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Combined Oxidized Bitumen: Technology, Chemistry and Properties

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Abstract

One of the important problems of the road industry is to improve the quality of bitumen used as a binder in the composition of asphalt mixtures. The aim of the work was to obtain and study the change in the composition and rheological characteristics of obtained products of a combined oxidation of a vacuum residue and a crumb rubber (CR). In this paper a new 2-stage combined oxidation of a vacuum residue is proposed: the 1st stage of the oxidation at 180 °C with small amount of the CR (2%) and the 2nd one at 260 °C with large amount of the CR (8%). This made it possible to obtain a road modified bitumen with improved high and low temperature performance: the values of the rutting parameter have been increased at temperatures from 46 °C to 64 °C and the stiffness has been significantly reduced to a temperature of -40 °C. The results of the analysis of the oxidation products by chromatography, nuclear magnetic resonance and infrared spectroscopy showed that unsaturated and sulfur-containing bonds in the rubber structure caused an intensive decrease in the content of oils and an increase in the content of condensed aromatic structures. Increasing the content of the condensed aromatic structures leads to increased high temperature resistance and the elastic rubber polymers have led to low temperature crack resistance.

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1. Introduction

Bitumen is a complex mixture of high boiling point range of organic compounds and molecules with a relatively low hydrogen-to-carbon ratio that is viscous, black and sticky. The terms of asphalt (asphalt binder) and bitumen (bitumen binder) are synonymous in the United States, while in Europe and Asia as well as in other areas, they have different meanings.[1-5] According to American Society for Testing and Materials (ASTM) definition that the bitumen as a generic class of amorphous, natural or manufactured, cementitious substances, dark colored composed principally of high molecular mass hydrocarbons, soluble in carbon disulfide. Meanwhile the European Standard EN 12597 defines the bitumen as a virtually in volatile, adhesive and water proofing material derived from crude petroleum, and very viscous or nearly solid at ambient temperature, which is completely or nearly completely soluble in toluene. It is not known to present any safety, health or environmental hazard. Asphalt is defined as a mixture of mineral aggregates and bituminous binder.[5-7]

Bitumen is widely used in many industries anywhere. The primary use of bitumen is for paving and roofing applications. Exactly 85% of all the bitumen is used as the binder in various kinds of asphalt pavements such as pavements for roads, airports, parking lots, *etc*. According to the statistic application, around 10% of the bitumen is used for roofing. The rest of the 5% bitumen is used for a different purpose; which sector is referred to as "Secondary Uses", for example, bitumen is also used for leak stops, pipe asphalt, joint filler, cable boxes,

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sealing accumulators and batteries, and others.[8,9]

There are well-known several manufacturing methods available to produce specification bitumens depending on the crude sources and processing capabilities available. Often used bitumen production technologies are as follows: distillation, solvent deasphalting, vacuum distillation of thermally cracked residue, and oxidized bitumen. Oxidized bitumen is made in a manufacturing unit known as the bitumen blowing unit or oxidizer air blowing unit, which is also commonly known as blown bitumen. Mentioned bitumen manufacturing depends on the feedstock viscosity and the processing conditions. The processes achieve this through varying degrees of chemical reactions, which result in an increase in the average molecular weight of the bitumen, leading to higher viscosity bitumen.[8-11]

Currently, there are four oxidized road bitumen producing enterprises in Kazakhstan. The biggest one is Caspi Bitum LLP, which is located in the western part of the country. The capacity of Caspi Bitum is about 400 thousand tons of oxidized road bitumen per year. Second is Pavlodar Petrochemical Plant LLP in the north, with a capacity of up to 350 thousand tons per year. Next is Qazaq Bitum, located in the south part, and its capacity is up to 280 thousand tons of bitumen. Asphalt Concrete 1 LLP is located in the southeast part of Kazakhstan, and its oxidized road bitumen-producing capacity is about 180 thousand tons per year. Kazakhstan is the 9th largest country in the world, covering an area of 2717,300 km^2, and state government programs have been agreed upon for the improvement of infrastructure and road construction across the country. As a result, the total demand for road bitumen in Kazakhstan could increase to 1.3 million tons in 2023. Imports from foreign countries fill the missing part of bitumen in our country. Characteristics of imported bitumen completely mismatch the climatic conditions of our country, *i.e.*, do not maintain sharp differences of temperatures from -40 up to +40 °C. Also, with a view to the preservation of quality and technological properties, bitumen is not recommended to be transported over greater distances. Bitumen shakes during long-distance transportation, which can change the grade of bitumen, as can mechanical mixing. In this connection, the production of bitumens of various marks on the basis of domestic raw material is an actual problem.[4-5,8,12]

Modern trends in the development of the oil industry, aimed at increasing the depth of oil refining, have a negative impact on the properties of residual oil products as raw materials for the production of oxidized bitumen. This is because the quality indicators of the latter largely depend on the group and chemical composition of the used raw materials. In addition, it is possible to obtain bitumen with improved adhesion and higher resistance to thermochemical oxidation by oxidizing oil feedstock at low process temperatures, but this leads to a decrease in the productivity of oxidized bitumen production plants.[13-15]

Using poor quality bitumens in asphalt concrete is the main problem in road building. One way to improve the quality of the bitumen is modification. It was found many modification processes and additives are currently used in bitumen modifications, such as styrene-butadiene rubber, ethylene vinyl acetate, styrene butadiene styrene, and crumb rubber (CR) modifiers.[16-18] As results of investigations that the properties of crumb rubber modified bitumen at a wide range of temperatures are considered to be somewhat unclear due to the various interaction effects of CR with a bitumen binder, depending on the chemistry of the bitumen, the CR percentage in bitumen, particle size of crumb rubber, the effect of mixture mixing type, dimensional changes of CR with bitumen, texture service of crumb rubber and the mixture blending interaction temperature and time. Modified bitumen has improved characteristics of heat, frost, and wear resistance. Its use in road construction will increase their service life by 1.5–2 times. Thus, using rubber crumbs in bitumen modification makes it possible to solve environmental problems and perform economically rational utilization processes. thereby increasing the quality of life of the population and reducing traffic accidents. It will be possible to improve the quality of the infrastructure.[19,20]

A term for crumb rubber is usually applied to recycled rubber obtained by mechanical shearing or grinding from automotive and truck scrap tires into small particles. While recycling scrap tires, the steel and fluff are removed, leaving rubber with a granular consistency. Using spent rubber technical materials, including automobile tires, is one of the most important environmental problems in the world because of the rapid growth of the world population and the volume of their consumption. Spent tires are bulky and highly toxic. They do not undergo natural degradation and decay. For these reasons, they accumulate in open landfills to occupy considerable ground areas or are scattered in ravines, forests, and water bodies to pollute the environment. According to published data, the world reserves of scrap tires are estimated to be more than 25 million tons, with an annual increment of 12 million (at least 7 million) tons. In Kazakhstan and the other Commonwealth of Independent States, the annual volume of discarded automobile tires exceeds 1 million tons.[20-24]

Nowadays, for protecting the environment and utilizing natural resources, many countries in the glove give priority to the reuse of waste rubber. In fact, the scrap tires are valuable secondary raw materials that contain 65-70% of rubber, 15-25% of technical carbon and 10-15% of metal materials. The effective processing of spent tires allows not only to solve ecological problems but also to perform economically rational utilization processes.[24,25]

Many potential scientists have been offered variety ways of recycling and utilization of rubber crumb from worn tires in the world. Including the well-known method is to burn the waste rubber to produce energy during the cement producing process. But, this type of “recycling” has to be reduced in the future and starting it. Often, crumb rubber is used in astroturf as cushioning; sometimes, it is referred to as Astro dirt. The work used[26] CR to remove xylene, ethylbenzene, and toluene from aqueous solutions at room temperature. Rubber crumb is used in the manufacturing of some auto parts, namely brake shoes, brake pads, and vehicle acoustic insulation. Small volumes of crumb rubber go into the manufacturing of new tires. On the other side, the cut tires are used to manufacture drainage tubes and soundproof walls along highways, tapes for the protection of cables and pipelines, and downslopes from erosion. Thermal methods are used for the secondary use of scrap tires. However, the combustion of tires to generate energy and pyrolysis under low temperatures allows the production of light distillate, solid fuel, carbon-containing materials, and metals.[27] The British group Dena Technology developed the modern nanotechnological process of reusing rubber wastes; they found a new method to produce high-quality building materials such as wood-replacement products and paper-replacement materials from spent tires. Using alternative materials in road and pavement construction, which is a large-tonnage product, will not only improve the bitumen binder properties and durability, but they also have the potential to be cost-effective as they are highly expensive materials.[28-30]

Improvement of production technology and quality characteristics, carried out through the reconstruction of existing installations or changes in technological parameters, are associated with significant material costs, as a result, increase the cost of bituminous binder. In this regard, such a way to control the performance of vacuum residue oxidation plants as the effect of modifying additives on the raw material seems to be more accessible. According to the literature data,[31-34] the introduction of small amounts of modifiers into the raw material can positively affect the properties of the resulting bitumen as following: plasticity, group and chemical composition are improved. However, for the most complete realization of the potential possibilities of modifying raw materials in the production of oxidized bitumen, systematic studies of these systems should be significantly expanded.[35-37] When deciding on the prospects of using new modifiers in the process of vacuum residue oxidation, the main criteria are a high oxidation rate, energy efficiency and rational resource consumption in terms of ensuring environmental safety. Therefore, from a scientific and practical point of view, it is important to study the effect of modifiers on the composition and properties of products of liquid-phase oxidation of vacuum residue.[38,39] Data on the physical and mechanical characteristics and compositions of the modified oxidation products are necessary to develop the optimal mode of the chemical-technological process.

In connection with the foregoing, this work aimed to study the change in the chemical composition and rheological characteristics of vacuum residue during oxidation with the addition of crumb rubber, which affects the structural organization of the original oil system.

2. Materials and methods

2.1 Vacuum residue

In the work, a vacuum residue (VR) from the Omsk oil refinery (Omsk, Russia), which is a raw material for the production of an oxidized bitumen at “Asphaltobeton-1” LLP in Almaty city (Kazakhstan), was used as a feedstock for the production of a bitumen by oxidation in laboratory conditions. The VR is a liquid with a density of 957.0 kg/m^3 at 20 °C.

