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Obtaining Compositions Based on Sulphur for Road Building Materials

Fozilov S.F.	Doctor of Technical Sciences, Professor at Bukhara Engineering and Technology Institute
Mavlanov B.A.	Associate Professor at Bukhara Engineering and Technology Institute
Raupov B.K.	Doctoral student at Bukhara Engineering and Technology Institute
Khayrullayev Ch.K.	Doctor of Technical Sciences, Associate Professor at Bukhara State Medical Institute

ABSTRACT

The article examines the production of a sulfur-based composition for road building materials. The use of sulfur compositions and polymer sulfur compounds with a modifier in the production of filled road materials will improve their properties and provide the opportunity to sell additional volumes of elemental sulfur on the domestic market, since the production of road materials is a very capacious and intensively developing branch of national industry

Keywords: compositions, polymers, consumption, chemical industries, production, materials, production technology.

In recent years, there has been increasing interest in filled building materials in which sulphur-based compositions are used as a binder. This is due to the technical advantages of the resulting composite materials - rapid hardening and strength gain, resistance to aggressive environments, hydrophobicity.

At the same time, elemental sulphur in its pure form is not used in the production of road materials due to its fragility. It is necessary to carry out chemical modification of sulphur by introducing various, mainly polymer, additives in order to give it additional properties, such as increased strength, oxidation resistance, adhesive and enveloping characteristics, as well as a stable structure, elasticity, and biostability.

Thus, the resulting modified sulphur is a composition of sulphur itself and its copolymer with an organic additive. The main starting component for obtaining the compositions is elemental sulphur, which is a by-product of processing sulphur-containing hydrocarbon local raw materials.

In 2022, the production of elemental sulphur in Uzbekistan amounted to 280.0 tons, while consumption was only 205 tons. In Uzbekistan, sulphur is used for the production of mineral fertilizers (2.3 million tons), in metallurgy (0.06), pulp and paper (0.05) and chemical industries (0.14). A surplus of 3.5 million tons is sold for export [1].

Excess sulphur production leads to an increase in sulphur inventories. Long-term storage of significant volumes of sulphur is undesirable, as it is accompanied by a decrease in its quality characteristics and also has a negative impact on the environment. In such conditions, an urgent task is to expand the areas of large-scale use of sulphur in road construction technologies.

The use of sulphur compositions and polymer sulphur compounds with a modifier in the production of filled road materials will improve their properties and provide the opportunity to sell additional volumes of elemental sulphur on the domestic market, since the production of road materials is a very capacious and intensively developing branch of national industry.

The available literature information on the production of sulphur compositions and sulphur copolymers with a modifier is scattered, is predominantly patent in nature, does not disclose the modification process, its laws, the influence of conditions and type of modifier on the composition and structure of the compositions, as well as methods for analyzing their qualitative characteristics. The information is reduced to a description of the technological conditions in a wide range and the physical and mechanical properties of the final composite materials. There is no single criterion for assessing the quality of compositions to compare their different types with each other [2,3].

Therefore, studying the process of obtaining sulphur compositions as a result of the interaction of sulphur with modifiers and identifying patterns reflecting the dependence of the yield of the polymer component on various conditions is an urgent task for the formation of a scientific basis for the development of a new domestic branch of sulfur-based road materials.

The purpose of this work was to study the features of obtaining sulfur-based compositions that are promising as binders for filled road building materials.

The developed sulfur-based compositions are promising as binders in the production of road building materials. The use of the compositions will improve the properties of materials and provide the opportunity to sell additional volumes of elemental sulfur on the domestic market, which will serve to reduce the consequences of excess production and the environmental burden from long-term storage of sulfur in large volumes.

Sulphur-based compositions are used for the production of sulfur-asphalt concrete and sulfur concrete mixtures as a binder material. The use of sulfur as a component of road materials is due to its properties, such as rapid hardening, hydrophobicity, resistance to aggressive environments, and low thermal conductivity [4-8].

Sulfur concrete mixtures are produced using hot technology at a temperature that ensures that the binder component (modified sulfur) is maintained in a liquid state. Typically the temperature is in the range of 130-150 °C. The production technology consists of mixing modified sulfur and a mineral part heated to operating temperature. The content of modified sulfur in the mixture can reach 25 wt.% [9].

