Oil-treated gravel road pavements

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Abstract. The following paper presents results of research carried out on oiled gravel aggregate. In Russia, the oil-treated aggregate mixture is called "loose-bound organic-mineral mixture" (hereinafter abbreviated as LOM). The aim of the research was to explore the possibility of using oil waste products and their heavy residues generated during oil transportation as a binder in oil-treated gravel aggregate or LOM. Currently, this waste is not used anywhere, it is widely burned, polluting the environment. Studies were carried out using Infra-red spectroscopy of samples of the original oil waste, heavy residues of oil waste and road oil bitumen of BND 90/130 quality type. The fractional composition of oil wastes and their heavy residues was studied during their distillation by heating to a temperature of +335 °C. It was found that for preparing LOM it is more effective to use oil residues. The number of LOM compositions samples were prepared and their main physical and mechanical indicators were determined. Based on the tests, it was concluded that the residues of oil waste can be used as a binder in the composition of LOM such as oil-treated gravel.

1. Introduction
Currently, the main road-building material is asphalt on a bituminous binder. However, bitumen has its drawbacks: it emits harmful gases when heated, and it is not a frost-resistant or heat-resistant material. A number of scientists have been studying the properties of bitumen [1]. To improve the qualities of bitumens, they are modified with various polymers and industrial production wastes [2-7]. In addition, bitumen due to rising prices for crude oil, is becoming an expensive and scarce material. Therefore, the cost of asphalt is also high. To reduce the cost of asphalt concrete, industrial waste [8-12] or alternative petroleum-based asphalt binder [13-16] are used.

It's a fact that in foreign countries oiled gravel road cover is widely spread. “Oil-treated or oiled gravel” is a conventional name, since this material composition does not contain pure oil and gravel, but a low-viscosity oil binder with adhesive additives and crushed stone from durable rocks. Oil gravel coatings in road construction are used extensively in Scandinavian countries. In Finland, for instance, more than half of the roads are paved with oiled gravel. These coatings have a number of advantages: oiled gravel is more environmentally friendly than bitumen, as it contains less volatile components; the possibility of producing mixtures ready to be transported to a warehouse with a shelf life of up to 5 years or more; high pace of road coating devices which use traditional technology.

In Russia, the oil-treated gravel mixture is called "loose-bound organic-mineral mixture" (hereinafter abbreviated as LOM). Economic efficiency in the installation of coatings made on the basis of LOM, compared to conventional asphalt concrete coating, is reflected in a reduction of costs.
by 1.5 times, decrease in the amount of organic binders by almost 2 times, lowering in the number of machines and mechanisms by 1.5 times and labor force by 3 times.

Oil-treated gravel aggregate is in many respects a special material, therefore the scale of its use is not very large. An oil product containing volatile matter is used as a binder in oiled gravel coating. Its composition is not publicly described in literature. The purpose of the binder is to prevent material separation and the removal of large grains. Binding in oiled gravel should be enough to bind the stone material, but not too tightly. The coating must be soft and flexible so that it can be cracked and opened any time when necessary. The binder must be mixed with cold materials and retain plasticity and softness during the entire period of operation, that is, light fractions from the binder must evaporate slowly. The oil product is hardened after mixing due to oxidation of the oil base.

Crushed rock with a low content of fines from strong acidic rocks is used as a stone material in oil-treated gravel. The adhesive ability of the oil binder to these rocks is insufficient. The most effective is the introduction into the binder adhesive additives of the amine type, which intensify chemisorption processes, hydrophobicize the hydrophilic surface of acidic stone materials, thereby providing better wettability of stone materials and provide a more reliable connection of oil-treated gravel components in the conditions of peeling effect of water.

In Russia technical specifications have been drawn up for LOM ingredients and composition [1]. The purpose of this research was to study the possibility of using oil waste and its heavy residues generated during the transportation of oil as a binder in the production of LOM. These waste products are generally received while cleaning pipelines. They are commonly aggregated into metal containers, where they may be stored for a long time. Heavy residues of these oil wastes are formed after the heavy fractions of oil are sinking to the bottom of these tanks. Currently, this oil waste products are not used anywhere in industry, they are generally burned which results in environment pollution. To improve the adhesion of these wastes with stone materials, amine-type adhesive additives were used.

