

Modified polyolefins to prevent paraffin deposits in pipelines

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Abstract

By chemical modification based on waste of polyolefins production, new reagents of complex action for oil production and transportation were developed. The structure of the obtained products was confirmed by ¹H NMR and IR spectroscopy.

Developed reagents were tested as inhibitors of ARPD and depressants. The assay object was highly paraffinic Kumkol oil that was characterized by low content of sulfur and asphaltene components.

The depressor activity of reagents was determined by standard ASTM D5853-09. The maximum decrease of the pour point and improvement of rheological properties was observed with the amount of the reagent 200–300 ppm; depression was 21°C.

The effectiveness of inhibitors of ARPD was analyzed by the “Cold rod” method according to RD 39-3-1273-85. The results indicated sufficiently high inhibitory activity of reagent: the inhibition rate was 73% at joint heat treatment and entering additives into oil.

With the use of the X-ray diffraction method, the effects of inhibitors on the structure of the samples of asphaltene deposits were controlled. It was revealed that the modified polyolefins were able to change the phase composition of deposits, thereby improving the rheological properties of oil.



There was a high degree of amorphization ARPD entering the modified reagent: the content of the amorphous phase increased from 44% to 63%.

Keywords: asphalt-resin-paraffin deposits (ARPD), inhibitor, depressants, structure of ARPD.

1 Introduction

The problem of dealing with deposits of organic nature has not lost its significance in connection with involvement in mining heavy viscous oils, which contain a significant amount of paraffins, asphaltenes and resins [1].

In Kazakhstan most oil fields contain high amounts of high molecular weight paraffins, which in combination with abnormally low reservoir temperatures lead to rapid coagulation and crystallization of asphalt-resin-paraffin deposits (ARPD) directly in reservoir, formation in bottom hole formation zone and on the surface of oilfield equipment.

This raises the need for new chemicals designed to inhibit the ARPD and improve the rheological properties of oil.

One of the main methods to combat such complications is the use of chemical reagents. That's why it is necessary to create a new generation of chemicals of complex action intended for inhibiting paraffin deposits and to improve the rheological properties of oil.

2 Main level

The object of study in this work is highly paraffinic oil of Kumkol, South Turgay oilfield characterized by low content of sulfur and asphaltene components.

The aim of the work is creating new complex action reagents by radiation-chemical grafting of ethylene glycol monovinyl ether on the macromolecule of acidified atactic polypropylene and evaluation of their effectiveness as inhibitors of ARPD and depressants.

2.1 Studying the structure of the reagents

Radiation-chemical modification of OAPP performed by simple grafting of vinyl monomers to the polymer matrix with different doses of irradiation in the presence of oxygen.

Electron accelerator ELV-4 was used as high-energy ionizing radiation. Standard radiation dose for all kinds of materials was 67 kGy and on the surface approximately 50 kGy. This dose was sufficient to form a free radical intermediate species, but insufficient for gelformation in the polymer. By passing radiation through a box, irradiation doses of 200, 400, 600 and 1200 kGy were achieved.

Graft copolymers were isolated by extraction in a Sokslett apparatus with organic solvents: o-xylol, chloroform, a mixture of chloroform and ethanol, also o-xylene with following extraction of residual polymer with chloroform. The time of extraction was 10 hours.



Analysis of samples of the graft copolymers was performed by IR and ^1H NMR spectroscopy.

IR spectra were recorded on "Spectrum 65" spectrometer of Perkin Elmer, at a temperature of 20°C ranging from 450 to 4000 cm^{-1} .

Figure 1 shows the IR spectra of OAPP and its radiation-grafted copolymers in o-xylol, chloroform and chloroform-alcohol.

