INTRODUCTION

In the Republic of Kazakhstan the construction of modern highways as per international standards has recently drawn much attention, however, in the acute climate conditions of spring and summer and especially in the autumn and winter periods, the air temperature changes from -40°C to + 40°C and the road covers heat up to 90°C to 100°C. This leads to a quick wear of the roads wear, which requires an annual renewal of the top layer, the asphalt. Thermal mechanical studies (Abdikarimov, et al., 1995) show that bitumen softens at 0°C, turns into a viscous fluid state at 20°C and a 100% destruction is observed at 40°C, and the area of highly elastic deformation is absent.

In this regard, the pressing challenge, which has both theoretical and practical interest, is the modification of bitumen with various polymers to attain a set of physical-mechanical and operational parameters as well as durability.

Knowledge of the laws of transformation of composite materials under a thermal degradation by applying modern techniques is important due to the growing scarcity of the road bitumen and attracted a lot of researchers’ attention due to a wide presence of OBR in Western Kazakhstan.

The method of infrared spectroscopy (IR) was used as the primary method of genetic typing of OBR and for the qualitative and quantitative assessment of ratios of the hydrocarbon and heteroatomic components (Nadirov, et al., 1985).


EXPERIMENT

The following OBR of Western Kazakhstan were used:

1. The sample number 1 (deposits Tyubkaragan) wells no. 606, interval 58 m to105 m, comprised of 5% to 15% bitumen and metal oxides. According to XRD OBR contains: silicon oxide-SiO$_2$, feldspar, hematite-Fe$_2$O$_3$, inclusions of mica and the hydrocarbon phase.

2. Sample number 46/91, contains 5% to 15% bitumen, metal oxides, and silicon-SiO$_2$.

3. Sample from the field Munaily Mola

Samples of OBR were fragmented and mixed with various additives at a room temperature. Extraction of bitumen was performed in a water bath with water, alkali and liquid glass for 40 min at 90°C.

The influence of inorganic and polymeric additives on the mechanism of thermal degradation of the OBR and the formation of chemical bonds by thermal analysis and X-ray diffraction was studied.

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Thermal analysis (thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA)) of bitumen, OBR, additives and modified compositions were performed using the derivatography equipment by F. Paulik, J. Paulik, L. Erdey, "MOM", Budapest. Heating of the sample was performed under the dynamic conditions (the temperature increase rate of 10°C per minute), sensitive measuring systems DTA=250 µv, DTG=500 µv, TG=100 mg 500 ÷ µv.

Radiography. To determine the phase composition of the mineral part of the OBR, X-ray diffraction phase analysis was carried out on a DRON-3M diffractometer using the СuKα filtered radiation, 30 kV, 20 ma, dial 2000 (c/s), with a 2.5-time constant.

IR spectroscopy. Infrared absorption spectra of bitumen, OBR and polymer compositions were obtained on an automatic dual-beam spectrometer UR-20 in the absorption interval of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

RESULTS AND DISCUSSION
Fig. 1 and 2 show the IR spectra of the original sample OBR number 2 and with the additive of PMMA (polymethylmethacrylate).

The high frequency field of infrared spectra is dominated by intense absorption band 2860, 2920 cm\(^{-1}\), related to the valence vibrations of methylene and terminal methyl groups, mainly due to cycloalkanes and aliphatic heterojunction instead of n-alkanes and isoprene (Nadirov, et al., 1985). Low in intensity and broad absorption bands 3400 cm\(^{-1}\) to 3460 cm\(^{-1}\) may pertain to valence vibrations of -OH and =NH. Characterized by the absence of peaks in the infrared spectra in the region of 1050 cm\(^{-1}\) to 1370 cm\(^{-1}\). A comparison of the spectra of two rocks in the sample number 2, the intensity of absorption bands is markedly increased, these are the above subsections of 2860 cm\(^{-1}\) to 2920 cm\(^{-1}\) and 3400 cm\(^{-1}\) to 3460 cm\(^{-1}\), which characterize the enhancement of the physical interaction of the addition of PMMA in the OBR.

