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Oxidation of Petroleum Resin based on Dicyclopentadiene Fraction

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Abstract

This work represents the results of obtaining modified petroleum resin based on dicyclopentadiene fraction. The modification is carried out by means of resin oxidation by the Prilezhaev's method. The possibility of epoxidation of dicyclopentadiene double bonds during the process in the residual hydrocarbons is experimentally established. Dependences of acid, bromine and epoxy numbers on oxidation process duration at various «oxidative system: resin PR_{DF}» component ratio is found. The modified resin structure is determined by IR and NMR spectroscopy.

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Keywords: dicyclopentadiene fraction; liquid pyrolysis products; petroleum resin; modification; peracetic acid

1. Introduction

The composition of components of liquid pyrolysis products can vary within wide limits depending on the used raw material and the pyrolysis conditions^{1,2}. Generally, fractions of aliphatic hydrocarbons (for example, C₅ fraction) or aromatic hydrocarbons (for example, C₉ fraction) are used to produce petroleum resin (PR). In addition to these fractions it is possible to use the original fraction of liquid pyrolysis products enriched with dicyclopentadiene – a so-called dicyclopentadiene fraction (DF)³. This fraction contains up to 55-56 % of dicyclopentadiene (DCPD). Also, in these fractions there are DCPD derivatives and a small amount of styrene, indene, vinyltoluene.

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Using fractions of different hydrocarbon composition, we can vary the quality of resin, i.e. receive light- and refractory resin, low and high molecular weight resin, different colours of resins and various brittle resins. However, these resins do not contain polar groups in the structure as well as the resin based on C₅ or C₉ fractions. Therefore, resin modification is necessary for improving its quality.

Petroleum resins with polar oxygen-containing groups are of great interest, because polar groups as a part of resin give them a number of valuable properties and expands areas of their application significantly^{4,7}. Such a modification is carried out by oxidation with oxygen, peroxyacids and other oxidants, ozonation, interaction with maleic anhydride.

Oxidation process is a widely used method of modification. Oxidation process with the peracetic acid obtained *in situ* proceeds in mild conditions based on the Prilezhaev's reaction. Modification of aliphatic resin based on C₅ fraction and aromatic resin based on C₉ fraction was performed by this method and was described in the works^{4,8,9}. It was established that the oxidant type and the petroleum resin structure have significant effect on the final result^{5,8}.

Petroleum resin based on dicyclopentadiene fraction is unsaturated cycloaliphatic resin, so its modification by oxidation with peracetic acid is possible. Therefore, the goal of this work is to study oxidation based on the Prilezhaev's method of petroleum resin obtained by polymerization of unsaturated dicyclopentadiene fraction compounds of liquid pyrolysis products and to study the properties of the modified resin formed in this process.

2. Experiment

2.1. Objects of research

We used the fraction of liquid pyrolysis products with boiling temperature of 110-190 °C as raw material for obtaining petroleum resin based on dicyclopentadiene fraction (DF). Technical DF was subjected to preparatory distillation, thus separating up 10-15 % of resinous compounds, dried with calcium chloride and incubated in the range of 72-96 hours.

Polymerization of DF unsaturated components was carried out in the following conditions: the catalyst system TiCl₄-Al(C₂H₅)₂Cl with the equimolar ratio of components, TiCl₄ concentration – 2 %, temperature – 80 °C, duration – 2 hours, pressure – 0.1 MPa. At the end of the interaction the TiCl₄-Al(C₂H₅)₂Cl catalyst system was deactivated by using propylene oxide. The interaction products of the catalytic complex and propylene oxide were not removed from the reaction mixture. The resin PR_{DF} was isolated from the reaction mixture by removal of residual hydrocarbons at pressures of 8-10 kPa.

Petroleum resin PR_{DF} modification was performed with the oxidative system using sulfuric acid as catalyst. Oxidation was carried out using the resin solution in the residual hydrocarbons or in 30 % toluene resin solution. The oxidative system that consists of hydrogen peroxide and acetic acid with the equimolar ratio of the components was dosed at 50-55 °C. After that, temperature increased to 70-75 °C and the process was carried out for 3 hours. After cooling to 20-25 °C, multiple washing of the obtained solution was performed with water to achieve neutral pH. The obtained modified resin (MPR_{DF}) was extracted from the organic layer by toluene removal.

2.2. Methods of research

The composition of fractions was determined using a GLC (GC-1000 «Chromos» gas chromatograph, PID, a steel capillary column of 5 m long, internal diameter of 0.25 mm, carrier gas – nitrogen, fixed liquid phase – apiezon L). The modified resin was investigated by standard methods¹⁰. NMR spectra was recorded by using NMR Fourier spectrometer AVANCE AV-300 «Bruker» in CDCl₃. IR spectra was recorded by IR Fourier spectrometer FT-801 «Simex» using KBr glass.

