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OXIDATIVE MODIFICATION OF PETROLEUM RESINS AND RECEPTION OF EMULSIONS WITH INDUSTRIAL OILS

Daria V. Fisenko, Anna A. Manankova*, Vladimir G. Bondaletov, Marina Y. Fillipova, Vera A. Yakimova

Institute of Natural Resources, Tomsk Polytechnic University, Russia

Abstract

In this paper, the petroleum resin modification process by oxidation with hydrogen peroxide under phase transfer catalysis has been studied. As a result of oxidation petroleum resins with various oxygen-containing groups (carboxyl, hydroperoxide and epoxy groups) have been obtained. The possibility of using oxidized resins as emulsifiers to stabilize oil-in-water emulsions has been shown. The optimum mixing ratio water/petroleum resin has been determined, and stable oil-in-water emulsions with modified petroleum resins have been obtained. The dependence of the emulsion stability on the acid number of the oxidized resins included in the composition of the obtained emulsions has been determined. The effect of the composition on the rheological characteristics of the emulsions: dynamic viscosity, shear stress, and the shear rate have been identified.

Keywords: petroleum resins; modification; phase transfer catalysis; stable oil-in-water emulsions.

1. Introduction

Using by-products of petroleum chemical manufactures decreases the environmental load significantly and can serve as a source of extra income when organizing a technological process correctly. At present multipurpose utilization of raw materials in petroleum refining industry is especially actual for saving non-renewable oil resources. Skilled use of pyrolysis by-products is the basic problem that can greatly affect the profitability of both the main products and products of deeper processing [1].

As a raw material for petroleum resin (PR) synthesis, products of refined and petrochemical industries containing unsaturated hydrocarbons are used. PR can be obtained by methods of thermal, catalytic and initiated polymerization [2]. A method of thermal polymerization is cheaper than a cationic method, but it tends to produce darker resins. The advantage of it is that catalyst or initiator preparation and subsequent removal steps are eliminated from the process. However, thermally polymerized resin properties are not comparable to those of the cationic resins due to limited controlling parameters of the polymerization. The catalytic polymerization processes in contrast to the methods of thermal and initiated polymerization provide stable high yields of PR at low temperatures of synthesis, which is especially important for regions with average annual low temperatures [3].

Depending on the raw materials and polymerization conditions, petroleum resins can vary considerably. The presence of reactive cyclopentadien (CPD) in the fraction can be the reason to control the process the oligomerization fraction of pyrolysis liquid products is investigated using the modified catalyst system [4].

Petroleum resins contain carbon and hydrogen atoms predominantly, but no polar or functional groups. Modified resins either are obtained from special, modified feed stream or modified after polymerization [5].

The simplest method of modification is a method of PR oxidation by hydrogen peroxide under phase transfer catalysis. Under these conditions in the structure of PR a hydroxyl, carboxyl, and epoxy groups are formed [6-7]. In this connection, the development of chemical modification methods has a great importance to make new physico-chemical properties of PR and thereby extend the area of their practical use.

Modified PRs are considered to have surfactant properties and be applied in the stabilization of oil-in-water emulsions based on mineral oil. An important characteristic of the emulsions is their stability that is the ability not to break down for certain time and not to separate into two immiscible phases. That is why substances which increase the stability of emulsions - stabilizers are used. Moreover, the stability of formed emulsion depends largely on the concentration of stabilizers and their composition [8-9].

This paper presents the results of modified PR obtaining and investigation of the rheological properties of the oil-in-water emulsions in the presence of small additions (1.2 wt.%) of modified PRs.

2. Experimental

The object of the investigation is the PR obtained by initiated and thermal polymerization of C_9 fractions of pyrolysis liquid products, and by catalytic polymerization of the fraction with the content of dicyclopentadiene (DCPD) more than 50 %, the so-called dicyclopentadiene fraction (DCPDF).

