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Iron oxide pigment as a coloring nanofill for decorative concrete products

Elmira K. Aminova*, Lilia Z. Kasyanova, Aigul A. Islamutdinova, Lilia R. Asfandiyarova
Branch of the Ufa State Petroleum Technological University in Sterlitamak, Sterlitamak, Russia
* Corresponding author: e-mail: k.elmira.k@yandex.ru

ABSTRACT: Introduction. Current research on the performance properties of decorative concrete, when added to the concrete mixture of nano pigments are more recommendatory. In the academic literature, it is recommended to introduce pigment in the amount of about 5% of the total cement mass when creating improvement elements. The recommendations described above often demonstrate the potential for using nano pigments in terms of the influence of the amount of nano-additive applied on the uniformity of the coating texture. Characteristics such as intensity and retention time of the resulting color are also taken into account. In RF we do not have approved regulations on how to use pigments for concrete coloring. Pigments are obtained mainly from iron oxides due to their availability and low toxicity to the human body, and are promising nanomaterials in construction. **Methods and materials.** The study is aimed at the use of iron oxide pigment obtained from a spent iron oxide dehydrogenation catalyst as a coloring nanofiller and improving the strength characteristics of decorative concrete products. Spent iron oxide catalysts containing iron oxide particles are considered as a by-product of chemical production. The purpose of this study is to use a pigment (in the form of Fe_2O_3 and Fe_3O_4) obtained from the composition of a spent iron oxide catalyst as an additional binder and coloring nanomaterial in the composition of decorative concrete products. The effect was evaluated by testing mechanical properties such as strength, color, water absorption, water and frost resistance. **Results.** The research results have shown that the use of nanopigment in the technology of concrete production improves the properties of cementing composites (cement) and allows you to change the color of products. **Conclusion.** This study consists in the application of an iron oxide nanopigment obtained from a spent catalyst for the dehydrogenation of olefins and alkylaromatic hydrocarbons in decorative concrete products with the provision of mechanical characteristics and chromaticity of products.

KEYWORDS: decorative concrete products, spent catalyst, nanopigment.

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INTRODUCTION

The improvement of construction technologies today occupies one of the main directions in the research process. Great importance is given to the construction of residential buildings and public facilities. Finishing the facades of such structures plays an important role, and strict requirements are imposed on it. The color scheme of modern construction structures and art objects has very wide possibilities. For this purpose, colored dry mixes are used for construction and finishing works, such as building walls, panels, building blocks and other building structures. Decorative concrete charge is obtained in practice using painted cements or by introducing dyes into the composition of building mixes [1–2]. The Portland cement medium is alkaline, so the additive introduced into it must be resistant to an alkaline environment. Also, one of the important characteristics in the preparation of the charge is to take into account the coating capacity, which is characterized not by a decrease in the strength characteristics of decorative concrete products, but by their improvement, also taking into account the consumption rate of the binder. In the manufacture of most decorative concrete materials, yellow, red, black and brown colors are used, the basis of which is an iron oxide pigment. These pigments can be both natural and synthetic. Natural pigments are rarely used in the production of concrete coatings, due to their low performance characteristics, such as moisture capacity, low brightness of such materials and quality variability. The future of decorative concrete products in their production lies in the use of specific nanopigments with variable capabilities according to customer requirements. It should be noted that synthetic pigments have a high coloring and covering ability.

The improvement of the technology of using pigments in building materials has led to the development and application of pigments that are particles less than 100 nanometers in size. The use of nanopigments in concrete has a number of advantages, such as a deeper and richer color, improved UV resistance and durability of the material [3–9].

Experiments with pigments in concrete began in the late twentieth century. However, they were initially limited to laboratory applications and had no industrial applications.

With the advent of new technologies and the development of technologies in recent decades, the use of nanopigments in concrete has become increasingly popular. With the help of nanopigments, it became possible to achieve a wide range of color shades and create unique design solutions for decorative elements made of concrete.

Due to their small size, nanopigments are mixed with the concrete mixture at the molecular level, ensuring uniform color distribution in the material. This allows you to create a deeper and richer color that surpasses traditional pigments in the quality of concrete coloring. One of the main advantages of using nanopigments in concrete is their high resistance to ultraviolet radiation and external influences. Due to this, the concrete surfaces painted with pigments retain their brightness and color stability for a long time.

In the recent past, construction companies used synthetic stone material obtained on the basis of water, sand and crushed stone in the production of concrete mixtures. By mixing these components, solid and durable compositions are obtained. Such compositions characterize themselves well when obtaining foundations, walls, ceilings, cladding materials for internal and external surfaces. Currently, high requirements for the service life of building materials are imposed, as a rule, not less than ten years. They are mainly used in the design of homesteads, parks, shopping centers, squares that are under the influence of an aggressive environment.