2. Materials and methods
For the preparation of LOM, the following raw materials were used:
1. As a coarse aggregate, crushed stone was used, which was obtained by crushing the gneisses of the “Cardon” open pit of the Uyar town;
2. Small aggregate - sifting of crushing of gneisses of the same quarry.
3. The chemical composition was investigated, an X-ray structural analysis was performed, and the physical and mechanical properties of the aggregates were determined. For all characteristics, the fillers met the requirements of the relevant State Standards.
4. The binder was waste generated in oil pipelines during the transportation of oil;
5. Triethanolamine N \((C_2H_4OH)_3\) and ammonium acetate \(CH_3COONH_4\) were applied as surfactants.
6. Determination of the physical and mechanical properties of LOM aggregate was carried out in accordance with the technical conditions.

3. Results
In order to study the chemical composition of oil waste and compare it with the chemical composition of bitumen, infra-red spectroscopy (IR-spectroscopy) studies of samples of the original oil waste, their heavy residues and oil road bitumen of the BND 90/130 quality type were carried out.

Registration of IR spectra in the range of 400–3900 cm\(^{-1}\) was performed on a Specord 75JR spectrophotometer. The recording conditions of the spectra were selected in such a way that the hardware distortions were minimized. Samples were recorded between potassium bromide plates.

IR spectrum of initial oil wastes (Figure 1) is mainly (65 – 70%) absorption bands of vibrations of volatile saturated hydrocarbons with a chain length \(n>6\) in the range of 720 cm\(^{-1}\) and a doublet in the range of 1460, 1467 cm\(^{-1}\), and there is also a high intensity of bands in the domain of 2880 – 2960 cm\(^{-1}\), which corresponds to the vibrations of \(CH_2\) and \(CH_3\) – groups [17].
The composition of oil residues consists of small amounts of oxygen-containing products (absorption bands in the range of 3400 – 3600 cm\(^{-1}\)), as well as condensed aromatic systems (absorption bands in the range of 3020 – 3060 cm\(^{-1}\)) in the absence of strong absorption bands in the range of 1600 cm\(^{-1}\) and 700 – 900 cm\(^{-1}\). Weak absorption in the domain of 1640 and 810 cm\(^{-1}\) may indicate the presence of conjugated double bonds [18].

Aromatic polycyclic structures are present in a significant amount in the composition of heavy residues of oil waste. This is evidenced by the presence in the spectrum of the residue (Figure 2) of the absorption bands in the range of 1602, 1575 and 1450 cm\(^{-1}\).

Despite the impossibility of direct identification in the IR spectra of the residue of asphaltene-naphthenic structures, their presence can be assumed on the basis of high overall cyclicity [19].

The comparison of the IR spectra of the original oil wastes and the heavy residues of these wastes (Figure 1 and Figure 2) shows a significant decrease in the proportion of aliphatic hydrocarbons in the composition of the residue. The proof is a decrease in the intensity of the absorption bands in the range of 2800 – 2960 cm\(^{-1}\) and 1460 cm\(^{-1}\) for the remainder. The relatively high intensity of the absorption bands in the range of 1602 cm\(^{-1}\), as compared with that in the IR spectrum of oil waste (Figure 1), which furthermore confirms the presence in the composition of the residue of highly condensed aromatic nuclei [20].

IR spectrum of bitumen (Figure 3) is represented mainly by the absorption bands of vibrations of CH\(_2\) and CH\(_3\) - aliphatic groups in the range of 2800 – 2960 and 1375 – 1460 cm\(^{-1}\). Analysis of their intensities, as well as the presence of a doublet of 720 and 745 cm\(^{-1}\), suggests that paraffin hydrocarbons are the main component of bitumen. Along with the paraffin chains of the normal structure of bitumen, asphaltene-naphthenic fragments are present in small quantities. This is evidenced by the presence of absorption bands which range at 1735, 1602, 860 and 810 cm\(^{-1}\).

Oxygen-containing products are represented in bitumen, in contrast to oil waste, in very specific groups:

- OH (absorption band 3380 cm\(^{-1}\));
- carbonyl (complex absorption band in the region of 1602 cm\(^{-1}\));
- ethereal (absorption band 1030 and 1310 cm\(^{-1}\)).

![Figure 2. IR spectrum of heavy residues of oil wastes.](image)

![Figure 3. IR spectrum of bitumen BND quality type.](image)

It should be noted that the amount of oxygen-containing products in bitumen, compared with oil wastes and heavy residues, is very small (17 – 20%), which indicates the possibility of better adhesion of oil wastes and especially their heavy residues with stone materials.

