

## PAINT MATERIALS BASED ON PETROLEUM RESINS

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Received March 22, 2018; Accepted May 31, 2018

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### Abstract

Petroleum resins synthesized by ionic polymerization (catalyst –  $\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ ) of different fractions of liquid pyrolysis products have been modified using peracetic acid prepared as a product of *in situ* reaction between hydrogen peroxide and acetic acid in the presence of sulfuric acid.

This modification leads to the introduction of the following polar groups into the resin: carboxyl (acid number 3.7-16.8 mg/g) and epoxy (epoxy number 2.9-8.9 %) groups. It has been shown that initial and modified petroleum resins are suitable for the formation of paint and varnish coatings. Modified resin coatings have improved elasticity and increased adhesion to metal surfaces and can be used as a part of bitumen-resin compositions.

**Keywords:** fraction of liquid pyrolysis products; petroleum resin; modification, bitumen, bitumen-resin composition.

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## 1. Introduction

A promising direction of utilization of petrochemical industry waste or by-products is their use in the synthesis of new organic compounds. By-products of pyrolysis plants with ethylene and propylene as their target products contain 30-50 % of unsaturated compounds, so their prospective processing is polymerization with the formation of petroleum polymer resins (PR). A distinctive feature of the petroleum resin production is that the industry's by-products (feedstock for polymerization) have a complex composition. The feedstock contains a significant amount of differently structured monomers that have different reactivity in a mixture with unpolymerizable hydrocarbons. Thus, the synthesis of PR represents the copolymerization process of monomers in solution [1].

The by-products of pyrolysis plants, the so-called liquid pyrolysis products, are divided into narrow fractions of saturated, unsaturated and aromatic hydrocarbons. The composition of different fractions varies considerably depending on the pyrolysis conditions and the type of raw material used in the pyrolysis process. The hydrocarbon fraction  $\text{C}_5$  (initial and final boiling point of 25-35°C and 70-75°C respectively) contains a considerable amount of diene monomers (isoprene, cyclopentadiene, pentadienes, etc.). Their content varies within a fairly wide range, which is explained by different conditions of sampling and storage of fractions. In the higher-boiling fraction  $\text{C}_9$  (initial and final boiling point of 120-125°C and 200-205°C respectively) reactive arylalkenes and dicyclopentadiene are present. In accordance with the classification of PR, aliphatic resins are obtained in the polymerization of unsaturated hydrocarbons of the  $\text{C}_5$  fraction, aromatic resins – of the  $\text{C}_9$  fraction, copolymer resins – of the  $\text{C}_5$  and  $\text{C}_9$  fractions. Copolymer resins can also be obtained by polymerization of unsaturated hydrocarbons of wide  $\text{C}_{5-9}$  fraction (initial and final boiling point of 25-35°C and 200-205°C respectively). The properties of resins produced from different fractions vary significantly. Aromatic resins in comparison with aliphatic resins have a higher density, softening point, heat resistance and lower bromine number, which determines the unsaturated nature of the resins. Copolymer resins obtained by copolymerization of aliphatic and alkenyl aromatic monomers contained in  $\text{C}_5$  and  $\text{C}_9$  fractions respectively occupy an intermediate position according to their properties [2].

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One of the drawbacks that limit the use of PR in the composition of polymer materials is their poor compatibility with many, usually polar, substances. This property is explained by the absence of functional groups in the resin structure. Therefore, the development and implementation of new types of resins and, above all, modified ones is an urgent task at present.

Modified petroleum resins are obtained by copolymerization [3-4] of liquid pyrolysis product fractions and polar monomers (vinylacetate, maleic anhydride, acrylic, methacrylic and other  $\alpha$ ,  $\beta$ -unsaturated acids, methyl methacrylate, butyl methacrylate, acrylonitrile) or by treatment [5] of the petroleum resins with chemical agents (oxygen, ozone, hydrogen peroxide,  $\alpha$ ,  $\beta$ -unsaturated dicarboxylic acids and anhydrides). The most common method of the PR functionalization is oxidation. The presence of unsaturated bonds in the PR composition makes it possible to use them in the process of oxidation by hydrogen peroxide according to the Prilezhaev's reaction [6]. Thus, the modification of aliphatic and aromatic resins with hydrogen peroxide by the Prilezhaev's reaction leads to the introduction of carboxyl and epoxy groups into their composition and to the decrease in the overall unsaturation of the resins, which entails a change in the properties of paint coatings based on them.

