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Study of petroleum resins modification by ethanolamins

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Abstract

Possibilities of synthesis and properties of the products of the ozonated petroleum resins modification by ethanolamines was considered. It is founded that ethanolamines interact both with decomposition products of the ozonized groups obtained from ozonated resins, and directly with the ozonized groups themselves. The obtained modified petroleum resins can be used as adhesive and film-forming components in paint materials.

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Keywords: petroleum resin, ozonation, modification, amination, ethanolamines;

1. Introduction

One of the significant directions of liquid pyrolysis products utilization is their polymerization to produce petroleum resins (PR). Widespread use of PR is due to their valuable physical and chemical properties[1]. Along with the advantages resins have a low adhesion to a various surfaces and reduced resistance to air oxidation. For improvement of operational characteristics PR and extension of the application field it is necessary to implement their modification[2,3].

One of the possible and promising areas of PR modification is ozonation[4]. This is due to the fact that ozone reacts with almost all organic compounds reacting with them either in electrophilic addition reactions, or radical chain oxidation reactions[5,6]. Modifying of PR by ozonation reduces uncontrolled oxidation of resins by atmospheric oxygen by reducing the number of double bonds and improves the adhesive properties by the insertion of oxygen-

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containing groups, and the formation of the molecule structure of reactive groups gives the possibility for further controlled chemical modification and directional regulation of this process.

In this paper are presented the study results of the modification process of ozonated aromatic petroleum resins by ethanolamines. Characteristics of synthetic film formers obtained on the basis of modified resins are considered.

2. Experimental

The study object in this paper was the PR obtained by polymerization of unsaturated compounds of the C_9 fraction using catalytic system $TiCl_4 – Al(C_2H_5)_2Cl$.

The ozonized PR (OPR_{C9}) was obtained by ozonation of 10 % solution in xylene PR by means of an ozone-oxygen mixture (flow rate of O_2-O_3 – 0.05 s^{-1}, the concentration of O_3 – 2 % vol.) in the bubble type reactor at a temperature of 5 °C and the process time of 40 minutes.

Amination of OPR_{C9} was carried out in a glass reactor equipped with a reflux condenser and a stirring device. The process proceeds at a temperature of 80 °C for 2 hours at a ratio of OPR : EA – 10 : 1 mass., respectively. Monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were used as an aminating agent.

Methods of IR and ^{1}H NMR spectroscopy were used for study of the initial and modified PR structure. IR spectra were recorded by of Fourier IR-spectrometer NICOLET 5700 in the wavelength range of 400–4000 cm^{-1}. ^{1}H NMR spectra were recorded by a NMR-spectrometer AVANCE–300MHz («Bruker»).

3. Results and Discussion

Initial petroleum resin (PR_{C9}) has the following physicochemical characteristics:

Bromine number, g Br_2/100 g	50
Softening point (ring and ball method), °C	62
The molecular weight	450
Color of a 50 % solution in xylene, mg I_2/100 mg KI	900

For structure and structural composition analysis of the PR, i.e., a character and combination of saturated, unsaturated and aromatic fragments in their molecules the methods of IR spectroscopy and ^{1}H NMR spectroscopy were used. In the ^{1}H-NMR spectra PR six types of protons were allocated and were determined the values of normalized integrated intensities (%):

Aromatic A (6.2..8.0)	20.89
Olefin B (4.0..6.2)	7.04
Methyl and methylene at α-position to the benzene ring C (2.0..3.6)	30.07
Methine paraffin's and naphthenes D (1.5..2.0)	19.59
Methylene paraffin's and naphthenes E (1.05..1.5)	13.11
Methyl F (0.5..1.05)	4.96

It is obviously that the structure of PR_{C9} contains significant amounts of protons of aromatic fragments (type A and C) and the olefin protons (type B). Paraffin chain branching, a number of CH_3 groups is insignificant (type F). The character of ^{1}H NMR spectrum is consistent with the data of IR-spectroscopy. The presence of a strong absorption band in the spectrum of PR at 2930 cm^{-1} and the average intensity of the band at 1450 cm^{-1} related, respectively, to the stretching and deformation vibrations of CH_2 groups, as well as a weak absorption band in the region of the deformation vibrations of CH_3 groups (1370 cm^{-1}) indicates slight branching of the hydrocarbon chains. The presence of aromatic structural fragments is detected by the average intensity of the absorption bands in the area 1600 cm^{-1} and strong intensity in the area of 650–750 cm^{-1}, Fig. 1.