2.2 Crumb rubber

A crumb rubber (CR) obtained by “Q-Recycling” LLP (Almaty) was used as a modifier of the VR and bitumen. The choice of CR is since it acts, firstly, as a modifier, and secondly, as a catalyst, somewhat accelerating the oxidation process.

2.3 Combined oxidation

The oxidation process adopted in the work is implemented in the following sequence: 1) the first portion of CR in the amount of 2% by weight is added to the VR and continuously mixed for 0.5 hours at a temperature of 180 °C. This temperature ensures the complete distribution of rubber particles in the VR and creates conditions for rubber swelling due to the absorption of the bitumen liquid phase. This is a preparatory process before oxidation; 2) the resulting mixture of VR and CR (2%) is oxidized by air for 2 hours at 260°C. The air consumption was 7.5-10 l/min. At the oxidation temperature, the dissolution of CR is improved under the action of asphaltogenic acids and atmospheric oxygen; 3) the second portion of CR in the amount of 8% is added to the product of the joint oxidation of VR and CR (2%) and continuously mixed for 0.5 hours at a temperature of 180 °C. At this stage the bitumen and CR interact with each other and the bitumen is modified.

The described technological method allows, to some extent, to combine the oxidation process of a VR with the process of bitumen modification, which are usually carried out separately.[40] Therefore, this method can be called "combined oxidation". Combined oxidation was carried out on a specially designed unit. The scheme and detailed description of the combined oxidation unit are given in the work.[41]

The combined oxidation method, compared to traditional oxidation and modification processes carried out separately, has the following advantages: firstly, the duration of the process is reduced (from 0.5 to 1 hour); secondly, energy consumption is reduced; thirdly, thermal pollution of the atmosphere and harmful emissions into the environment are reduced.

The combined oxidation method can mainly be used in bitumen plants that produce bitumen by oxidation and modify it with CR, polymers and other modifiers. In the future, different options for the combined oxidation can be studied with changes in the duration of its stages, temperature, dispersity (particle sizes) of CR (for example, to nanosized), with different polymers instead of CR and in combination with CR in different proportions.

2.4 Gas chromatography

Gas chromatography with mass spectrometric detection using a Agilent 7890A/5975C chromatograph was used to determine the hydrocarbon composition of the VR and its oxidation products without and with the addition of CR. Analysis conditions: a sample volume is equal to 0.5 µl, the sample injection temperature is 250 °C, no split flow. Separation was carried out using a DB-35MS chromatographic capillary column with length of 30 m, with inner diameter of 0.25 mm and film thickness of 0.25 µm at a constant carrier gas (helium) velocity of 1 ml/min. The chromatography temperature is programmed from 40 °C (0 min hold) to 280 °C with heating rate of 10 °C/min (25 min hold). 1 g of the test sample was extracted with 5 ml of chloroform solution and transferred into a 2 ml vial. Detection in SCAN mode m/z 10-850. The Agilent MSD ChemStation software (version 1701EA) was used to control the gas chromatography system, record and process the obtained results and data. Data processing included determination of retention times, peak areas, and processing of spectral information obtained using a mass spectrometric detector. To interpret the obtained mass spectra, the Wiley 7th edition and NIST'02 libraries were used (the total number of spectra in the libraries: more than 550 thousand). Group analysis of samples by gas chromatography with mass spectrometric detection was performed according to the calculation method described.[42]

2.5 IR spectroscopy

The Perkin Elmer Spectrum 100 Fourier transform infrared (FTIR) spectrometer was used to identify the chemical functional groups of the VR and its oxidation products. The wavelength of the reflected beam is characteristic of each element and indicates the presence of specific functional groups. Samples for FTIR were prepared as potassium bromide (KBr) pellets, containing 0.1 to 0.8 wt.% of powdered sample. Mixtures of sample/KBr were prepared in a clean and dry agate mortar. The FTIR spectrum was obtained in the spectral range between 4000 and 600 cm^{-1} with a scanning resolution of 4 cm^{-1} averaging five scans for each measurement in order to increase the signal-to-noise ratio of the measurements. Then the spectrum was normalized to allow the quantitative analysis of the results.

2.6 NMR spectroscopy

The nuclear magnetic resonance (NMR) spectra of the ^{1}H hydrogen and ^{13}C carbon nuclei of the samples were taken on a JNM-ECA Jeol 400 spectrometer (Japan) at temperature of 25 °C. The operating frequencies for the ^{1}H and ^{13}C nuclei were taken to be 399.78 MHz and 100.53 MHz respectively. Samples of the materials (60 mg) were dissolved in deuterated chloroform ($CDCl_3$) with a volume of 0.5 ml.

The chemical shifts of the ^{1}H and ^{13}C nuclei were measured relative to the signals of the residual protons or carbon atoms of deuterated chloroform. The limits of chemical shifts of the ^{1}H and ^{13}C nuclei used to identify and determine the amounts of functional groups in the samples are given in Tables 1 and 2.

By integrating the spectra within the specified limits of chemical shifts (Tables 1 and 2), one can calculate the relative number of hydrogen and carbon atoms belonging to the corresponding functional groups.[43,44] The total integrated intensities of the signals of hydrogen and carbon atoms are calculated by the expressions respectively:

$$\overline{H}_{sum} = H_{ar} + H_{\alpha} + H_{\beta} + H_{\gamma}, \quad (1)$$

$$\overline{C}_{sum} = C_{pm} + C_{p\alpha} + C_{a\ell}, \quad (2)$$

Table 1. Limits of variation and interpretation of chemical shifts of ^{1}H nuclei.

δ (^{1}H), ppm	Notation of atoms	Functional group
0.5-1.0	H_{γ}	Methyl groups of saturated compounds. Methyl groups in γ and further positions to an aromatic ring.
1.0-2.0	H_{β}	Methylene and methine groups of saturated compounds. Hydrogen atoms in methyl groups in β position to an aromatic ring. Hydrogen atoms of methylene and methine groups in β and further positions to an aromatic ring.
2.0-4.0	H_{α}	Hydrogen atoms in α position to aromatic and carbonyl carbons, heteroatoms
4.5-6.3	$H_{o\ell}$	Hydrogen atoms of olefinic groups
6.3-9.0	H_{ar}	Hydrogen atoms of aromatic nuclei and phenolic hydroxyls

Table 2. Limits of variation and interpretation of chemical shifts of ^{13}C nuclei.

δ (^{13}C), ppm	Notation of atoms	Functional group
7-17	C_{pm}	Carbon atoms of methyl groups linked with a methylene group
17-25	C_{pa}	Carbon atoms of methyl groups linked with a methine group or an aromatic ring
25-50	$C_{a\ell}$	Quaternary aliphatic carbon atoms

The contents (%) of aromatic and aliphatic hydrogen atoms are determined by the formulas respectively:

$$\overline{H}_{ar} = \frac{H_{ar}}{\overline{H}_{sum}} \cdot 100\ \%, \quad (3)$$

$$\overline{H}_{a\ell} = \frac{H_{\alpha}+H_{\beta}+H_{\gamma}}{\overline{H}_{sum}} \cdot 100\ \%, \quad (4)$$

The contents (%) of hydrogen atoms (H_{α}, H_{β}, H_{γ}) are determined by the formulas respectively:

$$\overline{H}_{\alpha} = \frac{H_{\alpha}}{\overline{H}_{sum}} \cdot 100\ \%, \quad (5)$$

$$\overline{H}_{\beta} = \frac{H_{\beta}}{\overline{H}_{sum}} \cdot 100\ \%, \quad (6)$$

$$\overline{H}_{\gamma} = \frac{H_{\gamma}}{\overline{H}_{sum}} \cdot 100\ \%, \quad (7)$$

$$\overline{\mathrm{H}}_{ol} = \frac{H_{ol}}{\overline{H}_{sum}} \cdot 100\ \%. \quad (8)$$

The contents (%) of carbon atoms (C_{pm}, C_{pa}, $C_{a\ell}$) are determined by the formulas respectively:

$$\overline{\mathrm{C}}_{pm} = \frac{C_{pm}}{\overline{C}_{sum}} \cdot 100\ \%, \quad (9)$$

$$\overline{\mathrm{C}}_{p\alpha} = \frac{C_{p\alpha}}{\overline{C}_{sum}} \cdot 100\ \%, \quad (10)$$

$$\overline{\mathrm{C}}_{\alpha\ell} = \frac{C_{\alpha\ell}}{\overline{C}_{sum}} \cdot 100\ \%, \quad (11)$$

2.7 Liquid adsorption chromatography

The group chemical composition of the VR was determined using a Gradient-M liquid adsorption chromatograph (Ufa, Russia). First, a sample to be analyzed is heated, stirred, and a weighed portion of 0.1 g is taken, which is diluted with benzene at the rate of 7 ml of benzene per 1 g of a sample portion. In this case 2 μl of the sample solution is injected into the column. The sample is injected into the column with a microsyringe. The microsyringe is thoroughly washed with benzene or an alcohol-benzene mixture and blown with purified air. A solution of the analyzed sample is pumped through a clean syringe several times. With a microsyringe1 or 2 μl of VR is carefully introduced into the top layer of silica gel in the column. Silica gel is added to the column to the marked level of the tank in order to avoid displacement of the upper layer of the adsorbent with asphaltenes when the pressure is removed before the second solvent is supplied. Carefully inject 1.5-2 ml of the first eluent into the tank of the chromatographic column with a medical syringe. The column prepared in this way is placed in the column fixator of the chromatograph. Then pressure is applied. The operating pressure ranges from 0.3-1.2 MPa and depends on the grinding of silica gel, on the degree of packing of the column. The finer the silica gel and the denser the packing of the column, the greater the operating pressure. After all the separated components of the maltenic part exit the column and six chromatographic peaks are recorded on the cartogram of the recorder, the pressure is carefully removed. Remove the column and remove the remaining solvent with a syringe. Then 1-1.5 ml of the second solvent is introduced, the column is again installed in the chromatograph and pressure is applied. The exit order of the groups is as follows: paraffin-naphthenic hydrocarbons, light aromatic hydrocarbons, medium aromatic hydrocarbons, heavy aromatic hydrocarbons, neutral resins, acid resins, asphaltenes. After the peak of asphaltenes (the seventh peak) is fixed on the cartogram, the column is removed, dried, and silica gel is removed from it.