Petroleum resins as film-forming agents hold a special place among synthetic vegetable oil substitutes in the paint and varnish industry and are widely used in the development of oil-resin or bitumen-resin compositions. The developed polymerization methods and the different compositions of the initial fractions of liquid pyrolysis products determine the variety of chemical structures and properties of the resins. Therefore, different types of PR have different properties as film-forming substances.

Consequently, the purpose of this paper is to study the technical characteristics of paint coatings based on the initial and modified resins obtained by polymerization of the  $C_5$ ,  $C_9$ ,  $C_{5-9}$  fractions and the dicyclopentadiene fraction, and to study the possibility of using these resins as part of bitumen-resin compositions.

## 2. Experimental

### 2.1. Objects of research

The object of the study is petroleum resin obtained by polymerization of unsaturated compounds of various hydrocarbon fractions:  $C_5$  fraction (boiling point of 30-70°C),  $C_9$  fraction (boiling point of 110-190°C),  $C_{5-9}$  wide fraction of hydrocarbons (boiling point of 30-190°C) and enriched with dicyclopentadiene fraction (DF, boiling point of 110-190°C). The polymerization of unsaturated compounds of the fractions was carried out in a solution of saturated hydrocarbon under the action of the  $TiCl_4-Al(C_2H_5)_2Cl$  catalyst system.  $TiCl_4$  concentration was 2 %, the component ratio of the catalytic system was 1: 1. The process temperature was maintained at 80°C, and the process duration was 2 hours. Polymerization of high-boiling fractions ( $C_9$ , DF) was carried out at atmospheric pressure, polymerization of fractions  $C_{5-9}$  and  $C_{5-9}$  – at a pressure of 0.13 MPa. The catalytic system was deactivated with propylene oxide at the end of the process; the reaction product was kept in the composition of the obtained resins.

The modification of petroleum resins ( $PR_{C_5}$ ,  $PR_{C_{5-9}}$ ,  $PR_{C_9}$ ,  $PR_{DF}$ ) synthesized on the basis of different fractions ( $C_5$ ,  $C_{5-9}$ ,  $C_9$ , DF) was carried out with peracetic acid obtained *in situ* at an equimolar ratio of hydrogen peroxide and acetic acid in the 30 % toluene solution of the resin. The process duration was 3 hours; the process temperature was 70-75 °C. The weight ratio of resin to the oxidative system was 1 to 0.25. At the end of the process, the reaction mass was washed from acid impurities, and the resin was isolated by removal of the solvent [7].

BN 90/10 bitumen was used (GOST 6617-76 "Petroleum construction bitumens. Technical specifications"). The bitumen-resin composition was prepared by mixing 40 % bitumen solutions and 40 % resin solutions (solvent – xylene).

### 2.2. Methods of research

The functional numbers of the modified resins ( $MPR_{C_5}$ ,  $MPR_{C_{5-9}}$ ,  $MPR_{C_9}$ ,  $MPR_{DF}$ ) were determined by standard methods [8].

The paint coatings were obtained on metal plates (plate size – 9 x 16 x 0.1 cm), using a core applicator for liquid paint materials. The metal plates had been cleaned and degreased by gasoline and acetone beforehand.

The thickness of the liquid paint material was monitored with the “Measuring comb” instrument, the thickness of the dry paint material (the paint coating) with the “Thickness gauge-pencil Constant M1” instrument. The coating was dried in air, and then the strength characteristics were determined. The thickness of the bituminous or bituminous coatings was 100-140  $\mu\text{m}$ , the resin coating thickness – 20-25  $\mu\text{m}$ .

The adhesion strength of the coating was measured by the detachment method with the “Adhesimeter OR” device (GOST 32299-2013 (ISO 4624: 2002) “Paint materials. Pull-off test for adhesion”) or by the method of lattice incisions (GOST 15140-78 “Paintwork materials. Methods for determination of adhesion”).

