on Coloring Properties of Polymeric Superconcentrates

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Abstract. The article considers methods of manufacturing non-toxic films of a given color that meet technological requirements. The problem of reducing the shrinkage of the colored polymer in the casting mould during cooling and maintaining its technical characteristics is experimentally solved. To this end, the influence of the nature of pigments on the degree of polymer coloring is studied, and ways to improve the quality of color are investigated. The object of the study was selected pigment concentrate based on high pressure polyethylene brand 15803-003. The pigment has chosen technical carbon grades N220, P803. Surfactants were modifying additives. Tests of samples to determine the light fastness of dye, migration resistance, the number of agglomerates of pigments, toughness and strength, physical and mechanical properties showed that the most effective additive to improve the coloring properties of soot pigment brand N220 and improve the appearance of finished products introduced into the superconcentrate calcium stearate, which at the stage of mixing in the extruder acts as a surfactant and prevents the adhesion of the pigment and the formation of agglomerates in the polymer melt.

Introduction

To obtain colored polymeric materials, there are two possibilities of introducing colorant: by coloring the polymeric material in bulk or adding a concentrate, which includes a polymer, colorant and special additives [1, 2, 3].

Coloring of polymers with the help of pigment concentrates has become widespread in the production of consumer goods. This is facilitated by the availability of concentrates provided by a large number of their manufacturers. To choose a concentrate to obtain a product of the desired color, you must first study all the characteristics of the product, taking into account the special requirements that the customer often takes into account when concluding a contract for the production of painted polymer products.

The quality and color of the polymer directly depends on the properties and nature of the pigments that are part of the concentrate [4].

Inorganic pigments can be classified according to the following characteristics:

1) by origin pigments are divided into natural, obtained by grinding, enrichment or heat treatment of rocks and minerals, and synthetic, obtained by chemical reactions;

2) by purpose pigments are divided into decorative, protective-decorative protective and special purpose;

3) distinguish color by achromatic (white, black, neutral gray) and chromatic (all color) pigments;

4) the chemical composition of pigments is divided into oxides, salts, metals.

Organic pigments have only decorative properties and are classified by color and class of organic compounds.

Technical products used as pigments must have a set of properties that varies depending on the purpose of the pigments, the composition and properties of the polymer, and the operating conditions of the product [4, 5, 6].

Physical properties: crystal structure; refractive index; color; density; hardness; particle shape and size (dispersion); specific surface; bulk density; solubility;

Chemical properties: pH of water extract; resistance to water and chemical reagents (acids, alkalis); reactivity; acid-base properties of the surface.

Physico-chemical properties: wettability (hydrophilicity or olephilicity); density and strength of packing of particles in units; adsorption capacity (adsorption potential) of the surface; photochemical activity; light fastness; phototropy; ability to change the electrode potential of the surface (passivating action).

Technological properties: coverage (hiding power); coloring ability (intensity); oil content; dispersion; critical volume content; structuring ability; atmospheric stability; compatibility with other components.

Environmental requirements: harmlessness; volatility; non-toxicity; absence or full use of waste and by-products in production.

Assessment of colorant toxicity is constantly being reviewed as new analytical methods in the field of ecology appear. Thus, lead chromates and sulfochromates, cadmium pigments and disazopigments, which are widely used in the past, are currently banned due to their high toxicity [5].

Manufacturers of food multilayer polyethylene film (film for packaging dairy products) need high-quality rich color and guaranteed non-toxicity. Therefore, the study of the possibilities of manufacturing non-toxic films of a given color that meet technological requirements is relevant [6, 7].

Formulation of the problem

As already mentioned, concentrates are usually used for dyeing polymers. When determining the composition of concentrates of great importance is the correct choice of colorant. Only in this case it is possible to meet the various requirements of the customer, the main of which, of course, is the implementation of the selected color, as well as color fastness, pigment migration, shape fastness, toxicological safety.

A large number of substances (in particular, some organic pigments) act as crystallization centers in partially crystallized polymers, such as polyolefins, initiating the formation of crystallites. Some superficial phenomena play an important role in the formation of crystallites. Individual growing crystallites form supramolecular formations - spherulites, the increase in the number of which indicates an increase in the degree of crystallinity of the polymer [7, 8, 9]. The shrinkage of the polymer, in addition to factors such as temperature, cooling rate, pigment concentration, is determined mainly by the degree of crystallinity. Any defects in crystallization lead to distortion. Among the many causes of distortion, the main ones are: the appearance of needle colorant crystals and the thickness variation of polymer products that are not bodies of rotation [10, 11]. Polymers are known to have low thermal conductivity, and therefore the molded polymer product slowly cools, causing shrinkage.

The problem that needs to be addressed is that to reduce shrinkage during cooling, it would be logical to increase the cooling time in the mold. However, it is practically impossible to do this for economic reasons [12]. It should be noted that the amount of shrinkage and possible distortion of colored polymer products can not be calculated, but can only be determined experimentally.

The purpose of this research is to study the influence of the nature of pigments on the degree of color of the polymer, and to study ways to improve the quality of color.

For this work was taken as one of the indicators that affects the degree of staining - the dispersion of the pigment and the ability to combine into agglomerates in the polymer melt. In order

to improve the dispersion of the pigment in the melt was introduced into the surfactant system.

It is necessary to determine the most effective additives and the concentration in the superconcentrate of the pigment obtained on the twin-screw extruder. It is necessary to investigate the degree of distribution of pigment in the mass of the painted product, to determine the coloring ability, color and amount of agglomerates of pigments [13].

The resulting pigment superconcentrate must meet the following requirements:

– mix well with the polymeric material in order to ensure uniform distribution of pigment in the mass:

– do not affect the physical and chemical properties of the product;

– have high thermal and light stability;

– have a rich color;

– be harmless in the finished product (product);

– have a small dosage.