Oligomerization catalyst systems based on titanium chloride and diethylaluminumchloride $TiCl_4$ - $Al(C_2H_5)_2Cl$ were used as catalysts for DCPD fraction. The presence of CPD in the fraction determines its high reactivity and creates difficulties in the oligomerization process using a catalyst system $TiCl_4$ - $Al(C_2H_5)_2Cl$. To solve the problem related to the high reactivity fraction loading of the catalyst system was carried out by dosing in regular intervals of time. This allows not only reducing a thermal effect of carrying out oligomerization of reactive components of the faction, but also reducing the process temperature to 30°C. It is known that the use of $Al(C_2H_5)_2Cl$ as a co-catalyst allows obtaining a light resin with a higher yield, molecular weight, higher value of bromine number, indicating high unsaturation of PR and possibility of its further modification.

The modification of PR was carried out by oxidation of 30 % resin solution with hydrogen peroxide (39 % aq.) in the emulsion in the presence of a typical oxidation catalyst - ammonium molybdate in an amount of 0.05 – 0.2 % of total reaction mass. The concentration of hydrogen peroxide was varied from 0 to 7–9 % by weight of the resin. For efficient homogenization of the reactive medium a phase transfer agent - tetrabutylammonium iodide in an amount of 1 % by weight of the organic phase was used. Adding H_2O_2 was carried out by dosing at a temperature of 40-45°C, and then the reaction mixture was kept under constant stirring at 75°C for 1 hour.

The initial and modified samples of PR were examined by ^{1}H NMR spectroscopy using a device AVANCE AV-300 "Bruker" and by IR spectroscopy using an IR Fourier spectrometer (FT-801 "Simex"). Besides, the samples of initial and oxidized PR were investigated by titrimetric methods for the content of double bonds and the presence of oxygen-containing groups.

To investigate the possibility of using PR as stabilizers of oil-in-water (o/w) emulsion, the emulsion based on mineral oil I-20A was prepared. For the preparation of o/w emulsion, a sample of mineral oil was mixed with a certain amount of petroleum resin and then distilled water was added. Stirring was carried out using a rotary disperser IKA ULTRA TURRAX T18 for 10 minutes at 16.000 rev/min.

Rheological characteristics (dynamic viscosity, shear stress, and shear rate) of o/w emulsion were determined by a Brookfield viscometer DV-II + PRO. The hydrophilic properties of emulsions were assessed using a contact angle. The contact angles were measured using the image of a sessile drop with the use of a KRUSS DSA 25 device.

3. Results and discussion

Comparative characteristics of the initial petroleum resins obtained in many ways are presented in **Tab. 1**.

Table 1. The properties of the initial PR

Petroleum resins	Bromine number, g of Br$_2$/100 g of PR	Hydroperoxide number, %	Acid number, mg of KOH/100 g of PR	Epoxy number, %
PR$_{DCPDF}$	60.8	1.54	4.10	0.56
PR$_{C9}$ thermal	37.2	0.29	2.61	2.56
PR$_{C9}$ initiated	34.4	0.23	3.66	1.81