2.8 Microscopy

To obtain information about the morphological structure of CR, we used a Leica DM6000 M fluorescent microscope (Leica Microsystems Wetzlar GmbH, Germany) and a Quanta 3D 200i scanning electron microscope at an accelerating voltage of 20 kV (FEI Company, USA).

2.9 Short-term aging

Short-term aging of the bitumen in the vertical rolling thin film oven have been performed under the standard,[45] which models the bitumen aging during preparing of an asphalt concrete mix, its transportation, laying and compaction. The samples of the bitumen were in the oven at the temperature of 150 °C for 75 minutes.

2.10 Long-term aging

Long-term aging of the bitumen in the special pressure aging vessel has been performed under the standard,[46] which models the bitumen aging during operation of the asphalt concrete pavement. The samples of the bitumen, after the short-term aging, were in the vessel under the pressure of 2070 kPa and at the temperature of 100 °C for 20 hours.

2.11 Bending beam rheometer

To evaluate the resistance to low temperature cracking, samples of the bitumen obtained by combined oxidation were tested on a bending beam rheometer (BBR) at temperatures of -24, -27, -30, -33, -36 and -39 °C according to the standard.[47] Currently, BBR is widely used for the experimental determination of low temperature characteristics of bituminous binders.[48-50] In accordance with the requirements of Superpave,[51] before testing on BBR bitumens must be subjected to double aging: short-term aging according to the standard[45] and long-term aging according to the standard.[46] Values of bitumen stiffness are calculated by the formula:

$$S(t) = \frac{P \cdot \ell^3}{4 \cdot b \cdot h^3 \cdot \delta(t)}, \quad (12)$$

where, *S(t)* is a bitumen stiffness at time t (MPa), *δ(t)* is a maximum deflection of the bitumen beam at time t (mm), *P* is load (0,98 H), *h, b, ℓ* are height, width, length of the bitumen beam, respectively (mm).

Bitumen relaxation rate m (m-value) is determined by the expression:

$$m = \frac{d\ \ell og[S(t)]}{d\ \ell og(t)}. \quad (13)$$

2.12 Dynamic shear rheometer

To evaluate high temperature performance the bitumen samples were tested on a dynamic shear rheometer of model SmartPave 102 (Anton Paar GmbH, Austria) at the temperatures of 46, 52, 58, 64 and 70 °C in the virgin (unaged) condition and after aging in RTFOT. The controlled strain mode was accepted. Target strain and angular frequency were equal to 12% and 10 rad/s respectively. Two metal plates were used with the same diameter (25 mm) and 1 mm gap between them.

3. Results and discussion

3.1 Vacuum residue

The group, hydrocarbon and fractional compositions of VR are presented in Table 3. The group composition of the VR was determined by an adsorption chromatography. As it can be seen from Table 3, according to the group composition in the VR, the total content of oils is 56.7%. Aromatic oils (30.8%) predominate compared to paraffin-naphthenic oils (25.9%). Heavy aromatic oils have a high content (18.1%) among the aromatic oils. As a heavy oil residue, the VR is characterized by a high content of resins (31.5%) and asphaltenes (11.8%). Among the resins, the content of acidic resins (20.3%) prevails over the content of neutral resins (11.2%).

The hydrocarbon composition of the VR was determined by a liquid chromatography. Based on the chromatogram (Fig. 1), the contents of hydrocarbons were calculated, which are shown in Table 3. Among the classes of hydrocarbons, aromatic hydrocarbons (44.52%) and cycloalkanes (41.07%) turned out to be almost 3 times more than alkane hydrocarbons (14.41 %).

According to the fractional composition, the VR is represented mainly by heavy oil fractions with a boiling point of 350 °C and higher (60.1%). The total content of light distillates with a boiling point up to 350 °C in the VR is 39.9%. The results of IR spectroscopic analysis also confirm the composition of the VR. The IR spectrum (Fig. 2) is represented by intense absorption bands of aliphatic structures by vibrations of C-H bonds in CH_2 and CH_3 groups at 721, 1375, 1457, 2850 and 2919 cm^{-1}. The spectrum also contains absorption bands of aromatic structures at 745, 810, 865 and 1616 cm^{-1}.

Thus, VR is a heavy oil residue with a high content of aromatic hydrocarbons (44.52%) and cycloalkanes (41.07%) found in oils, resins, and asphaltenes.

3.2 Crumb rubber

Pictures of the CR obtained on optical and scanning electron microscopes are shown in Figs. 3 and 4. These pictures show the CR has a heterogeneous, complex and porous morphological structure. A conglomerate of heterogeneous grain sizes represents the material; most grains are nanoscale and have open (not bonded) surfaces due to their porous structure, which determines their high reactivity, especially at high temperatures (180 °C and 260 °C).[52]

Table 3. Group, hydrocarbon and fractional compositions of VR.

Indicator	Content in VR, wt.%
Oil content, wt.%:	56.7
paraffin-naphthenic	25.9
light aromatic	9.9
medium aromatic	2.8
heavy aromatic	18.1
Resin content, wt.%:	31.5
neutral resins	11.2
acidic resins	20.3
Asphaltene content, wt.%	11.8
Hydrocarbon content, wt.%:	
alkanes	14.41
cycloalkanes	41.07
aromatic	44.52
The content of fractions, wt.%:	
the beginning of boiling – 180 °C	7.0
200-350 °C	32.9
350 °C - end of boiling	60.1

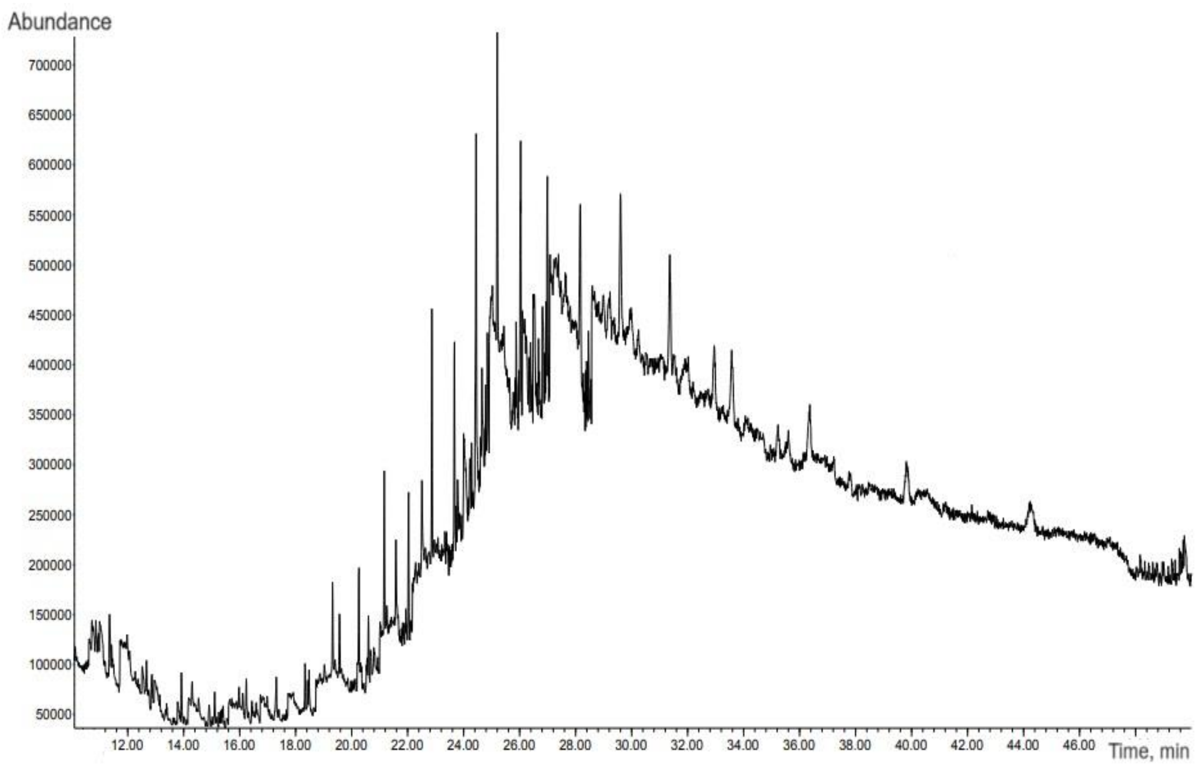

Fig. 1 Chromatogram of the VR.

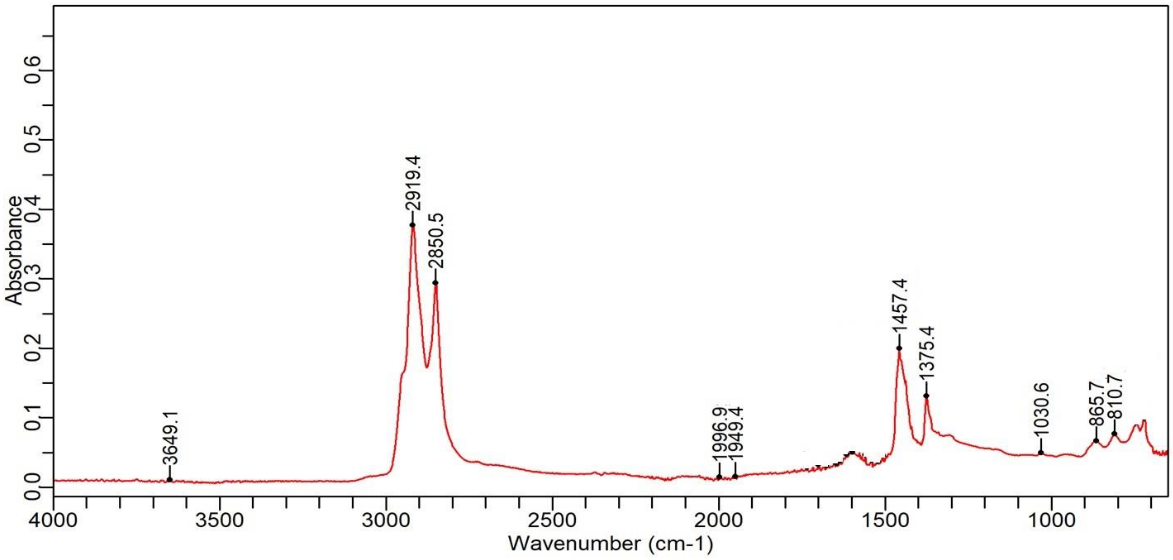

Fig. 2 IR spectrum of the VR.

