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Properties of Bitumen Composition Modified by Petroleum Resins

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Abstract. It was advised to use aliphatic, cycloaliphatic, aromatic petroleum resins and their derivatives obtained by oxidation of resins with a mixture of hydrogen peroxide and acetic acid as bitumen polymer-modifiers. Petroleum resins were obtained by ionic polymerization of unsaturated compounds of liquid pyrolysis products under the influence of titanium tetrachloride-diethylaluminium chloride catalyst. It was established that the maximum values of adhesion of modified bitumen coatings to metal substrates, corresponding to the minimum values of the wetting angle of the metal surface coated with solutions of bitumen compositions with different content of the polymer modifier were achieved using oxidized resins. All modified bitumen coatings have low water absorptivity and high acid resistance, alkali resistance and salt resistance, which allow using them as protective coatings.

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

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Свойства битумных композиций, модифицированных нефтеполимерными смолами

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Аннотация. Показано использование алифатических, циклоалифатических, ароматических нефтеполимерных смол, полученных ионной полимеризацией непредельных соединений различных фракций жидких продуктов пиролиза под действием каталитической системы тетрахлорид титана – диэтилалюминийхлорид и их окисленных смесью пероксида водорода и уксусной кислоты производных в качестве полимеров–модификаторов битума. Установлено, что максимальные значения адгезии модифицированных битумных покрытий к металлическим подложкам, соответствующие минимальным значениям краевого угла смачивания подложек битумным раствором, достигнуты при использовании окисленных смол. Все модифицированные битумные покрытия обладают низким водопоглощением и высокой кислото-, щелоче- и солестойкостью, что позволяет использовать их в качестве защитных покрытий.

Ключевые слова: битум, нефтеполимерная смола, фракции жидких продуктов пиролиза, модификация, битумно-смоляные композиции.

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Introduction

Corrosion of metal annually leads to billions in losses as a result of the destruction of machines and mechanisms. Currently, the simplest and most common method of protecting metals from corrosion is to apply protective coatings on their surfaces. But paint and varnish coatings are not able to prevent corrosion, but only reduce its speed, inhibit corrosion. Therefore, such qualities of the coating as uniformity, adhesion strength to the surface of the metal substrate, the ability to swell in water, are of paramount importance.

Artificial and natural bitumens have found quite wide application in the paint and varnish industry. One of the main advantages of coatings based on bitumen mastics is the low cost of raw materials – bitumen, which can be more than 20 times lower than the cost of a polymer coating (for example, polyethylene). The disadvantages of such coatings include their low durability: paint and bituminous coatings are destroyed in corrosive, especially alkaline, environments or wet soils. Gaseous products of corrosion cause delamination of coatings, which further leads to their destruction.

One of the ways to improve the quality and durability of bitumen coatings is to modify bitumens with mineral and synthetic polymeric materials. For example, primary carbon nanomaterials increase the physical and mechanical properties of petroleum bitumen and construction materials based on it, provided they are evenly distributed in bitumen [1]. Thermoplastic linear polymers, general purpose rubbers and thermoplastic elastomers are mainly used in bitumen-polymer compositions [2, 3]. Thermoplastic polymers, in particular atactic polypropylene, recycled polyethylene [4-6], or thermoplastic elastomers, for example, divinyl styrene rubbers have become widespread both in Russia and abroad [7-9]. The introduction of modifiers perfects the basic parameters of polymer-bitumen compositions: increases the softening temperature, reduces the brittleness temperature, and improves adhesion [10, 11] and stability of modified bitumen at different temperatures [12, 13].

Oligomeric products can also be used as bitumen modifiers: indene-coumarone, petroleum, phenol-formaldehyde, epoxy, and other resins [3, 10, 14]. The influence of petroleum resins (PR) on the physical and mechanical characteristics of various petroleum road bitumen is examined in articles [3, 15, 16], and it is concluded that the PR is a modifier optimizing the structure of road bitumen. The possibility of using modified PR with terminal epoxy, hydroxyl and carboxyl groups to improve the properties of bitumen has been shown [17].

The purpose of the work is to develop bitumen compositions modified with petroleum resins oxidized by hydrogen peroxide and to obtain anti-corrosion coatings with improved properties based on them.

Experimental

Objects of research

Polymer-bitumen compositions were obtained by mixing solutions of the components at a temperature of 20-25 °C. Bitumen and resin, taken at a given ratio, were used as a 40% solution in xylene. The amount of bitumen modifier (polymer) varied in the range from 0 to 15% wt.