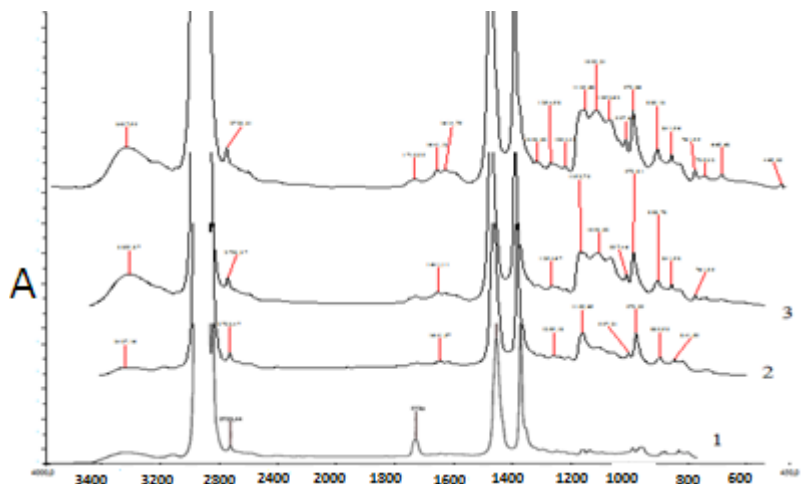


Figure 1: IR spectra of OAPP and radiation-grafted copolymers. (1 – OAPP; 2 – radiation-grafted copolymer of the o-xylol fraction; 3 – radiation-grafted copolymer of the chloroform fraction; 4 – radiation-grafted copolymer of the chloroform-alcohol fraction.)

At IR spectra of all copolymers there are bands [2, 3]:

- in the area of 3407 cm^{-1} there is a characteristic absorption band of high intensity stretching vibrations of the hydroxyl group, related to alcohol;
- Absorption bands in the area of $2955\text{--}2840\text{ cm}^{-1}$ are characteristic absorption bands of stretching vibrations of C-H in groups - CH_2 and CH_3 ; the presence of large amount of aliphatic structures confirmed with intensive adsorption in the area of 1460-- and 1377 cm^{-1} ;
- in the area of 1720 cm^{-1} there is an absorption band of medium intensity which is characteristic of stretching vibrations of C=O of carbonyl group;
- in the area of $1641\text{--}1614\text{ cm}^{-1}$ there is typical absorption of C=C;
- absorption band at $1300\text{--}1052\text{ cm}^{-1}$ is the absorption band of C-O of ethers;
- absorption bands at $972\text{--}997\text{ cm}^{-1}$ is characterized by the presence of vinyl double bonds $-\text{CH}=\text{CH}_2$;
- absorption bands at $841\text{--}889\text{ cm}^{-1}$ is characterized by the presence of vinylidene double bonds $-\text{CR}=\text{CH}_2$;
- absorption bands at $669\text{--}761\text{ cm}^{-1}$ correspond to pendulum oscillations of $-\text{CH}_2-$ groups.

Thus, the comparative analysis of the IR spectrums of the samples of acidified atactic polypropylene and radiation-grafted copolymers of vinyl ethers on a matrix of acidified atactic polypropylene confirms the formation of new ester group after graft polymerization.

^1H NMR spectrums of the initial materials and the graft polymers have been done by multinuclear NMR Fourier spectrometer of high resolution UltraShield-400 of Bruker production.

^1H NMR spectrums were recorded at 60°C for 6.5% solutions of polymers in deuteriotoluole (Tol-d_8).

The signals with a chemical shift $\delta = 7.09$; 7.00 ; 6.98 and 2.09 ppm correspond to the protons of the solvent Tol-d_8 .

Characteristic absorption regions diagram of protons (δ -scale) in organic compounds was used for the interpretation of NMR spectrums [4].