Figure 5 shows the CR's infrared spectrum. It is distinguished by a set of high-intensity absorption bands at 964 and 1062 cm^{-1}. The absorption band at 964 cm^{-1} belongs to the vibrations of double C=C bonds of rubber compounds, and the absorption band at 1062 cm^{-1} is due to the presence of sulfoxides formed during the vulcanization of rubbers to produce rubber. The technical indicators of the CR meet the requirements of the Kazakhstan standard[53] and are shown in Table 4.

3.3 Gas chromatography

The hydrocarbon compositions of the VR and its oxidation products without and with the CR was determined by a gas chromatography with mass spectrometric detection. The products of the VR oxidation without and with the CR were obtained at a temperature of 260 °C for 3 hours.

Table 4. Technical indicators of the CR.

Indicator	Value	Requirements of the ST RK 2028-2010
Mass fraction of cord fiber residues (viscose and nylon), %	0.02	no more than 1.0
Mass fraction of rubber (%), sifted through a mesh sieve:		
1.4		
1.0	100.0	at least 100
0.63	92.6	at least 90
0.315	50.0	at least 50
	8.5	not standardized
Mass fraction of ferrous metal particles after magnetic separation, %	not found	no more than 0.005

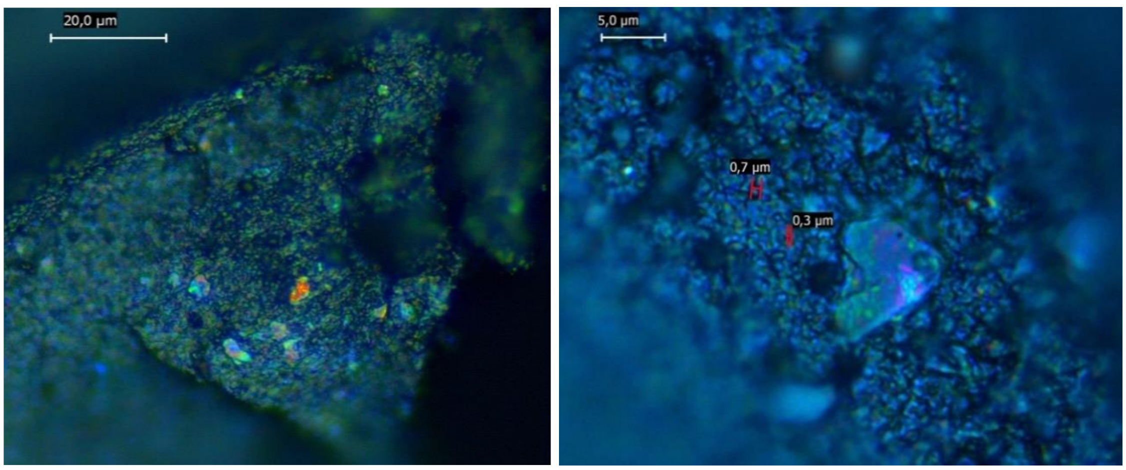

Fig. 3 Optical microscope images of the CR samples.

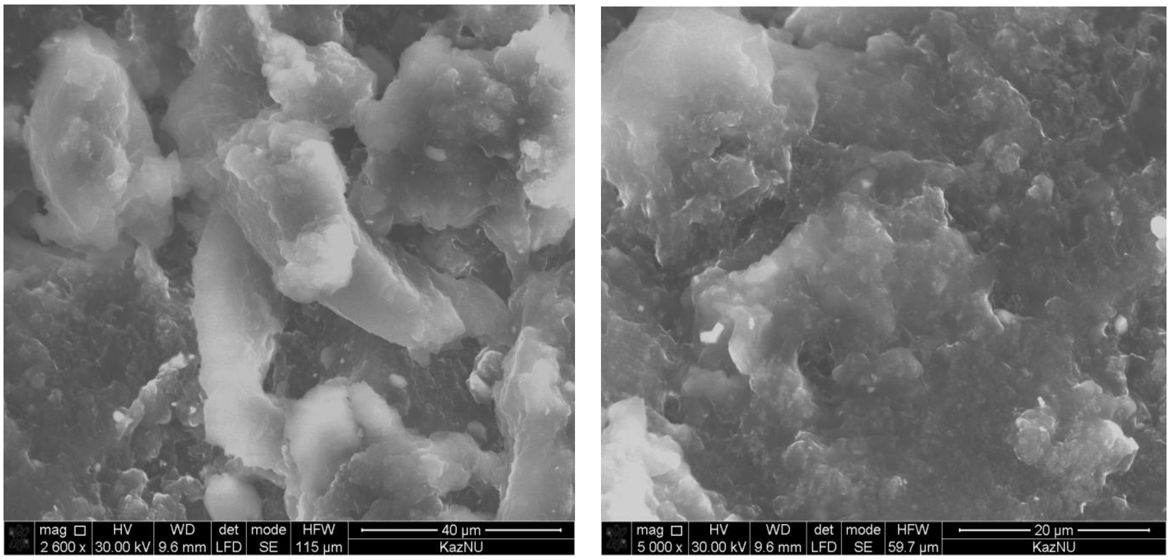

Fig. 4 Electron microscopic images of the CR samples.

From Fig. 6, the same change is observed in the total amount of cycloalkanes, their total content decreases, the largest decrease is observed in the product of VR oxidation with addition of the CR - by 3.63%, while in the oxidation product without the CR cycloalkanes decreased by 2.17%. Among the cycloalkanes (Table 5), the maximum content is shown by non-condensed cycloalkanes, their content in the VR was 17.24%, in the oxidation products without and with CR - 15.93 and 14.98%, respectively. Unlike other types of cycloalkanes, the amount of condensed cycloalkanes with three rings in the oxidation products of the VR slightly increases: in the initial VR - 11.29%, in its oxidation products - 11.57 and 11.61%.

Unlike alkanes and cycloalkanes, the total number of aromatic hydrocarbons increases. Here, the greatest increase in the content of aromatic hydrocarbons is manifested in the product of the VR oxidation with the CR. The content of arenes in the feedstock was 44.52%, and in the oxidation products of the vacuum residue with the CR - 49.56%, *i.e.* the content of arenes increased by 5.04%. In the oxidation product of the VR without the modifier, the content of aromatic hydrocarbons is 47.56%, which led to an increase in their content by 3.04%. Almost all classes of aromatic hydrocarbons have a decrease in their amount, except for benzenes: the content of benzenes in the VR was 7.81%; after oxidation, their content decreased slightly - to 7.66%.

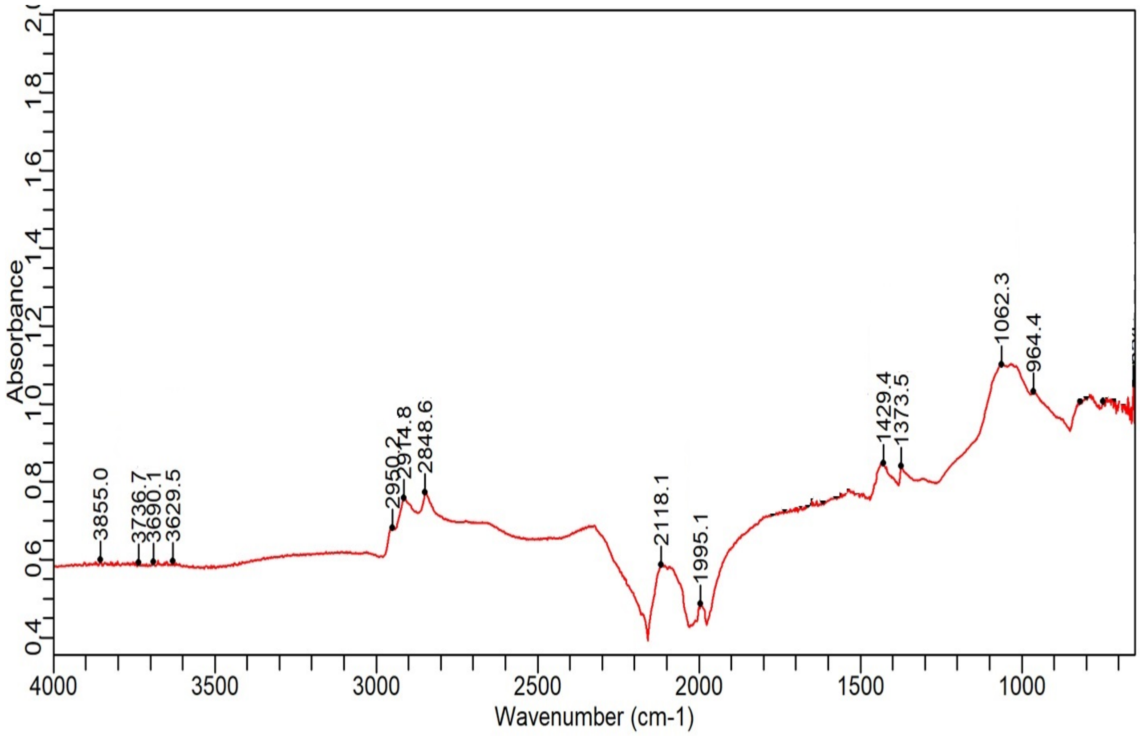

Fig. 5 IR spectrum of the CR.