Today, the use of nanopigments in concrete has found wide application in the construction industry. They are used to create decorative elements such as sidewalk slabs, wall panels, building facades and other architectural structures. Yellow oxide nanopigments open up new opportunities for designers and architects, allowing them to create unique and visually attractive elements from concrete.

In general, the use of pigments based on a mixture of Fe (II) and Fe(III) in concrete is a modern technology that allows achieving high aesthetic appeal and durability of painted concrete surfaces. This technology continues to evolve, and it is expected that in the future its application in construction and design will become more widespread and innovative.

Industrial production of nanomaterials during finishing works is currently growing rapidly. Decorative cement concrete products are in great demand, the main disadvantage of which is low resistance in aggressive environments, in conditions with variable temperature changes, such as freezing and thawing, as well as resistance to impact and abrasion. Therefore, obtaining mixtures for the manufacture of decorative concrete products with improved characteristics is an urgent and promising task.

To date, there are no regulatory documents and quality standards for the use of pigments in painting decorative concrete and other building materials in our country. European companies use in the production of these materials the international standard EN 12 878 “Pigments for coloring building materials on cement and lime binder” [10–11], the United States uses the standard ASTM C 979 “Pigments for Integrally Colored Concrete” [12]. When applying these standards, the effect of the pigment on the curing time of the cement mixture and on the strength of the final product is taken into account.

An analysis of studies that relate to the application of nanopigment additives in concrete and decorative mixtures shows that this topic is poorly studied and is interesting and useful from the point of view of industrial waste disposal.

Due to the demand of the population, every year more and more attention is paid to the construction of both civil and public facilities, squares and parks, where decorative concrete materials of various colors are an integral part of the decoration [13–20].

METHODS AND MATERIALS

The paper proposes a method for environmentally friendly processing of catalyst waste hydrogenation of unsaturated hydrocarbons to obtain a valuable product – nanopigment. Pigment – iron oxide nano-additive – improves the strength properties of concrete and allows you to get bright solid concrete masses. Reducing efflorescence is also a positive aspect of its use.

One of the pigments widely used in decorative concrete is iron oxide pigment. It is necessary to note some features of iron oxide pigments and their use in decorative concrete. It is iron oxide pigments that offer a wide range of colors, including shades of red, yellow, brown and black. This allows designers and architects to choose the right color to create aesthetically attractive and individual surfaces made of decorative concrete. In addition, they are highly resistant to UV rays, fading, moisture, chemicals and mechanical wear. This makes them an ideal choice for use in open spaces, including building facades, sidewalks, playgrounds and other landscape elements. Environmental safety is quite important. Iron oxide pigments as nanofillers are environmentally safe and do not contain heavy metals or harmful chemical compounds. They do not have a negative impact on the environment and human health, which makes them the preferred choice for use in construction and repair. In this work, an iron oxide pigment obtained from a spent iron-containing catalyst is used, which increases the attractiveness of the work in connection with solving the problems of solid waste disposal and obtaining environmentally friendly products for construction.

Spent iron oxide catalysts, depending on their modification, contain up to 80% iron oxides in the form of hematite and magnetite. The water-soluble components of the catalyst form an alkaline medium. Freed from water-soluble components, followed by drying and grinding in a disintegrator up to 3–20 microns, the product is a mixture of iron oxides in the form of Fe_2O_3 and Fe_3O_4.

The Portland cement medium is alkaline, so the additive introduced into it must be resistant to an alkaline environment. And when preparing the charge, it is necessary to take into account the coating capacity, which does not reduce the strength characteristics of decorative concrete products, as well as taking into account the consumption rate of the binder [8].

RESULTS

The most popular colors for the consumer are yellow, red, brown and black. The nanopigment obtained by us from the spent iron oxide catalyst is a red-brown product, the characteristics of which are presented in Table 1.

Bayer pigments are used in Europe. These pigments demonstrate high quality, but are very expensive. Thus, when used on a large scale in the production of building materials, in particular decorative concrete products, it leads to high costs for the consumer.

The attractiveness of the proposed nanopigment is its low cost due to the use of a spent iron oxide catalyst as a raw material.

The assessment of the quality of the obtained pigment as a nanofiller for decorative concrete products was carried out by preparing concrete products with subsequent testing of the obtained samples according to the following indicators: testing of mechanical properties, such as strength, color, water absorption, resistance to changes in climatic conditions, such as heat and frost resistance.

Table 1
Physico-chemical parameters of the pigment obtained from spent iron oxide catalysts

Indicator	Pigment
1. Fe_2O_3 content, % by weight.	83.79
2. Water-soluble compounds, % by weight	0.7996
3. pH of the water extract	6.0
4. The residue after dry sieving on a sieve with a grid 016, %	1.3

To do this, a series of experiments were carried out, including the preparation of concrete products with different concentrations of pigments.