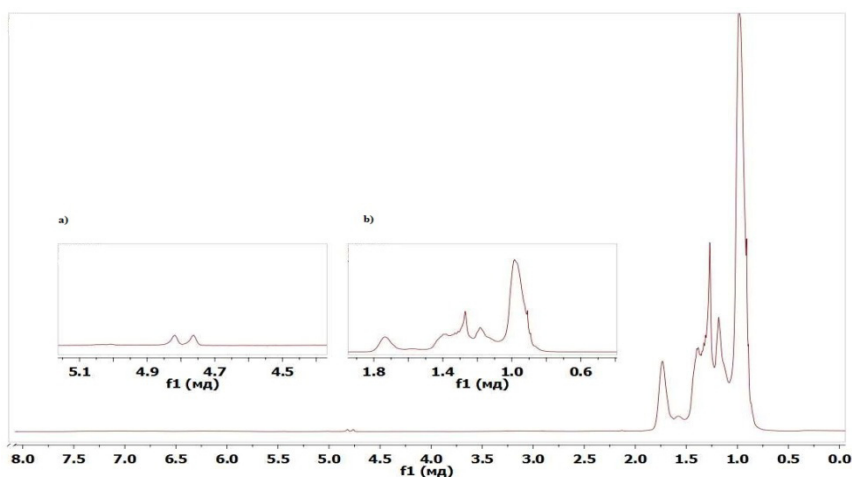


Figure 2: ^1H – NMR spectrum of the OAPP sample. a) a fragment of ^1H NMR spectrum for the group $-\text{H}-\text{C}=\text{C}-$; b) a fragment of ^1H NMR spectrum for the groups: CH , CH_2 , CH_3 .

In Figure 2 of ^1H NMR spectrum signal with chemical shift $\delta = 4.7675$ – 4.8227 ppm assigned to the proton group $-\text{HC}=\text{C}-$, the double bond. The signal from the chemical shift $\delta = 1.7349$ – 1.7648 ppm assigned to the proton $-\text{CH}-$. Signals of methylene protons located in a weak field - at $\delta = 1.1894$ ppm and split into two peaks. These results are explained as follows [5]: longer chains take folded form, but not a static tangle conformation in solution, that's why less shielded signal corresponds to the methylene protons in the folded part of the circuit. Signal with a chemical shift of $\delta = 0.9972$ ppm assigned to the methyl group.

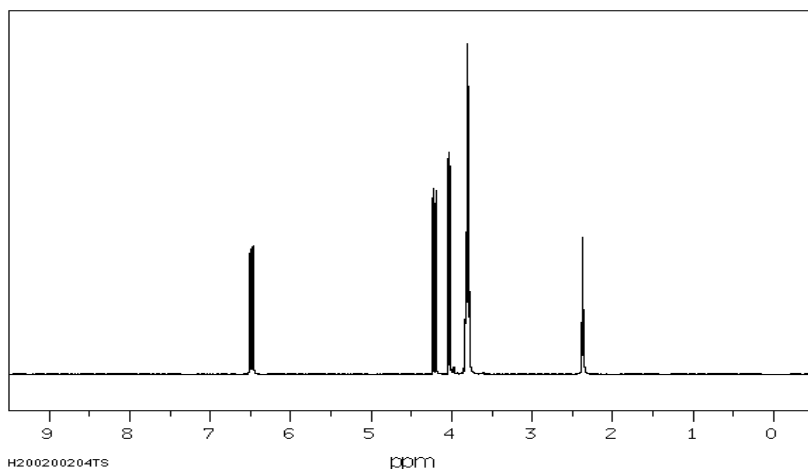


Figure 3: ^1H -NMR spectrum of ethylene glycol monovinyl ether.

^1H -NMR spectrum of ethylene glycol monovinyl ether (figure 3) comprises a signal with chemical shift $\delta = 6.497$ ppm attributed to the proton of group $\text{OCH} =$. Signals with chemical shifts $\delta = 4.230\text{--}4.044$ ppm assigned to the protons of group $=\text{CH}_2$, $\delta = 3.814$ ppm assigned to the proton of group $-\text{CH}_2$, $\delta = 2.386$ ppm assigned to the proton of group $-\text{OH}$.

^1H NMR spectrum of OAPP sample after radiation grafting on its macromolecule of ethylene glycol monovinyl ether is shown in figure 4.