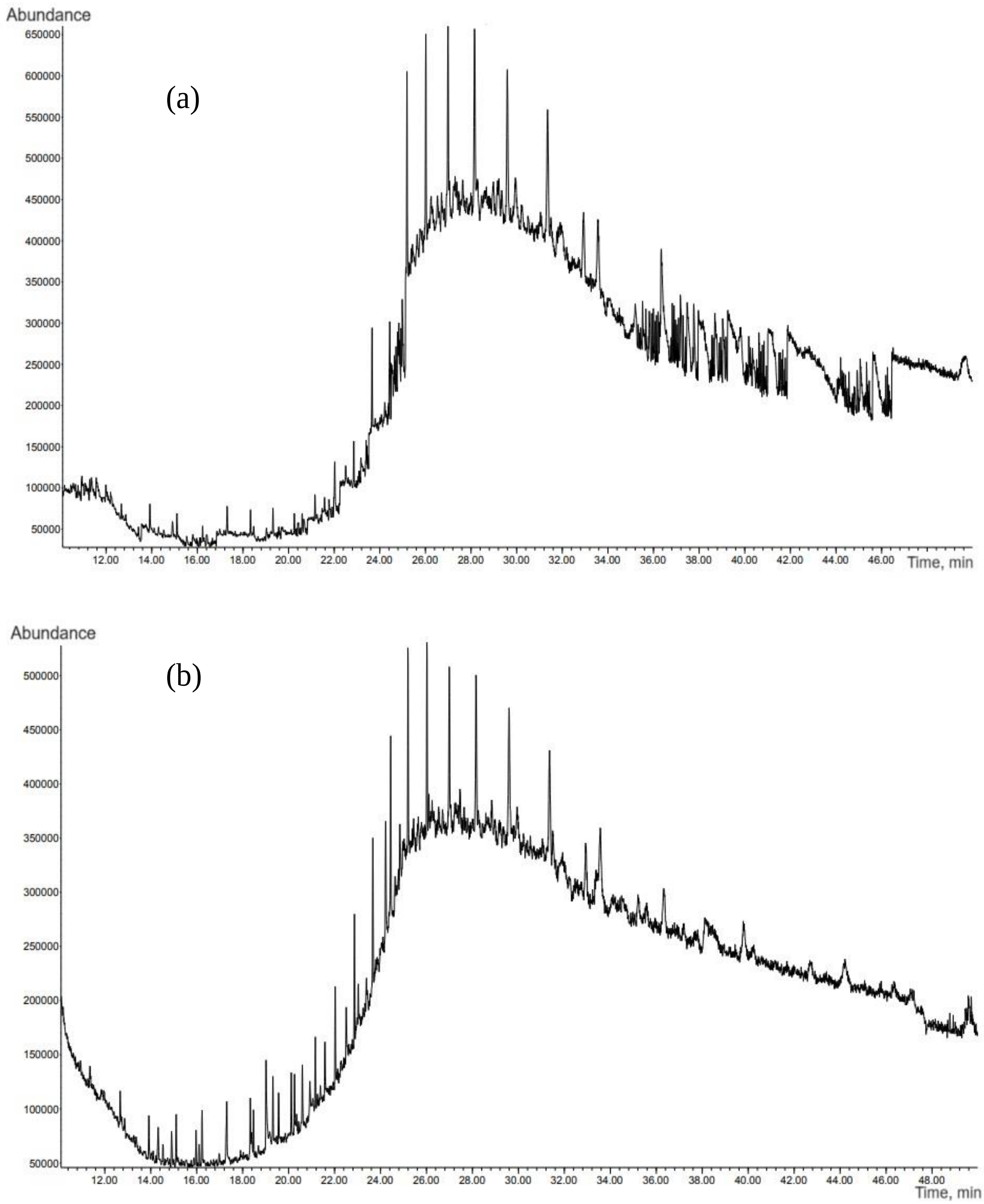

Fig. 6 Chromatograms of oxidation products of VR without (a) and with (b) the CR.

Among the various classes of aromatic hydrocarbons, naphthenobenzenes have the maximum content: their amount in the feedstock is 7.91%, in the oxidation product of the raw material - 8.27%, in the oxidation product with CR - 8.76%. Naphthalenes have the smallest amount, their content in the VR is 3.98%, it increases to 4.48% in the oxidation product without the modifier, and it increases to 4.75% in the oxidation product with the CR.

3.4 IR spectroscopy

An IR spectroscopic analysis was carried out to establish the changing dynamics in the VR's composition during oxidation.

Figure 7 shows the IR spectra of the VR mixed with 2% CR for 0.5 hours at 180 °C, then after 1 and 2 hours of oxidation at 260 °C, also mixed for 0.5 hours at 180 °C after addition of 8% CR.

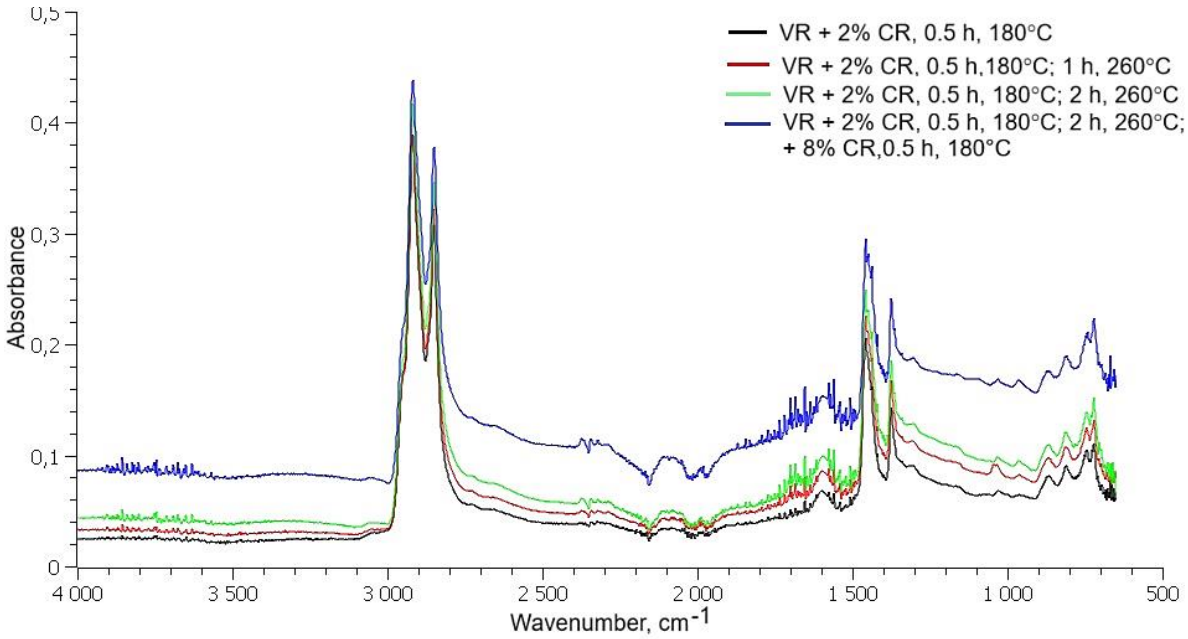

Fig. 7 IR spectra of the VR with 2% CR for 0.5 hours at 180 °C (black line), after 1 (red line) and 2 hours (green line) oxidation at 260 °C, after oxidation for 0.5 hours at 180 °C with 8% CR (blue line).

Table 5. Results of the chromatographic analysis of the VR and its oxidation products without and with the CR.

Classes of hydrocarbons	Vacuum residue (VR)	Oxidation product of VR without CR	Oxidation products of VR with CR
Alkanes	14.4	13.53	13.0
Uncondensed cycloalkanes	17.24	15.93	14.98
Condensed cycloalkanes with 2 rings	12.54	11.4	10.85
Condensed cycloalkanes + all cycloalkanes with 3 rings	11.29	11.57	11.61
Total number of cycloalkanes	41.07	38.9	37.44
Benzenes	7.81	7.66	7.72
Naphthenobenzenes	7.91	8.27	8.76
Dinaphthenobenzenes	6.46	7.33	7.92
Naphthalene	3.98	4.48	4.75
Acenaphthenes	6.58	7.03	7.17
Fluorenes	6.05	6.59	6.82
Phenantrenes	5.73	6.2	6.42
Total number of aromatic hydrocarbons	44.52	47.56	49.56

Table 6 compares the absorption band intensities observed in the IR spectra of the samples. As it can be seen from the table data, in the samples of oxidation products with the CR, a gradual increase in the intensities of the lines of all absorption bands is observed, which indicates an increase in the content of resins and asphaltenes in their composition, which consistof condensed aromatic structures.

Absorption bands at 659 and 964 cm^{-1} appear in the IR spectrum of the final product of the VR oxidation with CR, which are absent in the spectrum of other samples. The appearance of these bands, characteristic of the IR spectra of rubbers, is due to vibrations of double C=C bonds in the cis- and trans-positions, which should be attributed to the rubber destructured as a result of heat treatment and the resulting rubber substances.

3.5 NMR spectroscopy

The NMR spectra of ^{1}H hydrogen and ^{13}C carbon atoms of the VR (a), the CR (b) and the oxidation products without (c) and with the CR (d), built from the results of measuring the corresponding chemical shifts, are shown in Figs. 8 and 9 respectively.

The contents of ^{1}H and ^{13}C nuclei in the functional groups present in the VR, the CR and oxidation products without and with the CR are presented in Tables 7 and 8.

The analysis of tabular data shows that hydrogen atoms in the samples are presented mainly in aliphatic fragments, their amount in the VR is 99.8%, which decreases as a result of oxidation to 92.4%. Among these atoms the largest number (58.7-66.8%) is in the methylene (CH_2) and methine (CH) groups of saturated compounds and in the composition of these groups in β and further positions to an aromatic ring; their decrease by 4.6-5.4% is also observed after the oxidation process. 16.5-21.7% of hydrogen atoms are in the methyl (CH_3) groups of saturated compounds, as well as in γ- and further positions to an aromatic ring; here an increase in their content during oxidation by 4% is observed. 8.9-15.0% of hydrogen atoms are bonded in the α-position to aromatic and carbonyl

Table 6. Intensities of absorption bands in the IR spectra of vacuum residue mixed with 2% CR for 0.5 hours at 180 °C (1), then after 1 (2) and 2 hours (3) oxidation at 260 °C, also after oxidation with 8% CR for 0.5 hours at 180 °C (4).

