

**INTERACTION OF SULFUR WITH ORGANIC FEED.
PART I – THEORETICAL BASIS**

A.V. Osipov

Ufa State Petroleum Technological University

V.A. Budnic, V.V. Zolnicov

*Scientific Technical Centre «Salavatnefteorgsintez», Salavat
email: 48bva@snos.ru*

A.V. Gorbunov, B.S. Zhirnov

Ufa State Petroleum Technological University, Salavat branch

In this work prospects of implementation of sulfur as a component of road binders have been presented; also theoretical background of reaction of sulfur with different hydrocarbons has been reviewed; and further direction of researches of sulfurization processes has been shown.

Keywords: sulfur, bitumen, interaction, binders, temperature, modifying, composition, stability, properties, improving

World sulfur market has now the steady tendency of sulfur production excess in comparison with sulfur sales. It is connected with deep gas and refinery products treating, sulfur-contained oil and gas fields mining, fuel gas treatment. In Russia the situation is similar. That's why nowadays it becomes more profitable to use sulfur in building industry and in road construction [1, 2].

Up to date the interaction of sulfur and organic compounds is insufficiently studied. Sulfurizing reactions study is obstructed because of sulfur structure complexity; its ability to react in several directions simultaneously with hydrogen sulfide and polysulfones emission, to conjure side reactions (addition, hydrogenation, condensation, polymerization), instability of some of intermediate sulfurizing products that often are being converted into resinous substances; difficulty of final products separation. Age-old experience of sulfur usage for the improvement of the organic binder properties didn't allow to come to the one opinion about the character of the interaction processes and their optimal conditions [3].

Processes of sulfur-carbon bonds formation during chemical interaction of sulfur and oil are based on the interaction of sulfur and unsaturated compounds – resins and

olefins that are presented in small amounts in heavy aromatics. The main structure elements of resins consist of aromatic, olefinic and heterocyclic rings linked by short aliphatic bridges so they are the most probable components of interaction with sulfur [4].

The process of interaction of sulfur with organic binders especially – sulfur cracking at high temperatures hypothetically can course by ionic and radical mechanisms. In the first case during the cycle opening electron pair can remain near one sulfur atom, in the other side of the formed chain a lack of electrons is being created. In the second case each of the end sulfur atoms can attach one electron [4].

As a result of sulfurizing reactions reduction of amount of resins and a gain of amount of high-molecular weight compounds that lead to growth of disperse phase can be observed. Dehydrogenation process promotes the other way of interaction of sulfur with oil: during the heavy crude oil heating hydrogen sulfide is being formed that adds to the unsaturated hydrocarbons with further conversion of the formed ions into sulfur-organic compounds (mercaptans with their further decomposition into sulfides) [5, 6].

Researches that have been carried out in the State Road Scientific-Research Institute gave an opportunity to estimate two main variants of organic binder modification by sulfur: plasticization and densifying [5].

Plasticization by sulfur is recommended in case of viscous bitumens usage (BN and BND sorts) for the bituminous concrete mixtures preparation in Northern regions of European and ISC states. It is required to reduce the brittleness temperature for the prastificated bitumens in order to increase the fracture strength of the road pavements, to increase the penetrability for the improvement of the overlapping conditions of the organic binders and cold mineral materials during the blending process [7].

Densifying by sulfur is recommended in case of viscous bitumens usage (BN and BND sorts) for the bituminous concrete mixtures preparation in Southern regions of European and ISC states, where it is necessary to increase the melting point in order to improve the anti-shear properties of layers of road binders and to improve the adhesion ability of binders used for the construction of the road layers by the means of mixing on the road. This variant of improvement of organic binder properties is effective in case of low-viscous organic components usage such as heavy crude oil, vacuum residue from the distillation unit, liquid bitumen. They are modified by adding 15 - 25 % of sulfur when obtained products can replace conditional binders – viscous bitumens [8, 9].

There are at least three reasons why sulfur usage will be successful. First reason is in reduction of bitumen consumption – bitumen content in sulfur-bitumen binders decreases because of adding of sulfur that is cheap and available in high amounts. And as a result the cost of the road closes construction decreases [10, 11].

The second reason is in the inaccessibility of stone materials used in the layers of pavement, which are usually brought from other remote areas. Because of a application of the sulfur-bitumen binders, local sandy soils, weak stone materials, ash and slag can be widely used in road construction which also provides substantial economic effect [10, 12].