Experimental

The object of the study was selected pigment concentrate based on high pressure polyethylene brand 15803-003. Pigment is selected carbon black brand N220, P803, as one of the most problematic for the uniform distribution in the films.

The following modifying additives were selected [13]:

– as surfactants: calcium stearate, glycerol monostearate (MSG), high molecular weight polyethylene glycol (PEG), sodium salt of lauryl sulfonic acid (lauryl Na);

– as a dispersing agent: polyethylene wax brand WP2E.

Samples of superconcentrates were made on a twin-screw extruder with a ratio of L/d = 36, a filter mesh with a nest diameter of 0.2 mm, and a die diameter of 4 mm. The temperature at the outlet of the auger 160–170 °C.

Determination of the quality indicators of pigment superconcentrates was performed on the high-pressure polyethylene samples of grade 15803-020 not lower than the first grade. Film samples were made by extrusion.

Color control was performed in daylight reflected visually and using a spectrophotometer by comparing the obtained sample with the corresponding sample – the color standard. The color of the sample must match the color of the reference sample. The comparison was performed in the CIELAB color model. Printex U gas soot was the standard, which was the most suitable in terms of tone and degree of painting.

Determination of heat resistance of the dye was performed in a closed removable mold equipped with a thermocouple or thermometer.

To do this, make 3 samples by extrusion. Gaskets made of aluminum foil, cellulose or polyethylene terephthalate film were used to prevent the samples from sticking to the surface of the heated mold.

One of the samples was placed in a preheated to 40-50 ^{o}C mold and heated to (220±5) ^{o}C at a specific pressure of 3.43 MPa. The sample was kept in a closed mold for 15 minutes at a temperature of (220±5) ^{o}C and a specific pressure of 3.43 MPa, after which the mold was cooled at room temperature to 145-150 ^{o}C, and after reaching this temperature further cooling to 40-50 ^{o}C was performed in a cold press at a specific pressure of 3.43 MPa.

The second sample was heated to (250±5) ^{o}C and kept at this temperature and specific pressure of 3.43 MPa for 3 minutes. Heating and cooling of the second sample was performed similarly to the first. The third sample was considered control.

After the visual comparison tests, the color of the samples must not change in comparison with the color of the control sample.

Determination of light fastness of painting was performed on painted samples with a size of (20×50) mm.

The samples were kept for 96 hours. in a chamber equipped with a mercury-quartz lamp DRT-400. A drum rotates around the lamp at a speed of 10 rpm. The test specimens were fixed with

clamping plates on the inner surface of the drum, at a distance of 200 mm from the lamp. The temperature of the air inside the drum at the level of the samples should be (50±5) ºC, and the illumination of the surface of the samples, measured with a luxmeter, should be (20000±2000) lux. Intermittent irradiation is allowed.

Irradiation should be carried out with proper supply and exhaust ventilation. Before irradiation, the new lamp must work idle for 50 hours. The useful life of the lamp is 500 hours.

Other design of the installation for irradiation is allowed, but with application of the DRT-400 lamp of the same light and temperature modes.

Evaluation of light fastness is performed by changing the color in daylight reflected by visual comparison of irradiated samples with the original non-irradiated [14].

The resistance of the painted polymer to light is evaluated by an eight-point system (table 1).

Table 1. Light resistance evaluation system

Mark	Type and depth of the observed change
8	Invariant color of the sample corresponding to the color of the original sample.
7	Very weak discoloration, which is noticeable only when compared with the original sample.
6	Weak discoloration, which is noticeable when compared with the original sample.
5	Noticeable discoloration, which is manifested without comparison with the original sample, but the polymeric material still retains commercial and industrial value.
4	Significant discoloration, the polymer material is mostly unusable.
3	Strong discoloration.
2	Very strong discoloration.
1	Almost complete discoloration
0	Complete discoloration, the polymer material acquires the color of the polymer itself.

Determination of the migration stability of superconcentrates of pigments was performed on painted samples of polyethylene size (10×10) mm and polyethylene painted white UPC size (20×20) mm.

The stained sample was placed between two samples of white polymer. The samples were loaded at a rate of 9.8 N and kept in a thermostat at a temperature of (80±5) ºC for 24 hours. At the end of this time, the cargo was removed and white samples were examined. Migration was determined in daylight scattered by visual comparison of the original white sample and samples that were in contact with the tested stained sample. White samples should not be stained.

Determination of the number of agglomerates of pigments. The method is based on determining the number of pigment agglomerates with a size of 0.2-0.5 mm and more than 0.5 mm in a thin polyethylene film, which is extruded from a mixture of polyethylene granules and pigment superconcentrates [15]. High pressure polyethylene was manually mixed with a superconcentrate taken in an amount of 2% by weight of the polymer.

From the mixture of granules on the extrusion film unit by pneumatic stretching was obtained painted film with a thickness of 80-100 μm (two layers) at the temperature specified in (table 2):

From the obtained film (from the most intensely colored area) a film weighing (10.0±0.2) g (approximately 20×50 cm) was selected and cut on one side for single-layer viewing.

The film was visually viewed in transmitted light, for which it was placed between an observer and an electric lamp with a power of 50-75 W.

The size of the agglomerates of pigments was determined using a measuring magnifier or measuring microscope BCH-2. Then calculated the number of agglomerates ranging in size from 0.2 to 0.5 mm and more than 0.5 mm

Tests of the painted film were performed in parallel with the unpainted one.

An extrusion plastomer was used to determine the melt flow index (MFI), the measuring unit of which consists of an extrusion chamber, a piston, a capillary and an additional load.

Table 2. Temperature regime

Heating zones	Processing temperature, [°C]
1 zone	80 ± 10
2 zone	120 ± 10
3 zone	150 ± 10
4,5,6 zones	160 ± 10

A Dinstat-type device was used to determine the toughness and flexural strength.

To select the optimal composition used a generalized desirability function, which is a unique, unique and universal indicator of the quality of polymeric materials, which allows taking into account the degree of weight of a finished product and the requirements of consumer industries [16].

