

**PLASTICIZING ADDITIVES FROM PHTHALIC ANHYDRIDE RESIDUE
AND 2-ETHYLHEXANOL RESIDUE FOR IMPROVEMENT
OF PROPERTIES OF ROAD PETROLEUM BITUMENS**

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The article is about production of plasticizing additives which was received from phthalic anhydride residue and 2-ethylhexanol residue for improvement of properties and structure of road petroleum bitumens grades 60/90 and 90/130 - most often used in the road constructions. Method of receiving of plasticizing additives was described, their properties were researched, and influence of plasticizing additives on operating abilities and physicochemical properties of road petroleum bitumens was showed.

Keywords: phthalic anhydride residue, 2-ethylhexanol residue, plasticizing additive, esterification, road petroleum bitumen, modification

Actual problem is building new of high quality roadway coverings in connection with increasing of a share in motor transport in total amount of cargo transportation and growing of an automobile park of Russia [1].

Over third of a length of federal highways and bridge constructions demands the increasing strength properties by reason of the accelerated degradation of road constructions and decreasing life duration between repairs by reason of increasing of a share of heavy cars and articulated trucks in the traffic flow. About 76 percent of regional (intermunicipal) highways mismatches to normative requirements on road-service qualities, that leads to increasing of the cost price of automobile transportations and decreasing in competitiveness of production of the enterprises.

At level of the government of the Russian Federation the federal target program is accepted till 2015 which provides for increasing in volume of building and reconstruction of highways more than in 1,5 times [2].

For manufacturing reliable road bitumen coverings are necessary bitumens with high qualities (with the higher frost resistance, thermal stability and stability to cracks formation). One of the perspective ways for improvement air-blown road petroleum quality along with optimization and raw material for oxidation is adding different modifiers to them [3].

It is known, that compounded bitumens have a high tensile strength and improvement adhesion properties. main advantage of the modifying bitumens are strong gluing and reliable keeping some particles of mineral material in the long time in real weather impact in wide range temperature [4]. Selection of the components, that constituents at the modifying additives, in the first place based on their availability and cost [5].

The purpose of this work is qualified using of phthalic anhydride residue (PA residue) and 2-ethylhexanol residue (2-EH residue) and producing from their additives which can be used for modifying of properties of road petroleum bitumen.

Researches on producing plasticizing additives (PAdd) from phthalic anhydride residue and 2-ethylhexanol residue, which are a waste of large-tonnage manufactures of a gas-chemical plant's of JSC "Salavatnefteorgsintez", was carry out in Research and development centre of JSC "Salavatnefteorgsintez".

At the present phthalic anhydride residue is not qualified utilized and considering us a production waste. Inexpensive plasticizer additives producing on the base PA residue could find application in various industries (paint and varnish, shoe, fuel and et al.) [6, 7, 8]. In particular, we are offered using PAdd as modifiers for improvement of properties of road petroleum bitumens grades 60/90 and 90/130, most often used in the road constructions.

PA residue's characteristics are presented in Table 1.

Table 1

Phthalic anhydride residue's characteristics

Characteristics	Value
1. A mass fraction of oil, %	Absence
2. A mass fraction sour, %	98,88
Including Phthalic anhydride	97,07
Phthalic acid	2,03
3. Crystallization temperature, °C	123,4

It is necessary to pay attention to high enough content of phthalic anhydride in phthalic anhydride residue – 97,07 %. So, State Standard 7119-77 normalized the mass content of phthalic anhydride in high quality phthalic product not less than 99,8 %, that all on 2,83 % above, than in PA residue. Also structure PA residue includes tarry

matters which can deteriorate chromaticity and other properties of the products producing on its basis [9].

2-EH residue's characteristics are presented in Table 2.

Table 2

2-ethylhexanol residue's characteristics

Characteristics	Value
1. Water content, Wt. %	0,02
2. A mass fraction parts of alcohols to C ₄ , %	Absence
3. The part's sum of alcohols to C ₄ , % mass.	Absence
4. A mass fraction parts of alcohols to C ₈	Absence
5. A mass fraction of alcohols C ₈ , % mass.	18,34
Including 2-ethylhexanol	18,34
2-ethyl-4-methylpentanol	Absence
6. A mass fraction parts of alcohols above C ₈ , % mass.	81,64
7. A mass fraction of unsaturated hydrocarbons, % mass.	0,50
8. A mass fraction of aldehydes, % mass.	2,89
9. Acidity index, mg KOH/g	0,19

2-ethylhexanol residue contents 18,34 % pure 2-ethylhexanol, that in 5 times it is less, than in the target product according to State Standard 26624-85 [10]. However in the structure 2-EH residue including enough large quantity of parts (alcohols above C₈) – 81,64 % mass, including 6 – 7 % mass. dodecanols, which also can enter into reaction esterification. 2-ethylhexanol residue contents unsaturated hydrocarbons and high-boiling components as impurities which are undesirable parts for esterification process.