Different petroleum resins and their oxidized derivatives were used as a polymer-modifier of bitumen. Petroleum resins were obtained by polymerization of unsaturated compounds of various fractions of liquid pyrolysis products: aliphatic C_5, cycloaliphatic with a high content of dicyclopentadiene C_{DF}, aromatic C_9 and broad fraction $C_{5\text{-}9}$ [18]. The catalyst concentration was 2%, the ratio of the catalyst components was 1 : 1. The catalyst was decomposed with propylene oxide, the deactivation products were not removed from the reaction mass. After removal of unreacted hydrocarbons at low pressure, the separated petroleum resins were modified.

The resin was oxidized for 180 minutes at a temperature of 70 °C. An equimolar mixture of hydrogen peroxide and acetic acid, obtained in situ, was used as the oxidizing agent. The ratio of resin : oxidizer was 1: 0.5 [19].

Bitumen used brands BN 90/10 (GOST 6617-76 "Petroleum construction bitumens. Specifications").

Bituminous coatings were applied to carefully prepared metal plates by a method of watering and dried in a vacuum oven.

Methods of research

The thickness of the dried coating was controlled by the device "Constant M1 Pencil Thickness Gauge".

Adhesion was determined by the pull-off test – GOST 32299-2013 (ISO 4624: 2002): Paint materials. Pull-off test for adhesion. Determination of the surface wetting angle was carried out by the method of lying drop at a temperature of 25 °C on the device DSA 25-Kruss – Drop shape analysis. Water absorption of bituminous coatings was evaluated after maturation in distilled water at 20 °C for 24 hours by the method: GOST 21513-76: Paint materials. Methods for determination of paint film water and moisture absorptivity. The acid resistance of the bitumen coating was evaluated after its maturing in an aqueous solution of H_2SO_4 (10% wt), the alkali resistance – in an aqueous solution of NaOH (10% wt), the salt resistance – in an aqueous solution of NaCl (3% wt) at a temperature of 20 °C. The value of acid resistance (alkali resistance / salt resistance) was defined by the time, during which the coating did not deteriorate (white matt spots, flaking, rashes, blisters, etc. are not allowed) – GOST 9.403-80: Unified system of corrosion and ageing protection. Paint coatings. Test methods for resistance to liquid static effect.

Results and discussion

Dependences of adhesion on the composition of bitumen compositions are shown in Fig. 1. The following polymers were used as a bitumen modifier: initial (PR_C5) and oxidized (OPR_C5) aliphatic petroleum resins; cycloaliphatic resins (PR_DF), obtained by polymerization of unsaturated compounds of fractions with a high content of dicyclopentadiene, and their oxidized derivatives (OPR_DF); initial (PR_C9) and oxidized (OP_C9) aromatic petroleum resins; the initial resin (PR_C5-9), obtained by polymerization of unsaturated compounds of a wide C_{5-9} fraction of hydrocarbons, and their oxidized derivatives (OPR_C5-9).

The results showed that bitumen coatings with 10% aliphatic (PR_C5, OPR_C5), cycloaliphatic resins (PR_DF, OPR_DF) and resins based on a wide fraction of hydrocarbons (PR_C5-9, OPR_C5-9) have maximum adhesion to the metal substrate. Bituminous coatings modified with aromatic resins (PR_C9, OPR_C9) have lower adhesion values, the maximum of which is observed when using 3% modifier. This fact is probably related to the higher brittleness of aromatic resins containing a significant

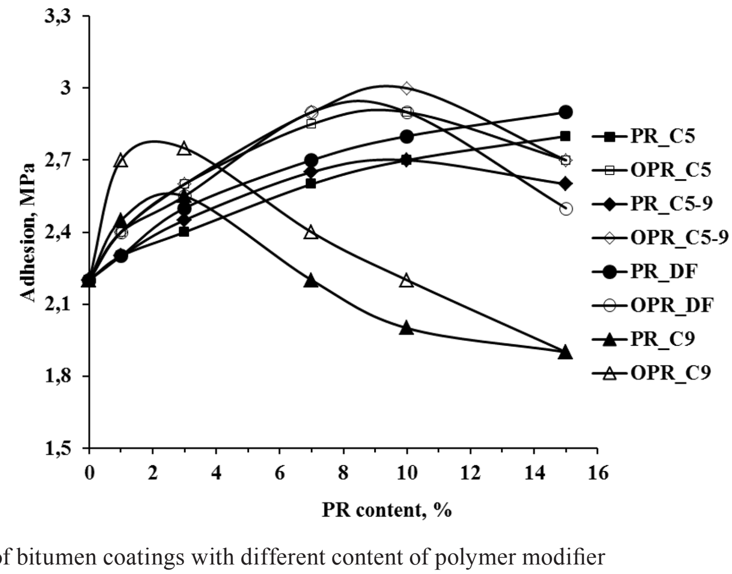

Fig. 1. Adhesion of bitumen coatings with different content of polymer modifier

number of styrene links, and deterioration of the coating quality with increasing resin content in the bitumen composition.