3. Results and Discussion

56 % petroleum resin solution in residual hydrocarbons is formed during polymerization of the dicyclopentadiene fraction. The residual hydrocarbons contain significant amounts (up to 40%) of dicyclopentadiene (DCPD)

according to the GLC. Therefore, 17-18 % of DCPD remain in the reaction mixture compared to the initial DF fraction.

The influence of oxidative system quantity on the property of the modified resin (MPR_{DF}) formed in the oxidation process was studied at the following «oxidative system : resin PR_{DF} »: 0.1:1; 0.25:1; 0.5:1; 0.75:1 component ratio and at the different process duration.

Dependences of acid (AN, mg/g), bromine (BN, g/100 g) and epoxy (EN, %) numbers on oxidation process duration at various components ratio are presented in Fig. 1. In this case, the resin dissolved in residual hydrocarbons (PR_{DF}) was subjected to oxidation.

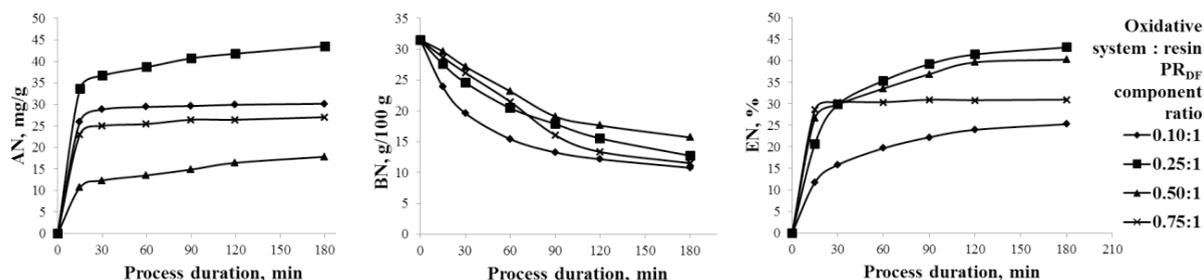


Fig. 1. Dependences of acid (AN), bromine (BN) and epoxy (EN) numbers on oxidation process duration at various components ratio

The data (Fig. 1) show that the oxidative system : resin PR_{DF} component ratio affects the properties of the modified resin. The maximum oxidation rate is recorded within the first 30 minutes and then monotonous change of the studied properties is noted.

Dependences of acid and epoxy numbers on components ratio have extreme character (Fig. 2). The maximum numbers are achieved when the oxidative system and PR_{DF} component ratio is (0.25-0.50) : 1.

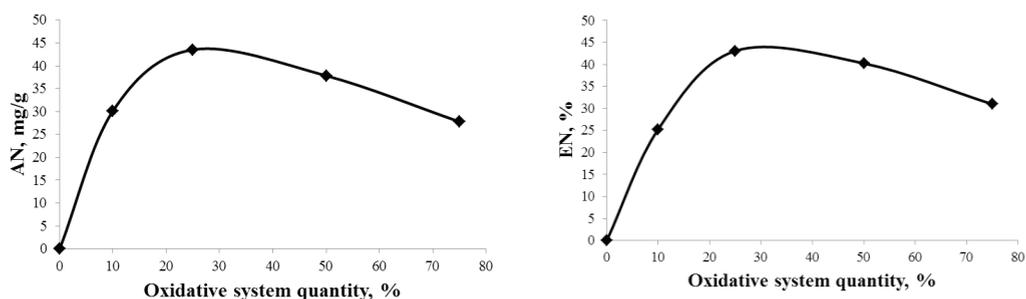
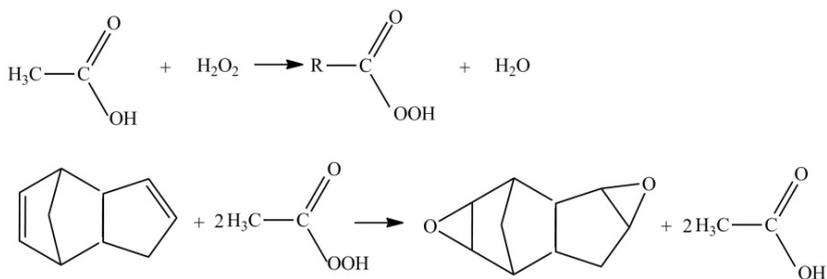


Fig. 2. Dependences of acid (AN) and epoxy (EN) numbers on oxidative system quantity during oxidation duration 180 min

The high values of epoxy numbers in comparison with epoxy numbers of the modified petroleum resin based on C_5 fraction⁸ and C_9 fraction⁹ are caused, probably, by dicyclopentadiene oxidation on double bonds. Simultaneously with epoxidation process at PR_{DF} double bonds epoxidation at DCPD double bonds happens in the Prilezhaev's reaction¹¹.



This fact is confirmed by the following data: lower values of property indicators of PR_{DF} are obtained during the oxidation of the resin dissolved in toluene (Table 1).