The bending strength of coatings was determined in accordance with GOST R 52740-2007 (ISO 1519-2002) “Paints materials. Method for determination of film strength while bending around cylindrical mandrel”. This property characterizes the elasticity of coatings.

The impact strength of coatings was measured in accordance with GOST R 53007-2008 “Paint materials. Rapid deformation (impact resistance) test method”.

The hardness test was performed according to ISO 6441-2 : 1999 “Paints and varnishes. Determination of micro-indentation hardness. Part 2: Knoop hardness by measurement of indentation depth under load”.

The water absorption measurement of the coating was carried out according to GOST 21513-76 “Paint materials. Methods for determination of paint film. Water- and moisture absorptivity”.

The wetting angle was determined on a Drop Shape Analyzer DSA 25-Kruss by the drop method at 25°C. The bitumen, resins or their bitumen compositions were dissolved in toluene at a material: solvent ratio of 1: 1.5.

### 3. Results and discussion

The analysis of scientific and patent literature on the PR application in the paint and varnish industry shows that there is high demand for them due to the availability of raw materials (petrochemical industries by-products containing unsaturated hydrocarbons) and their low cost. The application of PR in paint and varnish materials allow to effectively save the deficient monomers or the vegetable oils used to produce film-forming.

The advantages of using PR as paint materials include water resistance, acid-, salt- and alkali-inertness, high binding and adhesive capacity, good solubility in many solvents, high drying speed and coating hardness. The disadvantages are low light and weather resistance, brittleness, insufficient strength and adhesion characteristics, poor compatibility with drying or semi-drying oils and other polar substances. These disadvantages are eliminated by means of the introduction of polar groups or during the preparation of composite materials using low molecular weight, oligomeric and polymeric plasticizers: for example, phthalic and phosphoric acid esters, paraffin, waxes, transformer oils <sup>[9]</sup>, low molecular weight or oxidized rubbers <sup>[10]</sup>.

In the present work, petroleum polymer resins (PR<sub>C5</sub>, PR<sub>C5-9</sub>, PR<sub>C9</sub>, PR<sub>DF</sub>) obtained by polymerization of unsaturated compounds of various hydrocarbon fractions and modified resins (MPR<sub>C5</sub>, MPR<sub>C5-9</sub>, MPR<sub>C9</sub>, MPR<sub>DF</sub>) obtained by oxidation with peracetic acid obtained *in situ* by the Prilezhaev’s reaction were used. Characteristics (functional numbers) of the initial and modified petroleum resins – bromine number (BN, g/100 g), acid number (AN, mg/g), epoxy number (EN, %) are given in Tab. 1.

The modification leads to a decrease in the unsaturated nature of the resins and the introduction of polar (carboxyl and epoxy) groups in the polymer chain. The multicomponent composition of the initial fractions and different reactivity of the monomers in the polymerization process do not allow a strict correlation between the structure of PR<sub>C5</sub>, PR<sub>C5-9</sub>, PR<sub>C9</sub>, PR<sub>DF</sub>, MPR<sub>C5</sub>, MPR<sub>C5-9</sub>, MPR<sub>C9</sub>, MPR<sub>DF</sub> and functional numbers of the initial and modified petroleum resins.

Table 1. Functional numbers of initial and modified petroleum resins

Characteristics	Functional numbers of initial and modified petroleum resins			
	PR <sub>C5</sub>	PR <sub>C5-9</sub>	PR <sub>C9</sub>	PR <sub>DF</sub>
Bromine number, g/100 g	27.2	19.0	33.2	32.3
Acid number, mg/g	0.7	0.6	0	0
Epoxy number, %	0	0	0	0
	MPR <sub>C5</sub>	MPR <sub>C5-9</sub>	MPR <sub>C9</sub>	MPR <sub>DF</sub>
Bromine number, g/100 g	14.8	2.6	14.2	13.6
Acid number, mg/g	3.7	14.6	10.1	16.8
Epoxy number, %	5.0	2.9	8.2	8.9

Properties of coatings derived from 40 % solutions of initial and modified resins in toluene are given in Tab. 2.