According to the selected objects of study, formulations of concentrate compositions were developed for further studies, which are shown in table 3.

Table 3. Recipes for the preparation of superconcentrates

Sample	The content of active substances in the superconcentrate, [%]								
	PE 15803-003	Wax WP2E	Stearate Ca	Lauryl Na	PEG	MSG	Carbon N220	Carbon P803	Carbon Printex U
1 check	22	38	-	-	-	-	40	-	-
2 check	22	38	-	-	-	-	-	40	-
3 check	22	38	-	-	-	-	-	-	40
1 test	22	33	5	-	-	-	40	-	-
2 test	22	28	10	-	-	-	40	-	-
3 test	22	33	5	-	-	-	-	40	-
4 test	22	28	10	-	-	-	-	40	-
5 test	22	33	-	-	5	-	40	-	-
6 test	22	28	-	-	10	-	40	-	-
7 test	22	33	-	-	5	-	-	40	-
8 test	22	28	-	-	10	-	-	40	-
9 test	22	33	-	-	-	5	40	-	-
10 test	22	28	-	-	-	10	40	-	-
11 test	22	33	-	-	-	5	-	40	-
12 test	22	28	-	-	-	10	-	40	-
13 test	22	33	-	5	-	-	40	-	-
14 test	22	33	-	5	-	-	-	40	-

Research of physical and mechanical properties

For the study used compositions of low pressure polyethylene grade 273, containing 2 wt.% concentrate, mixed in a laboratory extruder. Data for soot brands P803 and N220 are shown in tables 4, 5 and figures 1-6. Tests of physical and mechanical properties were performed according to the method [16].

Table 4. Carbon black brand P803

Indicator	Check sample 3	Calcium stearate		Lauryl Na		Glycerol monostearate		Polyethylene glycol	
		5 %	10 %	5 %	10 %	5 %	10 %	5 %	10 %
Impact strength, [kJ/m^2]	38.7	41.2	41.0	41.2	49.8	43.2	41.0	37.4	38.8
Bending stress σ_{bs}, [MPa]	70.5	98.2	70.9	45.9	68.3	83.6	37.1	36.2	61.8
Shrinking, [%]	6.4	5.6	5.4	5.0	5.8	6.6	5.6	5.8	7.6

Table 5. Carbon black brand N220

Indicator	Calcium stearate		Lauryl Na		Glycerol monostearate		Polyethylene glycol	
	5 %	10 %	5 %	10 %	5 %	10 %	5 %	10 %
Impact strength, [kJ/m^2]	39.0	38.7	34.9	36.7	32.4	33.5	32.6	38.9
Bending stress σ_{bs}, [MPa]	31.2	43.1	63.2	65.7	85.7	55.5	69.6	68.8
Melt flow index (MFI), [g/10 minutes]	5.2	5.4	4.8	5.9	7.6	4.9	6.4	6

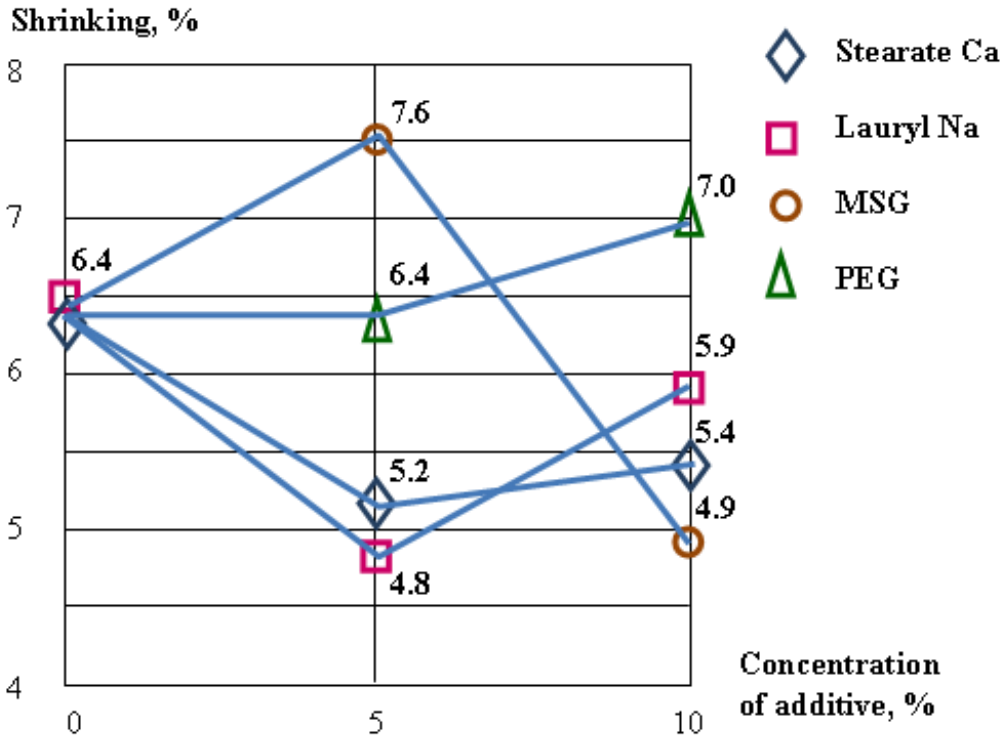

Fig. 1. Shrinkage of the composition based on carbon black brand N220 depending on the concentration of the additive