The technology for the production of sulfur-asphalt concrete mixtures consists of replacing part of the bitumen (up to 40%) with modified sulfur. In general, bitumen and sulfur are mixed with the remaining components of the mixture, or modified sulfur is directly added to the mixer.

The disadvantage of the technology is the possibility of releasing harmful substances (H2S, SO2), the presence of sulfur vapour during the production and use of materials, which makes the process a fire and explosion hazard. In the case of using elemental sulfur, the material loses its properties (strength, hydrophobicity) over time. Research in the field of improving the technology of production and use of sulfur-containing materials is carried out by industry institutes, sulfur producers, and manufacturers of building materials, as evidenced by a large number of patent literature [10].

Road construction materials based on sulfur are distinguished by higher performance characteristics, such as mechanical strength, water resistance, frost resistance, resistance to aggressive environments, and service life.

The use of sulfur as a binder in composite materials requires imparting a number of additional properties to it through chemical modification. This allows us to obtain a product with improved physical and mechanical characteristics, increased resistance to external factors, etc.

Chemical modification is carried out by reacting sulfur in the melt with various modifiers of organic nature. The most widely used modifiers are unsaturated compounds, for example, cyclic diene hydrocarbons and their oligomers [11,12].

The process of interaction of elemental sulfur with the modifier was carried out in a thermostated periodic tank-type reactor with a jacket and a mixing device (Fig. 1). A planetary mixer with a paddle mixer was used as a mixing device. A high-temperature inorganic coolant (mineral oil) was used as a coolant.

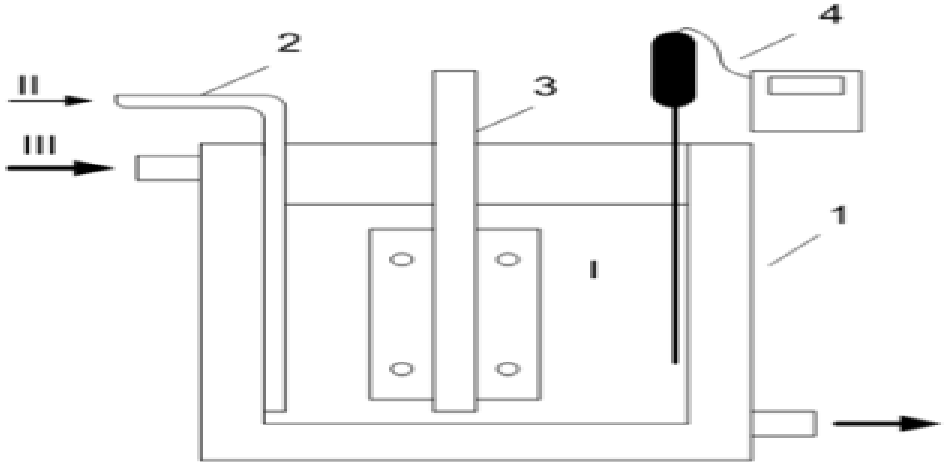
The modification was carried out in the liquid phase in molten sulfur. The melting point of sulfur is 120 °C. In this regard, the modifier must be thermally stable, non-volatile, and high-boiling (more than 120 °C).

The preparation of sulfur compositions with low molecular weight polypropylene was carried out as follows. A modifier was added to the sulfur melt. Next, mechanical mixing of the liquid reaction mass was carried out for a specified time with periodic sampling.

The optimal modification conditions found in the laboratory installation (Fig. 1) were then used to produce larger experimental batches of modified sulfur.

For this purpose, another experimental installation was used – a periodic capacitive-type reactor with a centrifugal pump and electrical heating (Fig. 2). The modifier was supplied to the pump suction line, and mixing and distribution in liquid sulfur took place in the area of the centrifugal pump impeller.

The minimum loading of sulfur into the reactor is 50 kg, the maximum is 100 kg. The installation produced experimental batches of modified sulfur weighing 50-60 kg.