Wave number, cm^{-1}	Line intensity, relative units				Link fluctuations and groups
	1	2	3	4	
659	0.07	-	-	0.17	Deformation vibration of a C=C bond in the cis-position
669	0.08	0.08	0.09	0.18	Deformation vibration of a N-H bond in primary and secondary amines
721	0.11	0.13	0.15	0.22	Deformation vibration of a C-H bond in long alkyl chains containing more than four CH_2 groups
745	0.10	0.12	0.14	0.21	Vibration of four H atoms adjacent to an aromatic ring
810	0.09	0.11	0.12	0.19	Vibration of two H atoms adjacent to an aromatic ring
865	0.08	0.10	0.11	0.18	Vibration of a H atom adjacent to an aromatic ring
964	-	-	-	0.17	Deformation vibration of a C=C bond in the trans-position
1031	0.07	-	0.10	0.17	Stretching vibrations of a S=O group
1375	0.14	0.17	0.18	0.24	Deformation vibration of a
1457	0.20	0.23	0.25	0.29	C-H bond in CH_3 and CH_2 groups
1595	0.07	0.09	0.10	0.15	Deformation vibration of a C=C
1616	0.06	0.08	0.10	0.15	bond in an aromatic ring
1700	0.05	0.07	0.09	0.15	Stretching vibration of a C=O group in ethers
1718	0.05	0.07	0.08	0.14	Stretching vibration of a C=O group in ketones
1734	0.05	0.06	0.07	0.13	Stretching vibration of a C=O group in aldehydes
2850	0.31	0.32	0.35	0.38	Valence vibrations
2919	0.39	0.39	0.42	0.44	C-H bonds in a CH_2 group
3629	-	0.03	-	0.09	Stretching vibrations of a OH
3676	-	0.03	0.05	0.10	group

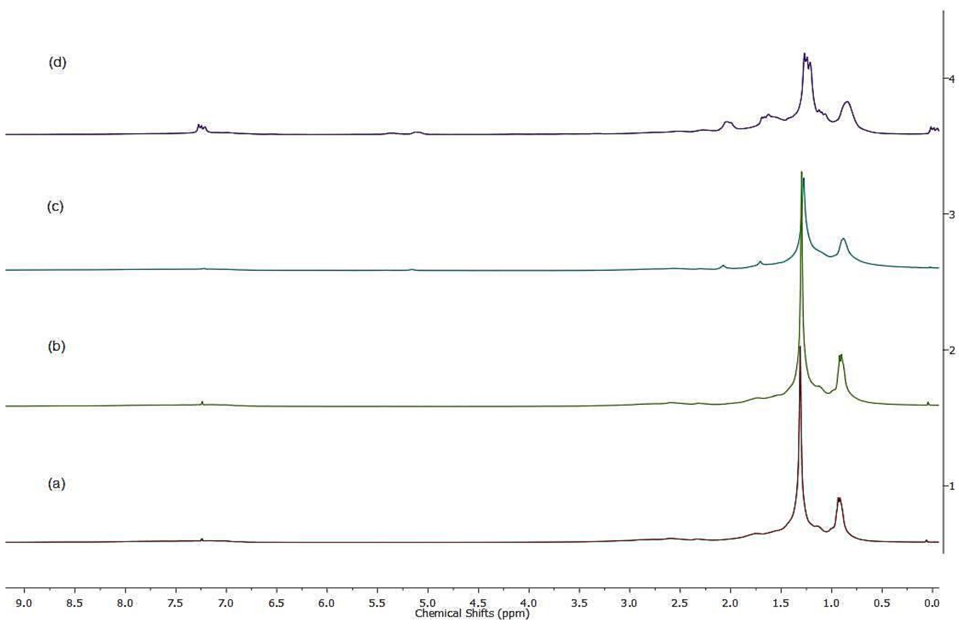

Fig. 8 ^{1}H NMR spectra of the VR (a), its oxidation products without (b) and with the CR (c), the CR (d).

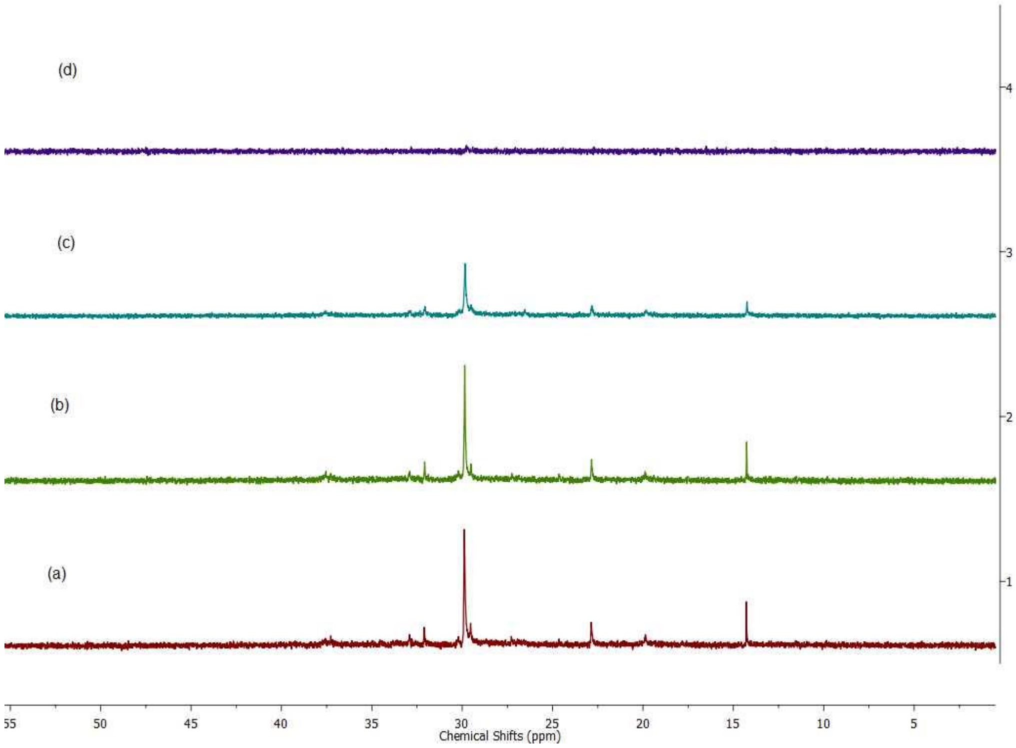

Fig. 9 ^{13}C NMR spectra of VR (a), its oxidation products without (b) and with the CR (c), the CR (d).

Table 7. Content of types of hydrogen atoms by number of ^1H (%).

Type of atoms	VR	CR	Oxidation products without the CR	Oxidation products with the CR
H_α	13.0	8.9	12.1	15.0
H_β	64.1	66.8	58.7	59.5
H_γ	16.5	21.7	20.5	17.0
H_{ol}	0.2	0.5	1.3	1.9
$H_{a\ell}$	99.8	97.9	92.6	92.4
H_{ar}	6.6	2.1	7.4	7.6

Table 8. Content of types of carbon atoms by the amount of ^{13}C (%).

Type of atoms	VR	CR	Oxidation products without the CR	Oxidation products with the CR
C_{pm}	14.4	-	10.2	7.2
C_{pa}	21.5	-	20.3	18.7
$C_{a\ell}$	64.1	-	69.5	74.1

carbon atoms, heteroatoms; here the influence of the addition of the CR is clearly pronounced, which increased the content of H_α atoms by 2%, while oxidation without the additive led to its decrease by 0.9%. Hydrogen atoms in the composition of olefin groups were found in a small amount, the oxidation of the VR with the CR increases their amount from 0.2 to 1.9%. As a result of oxidation a slight increase in the number of hydrogen atoms of aromatic nuclei by 1% is observed, *i.e.* from 6.6 to 7.6%.

A CR consists of saturated and unsaturated bonds of rubber hydrocarbons linked by sulfur bridges.[52] This is confirmed by the high content of H_γ (21.7%) and the low content of H_{ar} (2.1%). As a result of the oxidation of the VR with the CR, an increase in hydrogen atoms in the composition of olefin groups H_{ol} and hydrogen atoms in the α position to aromatic and carbonyl carbons, heteroatoms H_α was revealed, which confirms the formation of new bonds and functional groups involving unsaturated rubber structures.

Table 6 shows that oxidation without and with the CR significantly changes the distribution of carbon atoms in various functional groups contained in the samples. It turned out that as a result of oxidation (both without the CR and with it) in the VR the content of carbon atoms of methyl groups associated with a methylene group C_{pm} and a methine group or an aromatic ring C_{pa} decreases, while the content of quaternary aliphatic atoms $C_{a\ell}$ increases. In the VR the amount of C_{pm} was 14.4%, after oxidation it decreased by 4.2%, after oxidation with the CR it decreased by 2 times, *i.e.* up to 7.2%. There is a decrease in C_{pa} from 21.5% to 20.3% when oxidized without the CR and to 18.7% when oxidized with it. The content of $C_{a\ell}$ also greatly increases (by 10%) in the case of oxidation of the VR with the CR, while in the case of oxidation without it - by 5.4% only.

These results suggest that a decrease in the content of carbon atoms of methyl groups associated with methylene and methine groups (or an aromatic ring) and an increase in the content of quaternary (branched) aliphatic hydrocarbons increases (especially at low temperatures) the mobility of molecules and supramolecular structures of the obtained bitumen, *i.e.* enhances its relaxation ability.

3.6 High temperature stability

Figure 10 shows graphs of the rutting parameter (G*/sinδ) of the oxidized bitumen with the CR in the initial state and after short-term aging (RTFOT). The values of the bitumen rutting parameter (G*/sinδ) are determined from the results of the DSR test. According to Superpave in order for the asphalt concrete pavement with the considered bitumen to be resistant to rutting at the design high temperature, the bitumen in the initial state and after short-term aging must have a rutting parameter of at least 1 kPa and 2.2 kPa respectively.[51]

From Fig. 10, it was found that the limiting values of the rutting parameter for the oxidized bitumen with the CR in the initial state and after short-term aging correspond to temperatures of 68 °C and 64 °C, respectively. The territory of Kazakhstan is divided into eight zones[55,56] for which the following grades are established according to the operating conditions of bituminous binders (PG): 52-40, 58-28, 58-34, 58-40, 58-46, 64-28, 64-34, 64-40. As can be seen the resulting oxidized bitumen with the CR in terms of resistance to rutting can be used throughout Kazakhstan, which is one of the countries in the world with a huge area (the 9th place) with a sharply continental climate. This means that the resulting bitumen can be used in many countries around the world with difficult road operating conditions.

3.7 Low temperature resistance

It is known that, according to Superpave, a bituminous binder is considered resistant to low-temperature cracking if its stiffness (S) and relaxation rate (m-value) at a loading time of 60 seconds satisfy the following conditions: S < 300 MPa, m > 0.3.[51] The values of the stiffness and relaxation rate of the tested bitumen at a loading time of 60 seconds and at different temperatures are shown in Figs. 11 and 12. From these figures it can be seen that the tested bitumen at all temperatures has sufficient relaxing ability (m > 0.3). The bitumen stiffness at -36 °C (357.88 MPa) exceeds the required value (300 MPa), and at -33 °C (273.94 MPa) meets the condition. Considering a shift of 10 °C towards low temperatures (Superpave uses the principle of temperature-time superposition), the tested bitumen can be used in cold regions with an estimated winter temperature down to -43 °C.