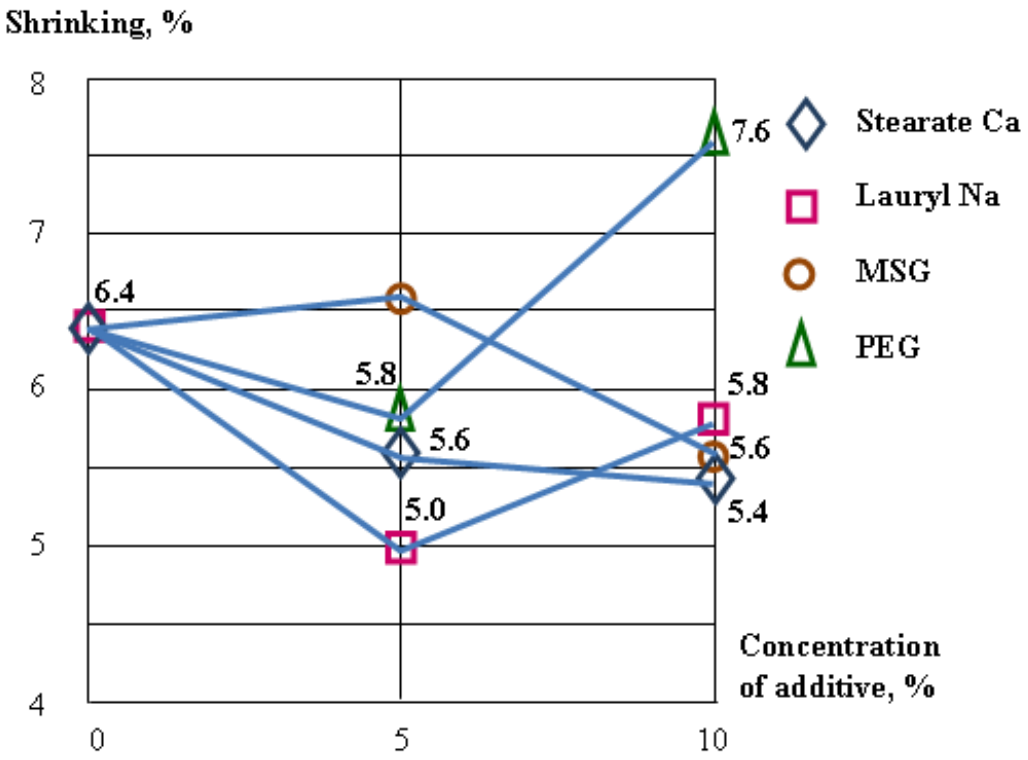

Fig. 2. Shrinkage of the composition based on carbon black brand P803 depending on the concentration of the additive

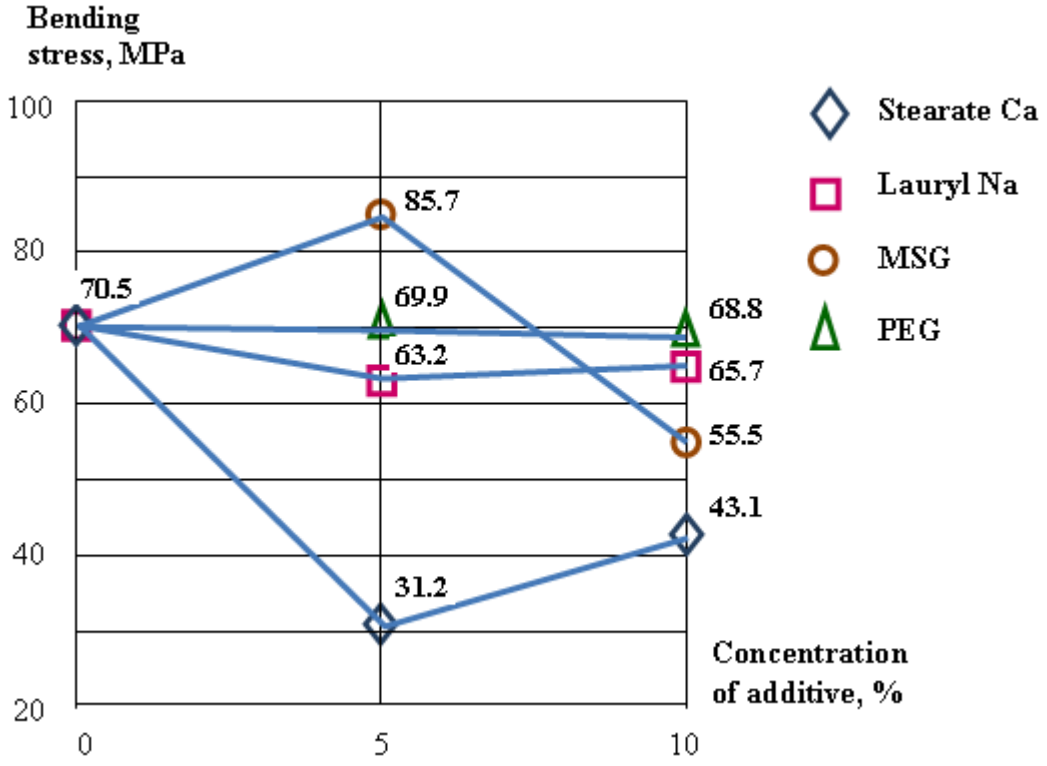

Fig. 3. Bending stress of the composition based on carbon black brand N220 depending on the concentration of the additive