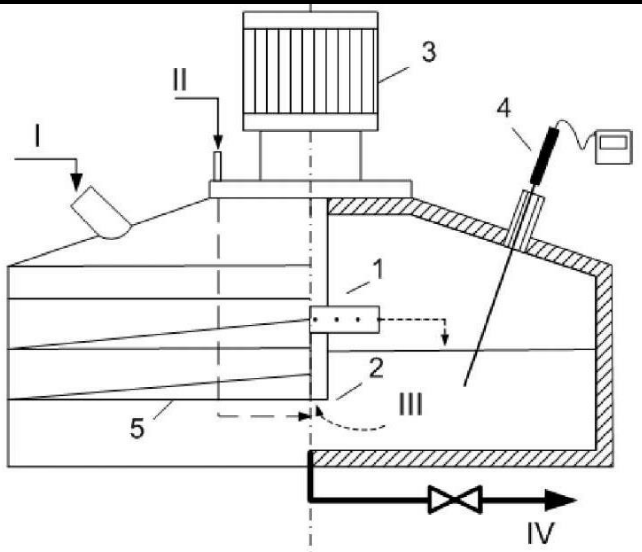


Reactor diagram
1 – jacketed reactor; 2 – modifier input pipe;
3 – mixing device (planetary rotation scheme);
4 – temperature control sensor.
I – reaction mass; II – input of liquid modifier;
III – coolant (oil).

Fig. 1 – Reactor for obtaining samples of compositions

The produced batches were used to produce prototypes of sulfur concrete and sulfur asphalt concrete, which were tested. Based on the results obtained, the quality of the resulting compositions and their suitability for use as a binder for composite materials were assessed.

Based on literature data, cyclic diene hydrocarbons – dicyclopentadiene (DCPD) and 5-ethylidene-2-norbornene (ENB) – were selected as organic sulfur modifiers at the first stage of the work. The use of such substances is due to their high reactivity, due to the presence of double bonds active with respect to sulfur.



1-pump impeller, emulsifier; 2 suction line; 3- electric motor; 4 - temperature control sensor; 5 electrical winding of the container (electric heating).
I – liquid sulfur; II – input of liquid modifier; III – reaction mass;
IV – finished products (compositions).
Fig. 2 – Diagram of the installation for producing experimental batches of sulfur and low molecular weight polypropylene compositions

Since the composition of impurities in the original sulfur depends on the method of its preparation, it is advisable to study its spectral characteristics. The qualitative composition of sulfur was studied using IR spectroscopy. The IR spectrum of a molten sample of the original granulated sulfur is shown in Fig. 3.