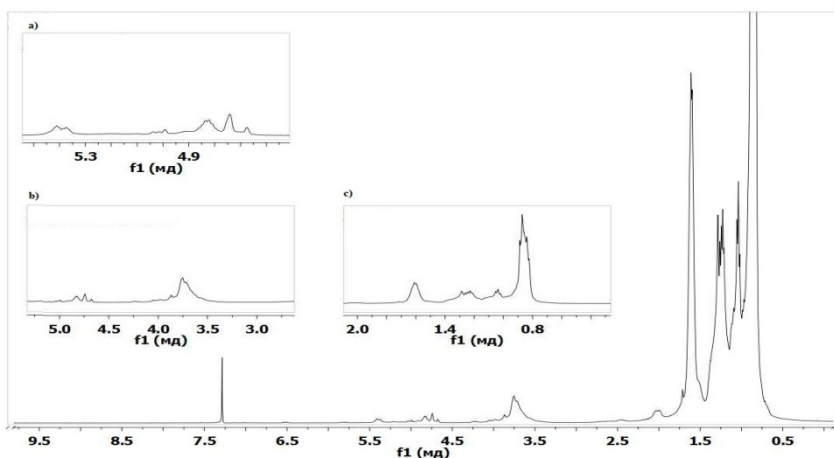


Figure 4: ^1H -NMR spectrum of the modified OAPP sample. a) a fragment of ^1H NMR spectrum for the group $-\text{H} - \text{C} = \text{C} -$; b) a fragment of the ^1H NMR spectrum for the group $-\text{OCH}_2$ of ether; c) a fragment of ^1H NMR spectrum for the groups: $-\text{OH}$, $-\text{CH}$, CH_2 , CH_3 .

Spectrum contains signals with chemical shift $\delta = 0.87$ ppm of protons of the methyl group, methylene protons located in a weaker field – at $\delta = 1.212$; 1.227 ; 1.243 and 1.284 ppm, the proton $-CH<$ located at $\delta = 1.6102$, proton- $CH=$ located in an area at $\delta = 4.99 - 4.6751$ ppm. The signal at $\delta = 3.8689$ and 3.7522 ppm corresponds to the ester group – OCH_2- . The presence of this group in the spectrum indicates grafting of ethylene glycol monovinyl ether on OAPP macromolecule. Having a signal at the chemical shift $\delta = 2.107$ ppm, which is attributed to the proton of the alcohol group - OH, also confirms the modification of the starting polyolefin matrix (OAPP).

IR spectroscopy revealed the presence of polar functional groups in macromolecule of OAPP samples and its modified forms.

2.2 Test reagents as depressants

Developed reagents were tested as inhibitors of ARPD and depressants for highly paraffinic oil of Kumkol oilfield. Depressor activity of the reagents was determined by ASTM D5853-09 [6].

Table 1: Change of the pour point.

Name of sample	Pour point, °C	Depression, °C
Oil without treatment	+15	-
Oil after thermochemical treatment with OAPP	0	15
Oil after the thermochemical treatment with grafted OAPP	-6	21
Additive concentration of 300 ppm		

From the analysis of the data in Table 1 was concluded that the additive reduces the pour point of Kumkol oil. Maximum depression is achieved by adding modified OAPP sample of 300 ppm at 21°C.

During reoviskozity studies has been found that the new depressant additives are good viscosity reducers. Dependence of the effective viscosity and shear stress from the temperature of oil and addition of OAPP is presented in figure 5. As can be seen from figure 5, after addition of OAPP effective viscosity declines from 9.7Pa·s to 0.1 Pa·s and the shear stress – from 46 to 0.1 Pa, and these indicators are not changed till further cooling oil to -5°C.

2.3 Definition of inhibitory properties of reagents

Effectiveness of inhibitors of ARPD was studied by method “Cold rod” of RD 39-3-1273-85 [7], according to which oil was poured into a stainless steel beaker at room temperature and then increased temperature to 30°C with magnetic stirring, after thermostating cooled rod made of stainless steel with constant

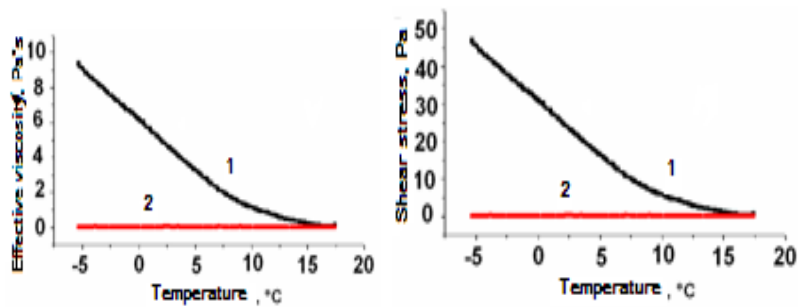


Figure 5: The effective viscosity and shear stress temperature. (1 – Kumkol oil after heat treatment at 60°C; 2 – Kumkol oil after heat treatment and addition of the reagent OAPP.)