As the table shows, all samples of the resins have a slight presence of oxygen-containing groups, which is caused by oxidation during the isolation of PR from the resulting solution, as well as the storage conditions of the initial resins. PR$_{DCPDF}$ is more unsaturated resin. The value of the bromine number is almost two times higher than that of PR based on the C$_9$ fraction. This is confirmed by ^{1}H NMR spectroscopy (Fig. 1).
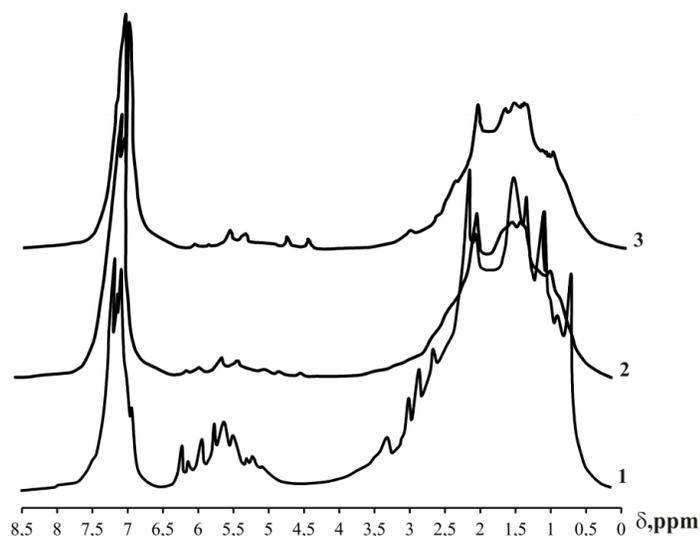

Fig. 1. ^{1}H NMR – spectra of the original samples: 1 - PR$_{DCPDF}$, 2 - PR$_{C9}$ thermal, 3 - PR$_{C9}$ initiated

The group of signals in the 4-6.2 ppm ^{1}H NMR spectrum corresponds to the protons of unsaturated bonds in the structure of PR. The value of the integral intensity of protons for the sample of PR$_{DCPDF}$ is twice more than the value of the integral intensity of protons for PR$_{C9}$. There is a group of signals in the 5.2-5.4 ppm related to acyclic double bonds in the spectrum of PR obtained by catalytic polymerization. This kind of signal is not typical for PR$_{C9}$. The signals in the 5.5-6.0 ppm are the protons of DCPD and its fragments in the oligomer. The signal at 5.97 ppm refers to the protons of norbornene double bonds. Based on the ^{1}H NMR spectra of PR it can be concluded that PR$_{C9}$ are aromatic, PR$_{DCPDF}$ is a high unsaturated cycloaliphatic resin with an aromatic moiety.

The comparative data of IR - spectra of the initial samples of PR are shown in Fig. 2.

All samples of PR are characterized by intensive absorption at 2928 cm^{-1} and medium intensity band at 1448 cm^{-1} which related to valent and deformation vibrations in the CH$_2$ groups, respectively. Also, there are absorption bands of weak intensity typical to deformation vibrations in the CH$_3$ groups (1375 cm^{-1}) indicating a predominant content of the methylene groups in PR molecule.
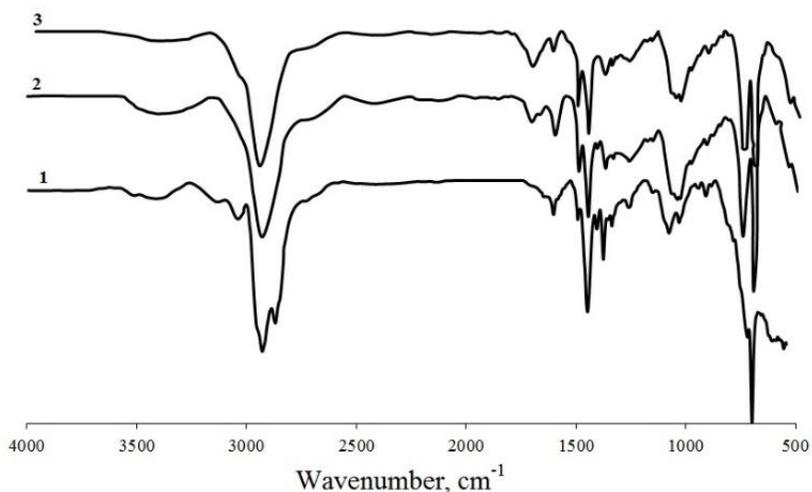
Fig.2. IR spectra of the original samples: 1 - PR$_{DCPDF}$, 2 - PR$_{C9}$ thermal, 3 - PR$_{C9}$ initiated