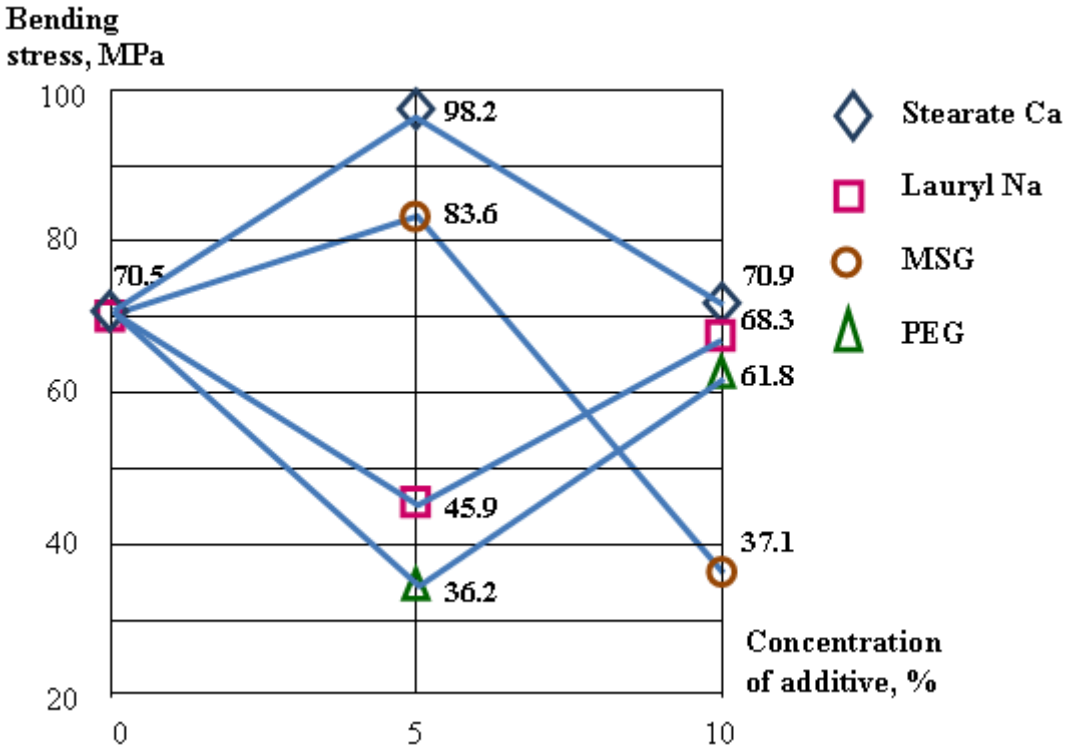

Fig. 4. Bending stress of the composition based on carbon black brand P803 depending on the concentration of the additive

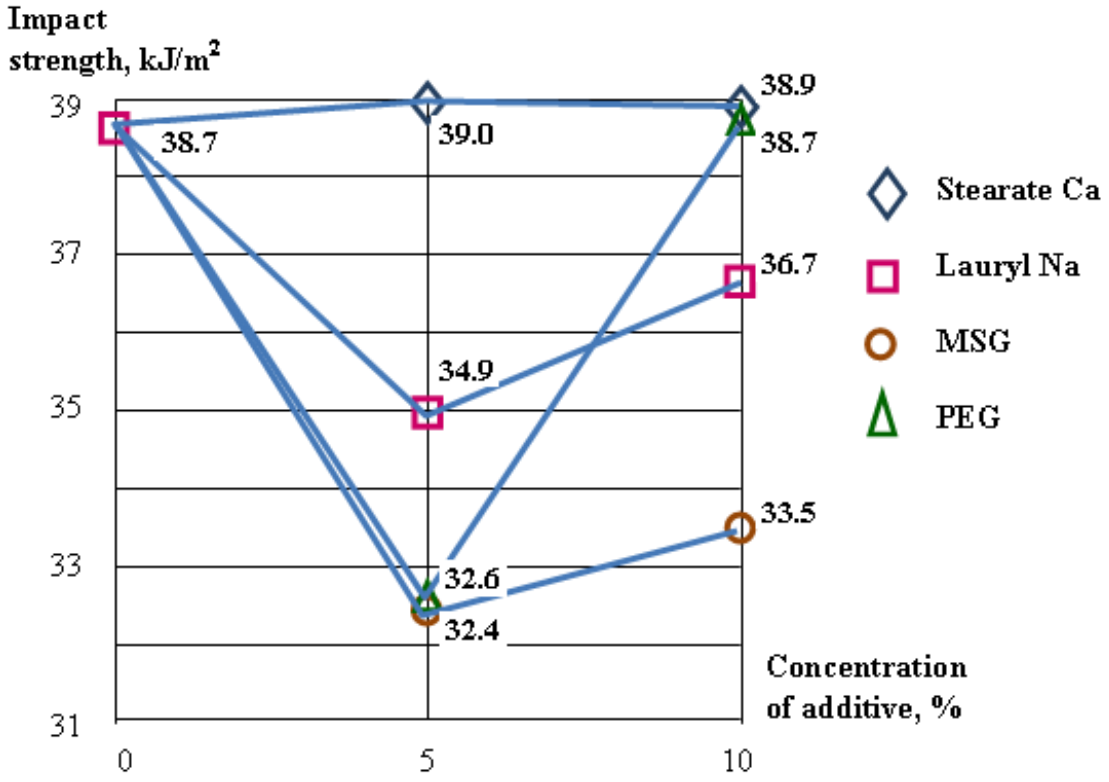

Fig. 5. Impact strength of the composition based on carbon black brand N220 depending on the concentration of the additive