The obtained values of adhesion are in good agreement with the values of the wetting angle (Fig. 2).

The relationship between the rupture work of an adhesive bond and the wetting angle is expressed by the Dupré-Jung equation, which shows that a smaller wetting angle corresponds to a greater adhesion [20].

The wetting angle of the surface coated with a solution of the bitumen composition modified with oxidized resins (OPR_C5, OPR_C5-9, OPR_DF, OPR_C9) has a lower value compared with the cases of using the original resins (PR_C5, PR_C5-9, PR_DF, PR_C9) as a modifier. The presence of free carboxyl and hydroxyl groups in the polymer-modifier contributes to the achievement of higher adhesion values (Fig. 1) and lower values of the wetting angle (Fig. 2) due to the appearance of an ion-dipole interaction between the polymers and the metal or the formation of hydrogen bonds between carboxyl groups of the polymer and polar groups (hydroxyl, oxide) on the metal surface. The influence

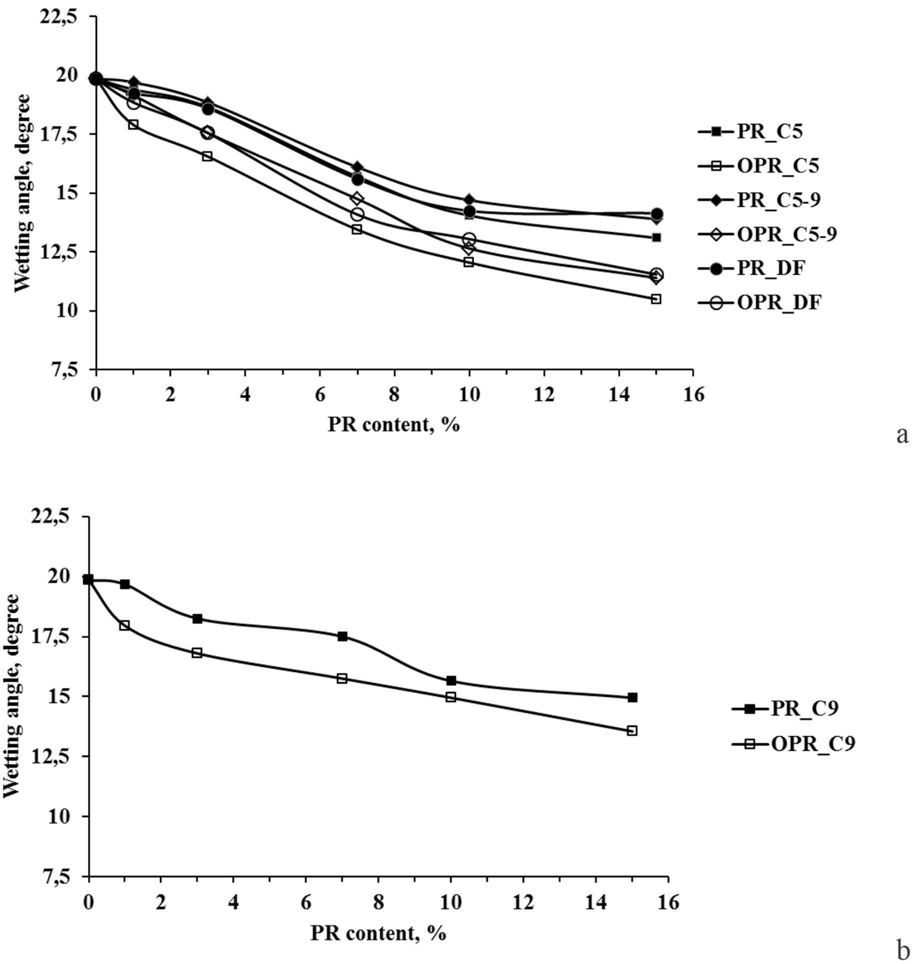

Fig. 2. Wetting angle of the metal surface coated with solutions of bituminous compositions with different content of the polymer modifier PR_C5, OPR_C5, PR_C5-9, OPR_C5-9, PR_DF, OPR_DF (a), PR_C9, OPR_C9 (b)

of the resin structure (OPR_C5, OPR_C5-9, OPR_DF) on these parameters is less pronounced. The wetting angle of the surface is significantly reduced to 10% of the polymer-modifier content in the bitumen composition (Fig. 2), which also agrees with the dependences of adhesion on the polymer-modifier content in the bitumen composition (Fig. 1). For comparison, the results of the study of bitumen compositions modified with aromatic resins (PR_C9, OPR_C9) are presented, and higher values of the wetting angle (Fig. 2, b) and lower adhesion values (Fig. 1) are noted when using aromatic resins, in which the main repetitive links are styrene units, giving increased brittleness to the polymer-modifier.