There is an absorption band in the IR spectrum of the resin, obtained by thermal polymerization at 1714 cm^{-1}, typical to C = C bonds. Absorption bands at 1490 and 1595 cm^{-1}, which must be attributed to skeletal vibrations of the aromatic ring, are observed. The absorption peak at 3051 cm^{-1} belongs to valent vibrations of the C-H aromatic ring. The series of sufficiently intense absorption bands at 700-800 cm^{-1}, which can be caused by deformation vibrations of unsubstituted C-H bonds in the aromatic ring, allows suggesting that the resin contains mono and dialkyl substituted aromatic compounds.

As for PR$_{DCPDF}$ sample, the presence of absorption bands at 900-1000 cm^{-1} suggests the presence of various compounds with C = C double bonds, and the doublet at 1360 and 1370 cm^{-1} indicates the content group = C (CH$_3$)$_2$. The absorption peaks at 1693 and 1603 cm^{-1} (cyclopentadiene double bonds) are caused by the presence both of exo- and endo-links in the structure. They are formed by reaction with the active species of norbornene double bond of DCPD on the reactions by direct connection on cyclopentene bond and by carbocation rearrangement. The absorption peaks at 720, and 700 cm^{-1} also indicate the presence both of exo- and endo-links of DCPD in the oligomer.

The results of PR modification by hydrogen peroxide, in the presence of ammonium molybdate and phase transfer agent - tetrabutylammonium iodide, are shown in Fig. 3.

As can be seen, in the resins modification process the bromine number value reduces significantly with increasing of the oxidant concentration and the content of carboxyl, epoxy and hydroperoxide groups increases for all resin samples. The formation of a significant amount of epoxy groups in the modified resin samples associates with the use of a catalyst based on salts of molybdic acid, which is a specific oxidation catalyst.

Due to the differences in the content of double bonds in the structure of resin, the character of curves describing the content of the various oxygen-containing groups is different for PR$_{DCPDF}$ and PR$_{C9}$ samples. Modification of PR$_{DCPDF}$ was carried out at the oxidizer concentration changes from 1 to 7 %. The results show that the values of acid, epoxy and hydroperoxide numbers exceed the values of the parameters for the resins of C$_9$ fraction when adding H$_2$O$_2$ in the amount of 7 %. The content of double bonds (28.2 g of Br$_2$/100 g of PR) is still enough to increase further the oxidant concentration. In the case of the resin based on a C$_9$ fraction, there is an inflection point at 5 % concentration of the oxidizing agent in graphs. After the point, the accumulation of oxygen-containing groups in the modified resin structure does not occur. This trend is confirmed for the PR$_{C9}$ samples with increasing concentration of H$_2$O$_2$ to 9%.

The results of the titrimetric analysis are in good agreement with the data of IR – spectroscopy (Fig. 4).

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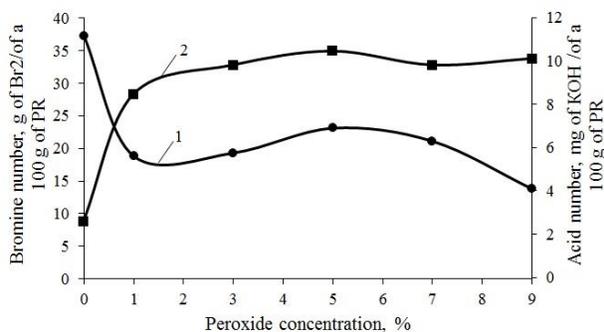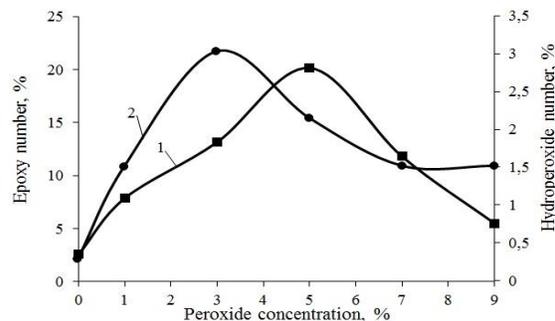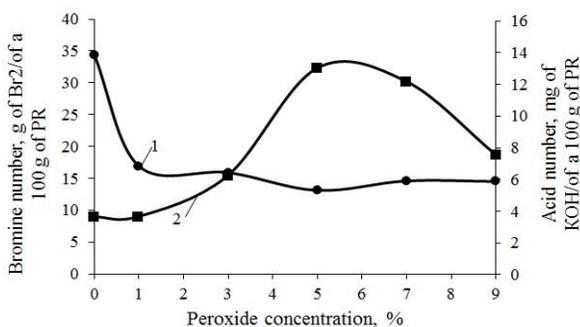
a) 1 – BN, 2 – AN

