Innovations in the technology for producing asphalt concrete based on neutralized catalyst as a condition for improving the quality of road surfaces

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Abstract. The conditions of safety and environmental friendliness of the operation of roads as an international key problem of our time are disclosed. Objective reasons are shown that reduce the quality indicators of the construction and operation of roads. A call to the technology for producing asphalt concrete based on spent alumina-chromium catalysts is a timely need, due to the increasing requirements of international and Russian standards for the quality of roads and their operating conditions. The main scientific idea is to obtain asphalt concrete based on reduced aluminum-chromium catalyst to improve the quality of road surfaces.

A safe method is proposed for converting toxic waste into safe raw materials, taking into account the conversion of chromium (VI) compounds to chromium (III), which makes it possible to use it as part of asphalt concrete coatings. The optimal amount of alumina-chromium catalyst in the composition of asphalt concrete (6.4 ÷ 12.5 wt. %) is shown. It is proved that the use of reduced aluminum-chromium catalyst in the composition of asphalt concrete increases the proportion of waste in the total raw material balance, expands the range of building materials used in atmospheric conditions.

Samples of asphalt concrete mixtures were prepared and tested according to ISST 9128-97 with the use of spent catalyst additives. The analysis of the current state of road surface coating technology is carried out. The optimal formulation for the preparation of asphalt mixes based on the spent catalyst having indicators of physical and mechanical properties is better than a standard sample of asphalt concrete. An effective method is proposed for removing toxic hexavalent chromium from spent catalyst as waste by transferring it to non-toxic trivalent chromium. One of the long-term problems of improving the quality of road surfaces with the inclusion of reconditioned spent aluminum-chromium catalysts, as a solution to the industrial and environmental safety of an industrial enterprise and improving the quality of operation and durability of road surfaces has been solved.

1. Introduction

Reconstruction and hopelessness - these are two brief statements for Russian roads, which are still relevant. Statistics show that 82% of modern roads require reconstructive modifications, which proves the need for the introduction of innovative achievements in both coating technology and material technology [1].
Today, well-known technologies have gained distribution: the use of asphalt concrete and cement concrete. At the same time, road surfaces are whole or assembled of their individual slabs. If we talk about the stages of construction operations, several obvious steps are obvious: preparatory work on the foundation of the road (compaction of the soil, distribution of the pillow - a layer of sand, then crushed stone).

To improve the quality and strength of coatings, a number of materials already created by scientists are used [2]. The most relevant is geotextile as a special protective material from erosion. It is possible to use other materials, for example, a geogrid, which is built between sand and gravel, which affects the durability of the use of roads. Next, the preparation of the base of the road cover is poured with a certain composition based on the bitumen mixture, and then it is required to apply asphalt concrete coating or make cement concrete coating according to the technology.

Cement concrete is the most advantageous coating for European countries and America. When conducting a literature review, we were interested in analyzing what discrepancies materials have for covering roads in America and Russia. The total percentage of cement concrete roads in America was 80%, which is very different from Russian data. In Russia, the total percentage of concrete pavement is only 3.2%.

2. Results and discussion

Our literature and patent searches have shown options for modern technological processes from classic to innovation, which are used in the construction of road surfaces [3].

Technological features of the production of classic coatings are modified: saturation of asphalt with special fibers (conductive), the inclusion of iron micro particles to eliminate cracks. The first technology is related to the fact that the fibers that conduct the current heat the bitumen, and it, in turn, glues the formed crack.

The second technology is associated with the action of an alternating magnetic field on iron particles.

If we take into account natural and climatic phenomena, then it is appropriate to note road options that are efficient in operation with the following components:

• water drainage (ground) to reduce rainfall;
• the use of special voids for the penetration of water and its quick discharge through a special trench;
• inclusion of communication with hot water circulation in the structure of the road surface;
• the use of special panels (Solar Roadways) with heating elements and LEDs operating at constant current (48 V);
• manufacture of special plastic waste (Plastic Road - environmentally friendly), which will be completely replaced with asphalt pavement (Holland);
• the inclusion of special polymer compounds for roads (Excusal Asphalt Protection) to reduce road risks in operation, eliminate icing (Holland).