Table 1. Property indicators of the modified resin MPR_{DF}

Oxidative system : resin PR_{DF} component ratio	Process duration, h	Property indicators		
		AN, mg/g	BN, g/100 g	EN, %
1 : 0.5	3	35.4	10.2	11.5

The formed dicyclopentadiene diepoxide is crystallized in the film later, substantially degrading the quality of the coating based on the resin oxidized in the residual hydrocarbons. These results allow us to conclude that the stage of resin isolating from the residual hydrocarbon solution is necessary for obtaining high quality paint and varnish coatings.

The $^1\text{H-NMR}$ spectra analysis (Table 2) of the obtained resin (PR_{DF} – unmodified resin, $\text{MPR}_{\text{DF+hic}}$ – modified resin in residual hydrocarbons, $\text{MPR}_{\text{DF+tol}}$ – modified resin in toluene) showed that normalized integrated intensity (NII) of olefin protons (proton type – B) decreased and NII of methine protons in the α -position to epoxy group oxygen (proton type – C) increased in the oxidation process. These data confirm the participation of double bonds in the process and the epoxide group formation.

Table 2. Normalized integrated intensity of resin protons

Proton type (ppm)	Petroleum resin		
	PR_{DF}	$\text{MPR}_{\text{DF+tol}}$	$\text{MPR}_{\text{DF+hic}}$
A (6.2-8.0)	2.3	2.1	1.8
B (4.5-6.2)	12.6	11.4	9.3
C (2.1-4.5)	31.7	33.8	44.5
D (1.5-2.1)	26.1	24.8	14.8
E (1.0-1.5)	18.3	21.5	22.4
F (0.5-1.0)	9.0	6.2	7.3
	100.0	100.0	100.0

The absorption bands of carbonyl ($1690\text{-}1703\text{ cm}^{-1}$), hydroxyl ($3365\text{-}3405\text{ cm}^{-1}$) groups and oxygen-containing ring ($1240\text{-}1250, 1045\text{-}1075\text{ cm}^{-1}$) appear in the IR spectra of the modified MPR_{DF} resin (Fig. 3, line 2, 3), that are not presented in the initial form of the PR_{DF} resin (Fig. 3, line 1). Moreover, the absorption band intensity of the $-\text{C}=\text{C}-\text{H}$ valent fluctuations ($3040\text{-}3046\text{ cm}^{-1}$), $-\text{C}=\text{C}-\text{H}$ deformation vibrations ($950, 850\text{ cm}^{-1}$) and the $-\text{C}=\text{C}-$ valent vibrations ($1612\text{-}1640\text{ cm}^{-1}$) decrease in the IR spectra of the modified resin in comparison with the IR spectra of the unmodified resin.

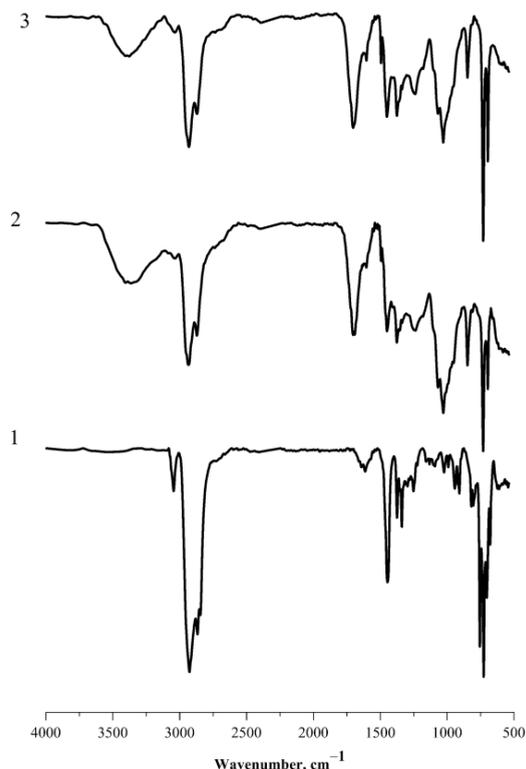


Fig. 3. IR spectra of the unmodified PR_{DF} (1) and the modified MPR_{DF} resins: oxidative system : PR_{DF} component ratio is 0.25 : 1 (2), 0.50 : 1 (3)

4. Conclusions

Oxidation of petroleum resin based on dicyclopentadiene fraction by the Prilezhaev's reaction leads to receiving of the modified resin with carboxyl and epoxy groups.

The presence of functional groups in petroleum resin is proved by IR and ¹H-NMR spectroscopy methods.

It is shown that the dicyclopentadiene oxidation proceeds simultaneously with the resin oxidation during the process in the residual hydrocarbon solution.

The number of the entered functional groups depends on the oxidative system: resin PR_{DF} component ratio and oxidation process duration.

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