By adding polymethylmethacrylate (PMMA) to the bitumen, a solid material with high Shore A hardness is obtained. These qualities are featured in the outdoor, sports and road coatings, thus the additive can be recommended as a modifier. Such a composite is obtained for the first time. Apparently, the PMMA as a polymer binder increases the physical connection, filling unsaturated bonds in bitumen, forming a solid monolith.

A thermal analysis of OBR was performed and the effect of different additives was studied. Fig. 3 shows the thermogram of the OBR number 2 (the original sample). Rock sample number 2 represents the formation of brown color and is easily crushed to the powder state. As determined by the thermal analysis, it contains gypsum, goethite, quartz, organic matter (OM) and thermal inert inclusions. The latter are poorly diagnosed using the specified thermal method. The inclusions include mica, feldspar, some oxides of silicon, iron, etc. The X-ray structure analysis confirms the presence of the above-mentioned thermal amorphous minerals in a rock number 2.
which is a characteristic of the phase state of gypsum, i.e. removal of the bound water, which is carried out with the endo-effect. During the first stage of dehydration, 0.66% of gypsum is lost by weight. The resulting hemi then completely gives up its water, changing the mass of sample by 0.37%. It should be noted that these values also contain the weighted values of the \( \text{H}_2\text{O} \) molecules, which are not a part of the gypsum structure.

A relatively small proportion of the value \( \Delta m \) (weight loss) indicates a low content of gypsum in the rock. This is indicated by a flat outline of the endothermic effect on the DTA curve and a strong flattening of the two types despite the overall bend.

The presence of goethite in the sample is indicated by the diffuse peak on the DTA curve within the 180°C to 3200°C range with a minimum at -2800°C. Within this range the DTA line should delineate a thermal peak, which corresponds with the intensity and the direction of the reaction of dehydroxylation of the hydrated form of the iron oxide. But due to the presence of the organic matter in the sample, which gives a thermal background in the temperature range of an exothermic nature, the specified peak degenerates to the shape that corresponds to a small degree. Data from thermogravimetric analysis (TGA) points out to the weight loss of 3%, which amounts to 15.8% (FeOOH) of goethite based on its stoichiometry.

The presence of a hydrocarbon phase (HPh) in the form of bitumen in the sample indicates the presence of a series of exothermic effects, which have been stretched through the temperature range between 3000°C and 7200°C, on a DTA curve. Reactions causing these manifestations are due to the oxidation of carbon. Endothermic processes, which produce light fractions of gaseous substances (peaks at 4000°C and 6000°C on the DTG-curve) are also observed. These processes are accompanied by the combustion of the organic matter. The most intense heat was noted in the range between 5000°C to 6000°C. Here DTA-curve is plotted with a clear peak at 5500°C. Next endothermic reaction is observed at 7100°C. It ends at 7200°C with a sharp enthalpy decrease to the level corresponding to the state of a pre-forced oxidation stage of degradation. The latter two are characterized by the effect of OM as a kerite formation, the structure of which has been seriously degraded by the oxidative processes that took place in its environment. Title kerites (household names—coal gangue, coal oil) is used as a collective for all products metamorphic mineral oil. Kerites are the minerals, lost the characteristic properties of bitumen-solubility and melting behavior. In their bulk, they are composed of kerogen and karboidy. Furthermore, kerites present in minor amounts of asphaltenes and oils, their conditional partial solubility. In appearance and physical properties kerites like coals. From the typical bitumen they differ almost complete insolubility in organic solvents and infusible.

The following sample weight reductions took place in the range between 7000°C to 8900°C. On the DTG curve, the rate of mass loss is reflected as a peak, which has a small amplitude and stretched throughout the temperature scale at the interval. In this case, in the paired with thermogravimetry area on the DTA curve there were no explicit thermal manifestations of any orientation. In this connection it should be assumed that the change in mass of the sample in the said temperature interval is due to the release of volatiles from the system formed by the oxidation of the portion of the substance which belongs to the more organized carbonaceous structures. Quartz is found in the order of its behavioral features in the temperature range of 5000°C to 5600°C. Near 5000°C, the DTA curve captures the effect of lowering the enthalpy of the system, which is a characteristic of the polymorphic transformation of SiO\(_2\). At this temperature the quartz present in the sample proceeds from modification \( \alpha \) to \( \beta \). The heat absorbed by the structure leaves a small diffused peak apex on the curve. The biased effect in the low-temperature range and blurred outlines of the peak indicate the incompleteness of the structure of the mineral.