The content of CH\(_2\) and CH\(_3\) groups of structural-group composition of bitumen in the approximation is quite close to oil waste. In the spectrum of the heavy residue is clearer than that of bitumen (Figure 2), the absorption bands characteristic of polyaromatic structures appear. As it is known, aromatic hydrocarbons are polarly active and are highly resistant to heating, oxygen and ultraviolet rays. Therefore, heavy residues should have greater stability when heated and better heat resistance than bitumen.
High content of paraffin hydrocarbons in the bitumen can lead to disruption of its structure. These hydrocarbons can be released from bitumen, as well as crystallize when temperature is lowered and reduce the adhesion of bitumen with stone material. This once again confirms the possibility of better adhesion of heavy residues with stone materials compared to bitumen.

To determine the fractional composition, the initial oil waste products and heavy residues of these wastes were distilled by heating to the corresponding temperatures and evaporation of volatile components from them. The data obtained during the distillation of these products are shown in Table 1.

| Distillation temperature of °C | The amount of the evaporated fractions volume% | Initial oil waste | Oil residues |
|-------------------------------|-----------------------------------------------|-------------------|--------------|
| up to 96                      | 10                                            | -                 |              |
| up to 97                      | 40                                            | -                 |              |
| up to 98                      | 50                                            | -                 |              |
| up to 100                     | 60                                            | -                 |              |
| up to 110                     | 70                                            | 5                 |              |
| up to 190                     | -                                             | 10                |              |
| up to 225                     | -                                             | 20                |              |
| up to 335                     | -                                             | 30                |              |

The kinematic viscosity at 60 °C of oil residues was also determined, which was 14.99 mm²/s. Thus, on the basis of the conducted research, it can be concluded that oil residues are better suited for preparing LOM coating according to the fractional composition, which, when the binder is heated to 90 − 100 °C, will not evaporate from the mixture and keep the composition constant. In the laboratory formulations of LOM composition were prepared. The selection of the grain composition of the mineral part of the LOM was carried out according to the principle of limit curves in accordance with the requirements of technical conditions. The limiting curves and the calculated composition of the mineral part of the LOM aggregate are shown in Figure 4. When preparing LOM, the binder was heated up to 90 − 100 °C. Mineral materials were not heated. Samples-cylinders, were formed from the LOM compounds; they were pressed out after storage in molds for a day at +5 °C. The molding of the samples was carried out on a press.

![Figure 4. Grain composition of the mineral part of LOM.](image-url)
Then, on the obtained samples, physical and mechanical properties were determined. Part of the mixture obtained was stored in a loose state for a day, then the index of adhesion of mineral materials binding to the surface was determined.

4. Discussions
During the research it has been established that the oil binder has good adhesion to stone materials compared to bitumen, but compacted samples have a large residual porosity. To improve the properties, adhesive additives — triethanolamine and ammonium acetate, were added to the binder.

The research results revealed that the application of amines increases the adhesion of the binder with stone materials and reduces the porosity of the LOM aggregate. On the basis of the tests conducted, it was concluded that it is better to use heavy residues of oil waste, since they are more stable and heat-resistant at the temperature of preparation of LOM compared to residual oil. To improve the properties in the oil binder, amines must be added to the composition. The developed compositions of LOM compounds were recommended to “Krasnoyarskavtodor” State company for further production implementation.

5. Conclusions
The main results of the present research are as follows:
1. Based on the conducted literature review, it has been established that road oil and gravel coatings are widely used abroad, which differ from ordinary asphalt concrete pavements by their much lower cost due to the high service life of coatings and the cold technology of oil-treated gravel aggregates.
2. As a binder in oil-treated gravel, oil waste generated during the transportation of oil has been studied. The results of physical and mechanical studies of these waste products have been presented.
3. Using infra-red spectroscopic studies, the chemical composition of oil wastes and their heavy residues was determined, which was compared with the chemical composition of bitumen. Based on these studies, it was found that oil residues should have better adhesion with stone materials and greater stability when heated compared with bitumen.
4. The results of determining the fractional composition of the original oil waste and their heavy residues are given. It is shown that heavy residues of oil wastes are better suited for the preparation of LOM in a fractional composition, which, when heated to 90 and 100 °C, will not evaporate from the mixtures and retain their composition.
5. The calculation of the composition of the LOM aggregate was carried out. In the laboratory, samples were prepared and molded, which were afterwards tested according to the main indicators.
6. It has been established that the oil binder has better adhesion with stone materials compared to bitumen, but compacted samples have a larger residual porosity. After the addition of triethanolamine and ammonium acetate to an astringent adhesive additive, the adhesion of the astringent to stone materials improved reasonably, and the residual porosity eventually was decreased.
7. The developed LOM aggregate compositions were recommended to “Krasnoyarskavtodor” State Company for further production implementation.

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7

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