With the advent of electric vehicles, the question arises of their timely charging. The construction of special rails included in the road surface for the transmission of electricity is no longer a new technology on the roads of Europe, America, and Russia.

Improving the quality of road marking materials is also an urgent task. Thus, the safety and environmental friendliness of the operation of roads is an international key problem of our time [4].

The technologies considered on the one hand will ensure safety and durability in moderate temperatures, in areas with a mild climate, which is typical for European countries. On the other hand, these are not economically viable technologies, since they are expensive processes.

There are various climatic zones on a Russian scale, which must be taken into account both within the framework of the technology for creating materials and as part of the operation of roads.

One can point to a number of existing objective reasons that reduce the quality indicators of construction and operation of roads: a) rationing, operating rules require processing; b) losses in the procurement of materials; c) low-quality bitumen, asphalt concrete, rapidly aging during operation; g) violations when covering asphalt concrete [5].
The existing reasons determined the relevance of the study - obtaining asphalt concrete from their petrochemical and chemical waste, to obtain better pavement, this is on the one hand, and on the other hand, solving the issue of rational disposal of spent catalyst as production waste will ensure the high environmental effect and the level of industrial safety at the enterprise.

These effects will ensure the quality of the environment through systemic, organized waste management; reduction of toxic components through the neutralization of toxic chromium; reduction of waste diversity (including hexavalent chromium); reduction in the number of unauthorized landfills; elimination of the source of environmental degradation of the enterprise, places of population. Today, official documents have been adopted on the strategy and future tasks for the development and safety of roads, with an implementation period of up to 2024 [6].

In addition to improving the quality of the environment and industrial safety of the enterprise, we note the fact that the waste itself - the spent catalyst contains valuable components that we use as secondary resources. In addition, this type of waste does not require additional construction of landfills, disposal tanks, which provides a high resource and economic effect to the modern enterprise. In addition, we note that the saved land, as practice shows, does not fall out of economic circulation for at least half a century.

However, the landfills used for solid industrial waste are special facilities designed to isolate and render waste harmless and do not guarantee the sanitary and epidemiological safety of the population around the industrial enterprise.

The main scientific idea is to obtain asphalt concrete based on reduced alumina-chromium catalyst to improve the quality of road surfaces [7].

In the processes of dehydrogenation of paraffin, isoparaffins in a fluidized bed of an aluminum-chromium catalyst, a significant amount of toxic waste is formed - a dust-like aluminum-chromium catalyst from 100 to 200 tons per month. This waste contains 15-20% of chromium oxide Cr$_3$O$_3$ (Cr$_2$O$_3$), alumina Al$_2$O$_3$, silicon oxide SiO$_2$, potassium oxide K$_2$O. The water-soluble part is about 5% (compounds of chromium, potassium, iron).

2.1 Methodology of work. Spent aluminum-chromium hydrocarbon dehydrogenation catalysts contain highly toxic chromium compounds Cr$_6$+ in an amount of from 0.1 to 1.5 wt. %, which limits their use as secondary raw materials.

An indispensable condition for environmental safety is the absence of toxic components in their composition. In this regard, the first stage in the preparation of the spent alumina-chromium catalyst is the stage of removal of toxic hexavalent chromium compounds from it.

We have developed an original method for the conversion of toxic hexavalent chromium compounds in the composition of the spent catalyst into nontoxic trivalent chromium compounds. For this, a chemical reduction method using an active reducing agent was chosen.

The aim of the research was to maximize the reduction of Cr$_6$+ content in the spent catalyst up to the absence. The goal was achieved by converting toxic Cr$_6$ + compounds into non-toxic Cr$_3$ + compounds by treating the spent catalyst with aqueous hydrazine solutions at temperatures up to 100 ºC, or rather, even at room temperature. Neutralization was carried out on two samples of catalysts - granular and dust-like.

The analysis of the content of Cr$_6$ + in the catalyst was carried out according to TU 6-68-170 "Determination of the mass fraction of chromium oxide (VI)".

The analysis of the content of Cr$_6$ + in the filtrate was carried out according to the measurement procedure: "Photometric determination of chromic anhydride and chromic acid salts in the air." The processing of spent chromium-containing catalysts by the proposed method allows achieving the degree of removal of toxic Cr$_6$ + compounds up to 100%.