Fig. 4 shows the thermogram rock number 2 with the addition of polymethyl methacrylate (PMMA) (Sample 2A). When dynamically heated, the sample responds to the heat by predominantly exothermic manifestations. It should be noted that the depolymerization temperature of PMMA to the monomer of methyl methacrylate (MMA) is 1000°C. It likely flows to absorb heat, but nevertheless the related concurrent reactions leading to formation of a new monolithic formation in the systems of PMMA + OBR or bitumen, which is part of OBR, flow with heat, therefore DTA curves are characterized by exothermic effects. Across the temperature field the effect of heat absorption by the system is not observed, which indicates the absence of any packages of \( \text{H}_2\text{O} \) and CO carbonate in any sample. Apparently, the forced introduction of organic carbon to the system, in this case PMMA, the displacement of named components (if any exist) took place in the structure. Depending on the technology of organic saturation into the formation, water may be substituted by carbon or is removed altogether by the active reagents.
Monitoring the kinetics of the burning of organic matter in the range of 200°C to 5000°C suggests a medium degree of entanglement of its units of the sample, but to a weaker extent. At the above temperature values, the contiguity of carbon takes place mainly on surfaces and at the dangling bonds, passing inside the crystalline forms of packaging. The latter method takes much energy. OM oxidation progresses in two main stages, in the ranges between 200°C to 3400°C, and 340°C to 5000°C. Thus at each destruction step 4.96% (by weight of the sample) of gas is released. The second phase of gas formation is complicated by the two-step process, as evidenced by double peaks in the DTG and DTA curves at 4000°C. Along with this, at 340°C the DTA curve registers a clear endothermic effect on the morphology of the line corresponding to the type of polymorphic transformation of the oxide formation.

Thermal analysis of rock samples number 3 of the deposit Munaily Mola, diluted with an inert substance Al2O3 in a proportion of, respectively, gives only the following most reliable information on the composition of rocks. Fig. 5 shows the thermogram of the OBR, sample number 3 from Munaily Mola. As can be seen from Fig. 5, the thermal degradation of OBR occurs with a small endo-effect in the temperature range 160°C to 180°C and with a significant endo-effect at 530°C to 5400°C, and with a heat release at temperatures of 340°C, 445°C, 500°C, 580°C, 758°C and 8600°C. This complicated thermochemical expression is detected on the DTG and DTA curves in the range of 3500°C to 5800°C. In this temperature range, the enthalpy change is due to the summary heat transfer processes that occur as a result of a thermal degradation of organic matter (OM) present in the OBR. This area in the DTA curve is characterized by the sum of a series of endothermic and exothermic effects of different intensities and the "density" of the heat flow. Amid exotherm effects there are two weak peaks (at 340°C and 4450°C) and one explicitly peak (at 5000°C). Each effect corresponds to the weight loss equal to 0.95%, 1.9% and 0.58% (for mixtures), and highly carbonized structures of bitumen-kerites. They are diagnosed by high-temperature thermal reactions. In our case, due to a small percentage of the formation the two exothermic effects on the DTA curve in the range of 740°C to 8700°C reduce to very small protrusions with extremes at 780°C and 8600°C. And the two peaks defining the rate of the weight change are identified as a weak trough of the curve in the mentioned temperature range. Quantity of the substance (kerites) in the sample does not exceed 1%, as indicated by thermogravimetry (100% sample, IG=1.13%).