Figure 13 compares the stiffness values (t=60 s) of the oxidized bitumen with the CR and a pure (non-modified) bitumen of 70/100 grade after double aging (RTFOT+PAV) at temperatures of -24 °C, -30 °C and -36 °C.[57] Bitumens of this grade are traditionally used in road construction in Kazakhstan and in many other countries of the world. As it can be seen from the figure, at all considered temperatures the stiffness of the oxidized bitumen with the CR is less than pure one. This

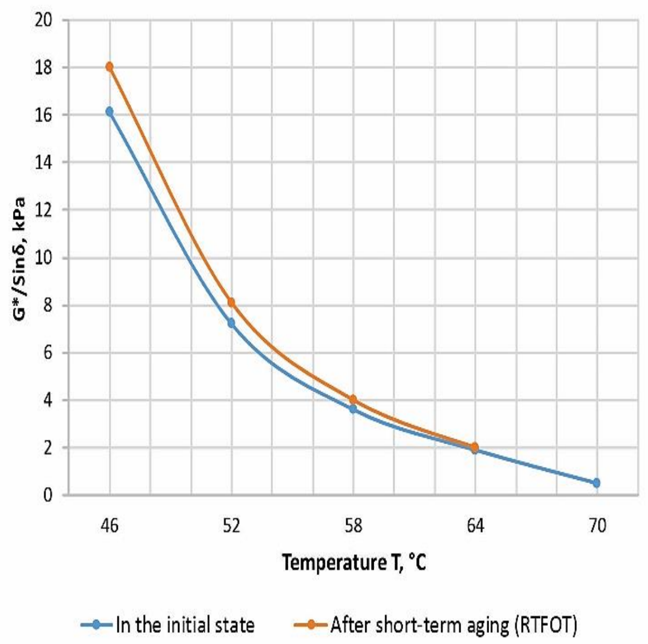

Fig. 10 Dependences of the rutting parameter (G*/sinδ) of the oxidized bitumen with the CR in the initial state and after short-term aging (RTFOT).

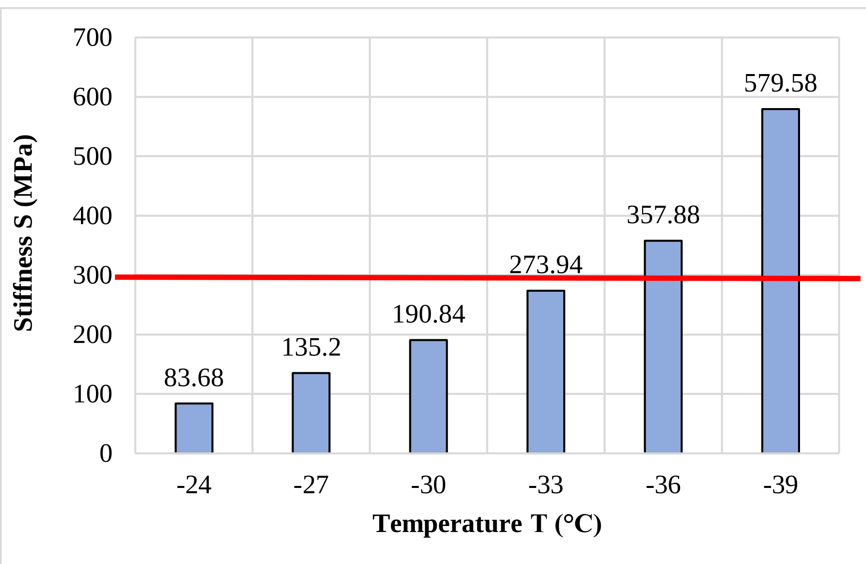

Fig. 11 Stiffness of the bitumen S (t=60 s) at different temperatures.

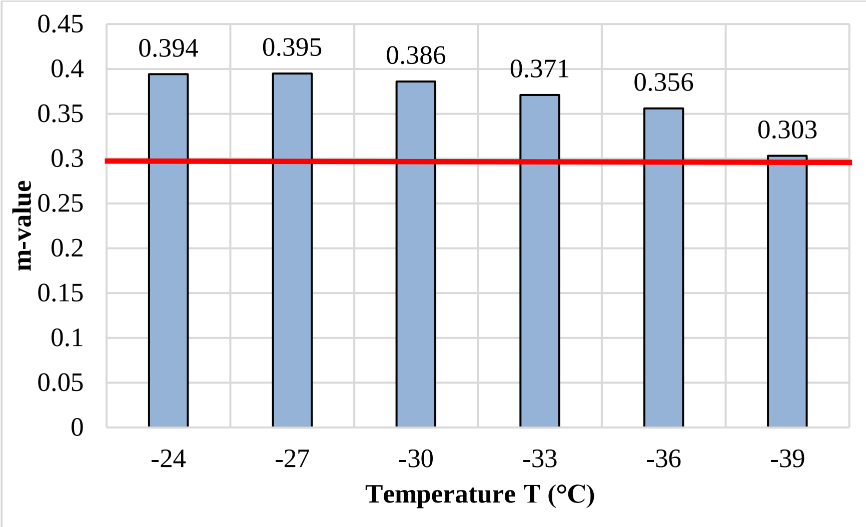

Fig. 12 m-value (t=60 s) of the bitumen at different temperatures.

fact shows that the low temperature resistance of the resulting oxidized bitumen with the CR is higher than the traditionally used 70/100 grade bitumen. Thus, the resulting bitumen with a resistance to low-temperature cracking can be used throughout the entire territory of Kazakhstan and in many countries of the world with a cold climate.

3.8 Chemistry of the process of oxidation of vacuum residue with crumb rubber

The results of analysis by chromatography, NMR and IR spectroscopy make it possible to explain some changes in the chemical composition of the VR during oxidation with the addition of the CR and the improvement in the characteristics of the oxidation products. Based on the data of chromatographic, NMR and IR spectroscopic analyzes, a reaction scheme was proposed (Fig. 14) and a general scheme of thermal-oxidative transformations of hydrocarbonic components was drawn up (Fig. 15).

As it can be seen from the scheme in Fig. 14, there are unsaturated and sulfur-containing bonds in the composition of rubber, which are involved in the accelerated formation of new condensed compounds of resins and asphaltenes, which ultimately leads to the intensification of the oxidation process. During the destruction of the rubber, fragments of the rubber molecules and sulfur additives are formed, which were used during vulcanization. As a result of the oxidation of the VR with the rubber components, a heterogeneous reinforcing spatial structure of the rubber-bitumen composite is formed. Improvement of the bitumen properties is achieved by creating a new bituminous composition. The rubber in it is a vulcanization mesh, which is a flexible polymer frame throughout the entire volume of the material. The grid is sparsely cross-linked. Therefore, the plastic properties of the bitumen, the components of which are embedded in this grid, are preserved. Thus, the liquid phase of the bitumen is enclosed in a spatial macrogrid and this ensures the stability of the entire composition.

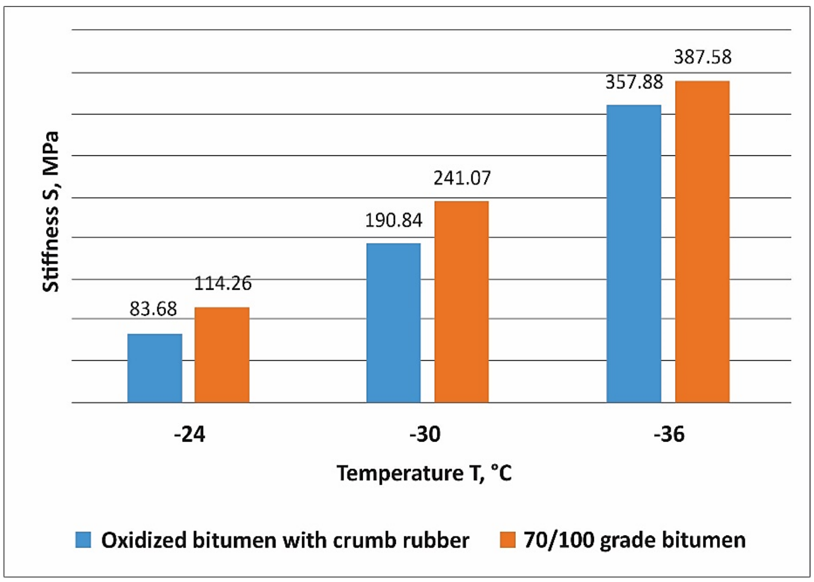

Fig. 13 Stiffness of the oxidized bitumen with the CR and a pure bitumen of 70/100 grade after double aging (RTFOT+PAV).