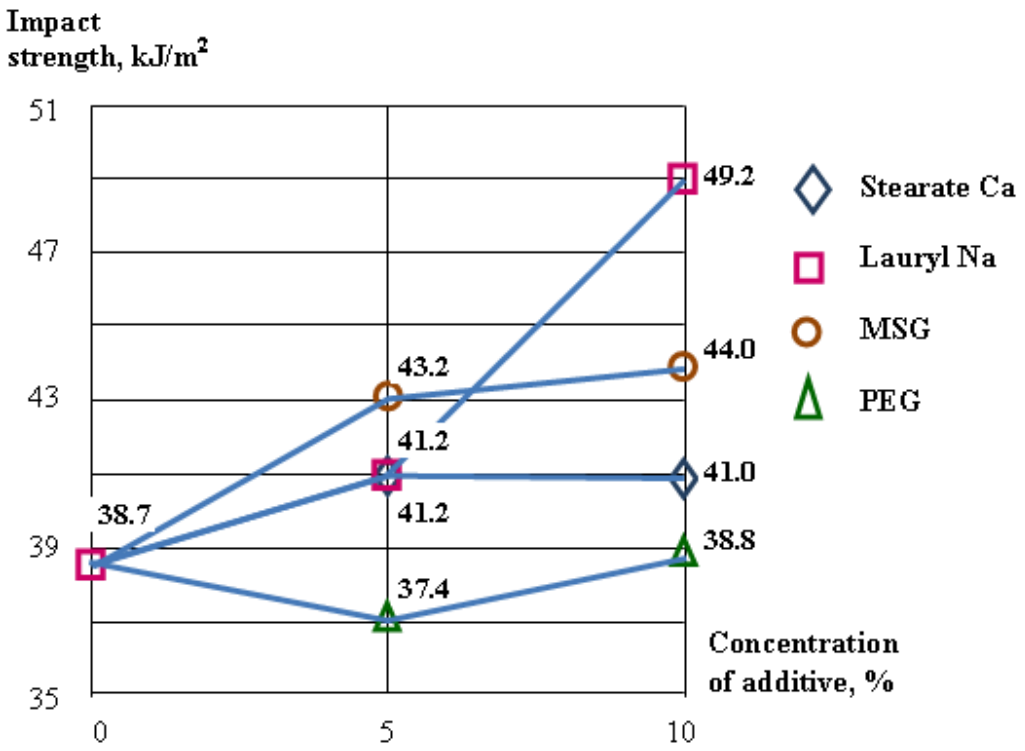

Fig. 6. Impact strength of the composition based on carbon black brand P803 depending on the concentration of the additive

As can be seen from the tables and figures, the selected modifiers ambiguously affect the properties of polyethylene samples. Thus, with the introduction of lauryl Na there is a decrease in shrinkage in the studied concentrations. The introduction of small amounts of glycerol monostearate (5 wt.%) leads to an increase in shrinkage compared to the base composition, but an increase in the content of this surfactant leads to a sharp decrease in shrinkage, which is observed for both types of carbon black. For carbon P803 (except PEG) the use of the proposed modifiers, all concentrations increases the toughness and flexural strength, and for N220 vice versa. In our opinion, this is due to the dispersion of carbon and methods of its production (carbon P803, in contrast to N220 is not subject to additional granulation and therefore better dispersed in the composition, respectively, has better performance compared to baseline).

Research of dyes of concentrates

For the study used compositions of high pressure polyethylene brand 15803-003, containing 2 wt.% concentrate. Research data are presented in Table 6 and Figures 7-10.

Table 6. Test results

Sample	Test methods											
	Color evaluation				Heat resis-tance at 250°C, [min.]	Light fast-ness, [mark]	Migration stability	The number of agglomerates, [pieces]		Specific density, [kg/m^3]	Bulk density, [kg/m^3]	MFI, [g/10 min.]
	a	b	L	ΔE				0.2-0.5 mm	more than 0.5 mm			
1	2	3	4	5	6	7	8	9	10	11	12	13
1 check	0.03	0.05	0.13	0.14	15	7-8	No migration	2500	300	1109	728	0.6-1
2 check	0.05	0.41	1.09	1.17	15	7-8	No migration	800	20	1098	725	0.5-1

1	2	3	4	5	6	7	8	9	10	11	12	13
3 check	-	-	-	-	15	7-8	No migration	50	-	1125	729	0.5-1
1test	0.02	0.04	0.09	0.08	15	7-8	No migration	500	100	1105	728	0.5-1
2 test	0.05	0.04	0.10	0.11	15	7-8	No migration	300	60	1100	727	0.3-0.8
3 test	0.07	0.36	1.25	1.34	15	7-8	No migration	200	-	1096	723	0.5-1
4 test	0.06	0.38	1.23	1.29	15	7-8	No migration	100	-	1093	722	0.4-0.9
5 test	0.06	0.06	0.13	0.16	15	7-8	No migration	3000	400	1103	729	0.6-1.1
6 test	0.02	0.05	0.12	0.13	15	7-8	No migration	4000	600	1106	730	0.5-1
7 test	0.02	0.12	0.98	0.98	15	7-8	No migration	500	100	1098	726	0.5-1
8 test	0.04	0.18	1.02	1.09	15	7-8	No migration	700	150	1096	727	0.4-0.9
9 test	0.03	0.05	0.12	0.14	15	7-8	No migration	1800	220	1105	725	0.6-1.2
10 test	0.03	0.02	0.13	0.13	15	7-8	No migration	1600	200	1100	724	0.5-1
11 test	0.07	0.42	1.05	1.14	15	7-8	No migration	600	-	1098	723	0.5-1.1
12 test	0.06	0.35	1.16	1.24	15	7-8	No migration	400	-	1096	722	0.5-0.1
13 test	0.06	0.03	0.10	0.11	15	7-8	No migration	1200	80	1105	726	0.5-1
14 test	0.07	0.43	1.11	1.19	15	7-8	No migration	120	-	1095	724	0.5-1