Along with this, small amounts of minerals of calcium sulfate, iron hydroxide (goethite) and silicon based on 100% ethyl sample, the thermogravimetry changes to 4.75%, 9.5% and 1.9%, respectively. Endothermic effects are associated with the removal of the light fractions of gaseous substances and carry out from the system the combustion products of carbon compounds. The composition of the OM can include oxide (quartz) are present in the sample. The thermal behavior of the sample number 1 is characterized by the presence of the expansion of endothermic reactions associated with the presence of gypsum and goethite in the sample in the initial stage (50°C to 3000°C). Gypsum is identified by its twin peak on the differential thermoanalytical (DTA) and differential thermogravimetric (DTG) curves with extremes at 100°C and 1200°C. Effects are due to the two-stage mineral dehydration: stage I of
dehydration occurs within the 50°C to 125°C range, phase II stage the range of 125°C to 1700°C. From the thermogravimetric (TG) curves it follows that the weight loss is 0.66% and 0.46%, respectively. The first stage of the weight change involves the production of water, which is present not only in a plaster. In this and the following stages of the gypsum dehydration, 0.46% of H₂O is removed, i.e. in total 0.92%, and the remainder of the water, 0.2% of the total sample belongs to the sample as a sorption share. The amount of sulfate is easy to count by using the gypsum stoichiometry and having a known part of the formula of 2H₂O = 0.92%.

Goethite (FeOOH) is used as another additive. It is detected by the endothermic reaction identified on the DTG and DTA curves in the shape of a clear peak at 250°C. The reaction is caused by dehydration of glandular inclusion (∆m=1.34%) and the transition of the system to the modification α-Fe₂O₃. Under 680°C this oxide undergoes a reversible polymorphic transformation into γ-Fe₂O₃. Accompanied by the absorption of heat energy, an endothermic effect is observed. Finally, a significant additive (quantitatively and by thermal behavior) is the organic matter (OM). Its presence is observed by an endothermic reaction in a wide temperature range (270°C to 900°C). According to the kinetics and the decomposition mechanism, this organic matter is a complex structure consisting of a series of bituminous minerals and their variations. The process of thermal degradation of OM is by stages, stage I in the range of 270°C to 330°C with the removal of CO₂ gas in the amount of 1.28% of the sample weight. The next stage takes place in two steps, with a corresponding weight loss of 5.28% in the temperature range of 330°C to 700°C. The final stage of destruction is in the range of 740°C to 900°C, with a removal of 0.86% by weight of a sample of carbon monoxide to the atmosphere. Apparently, this phase reveals the OM, which is the product of the highest stage of the bitumen carbonation, i.e. kerites and antraksmates. Along with the aforementioned entities, inert thermal inclusion are present in the rock, which do not allow for the chemical reactions within the temperature range or respond poorly to heat. These impurities can be a feldspar, mica and other anhydrous silicate formations detected by an X-ray of OBR sample 1.

CONCLUSIONS

1. Oil bitumen rocks were studied by the methods of thermal analysis, infrared spectroscopy and X-ray, the impact of inorganic and polymer additives on the mechanism of thermal degradation was studied.
2. It was investigated endo-and exothermic effects oil-bitumene rocks (OBR) c various additives. Amid exotherm allocated two weak peaks (at 3405 and 4450S) and one explicitly expressed (at 5000°C). Endothermic effects associated with the removal of the light fractions of gaseous substances and removal of products of combustion of carbonaceous compounds. The presence of bitumen and vysokokarbonizirovannyh structures-kerites. They are diagnosed by a high-temperature thermal reactions.
3. It is shown that the enthalpy change due to cumulative heat transfer processes that occur as a result of thermal degradation of organic matter (OM) present in the OBR. Establishes certain peaks endothermic and exothermic effects of different intensities and the "density" of heat flow.
4. A correlation of thermal methods of analysis of additives present in the OBR: feldspar, mica and other non-aqueous silicate formation detected as X-ray diffraction pattern OBR No. 1
5. Monolithic coatings based on OBR with a polymeric binder-PMMA were obtained for the first time.

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REFERENCES

Nadirov, N.K., Brawn, A.E. and Trokhymenko M.S.
ABDIKARIMOV ET AL.