a) 1 – EN, 2 – HN

b) 1 – BN, 2 – AN
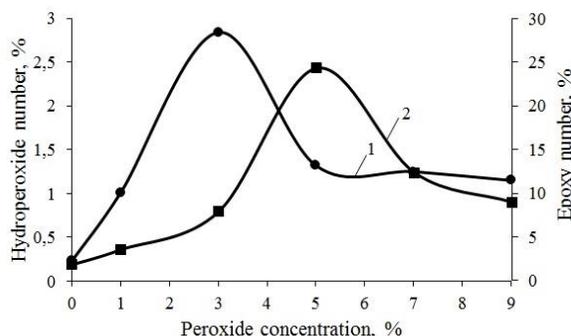
b) 1 – HN, 2 – EN
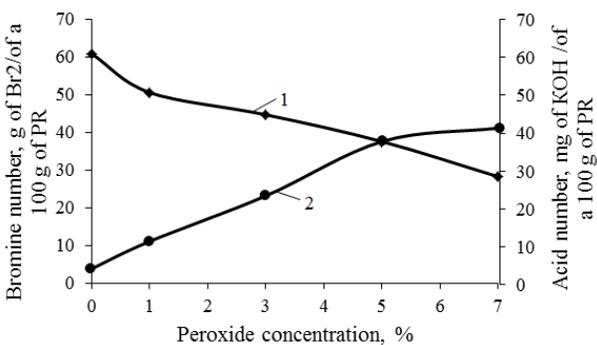
c) 1 – BN, 2 – AN
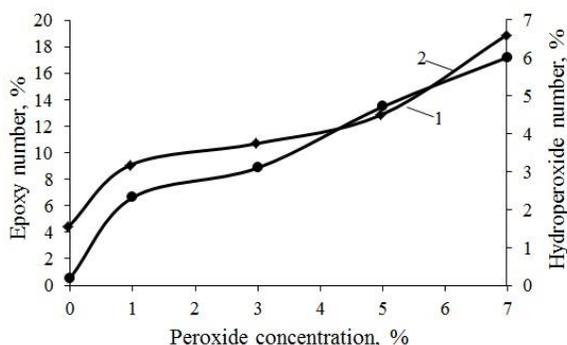
c) 1 – EN, 2 - HN

Fig. 3. Results of resin samples oxidation: a - PR_{C9} thermal, b - PR_{C9} initiated, c - PR_{DCPDF}

The IR spectra of the modified resin show appearance of a broad absorption band in the region of valent vibrations of the hydroxyl group (3500 - 3000 cm^{-1}), the intensity of which increases with the concentration of the oxidizing agent. The absorption band at 1690-1670 cm^{-1} corresponds to valent vibrations of the C = O bond. The appearance of absorption bands at 1250 cm^{-1} and 1030 cm^{-1}, corresponding to vibrations of the epoxy ring and asymmetric valent vibrations of the C-O bond, respectively, is observed as well.