Synthesis of plasticizer additive was carry out by following method. At I stage crushed phthalic anhydride residue and 2-ethylhexanol residue in various ratios was placed in 4-neck flask and the reaction mixture was mixed 1,0 - 1,5 hours at temperature 130 - 140 °C under atmospheric pressure. At II stage was added 5 % solution of tetrabutoxytitan in 2-EH residue and the reaction was continued for 9,5 - 10,0 hours at temperature 180 - 210 °C under atmospheric pressure. Then was carrying out the stage of neutralization of reaction mixture and tetrabutoxytitan decomposition in a phthalate-raw by 5 % water solution of NaOH at mixing 1,0 hour and temperature 95 - 100 °C, after that was carrying out the stage of washing by distilled water (the temperature 50 °C,

mixing at 10 - 15 min) and the reaction mixture was separated in the separating funnel. The stage of water and excess of alcohols distillation was caring out at the temperature 100 - 210 °C and residual pressure 100 - 150 mmHg, filtration stage – under vacuum.

For researches of bitumens properties was used the compounding method [11].

In the metal container was placed 100 g of investigated bitumen and the plasticizer additives in various ratios – from 1 % to 10 % from weight of bitumen. The mixture was mixed within 10-20 minutes at temperature of 120 ± 5 °C by stirrer until temperature of softening was receipted of constant value and selected test for definition Ring and Ball softening point.

Was received several grades plasticizing additives (PAdd-1, PAdd-2 and PAdd-3 at ratio PA residue and 2-EH residue 1:3, 1:6 and 1:9 respectively), differing on the properties. Properties of plasticizing additives are resulted in Table 3.

Table 3

Physical and chemical properties of plasticizer additives

Additives №	Specific gravity, g/sm ³	Kinematic viscosity at 50 °C, mm ² /sec	Flash point, °C	Acidity index of a phthalate-raw, mg KOH/g	Acidity index of a final product, mg KOH/g
PA-1	1,016	246,17	158	19,80	4,31
PA-2	0,969	56,64	140	12,22	1,92
PA-3	0,942	45,31	143	11,19	1,89

At producing plasticizer additive at ratio PA residue : 2-EH residue = 1 : 3 phthalate-raw's acidity index (product before neutralization stage) is equal to 19,80 mg KOH/g, that correspond that esterification was finished for 92 %. It confirms fact, that 2-ethylhexanol and other higher alcohols (above C₈) in 2-EH residue also was entered into reaction esterification.

Obtained plasticizer additives are viscous liquids with dark-brown colour. The flash point of produced phthalates (Table 3), which has been determined in open crucible, is less, than at dioctylphthalate (DOP) which equal 205 °C according to State Standard 8728-88 [12]. The acidity index of plasticizer additives as exceeds standard values to DOP extra/second quality (not more 0,07/0,10 mg KOH/g.)

For researching the influence of produced plasticizer additives on road petroleum bitumen properties was used two bitumens grades 60/90 and 90/130 which

produced on the plant of JSC "Salavatnefteorgsintez".

The quality properties of road petroleum of (State Standard 22245-90) are presented in Table 4 [13].

Table 4

Properties of viscous road bitumens grades 60/90, 90/130

The grade	Penetration, x 0,1 mm, at temperature		Penetration Index	Temperature of, °C		Loss of weight after heating, wt %	Adhesion, not worse than control standard sample №	Softening point drift, °C
	25 °C	0 °C		Softening	Brittleness			
60/90	63	21	- 1,4	47	- 33	0,46	1	2
90/130	118	28	- 1,4	43	- 37	0,66	2	5

The results of research of bitumen grade 60/90 and 90/130 with plasticizer additives are presented in Table 5 and Table 6.