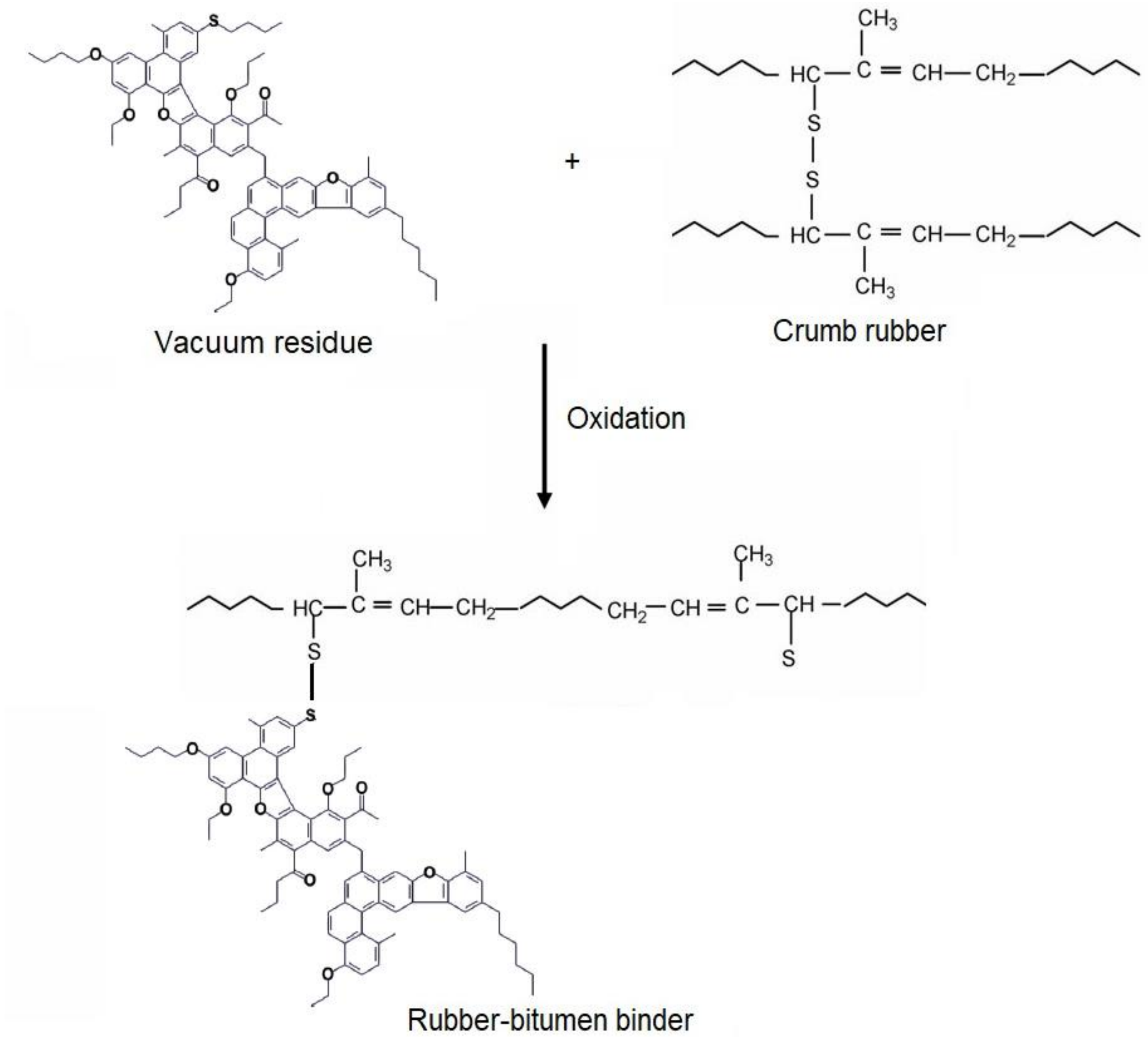

Fig. 14 Scheme of interaction reactions of CR with VR.

The scheme of Fig. 15 shows the possible ways of processes during the oxidation of the VR. Oxidation at 260°C results in chemical structural changes resulting in the formation of asphaltenes, maltenes and a small amount of gas. As is known, the oxidation of a VR leads to an increase in the content of high-molecular components (resins and asphaltenes), while the amount of low-molecular components (oils) decreases. The decrease in the amount of maltenes or oils is confirmed by the results of the chromatographic analysis, where there is a decrease in the content of alkanes. This is also confirmed by the results of NMR analysis, where a decrease in the number of carbon atoms of methyl groups associated with the methylene, methine groups, or aromatic ring is observed since they are connected by limiting unbranched structures. An increase in the content of resinous-asphaltene substances is confirmed by the results of IR spectroscopic analysis with an increase in the intensities of the absorption bands of the corresponding functional groups, as well as by the results of NMR analysis with an increase in the number of quaternary aliphatic carbon atoms that appear during the formation of branched condensed structures of resins and asphaltenes. The formation of stronger asphaltenes occurs by dealkylation of side long aliphatic chains of asphaltenes. The resulting strong asphaltenes in the presence of the CR molecules form high molecular weight maltenes. Then, gaseous oxidation products are formed from the high molecular weight maltenes and the stronger asphaltenes. The maltenes are converted at high temperatures by two reaction pathways: a cyclization of alkyl chains and an oxidative polymerization. The cyclization of the alkyl chains leads to the formation of an intermediate product - a naphthenic ring. Further the naphthenic hydrocarbons in the process of aromatization and dehydrogenation form more stable products - polycyclic aromatic hydrocarbons, which is confirmed by the results of the chromatographic analysis. With an increase in the concentration of the high-molecular maltenes the following reactions proceed in the system: a combination of radicals (polymerization) and a condensation of aromatic rings.

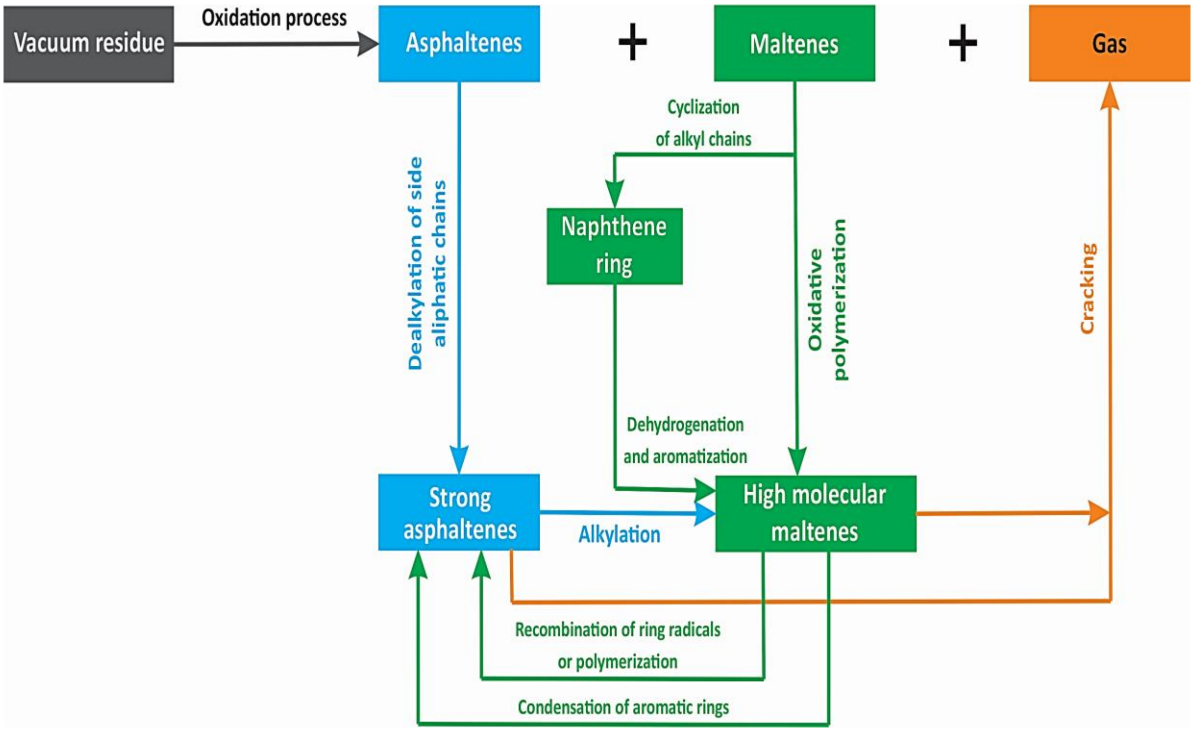

Fig. 15 Scheme of oxidation processes of VR with CR.

Here asphaltenes can be formed directly from aromatic compounds by radical processes. All these reactions lead to the formation of stronger the asphaltenes.

Thus, the oxidation of the VR includes primary and secondary reactions. The primary reactions during the oxidation of the VR mainly go in three directions: strong asphaltenes, maltenes and gases. Strong asphaltenes and maltenes can also undergo the secondary reactions such as dealkylation of side aliphatic chains, cyclization of alkyl chains, recombination of ring radicals or polymerization, dehydrogenation and aromatization of naphthenic rings, condensation of aromatic rings.

When vacuum residue and rubber crumb are mixed at 180 °C, rubber devulcanizes with the breaking of S-S, C-S bonds and the formation of rubber molecules with double bonds and sulfur. The rubber structure transforms from a network polymer to a linear one and polysulfides are formed, which, upon further oxidation at 260 °C, transform into stable cyclic sulfides. Next, the reaction of sulfides with naphthenoaromatic compounds leads to the formation of asphaltenes. When rubber devulcanizes in a bitumen environment, the content of benzene and alcohol-benzene resins, which are responsible for the elasticity of bitumen, increases and a bitumen structure that is resistant to force influences is formed.

In general, during combined oxidation, many reactions occur, such as oxidative dehydrogenation, dealkylation, oxidative polymerization, polycondensation, and cracking, with subsequent compaction of products. Oxidation begins with the formation of oxygen-containing substances, in which oxygen is in the form of carbonyl, ester and carboxyl groups. At the same time, they are slowly converted into resins through a condensation reaction mechanism with the release of oxygen in the form of water. With increasing oxidation, a relative increase in the content of compounds with short alkyl chains $(CH_2)_n$, where $n \leq 4$, is observed in bitumen, due to the elimination of alkyl groups of cyclic compounds with long alkyl chains. A relative increase in the proportion of benzene rings in the rings is also observed, which confirms the dehydrogenation nature of the reactions.

4. Conclusions

Combined (together with CR) oxidation of VR made it possible to obtain a modified road bitumen with improved high- and low-temperature performance characteristics: the values of the rutting parameter have been increased at temperatures from 46 °C to 64 °C and the stiffness has been significantly reduced to a temperature of -40 °C.

The improvement in the high- and low-temperature performance characteristics of the obtained modified bitumen can be explained by changes in the chemical composition of the VR during its joint oxidation with the CR, which chromatography, NMR and IR spectroscopy identified: the increased high-temperature stability is due to an increase in the content of resins and asphaltenes, as well as the presence of incompletely destroyed vulcanized structures and other rubber fillers, and the low-temperature cracking resistance is improved due to rubber elastic polymers.

When VR is oxidized together with CR (compared to oxidation without CR), the decrease in oil content and the increase in the content of resins and asphaltenes (condensed aromatic structures) occurs faster due to unsaturated and sulfur-containing bonds in the rubber.

The combined oxidation (compared to conventional oxidation and modification, which are carried out separately) is technically, economically and environmentally significantly beneficial, therefore, a promising technological method: 1) it is technically easy and relatively fast to achieve an improvement in both high-temperature and low-temperature performance characteristics of the final bituminous binder; 2) 10% of a bitumen (an expensive material) is replaced by CR, obtained as a waste material of processing; 3) recycling of old tires and the use of a obtained modified road bitumen in production (recycling) improves the environmental situation.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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