The spent alumina-chromium catalyst was used by us as part of the component of asphalt concrete mixtures.

The method for preparing the asphalt mixture was to mix heated mineral materials, introduce viscous bitumen and mix it with mineral materials in a heated state.
The aluminum-chromium catalyst, crushed in a ball mill, had a grain composition, wt. %: smaller than 1.025 mm - 99.9; other indicators of the properties of the mineral powder corresponded to ISST R 52129-2003 (porosity, %, not more than 35, swelling of samples from a mixture of powder with bitumen, % - not more than 2.5, water-resistance of samples from a mixture of powder with bitumen, % - not more than 0.7, bitumen consumption index, g - not more than 80, humidity, % by mass - not more than 1.0). Natural sand corresponded to ISST 8736-93; as a binder used bitumen road class BND, ISST 22245-90. Samples of asphalt concrete mixtures were prepared and tested according to ISST 9128-97 with the use of spent catalyst additives.

The results showed high-quality asphalt mixtures.

The optimal formulation of the asphalt mix, % mass: bitumen - 10%, spent catalyst 20%, sand up to 70%.

The manufacture and testing of samples (1-5) was carried out according to ISST 12801-98. Based on the results obtained, it can be concluded that samples of asphalt concrete mixtures, which include reduced alumina-chromium catalyst, have better physical and mechanical properties than standard samples (Table 1).

In the formulations of the mixture, the optimal amount of chromium-chromium catalyst should be in the range of 6.4 ÷ 12.5 wt. % (Samples 2-4). A decrease or increase in the catalyst content in the mixture leads to a decrease in physical and mechanical parameters: water saturation and water resistance coefficient (samples 1-5) (Table 1).

Table 1. Test results of samples of asphalt concrete mixtures based on reduced toxic chromium-containing waste.

| Indicators                      | Standard | 1   | 2   | 3   | 4   | 5   |
|--------------------------------|----------|-----|-----|-----|-----|-----|
| Density, g / cm³               | 2.34     | 2.32| 2.33| 2.34| 2.33| 2.38|
| Water saturation about, %      | 0.73     | 2.58| 2.57| 0.8 | 1.99| 6.13|
| Swelling, vol. %               | 0.0      | 0.8 | 0.0 | 0.0 | 0.1 | 1.3 |
| Tensile strength in compression, MPa, at temperature: 20°C | 5.1      | 4.1 | 5.1 | 5.3 | 5.3 | 3.6 |
| Tensile strength in compression, MPa, at temperature: 50°C | 2.7      | 2.1 | 2.6 | 2.8 | 2.6 | 1.6 |
| Water resistance coefficient   | 1.02     | 0.8 | 1.03| 1.12| 1.01| 0.8 |

The maximum value of the compressive strength at a temperature of 50 °C is achieved with the following range of values: the percentage of crushed stone (44 ÷ 51.1); water resistance coefficient (0.825 ÷ 0.864). The technical result obtained is the use of spent catalyst in the composition of asphalt concrete is reflected in patent 2403217 RU C1 C04B 06/26.

Prototypes of asphalt concrete were tested during the operation of pavements in the southern regions of the Tyumen region. The features of asphalt concrete of such compositions were laid hot, after which the coating was leveled and compacted by equipment. According to ISST 9128-2009, the temperature of the asphalt mix during installation was at least (103 °C). Lying was built in layers (from 5 to 7 cm), bitumen was used for the adhesion process.

3. Conclusions
As part of our research, we conducted a patent and literature review to identify proprietary technologies for improving the quality of asphalt concrete for road surfaces.
The analysis of the current state of road covering technologies is carried out; their advantages and disadvantages are revealed.

An effective method for removing toxic hexavalent chromium from the spent catalyst as a waste by converting it to non-toxic trivalent chromium is proposed. Optimal recipes for preparing asphalt concrete mixture based on spent catalyst have been developed, which have indicators of physical and mechanical properties better than the standard sample of asphalt concrete.

One of the long-term problems of improving the quality of road surfaces has been solved, taking into account the inclusion of recovered spent aluminum-chromium catalysts, as a solution to industrial and environmental safety of an industrial enterprise and improving the quality of operation and durability of road surfaces.

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