Table 2. Properties of coatings based on initial and modified resins

Characteristics	Properties of coatings based on initial and modified resins			
	PR <sub>C5</sub>	PR <sub>C5-9</sub>	PR <sub>C9</sub>	PR <sub>DF</sub>
Adhesion, points	2	2	3	3
Adhesion, MPa	1.0	1.2	0.8	0.9
Impact strength, cm	5	5	2	5
Bending strength, mm	3	1	3	3
Hardness, kg	0.2	0.2	0.7	0.2
Water absorption, %	0.5	0.3	0.6	0.5
	MPR <sub>C5</sub>	MPR <sub>C5-9</sub>	MPR <sub>C9</sub>	MPR <sub>DF</sub>
Adhesion, points	1	1	2	1
Adhesion, MPa	1.4	1.5	1.0	1.5
Impact strength, cm	10	10	4	10
Bending strength, mm	1	1	1	1
Hardness, kg	0.2	0.4	0.8	0.2
Water absorption, %	0.5	0.1	0.6	0.5

The test results showed that the type of resin affects the coating properties, but this effect is insignificant. For example, aromatic resins (PR<sub>C9</sub>, MPR<sub>C9</sub>) are more brittle and have lower adhesion values, but they are harder. In general, the results (Table 2) indicate an improvement of adhesion and strength properties (impact and bending strength) of coatings based on modified resins (MPR<sub>C5</sub>, MPR<sub>C5-9</sub>, MPR<sub>C9</sub>, MPR<sub>DF</sub>).

The improvement of adhesion properties is directly related to the change in the wetting angle (Tab. 3, Figure 1). Adhesion characterizes the interfacial interaction, as a result of the desire of the system to reduce surface energy. A quantitative measure of the interfacial interaction of a material with a metal surface is adhesion work, determined by the Dupre-Young equation [11]:

$$Wa = \sigma \cdot (1 + \cos\theta),$$

where: *Wa* – the adhesion work, mN/m<sup>2</sup>;  $\sigma$  – the surface tension of the material at the boundary with air, mN/m<sup>2</sup>;  $\theta$  – the wetting angle.

According to the above equation, the adhesion work increases with a decrease in the wetting angle, hence, the adhesion of the material to the metal surface increases.

Thus, a decrease in the wetting angle with the use of modified resins naturally leads to an increase in adhesion (Table 2, 3).

Table 3. Wetting angle values

Wetting angle values, degree			
PR <sub>C5</sub>	PR <sub>C5-9</sub>	PR <sub>C9</sub>	PR <sub>DF</sub>
8.6	9.2	11.1	8.5
MPR <sub>C5</sub>	MPR <sub>C5-9</sub>	MPR <sub>C9</sub>	MPR <sub>DF</sub>
7.4	8.3	9.9	8.2

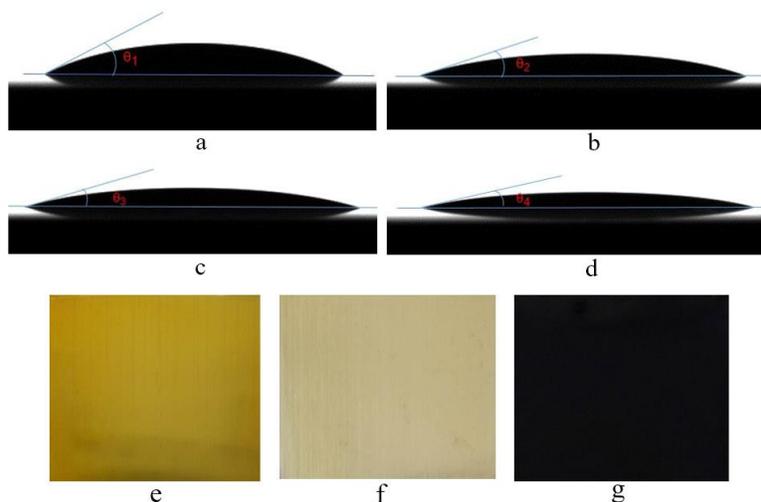


Fig. 1. Wetting angle by solutions of bitumen (a), bitumen-MPRc9 resin composites (b), initial PRc9 resin (c), modified MPRc9 resin (d) and surface view of initial PRc9 resin (e), modified MPRc9 resin (f), bitumen-MPRc9 resin composite (g)