Table 2: Inhibition of reagents.

Sample	Inhibition rate, %
Oil after thermochemical treatment with OAPP	43
Oil after the thermochemical treatment with grafted OAPP	73
Additive concentration of 300 ppm	

temperature 5°C was placed into beaker. Deposition was carried out for 5 hours. These inhibitory activities of additives of different brands on the Kumkol oil are shown in Table 2.

Studies indicate sufficiently high inhibitory activity of the modified OAPP reagent. ARPD of Kumkol oil: inhibition rate is 73% after joint heat treatment and addition of reagent to oil.

2.4 Studying the effect of reagents on ARPD phase composition

Effects of inhibitors on the phase composition of the samples of asphaltene deposits were controlled with the use of X-ray diffraction method.

By PDF-2 program was implemented selection of reference samples that could be attributed to possible normal paraffins with chemical formula (CH₂)_x, where x= 6-46.

By X-ray analysis (figures 6–8), it was demonstrated that in the tested samples sharp diffraction peaks which indicate the presence of crystalline phases in ARPD was observed.

It should be noted that with the addition of inhibitors the intensity peaks of crystalline n-paraffins in ARPD was markedly decreased, which indicates the transition of crystals of n-paraffins to the amorphous phase after addition of inhibitors to the oil.



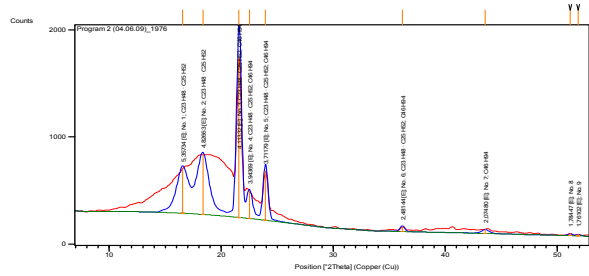


Figure 6: XRD pattern of the ARPD without treatment.

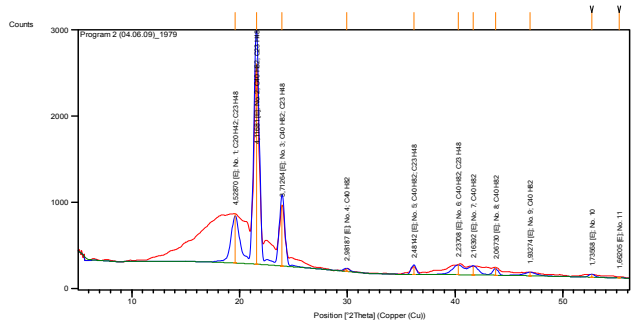


Figure 7: XRD pattern of the ARPD sample after adding OAPP reagent.

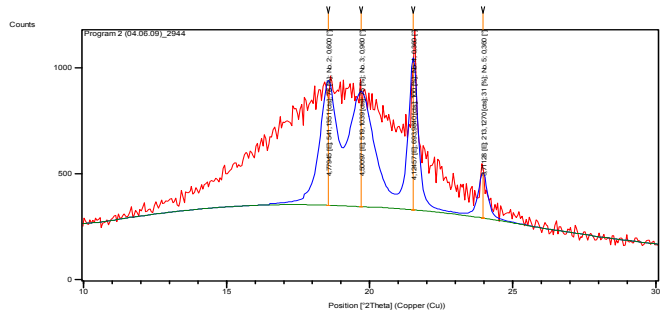


Figure 8: XRD pattern of the ARPD sample after entering chemically modified OAPP reagent.

It was revealed that the modified OAPP is able to change the phase composition of deposits, thereby improving the rheological properties of oil. There is a high degree of amorphization of ARPD after addition of the modified OAPP reagent: amorphous phase content increases from 44% to 63%.

Proposed reagent based on a cheap and accessible materials characterized by high reological properties and good inhibitory ability of ARPD, is a topical



solution to reduce the economic and technological costs of production and transportation of oil.

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