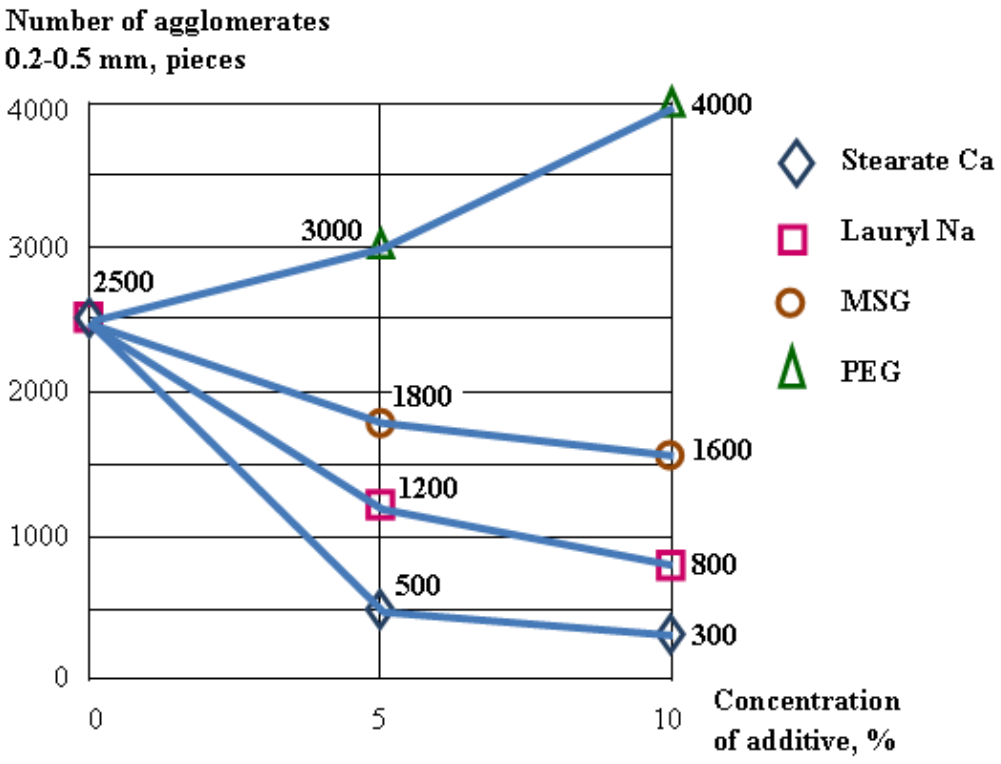

Fig. 7. The amount of agglomerates 0.2-0.5 mm in the painted sample concentrate based on carbon black brand N220 depending on the concentration of the additive

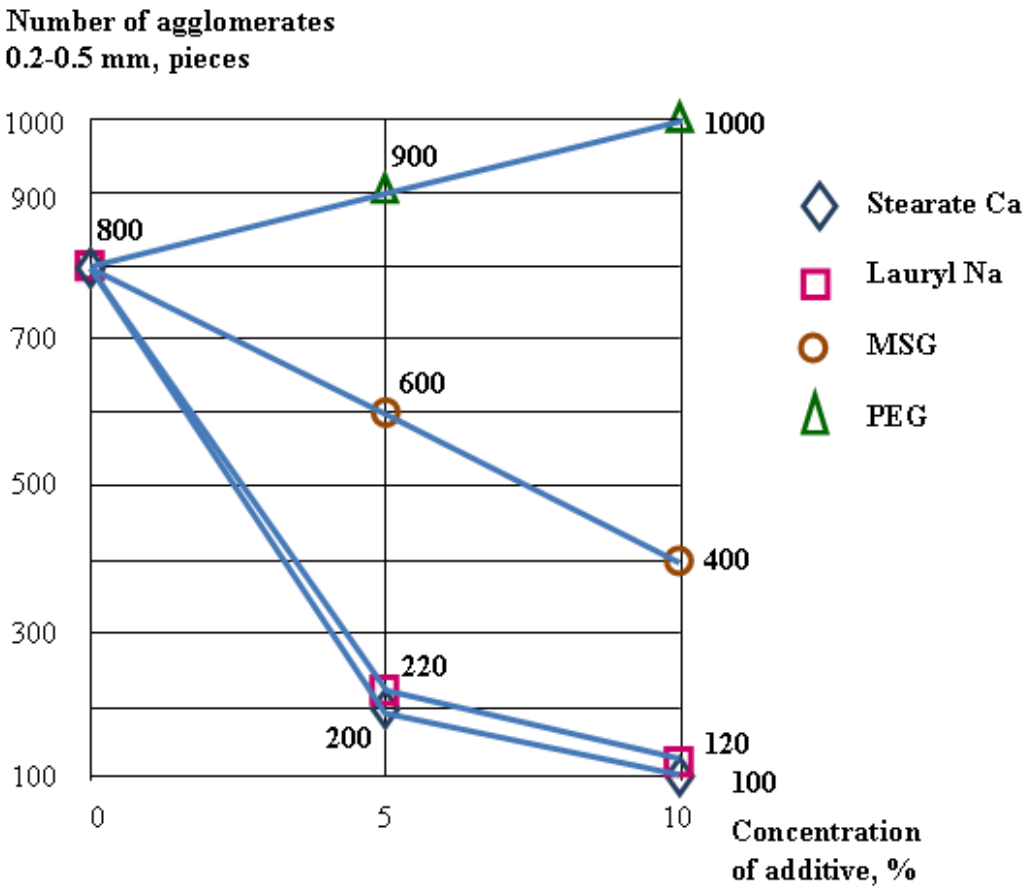

Fig. 8. The number of agglomerates of 0.2-0.5 mm in the painted sample concentrate based on carbon black brand P803 depending on the concentration of the additive