Modified PR, due to the presence in their structure of lyophilic and lyophobic centers, can be a link between oil and water in the process of emulsion stabilization.
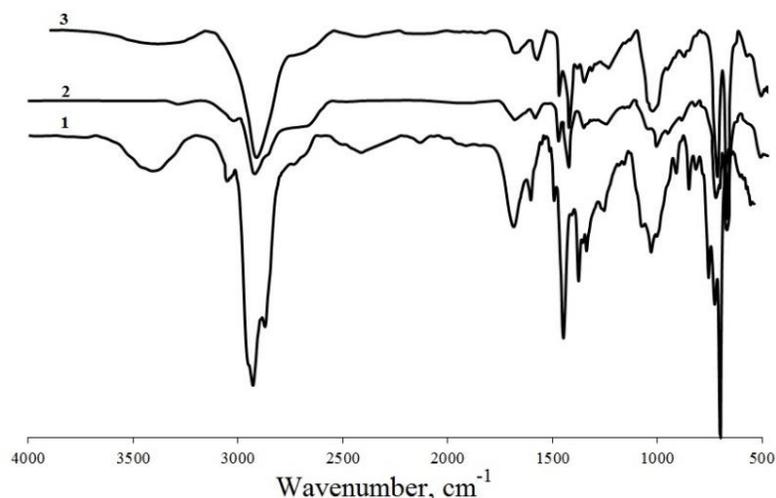
Fig. 4. IR spectra of the modified resin at a peroxide concentration 7 %: 1 - PR$_{DCPDF}$, 2 - PR$_{C9}$ thermal, 3 - PR$_{C9}$ initiated

The results of obtaining oil water emulsions based on mineral oil, the study of their viscosity and stability in the presence of small additions of modified petroleum resins are presented in this work.

PS$_{C9}$ obtained by thermal polymerization of unsaturated hydrocarbons of C$_9$ fraction was used as a sample of modified PR.

Patents analysis shows that, in order to prevent the process of emulsion destruction, complex synthetic mixtures of stabilizing compounds in an amount of 0.1 – 0.5 wt. % are introduced into their composition. Authors of the patent [10–12] have found the optimum ratio of water and resin: 70:0.5, the rest is used motor oil.

In order to get oil-in-water emulsions, a mineral oil I-20A with a viscosity of 86.5 mPa s was chosen. PR$_{C9}$ thermal, modified by hydrogen peroxide1, 3, 5, 7, and 9 %, was used as a stabilizer of oil-in-water emulsions.

Initially the stabilization of water-oil emulsion at a ratio of 70/30 by weight without emulsifier was investigated. The obtained emulsion was destroyed immediately. Further the stability of emulsions with a water content of 10 to 70 %, when the content of PR was 0.5 – 1.2 %, was investigated. The optimum ratio of oil/resin components was 57/1.2, in which emulsion was stable and homogeneous for a long time. Fig. 5 shows the results of measurement of the dynamic viscosity and shear stress of the obtai-ned emulsions according to shear rates at the different content of carboxyl groups in PR composition.
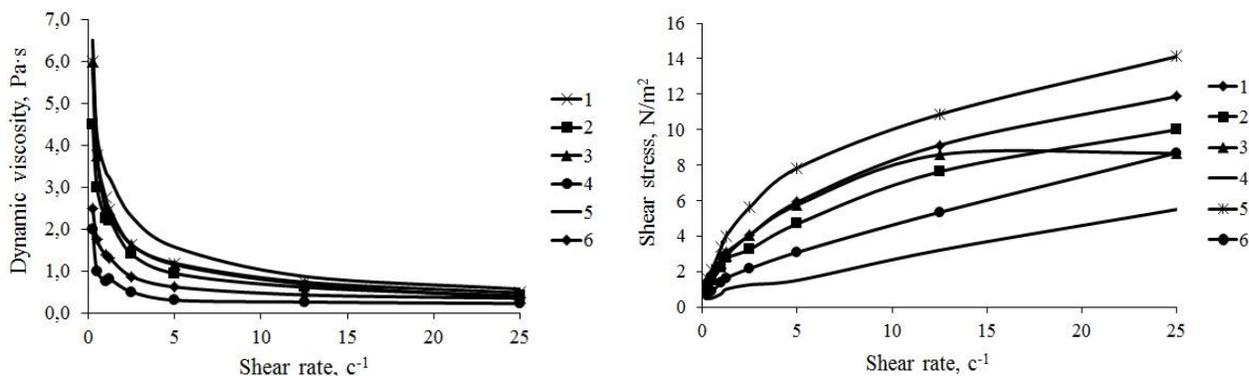