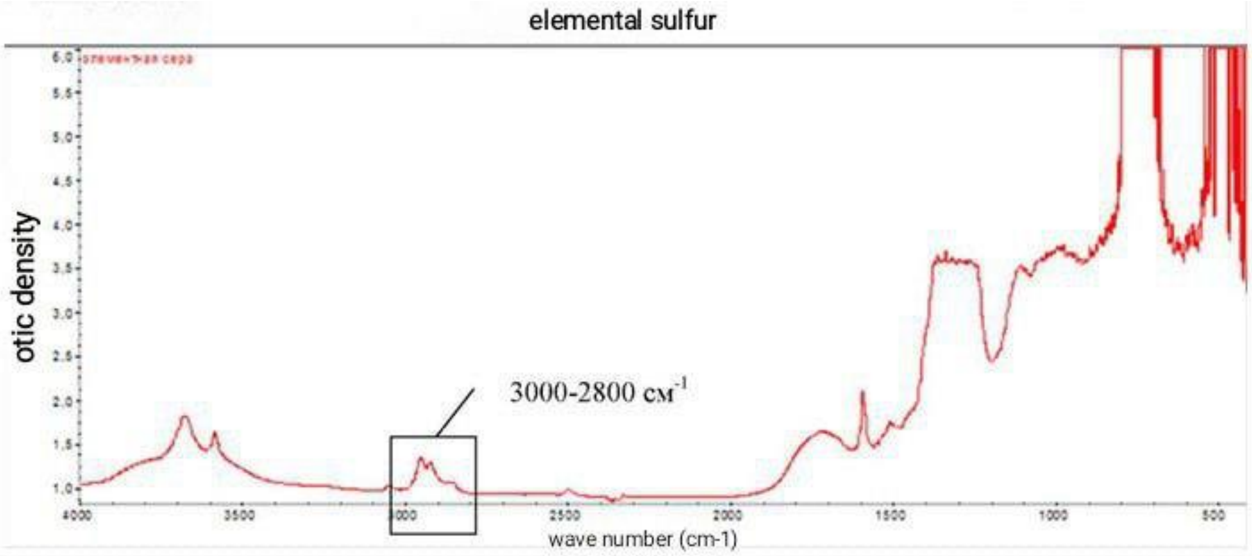


Fig.3. IR spectrum of the original sulfur sample

Absorption in the region of 3000-2800 cm-1 is characteristic of alkyl –CH2 bonds, which indicates the presence in sulfur of trace amounts of saturated hydrocarbons, which inevitably remain during the processing of hydrocarbon raw materials and the subsequent production of sulfur. Pure sulfur is characterized by significant absorption in the region of 1800-400 cm-1, which complicates a more detailed analysis of its compounds with high sulfidity and mixtures of sulfur with other substances using IR spectroscopy.

Due to the presence of organic impurities in sulfur, the behavior of sulfur was studied in a process similar to the production of modified sulfur, excluding the addition of a modifier. For this purpose, the sulfur melt was kept at 145°C for 18 minutes, after which the sulfur was left to cool to room temperature. The formation of dispersed black inclusions – karsuls – was observed on the surface of the sample. The formation of carsules in a molten gas sulfur is described in the literature [13]. These particles are a product of the interaction of sulfur with impurity hydrocarbons.

Figure 4 – Sample of initial sulfur after melting and crystallization

18 hours after melting
polypropylene share 3.1%

in 36 hours
polypropylene share 1.5%

To assess the stability of the resulting unmodified sulfur sample, the presence of an insoluble polymer fraction in the sample was studied 18 and 36 hours after melting. The results are presented in Fig. 4. 18 hours after the end of the experiment, it was visually possible to observe the presence of two forms of sulfur in the sample – orthorhombic and monoclinic, light and dark areas, respectively. After 36 hours, most of the sulfur was transformed into the orthorhombic crystalline α-form, which is stable under normal conditions. In this case, the proportion of the insoluble polymer fraction in the sample decreases from 4.0% immediately after cooling, to 3.1 and 1.5% 18 and 36 hours, respectively, after cooling due to depolymerization.

The presence of an insoluble residue, which was observed as a result of the extraction of elemental sulfur from the samples presented in Fig. 4 suggest that at a temperature of 140 °C, partial formation of polymer sulfur occurs in the melt mass. However, such polyolefins without a stabilizer are unstable and their depolymerization occurs within two days, as evidenced by the observed (Fig. 4) decrease in the proportion of the insoluble part. Consequently, the organic compounds present in this sample as impurities cannot stabilize the polymer fraction of sulfur from depolymerization.

Using the described extraction method, 4.0 wt.% of the insoluble part was obtained in the sample after melting at 140°C and cooling to room temperature, which is in good agreement with the literature data and confirms the reliability of the analysis method [14, 15, 16].

It should be noted that based on the results of this analysis, it was revealed that there is no polymer fraction in the original granulated sulfur and it is completely soluble in toluene.

Thus, the monoclinic β-form and polymers in modified sulfur must be stabilized, which is facilitated by the use of modifier additives – mainly unsaturated compounds with reactive double bonds.

The process of sulfur modification was carried out in a laboratory installation (Fig. 1).

The studies were carried out for modifiers in an amount of 0-5.0 wt.%, since this range is unexplored and practically undescribed in the literature. In addition, the use of modifiers in small quantities is advisable for economic and environmental reasons.

Mixing duration study. Mixing is necessary to distribute the modifier throughout the volume of the reaction mass. The liquid modifier was introduced into the layer of liquid sulfur with stirring for 1 minute. The modification process was carried out at a temperature of 140 °C for an hour, sampling was carried out every 15 minutes. All subsequent series, to allow comparison of results, were also carried out at 140 °C. The results obtained regarding the proportion of the insoluble part are shown in Fig. 5. According to, the formation of insoluble IUDs reaches maximum values already in the first 15-30 minutes. Process and with a further increase in the duration of the process changes slightly.

The nature of the presented curves of the dependence of the content of BMC in the reaction mass on the duration of the reaction suggests that a slight decrease in the mass content of BMC in the mixture is apparently due to destructive processes, due to the reversibility of the polymerization reaction.

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