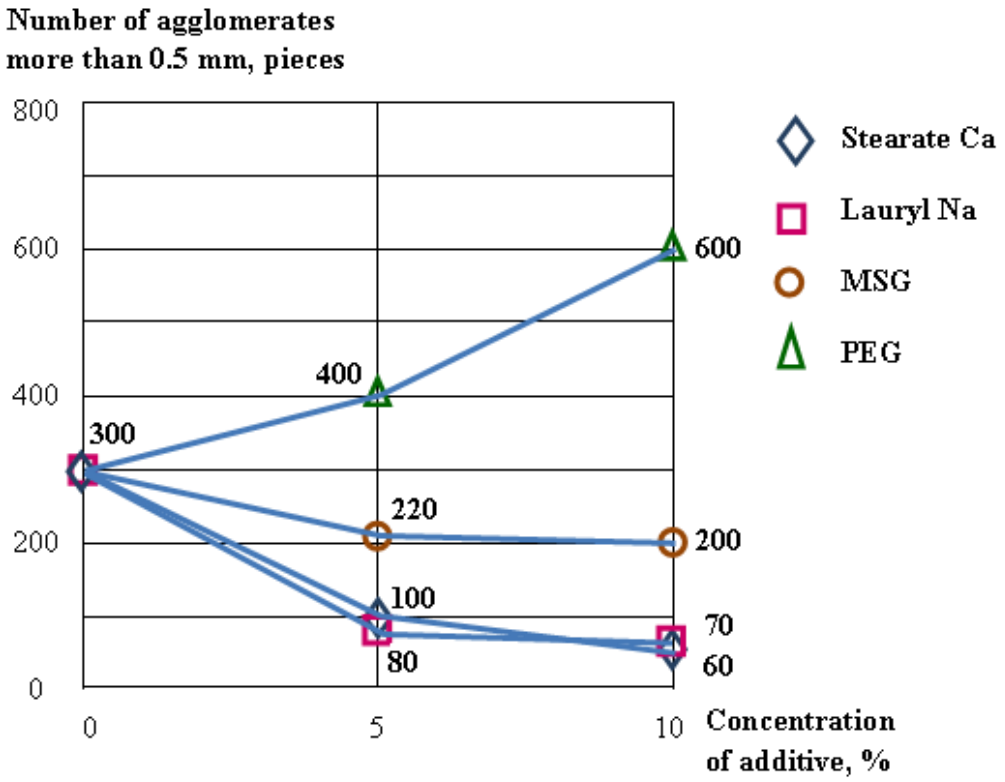

Fig. 9. The number of agglomerates over 0.5 mm in the painted sample concentrate based on carbon black brand N220 depending on the concentration of the additive

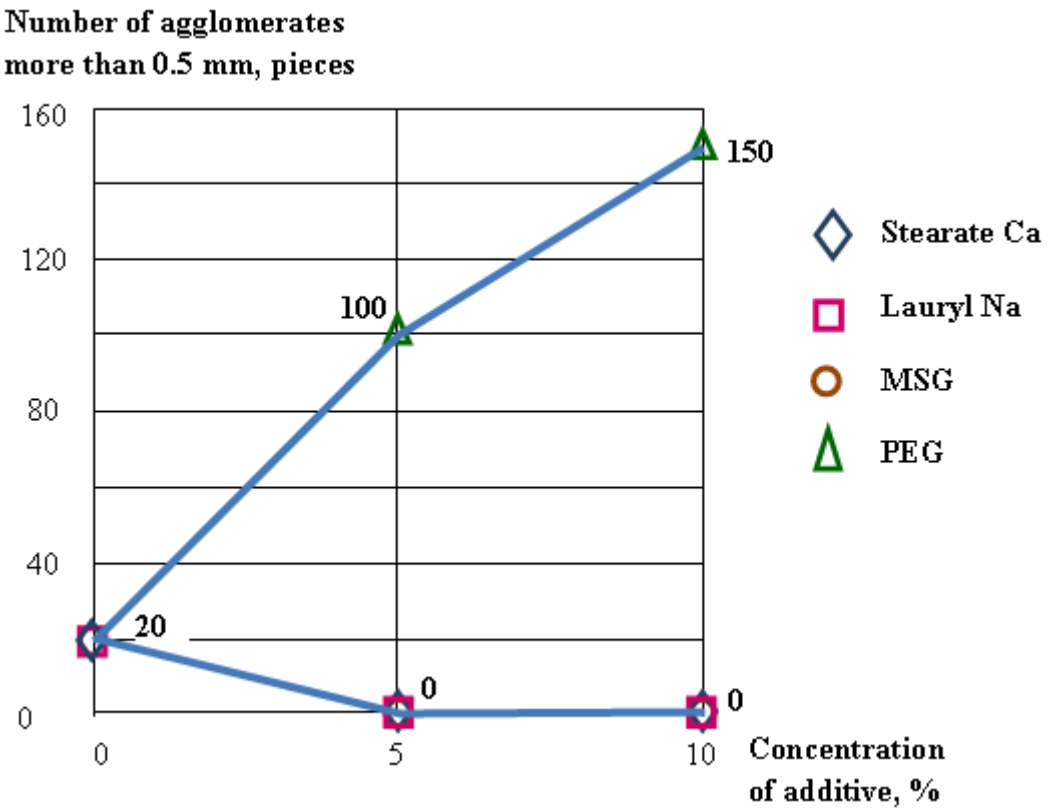

Fig. 10. The number of agglomerates more than 0.5 mm in the painted sample concentrate based on carbon black P803 depending on the concentration of the additive

According to the results of the experiment on the development and production of black superconcentrate, the analysis of films painted with concentrate samples was performed according to the main indicators: color, coverage, amount of agglomerates (pigment dispersion in polymer mass), and staining intensity.

Printex soot-painted film, which has no inclusions, has a uniform color and high coverage, was taken as a model.

The basic sample with the content of soot of the P803 brand very much differs from the accepted standard on color and degree of painting - coverage. The samples have a bluish tinge and low coverage but better dispersion of the pigment. Samples containing soot brand N220 have identical color and coverage, but have low dispersion of pigment in the polymer.

The introduction of PEG as a surfactant in the formulation led to an increase in the number of agglomerates and a deterioration in the intensity of staining.

The introduction of glycerol monostearate led to a slight reduction in agglomerates but added a new useful property for film producers – the surface became shiny and increased the sliding coefficient of the film.

The introduction of Ca stearate led to a significant improvement in the quality of staining and a significant reduction in the number of agglomerates.

The content of sodium lauryl also led to a significant reduction in agglomerates.

Conclusions

Thus, the most effective additive to improve the coloring properties of the soot pigment brand N220 and improve the appearance of the finished product painted with concentrate, experimentally isolated calcium stearate with 10 wt.% introduction into the superconcentrate.

At the mixing stage in the extruder, Ca stearate acts as a surfactant and prevents the adhesion of the pigment and the formation of agglomerates in the polymer melt.

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