As an independent film-forming compound or in combination with vegetable oils, natural resins or synthetic film-forming agents, bitumen is used in paintwork materials [12]. Previously rosin and products of its processing (natural resins) in combination with bitumen were mainly used, but at present, such materials are practically not applicable in industry. Natural materials (rosin, vegetable oils, etc.) in the bituminous composites are replaced with synthetic polymers without deterioration of the composite properties. The oil-free bituminous varnishes are divided into bitumen composite, which consists of bitumen and solvent, and bitumen-resin composite, which is a mixture of the bitumen and resin solution. The bituminous varnish is the basis for the production of the paint coating, which is reliable anticorrosive protection for metal surfaces and has good conservation properties at a reasonably low cost.

Initial and modified resins can also be used to prepare bitumen-resin composites. Examples of main properties of bituminous paint coatings, which contain 90% bitumen and 10% resin, are given in Tab. 4.

Table 4. Bitumen-resin coating properties

Characteristics	Properties of bitumen-resin coatings based on initial or modified petroleum resins				
	Bitumen – PR	Bitumen – PRc5	Bitumen – PRc5-9	Bitumen – PRc9	Bitumen – PRDF
Composition, %	100 – 0	90 – 10	90 – 10	90 – 10	90 – 10
Adhesion, points	1	1	1	1	1
Adhesion, MPa	2.4	2.7	2.7	2.1	2.8
Impact strength, cm	35	40	42	50	35
Bending strength, mm	1	1	1	1	1
Hardness, kg	0.2	0.4	0.4	0.4	0.3
Water absorption, %	0.8	0.1	0.1	0.1	0.1
	Bitumen – MPR	Bitumen – MPRc5	Bitumen – MPRc5-9	Bitumen – MPRc9	Bitumen – MPRDF
Composition, %	100 – 0	90 – 10	90 – 10	90 – 10	90 – 10
Adhesion, points	1	1	1	1	1
Adhesion, MPa	2.3	2.8	2.9	2.1	2.8
Impact strength, cm	35	45	47	50	45
Bending strength, mm	1	1	1	1	1
Hardness, kg	0.2	0.3	0.4	0.5	0.4
Water absorption, %	0.8	0.1	0.1	0.1	0.1

Higher adhesion values of coatings containing modified resins in comparison with coatings based on initial resins are well correlated with the wetting angle values of the metal surface with bitumen-resin composite solutions (Tab. 5, Fig. 1).

Table 5. Wetting angle values with bitumen-resin solutions (90 % bitumen, 10 % resin)

Wetting angle values, degree				
Bitumen	Bitumen – PRC5	Bitumen – PRC5-9	Bitumen – PRC9	Bitumen – PRDF
19.9	14.1	14.4	17.3	14.3
Bitumen	Bitumen – MPRC5	Bitumen – MPRC5-9	Bitumen – MPRC9	Bitumen – MPRDF
19.9	12.1	12.7	14.9	13.1

#### 4. Conclusions

1. Initial petroleum resins were synthesized by ionic polymerization of unsaturated compounds of various liquid pyrolysis product fractions with  $\text{TiCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  catalyst system. These resins were then further modified.
2. Resin modification with peracetic acid obtained *in situ* results in the introduction into the resin of polar groups: carboxyl (acid number 3.7-16.8 mg/g) and epoxy (epoxy number 2.9-8.9 %).
3. Initial and modified resins are suitable for obtaining paint and varnish coatings. It has been shown that coatings based on modified resins have increased adhesion to metal surfaces (1.0-1.5 MPa) and improved elasticity (bending strength – 1 mm) as compared to coatings based on initial resins (adhesion – 0.8-1.2 MPa, bending strength – 3 mm)

Obtained resins can be used in the bitumen-resin compositions to improve the protective coatings properties

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