Fig. 5. Change of dynamic viscosity and shear stress of oil-in-water emulsions according to shear rate and acid number of PR: №1 – PR$_{2,6}$; №2 – PR$_{8,5}$; №3 – PR $_{9,8}$; №4 – PR $_{10,5}$; №5 – PR $_{9,8}$; №6 – PR $_{10,1}$

According to the graphs from Figure 5, it can be concluded that when a shear rate increases the dynamic viscosity of the obtained emulsions decreases. These emulsions are non-Newtonian fluids and show a pseudo-plastic character of flow.

For stabilization of "oil-in-water" emulsions, a hydrophilic emulsifier is used. Therefore, the determination of the contact angle is a necessary condition for studying properties of emulsions used in various fields such as cutting fluids. When adding a hydrophilic emulsifier in the emulsion, a continuous layer of an emulsifier around the oil droplet, making it hydrophilic and enhancing its stability, is formed.

Fig. 6 shows the dependence of the contact angle of metal surface on the content of the carboxyl groups in PR composition.
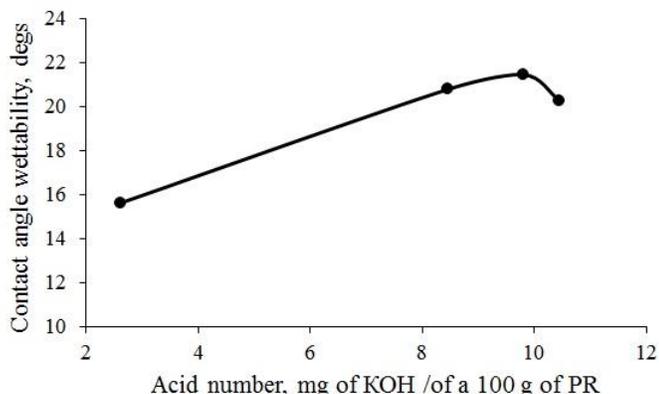

Fig. 6. Change of contact angle of oil-in-water emulsions according to acid number of PR: №1 – $PR_{2,6}$; №2 – $PR_{8,5}$; №3 – PR $_{9,8}$; №4 – PR $_{10,5}$; №5 – PR $_{9,8}$; №6 – PR $_{10,1}$

The value of contact angle is q <90 ° that indicates hydrophilic nature of the obtained emulsion samples.

4. Conclusion

The possibility of using PR as an emulsifier of oil-in-water emulsions has been studied. It has been found that when the content of oxygen-containing groups in the emulsion composition increases, their dynamic viscosity increases as well. It has been identified that emulsion, when using PR as an emulsifier, exhibits hydrophilic properties, which make it possible to apply this stable emulsion in metalworking processes.

Acknowledgments

Symbols

PR - petroleum resin;
DCPD – dicyclopentadiene;
DCPDF - dicyclopentadiene fraction;
BN - bromine number, g of Br_2/100 g of PR;

HN - hydroperoxide number, %;
AN - acid number, mg of KOH/100 g of PR;
EN - epoxy number, %.

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*Corresponding author, address: 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-3822) 606-121; fax: (+7-3822) 564-320; e-mail: amanankova@yandex.ru