Table 5

Physicochemical properties of bitumen 60/90 modified by additives

Additives №	% Additives to weight of bitumen	Temperature of, °C		Penetration, x 0,1 mm, at temperature		Loss of weight after heating, wt %	Softening point drift, °C	Adhesion, not worse than control standard sample №
		Softening	Brittleness	25 °C	0 °C			
PAdd-1	0	47	- 33	63	21	0,46	2	1
	1	46	- 42	46	33	0,50	6	1
	2	45	- 46	45	50	0,01	6	1
	3	45	- 44	50	36	0,58	5	2
	4	44	- 39	75	47	0,17	6	2
	5	43	- 43	78	53	0,05	3	2
PAdd-2	2	46	- 52	39	23	0,00	0	2
	4	44	- 56	58	29	0,09	3	1
	6	45	- 41	47	67	0,34	3	1
	8	34	- 71	98	52	0,38	15	1
	10	36	- 65	105	49	0,52	8	1
PAdd-3	1	42	- 54	49	23	0,09	9	2
	2	41	- 54	61	24	0,09	13	2
	3	42	- 46	73	22	0,14	10	1
	4	41	- 47	87	25	0,25	5	1
	5	39	- 53	100	44	0,36	4	1
	6	38	- 53	112	33	0,41	4	1

Table 6

Physicochemical properties of bitumen grade 90/130 modified by additives

Additives №	% Additives to weight of bitumen	Temperature of, °C		Penetration, x 0,1 mm, at temperature		Loss of weight after heating, wt %	Softening point drift, °C	Adhesion, not worse than control standard №
		Softening	Brittleness	25 °C	0 °C			
PAdd-1	0	43	- 37	118	28	0,66	5	2
	1	42	- 26	168	85	0,00	7	1
	2	41	- 32	171	30	- 0,12	5	1
	3	42	- 33	145	33	0,00	2	2
	4	39	- 44	155	37	0,86	4	2
	5	40	- 37	159	40	0,08	1	2
	6	39	- 42	168	38	0,12	8	2
PAdd-2	1	43	- 41	86	17	0,00	4	2
	2	42	- 45	81	33	0,00	3	2
	3	39	- 52	106	31	0,12	7	2
	4	38	- 52	126	30	0,08	1	1
	5	40	- 49	112	57	0,16	1	1
	6	38	- 47	156	69	0,16	5	1
PAdd-3	1	42	- 46	70	20	0,10	6	1
	2	41	- 47	88	27	0,22	8	1
	3	40	- 49	105	31	0,24	7	1
	4	39	- 52	106	32	0,27	7	1
	5	40	- 48	108	56	0,28	6	2
	6	38	- 54	124	47	0,00	12	2

Apparently from Tables 5 and 6, plasticizer additives reduce temperature of softening (melting point), increase plasticity and reduce temperature of brittleness (brittle point). Also improvements of adhesive properties to a mineral material that is very important at building of road coverings is observed. Plasticizer additives Padd-1, Padd-2, Padd-3 increase thermo stability of bitumen, reduce such quality indicators as a weight loss after heating (weight loss after heating within 5 hours at temperature 163 °C) and softening point drift (fallback).

Long-term experience in organization and maintenance of roadway coverings by using viscous road petroleum bitumens producing on Russian's petroleum refinery indicate that, for example, at value of temperature of brittleness equal -27 °C (that much more than limit value according to State Standard 22245-90) destruction of coverings already started on the first year of exploitation, case of insufficient properties of bitumi-

nous asphalt to stretching at the low temperatures (and this under stretching values according to quality standards at 25 and 0 °C) [14].

Modifying bitumens which obtained by compounding with plasticizer additives PAdd-1, PAdd-2, PAdd-3 have low temperature of brittleness – up to 65 °C, on good-quality of adhesion, that assumed probability of their application on the I climatic zone with average monthly temperature in the most cold season where low-temperature properties in the first place (not more – 20 °C).

It is established, that synthesized plasticizer additives PAdd-1, PAdd-2, PAdd-3 could influenced to physicochemical and operational properties of road bitumens: increased freeze resistance, improved adhesion and increased thermo stability at addition PAdd-1 and PAdd-2 in number of 4 % – 6 % from weight of initial bitumen grade 60/90 and at addition PAdd-1, PAdd -2, PAdd-3 in number of 4 % – 5 % from weight of initial bitumen grade 90/130. Whereas plasticizer additives reduced temperature of softening of bitumens a little, their can use in technology of production of bitumens "reoxidation → thinning", which is realized on the bitumen plant of JSC "Salavatnefteorgsintez" [15].

Researches are showed that from phthalic anhydride residue and 2-ethylhexanol residue is possible to produce the plasticizer additives which can be used to farther for improving of structure of viscous road petroleum bitumens.

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