The third reason is in significant improvements of the properties of asphalt concrete mixtures based on sulfur-bitumen binders:

- significant increase in compressive strength makes it possible to reduce the thickness of the layers of pavement;
- higher thermal resistance without a considerable increase in rigidity at low temperatures reduces the risk of formation of the layers of pavement cracks in the cold (winter) season, and plastic deformation in the hot (summer) period;
- the possibility of preparing mixtures based on sulfur-bitumen binders at a lower temperatures;
- greater stability of the sulfur-bitumen materials to dynamic loads;
- greater resistance to gasoline, diesel fuel and other organic solvents makes them suitable for device coatings on parking [10, 13-15].

A special features of asphalt concrete mixtures based on sulfur-bitumen binders are their good workability (viscosity of sulfur-bitumen binder at a certain temperature is less then viscosity the original bitumen at the same temperature) and compactibility.

Along with the advantages of oil-sulfur mixes, they have disadvantages that prevent their wide application. The main ones are the toxicity caused by the release of hydrogen sulfide and sulfuric anhydride, which limits the temperature regime of making and laying mixtures, high corrosion rate of technological equipment, the need for a partial change in the traditional binder preparation technology and in preparation of mixtures based on it; longer control the quality of such mixtures and binders because structure formation processes occur in them much longer then in traditional asphalt – concrete mixture [10, 16].

Sulfur in the sulfur-bitumen compounds can be in three types: chemically linked, dissolved in organic binder and in the form of undissolved bitumen filler. In every form of organic sulfur binder has different properties. In the chemical interaction with organic binder takes a slight (5 - 7 %, sometimes up to 10 % wt.) amount of sulfur. Analysis of the viscosity of organic sulfur binding on the sulfur content shows that the optimum content of sulfur is less dependent on the viscosity of the organic component. When the sulfur content in the binder is 5 - 10 % wt. plasticization of the organic component occurs. This quantity of sulfur is usually the most effective modifier, that greatly improves the thermal stability of binder and organic sulfur compounds based on them, increases the adhesive power binder. A further increase in the sulfur content of binder does not lead to improvement of its properties, there has been continued growth of softening point and fragility and decrease in distensibility [5, 17-18].

During the interaction of residue with sulfur two basic chemical reactions occur. The first – at temperatures below 140 °C the interaction of sulfur radicals with hydrocarbons in the direction of a sulfur-carbon bonds, i.e. the polar aromatic bonds. The probable structure of organic sulfur compounds are polysulfide compounds, which at higher temperatures move into cyclic sulphides with the structure of thiophene type, which includes the intermolecular cross-links. The second – at a temperature above 140 °C dehydrogenation of organic components occurs, which is a sign of hydrogen sulfide emission, formed as a result of reaction of sulfur with hydrogen. Dehydrogenated chains are subjected to cyclization, resulting in an increasing number of structure-forming complexes such as asphaltenes and other high-molecular compounds. At this stage a linkage of organic fragments by sulfur occurs [19].

These temperature limits are conditional, since in reality, both reactions occur simultaneously. In this case the dominant character of one of them depends on changes in temperature, that is, its growth or reduction, composition and structure of the components of resin, which leads to a definite change of binding properties by varying the degree of polymerization of the material [5, 20].

In sulfur-bitumen mixture excesses of sulfur are in the form of low-dispersed particles, which serve as a structure-forming filler. Sulphur content in this case can be more than half the total amount of added sulfur, and the efficiency of filling increases with decreasing viscosity of the organic component. The size of grains of sulfur, undis-

solved in the oil residue, has a significant influence on the properties of disperse system and especially on the strength properties of sulfur-bitumen mixtures [21, 22].

The size of the forming sulfur grains depends on the conditions of matching components (temperature, time, intensity of mixing) and the cooling rate of the compositions on their basis. This also explains the growth of strength of samples of asphalt concrete mixture with the addition of sulfur in time. Slow cooling of large samples leads to the formation of strong mechanical bonds because of the crystallization of sulfur. The structure of these bonds may be significantly damaged by very rapid cooling or mechanical breakdown, such as compaction, as well as by laying a mixture of pavement [5, 23, 24].

So this review allows to judge about the relative complexity of mechanism of interaction of sulfur with organic binders and about the prospects of researches of this direction. The direction of researches of oil residue sulfurizing process with road binders production is the most important. In this case, in prospects, two issues are decided simultaneously: sulfur utilization and increasing of yields and quality of road binders. Research of sulfurization process of such feed as straight-run residues (vacuum residue), oxidized bitumen and residues of secondary refinery processes will let, in the sequel, expand the assortment of oil refinery products and also reduce their cost.

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