For the preparation of the material, components were used, such as: M500 cement, OPTILUX superplasticizer C3 (OPTILUX) for concrete and mortar (meets the requirements of GOST 24211), nanopigment (from a spent iron oxide catalyst), water [21].

The preparation of the concrete mixture was carried out in a laboratory mixing plant. The mixing time was 2–3 minutes. The finished concrete mixture was placed in a mold to create samples. All samples were hardened under natural conditions.

Obtaining a spectrum of colors depends on the amount of pigment added. We studied the effect of the amount of pigment in the range of 3.3–40% by weight. with the production of products of a color range from light brown to dark brown. The formulation of the obtained samples is presented in Table 2.

With the addition of pigment above 40%, it was impossible to obtain samples of concrete products with a uniform smooth surface. For further studies, samples with a pigment content of 3.3, 16.67, 26.67 and 40% were selected.

To test the frost resistance, product samples were placed in a freezer for 2.5 hours at a temperature of minus 18±2°C. Then the samples were placed 20 mm apart and subjected to thawing. After saturation with water, the samples were drained with a cloth and placed at a distance of 20 mm from each other and the walls in a freezer. Then they turned on the camera and began to slowly lower the temperature. The initial freezing temperature of the samples is 16°C.

The studied samples were placed in a bath after freezing and subjected to thawing at a temperature of plus 20–22 degrees.

Calculations:

Calculation of the change in the mass of samples Δm, according to the formula

$$\Delta m = \frac{m - m_1}{m} \cdot 100,$$

where m is the mass of the sample before freezing and thawing, g; m_1 is the mass of the sample after freezing and thawing, g.

The average maximum permissible decrease in the mass of the samples should not exceed 2%.

According to the results presented in the table, samples with a pigment concentration of 13.3 and 26.6% meet the requirements.

The products were tested for water resistance by immersing the samples in a container with water for 24 hours. After passing this time , the following observations were made:

- samples do not stain the surfaces with which they interact;
- there were no visual changes;
- the water in which the samples were located has no changes in color;
- the strength characteristics of the samples with a pigment concentration of 3.3, 13.3 and 26.6% met the requirements of GOST 10180-90 [22].

The obtained samples were subjected to a heat resistance test.

The samples were placed in a drying cabinet with a set temperature of 50°C for 3 hours. After cooling the samples in natural conditions, the following conclusions were made: no visual changes were detected; no damage was detected by mechanical action (hands); no traces are left when they come into contact with surfaces.

The strength of the studied samples was determined according to GOST 10180-90.

The study of concrete samples for strength consists in measuring the minimum efforts that destroy pre-prepared decorative concrete samples prepared in accordance with regulatory documents. All samples were subjected to the study of strength characteristics after they were maintained at low and elevated temperatures. The samples of decorative concrete, being at rest, were subjected to static loading, the load increase occurred gradually, after which the stress was calculated under these conditions and assumptions of the elastic work of the obtained materials were put forward. The results of laboratory studies of the obtained samples for strength after tests for heat resistance and frost resistance are presented in Table 4.

The research results indicate that the addition of iron oxide nanopigment to the concrete mixture increases the strength of the products and does not change the properties of the samples obtained during tests for heat resistance and frost resistance. However, when a nanopigment is introduced in an amount of 40%, the samples crumble.

The pigment based on the applied nano-additive, in addition to coloring properties, fills the decorative con-

Table 2
Sample formulation

Pigment, g	Cement, g	Sand, g	Water, ml	Percentage of pigment, %
2	20.05	37.96	15	3.3
4	19.35	36.65	15	6.67
6	18.66	35.34	15	10
8	17.97	34.03	15	13.3
10	17.28	32.72	15	16.67
12	16.59	31.41	15	20
14	15.9	30.10	15	23.3
16	15.21	28.79	15	26.67
18	14.52	27.48	15	30
20	13.82	26.18	15	33.3
22	13.13	24.87	15	36.67
24	12.44	23.56	15	40

Table 3
Results of studies of samples for frost resistance

Percentage of pigment in the sample	Mass of the sample before tests (g)	Mass of the sample after the test, (g)	Change in the mass of samples, (g/%)
3.3%	62.2	60.4	2.2/3.5%
13.3%	61.5	60.5	1.0/1.6%
26.6%	60.4	59.7	0.7/1.1%
40%	60.1	58.4	1.7/2.8%

Table 4
Results of strength testing of samples

The amount of nanopigment in the sample, g	Percentage of pigment in the sample, %	Compression (sample before heat resistance and frost resistance tests) MPa	Compression (sample after heat resistance test), MPa	Compression (sample after frost resistance test), MPa
0	0	52.6	52.6	52.7
2	3.30	52.2	52.2	52.0
10	16.6	53.9	53.9	53.6
16	26.6	54.0	54.0	54.4
24	40.0	52.2	52.2	52.2

crete material at the initial stages of mixing, forms crystallization centers, the so-called embryos, then the growth of crystals, their hardening.