Initial resin may be attributed to aromatic type resins with negligible amounts of cycloaliphatic fragments. Judging from the molecular weight of the resin PR_{C9} is an oligomeric compound and contains a significant amount

of unsaturated bonds (Bromine number 50 g Br_2/100 g) indicating the possibility of carrying out the process of ozonization.

Ozonation of PR_{C9} under the above conditions leads to a modified product – ozonated resin (OPR_{C9}), which properties are presented below:

Active oxygen, %	1.68
Softening point (ring and ball method), °C	82
The molecular weight	500
Color of a 50 % solution in xylene, mg I_2/100 mg KI	700

It was established that ozonization process is accompanied by increasing of active oxygen content, i.e. by the formation of peroxide type compounds.The unsystematic changes in the molecular weight is due to the fact that under the ozonation of PR it is likely a simultaneous action both of degradation processes at double bonds and of cross-linking processes of oligomers involving the formed oxygen-containing functional groups.

In the IR spectra of OPR the increase in the intensity of the characteristic absorption band of 1080 cm^{-1} (Fig. 1) is observed, which confirms the occurrence of ozonide groups in the structure of the PR and corresponds to a change of the active oxygen content. Increasing of the intensity of the absorption bands in the range of 1710 cm^{-1} indicates the appearance of other oxygen-containing groups (carboxyl and carbonyl) probably formed as a result of the partial collapse of the ozonide groups (1,2,4-trioxolane).

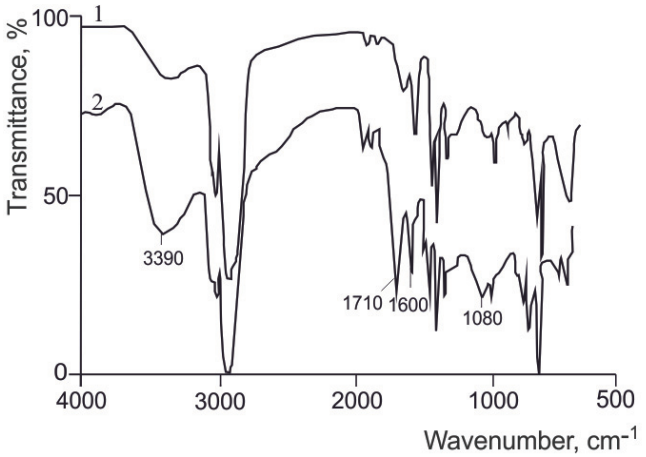
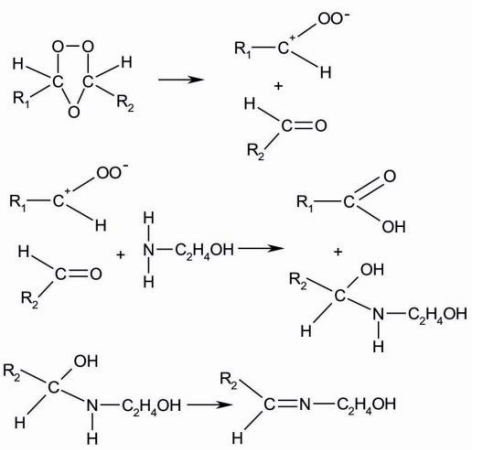


Fig. 1. (1) IR spectra PR_{C9} and (2) OPR_{C9}.

The insertion of ozonide, carbonyl and carboxyl groups to the structure of the PR allows conducting a secondary modification of resins, which in prospect will be responsible for interaction OPR with ethanolamines.

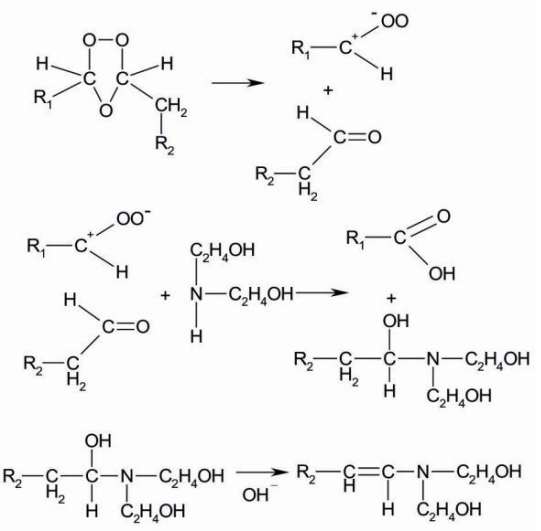
As a result of the interaction of degradation products of ozonide groups with ethanolamines the following reactions are possible[7]:

- Interaction of 1,2,4-trioxolane with monoethanolamine:



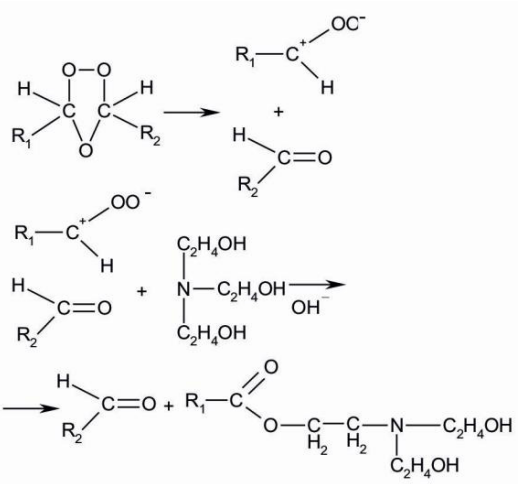
The reaction yields a Schiff base and a carboxylic acid.

- Interaction of 1,2,4-trioxolane with diethanolamine:



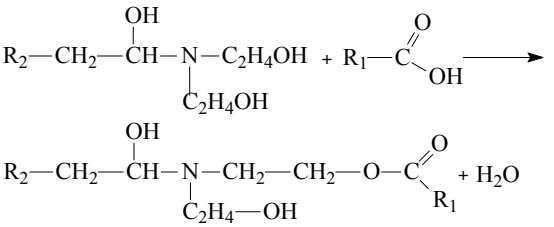
The formation of the tertiary amino alcohol and a carboxylic acid is observed.

- Interaction of 1,2,4-trioxolane with triethanolamine:



The reactions produces aldehydes and esters.

Also in the modification process the esters may be formed due to the etherification reaction:



Set of reactions significantly broader and is not limited presented the above. The properties of the aminated resins (APR) are presented in Table 1.

Table 1. Physical and chemical characteristics of aminated PR.

Characteristics	OPR_{C9}	APR_{MEA}	APR_{DEA}	APR_{TEA}
Active oxygen, %	1.68	0.08	0.13	0.24
Softening point (ring and ball method), °C	82	67	71	68
The molecular weight	500	570	550	720
Color of a 50 % solution in xylene, mg I_2/100 mg KI	700	1800	>2000	>2000

It is seen, that the amination process is accompanied by a significant decrease of active oxygen that mainly confirms by the suggested above the complex reactions. The process also causes a reduction of the softening temperature of APR and the increase of molecular weight.

According to ^{1}H NMR spectroscopy it was determined that for APR an increase of the integral intensity of protons in the range of 4.0–6.2 ppm due to the occurrence of protons of imine and amine groups, which exhibit absorption of protons in the range of 5–8 ppm[8]. Based on these data we can conclude that ethanolamines interact both with the degradation products of ozonide groups and directly with ozonide groups (Fig. 2).

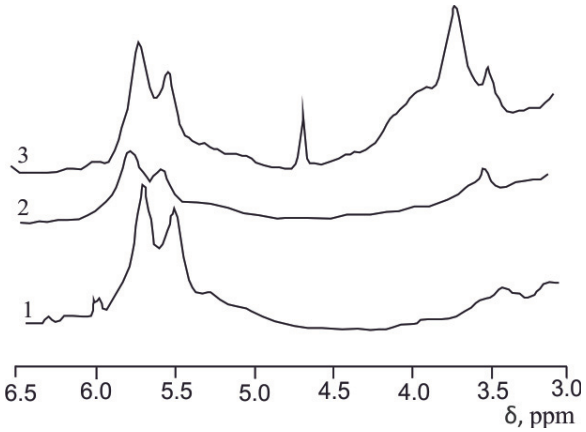


Fig. 2. (1) ^{1}H NMR spectra (1) PR_{C9}, (2) OPR_{C9} and (3) APR_{DEA}.

On the basis of initial and modified PR some coatings were obtained and their properties were investigated, as shown in Table 2.

Table 2. Physical and chemical characteristics of aminated PR.

Characteristics	PR_{C9}	OPR_{C9}	APR_{MEA}	APR_{DEA}	APR_{TEA}
Color of a 50 % solution in xylene, mg I_2/100 mg KI	900	700	1800	>2000	>2000
Adhesion, grade	4	4	3	1	1
Impact strength, cm	<3	<3	3	3	3
Bending strength, mm	20	20	8	1	1

Despite a substantial darkening, the secondary modification of PR leads to a significant improvement in elasticity, adhesion and strength properties of the coatings.

Thus, the process of modifying of the ozonated aromatic petroleum resins with the use of mono-, di- and triethanolamines allows, significantly improving the technical characteristics of the aminated resins and coatings based on them along with the changes in the functional composition.

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