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## A MODIFYING ADDITIVE TO ROAD BITUMEN

### МОДИФИЦИРУЮЩАЯ ДОБАВКА ДЛЯ ДОРОЖНОГО БИТУМА

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**Abstract.** The butadiene- $\alpha$ -methylstyrenated copolymer has been offered as a modifying additive in the road bitumen composition. The effect of the additive with various copolymer content, industrial oils' mixture and polyethylenepolyamine production wastes upon the main physical mechanical indices of the polymer – bitumen binder has been studied. With the modifier concentration rise in bitumens the depth of the needle penetration, the softening temperature increases, the brittleness temperature decreases and the temperature working interval of the road bitumen broadens substantially. As a result of the adhesive properties' study with the introduction of polyethylenepolyamine production wastes, the strength of adhesion with mineral material significantly improves. The patterns obtained have been also subjected to ageing test. On the basis of comparative investigations' analysis results, the polymer modifier effect upon the broken brick and mastic asphalt bitumen properties has been revealed. An optimal ratio of ingredients in the asphalt bitumen composition with improved working characteristics has been offered. The development has an applied value.

**Аннотация.** В качестве модифицирующей добавки в составе дорожного битума предложен бутадиен- $\alpha$ -метилстирольный сополимер. Исследовано влияние добавки с различным содержанием сополимера, смеси промышленных масел и отхода производства полиэтиленполиамин на основные физико-механические показатели полимерно-битумного вяжущего. С повышением концентрации модификатора в битумах увеличивается глубина проникновения иглы, температура размягчения, понижается температура хрупкости и

значительно расширяется температурный рабочий интервал дорожного покрытия. В результате исследования адгезионных свойств, при введении отхода производства полиэтиленполиамина существенно улучшается прочность сцепления с минеральным материалом. Так же полученные образцы подвергнуты испытанию на старение. На основании анализа результатов сопоставительных исследований, выявлено влияние полимерного модификатора на свойства щебеночно-мастичного асфальтобетона. Предложено оптимальное соотношение ингредиентов в составе асфальтобетонного покрытия с улучшенными эксплуатационными характеристиками.

**Keywords:** bitumen, polymer, modifying additive, compression strength limit, asphalt concrete

**Ключевые слова:** битум, полимер, модифицирующая добавка, предел прочности на сжатие, асфальтобетон

### **Introduction**

Use of modifiers is a promising route of modernization of road surfaces at the base of bitumens [1]. A substantial improvement of their properties, first of all, their strength is achieved by addition of such polymer compositions as styrene-butadiene-styrenated thermoelastoplasts, butyl-rubber and triple copolymers [2-5]. But the addition of some high-molecular modifiers can evoke the technological problems connected with nonuniform distribution of the polymer in the bitumen mass and with insufficient adhesion of crushed stone with surface resulting in surface layer destruction at the road sections with intense traffic.

The literature analysis made it possible to choose the optimum class of high-molecular compositions for production of polymer-bitumen binders (PBB). For example, the highly available copolymer of olefin and diene in concentrations providing preservation of the basic parameters of polymer-bitumen binders at technically justified level is a convenient modifying additive. So, the present study is devoted to investigation of the possibility of using the butadiene- $\alpha$ -methylstyrenated-copolymer as a modifier to road bitumen composition (and later – to asphalt concrete mixture composition) for achieving a high level of its operation characteristics.

### **Experimental part**

The experiments were conducted with the blown bitumen, which operation parameters are given a table 1, the  $\alpha$ -methylbutadiene-styrenated rubber; the industrial oil – a mixture of I-20 and I-40; the waste of polyethylenepolyamine production.

The waste of polyethylenepolyamine (PEPA) production had the following composition, % mas: polyethyleneamine - 20-35, mixture of carboxylic acids (oleinic acid and gossipole resin) - 10-20, amidoamines – 20-25, imidazolynes - 30-35.