Research in this field notes that the resulting nanoparticles, consisting of hydrated iron oxide, are in the α-form.

The α-form of hydrated iron oxide is the germ that initiates the processes of crystal formation and participates in the formation of the structurality of the material. These are the two factors that most affect the color gamut of the resulting nanopigment. For example, in order to get brighter shades and achieve color purity, it is necessary to obtain finely dispersed nanopigments. When the particles are enlarged, the color of the pigment becomes dull. Therefore, it is necessary to understand the need for preliminary grinding before use, since the processes of pigment caking are not excluded. Laboratory tests have shown that when forming a charge using gray cement, the introduced pigment improves the performance characteristics of concrete. It should be borne in mind that the clearest shades of decorative concrete materials can be obtained only when using white cement. The difference in the use of gray or white cement is minimal when obtaining brown or red concrete. When obtaining black concrete, it is preferable to use gray cement.

According to statistics, the brick-red shade of decorative concrete materials is in the greatest demand among consumers. The nanopigment obtained by us on the basis of iron oxide is the most promising from the point of view of its production on an industrial scale. It is possible to obtain samples with a sufficiently intense color even with its insignificant content (3–4%). This fact undoubtedly has economic attractiveness from the point of view of its practical application (Fig. 1).

According to the conducted studies, according to the intensity of coloring, all samples can be offered to potential consumers, depending on their preferences.

DISCUSSION

Obtaining iron oxide nanopigment from the waste of olefin dehydrogenation processes makes it possible not only to reduce the environmental burden, but also to obtain a valuable product – a coloring pigment widely used in the production of building materials. When iron oxide pigment was introduced into the composition of the concrete charge for the production of decorative concrete products, the following results were obtained:

– the introduction of a brick-red iron oxide nanopigment into the concrete mixture in an amount from 3.3 to 23.0% is accompanied by an increase in strength to 53–54 MPa, while the strength characteristics of

3.3% **13.3%** **26.6%** **40.0%**

Fig. 1. **Concrete samples obtained on the basis of white cement containing iron oxide nanopigment**

concrete products without the introduction of pigment turned out to be less durable;
- the introduction of iron oxide nanopigment into the concrete mixture allowed to reduce the consumption of raw materials;
- by varying the percentage of coloring pigment, it is possible to adjust the color intensity in accordance with the requirements of the consumer.

CONCLUSION

This paper shows the possibility of using iron oxide nanopigment as a coloring additive that improves the strength characteristics of decorative concrete products. It was found that with the addition of iron oxide nanopigment from 16...26%, it is possible to obtain samples with the best strength characteristics of decorative concrete products. In addition, reducing the cost of purchasing B25 cement when added to concrete mixes will increase hardening and strength by introducing iron oxide nanopigment up to 26%.

It is relevant to organize the production on an industrial scale of iron oxide nanopigments based on waste from petrochemical processes for their use not only as coloring and strength additives in the production of decorative concrete products, but also in the production of other building materials on an industrial scale using regional resources.

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INFORMATION ABOUT AUTHORS

Elmira K. Aminova – Cand. Sci. (Chem.), Associate Professor, Associate Professor, Department of General Chemical Technology, branch of the Ufa State Petroleum Technological University in Sterlitamak, Republic of Bashkortostan, Russia, k.elmira.k@yandex.ru**,** https://orcid.org/0000-0002-3105-3477

Liliya Z. Kasyanova – Cand. Sci. (Chem.), Associate Professor, Associate Professor, Department of General Chemical Technology, branch of the Ufa State Petroleum Technological University in Sterlitamak, Republic of Bashkortostan, Russia, kasyanova-liliya@mail.ru**,** https://orcid.org/0000-0003-1831-2793

Aigul A. Islamutdinova – Cand. Sci. (Tech.), Associate Professor, Associate Professor, Department of General Chemical Technology, branch of the Ufa State Petroleum Technological University in Sterlitamak, Republic of Bashkortostan, Russia, aygul_ru@mail.ru**,** https://orcid.org/0000-0003-3104-2097

Lilia R. Asfandiyarova – Cand. Sci. (Tech.), Associate Professor, Associate Professor, Department of General Chemical Technology, branch of the Ufa State Petroleum Technological University in Sterlitamak, Republic of Bashkortostan, Russia, asfand_lilya@mail.ru**,** https://orcid.org/0000-0002-8328-201X

CONTRIBUTION OF THE AUTHORS

Elmira K. Aminova – literary review; conducting the experimental part.

Liliya Z. Kasyanova – scientific guidance; final conclusions.

Aigul A. Islamutdinova – the concept of research; writing the source text.

Lilia R. Asfandiyarova – processing and analysis of experimental data.

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