Thus, when modifying bitumen with oxidized PR, the adhesion strength of bitumen coatings to metal substrates increases.

Protective properties of coatings are determined by their water and chemical resistance in various corrosive environments: salt, acid, alkaline. It has been established that the water resistance of bitumen coatings modified with petroleum resins is superior to that of pure bitumen coatings (Table 1). When 7-10% polymer modifier is added to bitumen, the water resistance of coatings reaches maximum values.

The introduction of all polymers-modifiers into bitumen leads to an increase of acid resistance (Table 2), alkali resistance (Table 3) and salt resistance (Table 4) bitumen coatings in comparison with indicators of a pure bitumen coating. The use of oxidized petroleum resin as a bitumen modifier increases the chemical resistance of the coating as a result of improved adhesion of the bitumen

Table 1. Water absorptivity of bitumen-resin coatings

Resin content in the composite, %	Water absorptivity, %							
	RR_C5	ORR_C5	PR_C5-9	OPR_C5-9	PR_DF	OPR_DF	RR_C9	ORR_C9
0	0,121	0,121	0,121	0,121	0,121	0,121	0,121	0,121
1	0,083	0,074	0,065	0,085	0,084	0,079	0,065	0,068
3	0,062	0,055	0,052	0,061	0,051	0,048	0,044	0,048
7	0,017	0,021	0,039	0,052	0,043	0,034	0,025	0,038
10	0,018	0,012	0,035	0,053	0,032	0,023	0,019	0,032
15	0,031	0,025	0,037	0,055	0,022	0,019	0,035	0,052

Table 2. Acid resistance of bitumen-resin coatings in a 10% H_2SO_4 solution

Resin content in the composite, %	Acid resistance, days							
	RR_C5	ORR_C5	PR_C5-9	OPR_C5-9	PR_DF	OPR_DF	RR_C9	ORR_C9
0	50	50	50	50	50	50	50	50
1	53	56	56	57	55	56	68	63
3	58	75	61	72	59	68	85	91
7	64	87	68	91	65	77	75	118
10	72	98	78	112	75	102	73	98
15	67	81	65	98	65	97	61	74

Table 3. Alkali resistance of bitumen-resin coatings in a 10% NaOH solution

Resin content in the composite, %	Alkali resistance, days							
	RR_C5	ORR_C5	PR_C5-9	OPR_C5-9	PR_DF	OPR_DF	RR_C9	ORR_C9
0	75	75	75	75	75	75	75	75
1	76	79	78	83	78	81	79	83
3	79	84	81	94	82	89	96	114
7	83	96	91	111	92	105	94	106
10	98	113	101	122	97	118	85	97
15	96	109	95	111	85	109	78	90

Table 4. Salt resistance of bitumen-resin coatings in a 3% NaCl solution

Resin content in the composite, %	Salt resistance, days							
	RR_C5	ORR_C5	PR_C5-9	OPR_C5-9	PR_DF	OPR_DF	RR_C9	ORR_C9
0	30	30	30	30	30	30	30	30
1	32	34	34	35	32	33	38	36
3	32	39	38	44	36	38	48	51
7	38	46	42	53	40	45	42	65
10	44	57	47	69	45	59	36	59
15	37	43	40	58	37	43	34	43

coating to the metal substrate. The maximum protective resistance (acid resistance – 98-118 days, alkali resistance – 113-122 days, salt resistance – 51-69 days) was noted when 10% oxidized aliphatic (OPR_C5), cycloaliphatic petroleum resin (OPR_DF) or resin obtained on the basis of a wide hydrocarbon fraction (OPR_C5-9) were added. When oxidized aromatic resins (OPR-C9) were used, 3% of the resin is required for maximum effect.

Thus, bitumen coatings modified with petroleum resins have low water absorptivity, good acid-, alkali- and salt resistance, which allow them to be used to obtain protective coatings with high physic-mechanical properties.

Conclusion

1. Modification of bitumen with aliphatic, cycloaliphatic, aromatic oil-polymer resins, and resins obtained on the basis of a wide hydrocarbon fraction, as well as their oxidized derivatives leads to increased adhesion of modified bitumen coatings to metal substrates. Maximum adhesion values have been achieved using oxidized resins.
2. The obtained adhesion values are in good agreement with the wetting angle of the metal surface with bitumen solutions.
3. Coatings based on modified bitumen have low water absorptivity and high acid-, alkali- and salt resistance, which allow them to be used as protective coatings.

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