The softening point of PBB was determined by the R&B method (GOST 11506-73)

The breaking point was determined by the Fraas method (GOST 11507-78).

The depth of needle penetration at 25 °C was determined by GOST 11501-78.

The tension at 25 °C was determined by GOST 11505-75.

The binding with mineral filler was determined by GOST 11508-74.

The stability of bitumens at durable storage and increased temperatures (163°C, 5 hours), estimated by its quality parameters, was determined by GOST 18180-72.

## Results and discussion

For better understanding of the work of polymer in PBB composition (later-asphalt concrete mixture) we studied its physical-mechanical parameters. At first, we examined the effect of the butadiene- $\alpha$ -methylstyrenated-copolymer on operation parameters of the binders. As it is seen from figure 1, the depth of needle penetration, determining its grade, increases with increase of the modifier concentration.

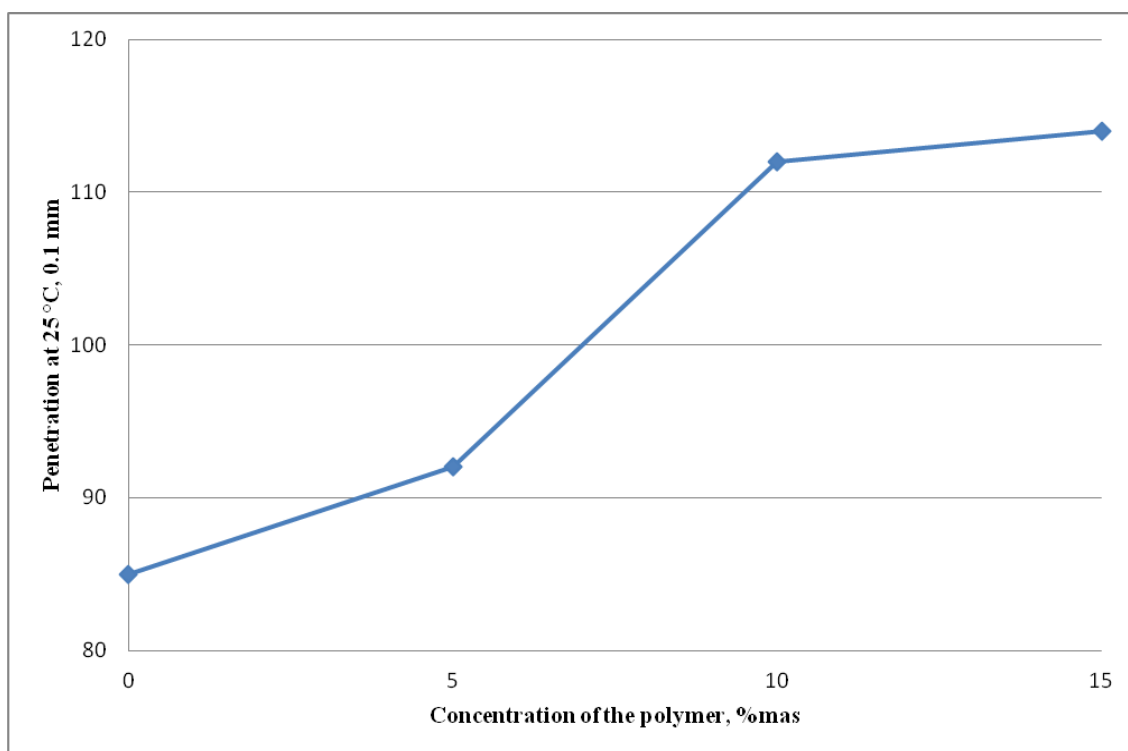


Figure 1. Dependence of the needle penetration depth from the polymer concentration in PBB

Because the softening point, reflecting the transition from viscous-plastic condition to viscous one, is the basic parameter of thermal stability, we studied the effect of the quantity of the introduced high-molecular compound on this parameter. It was shown that the increase of polymer content favors the increase of softening point ~13 °C (figure 2).

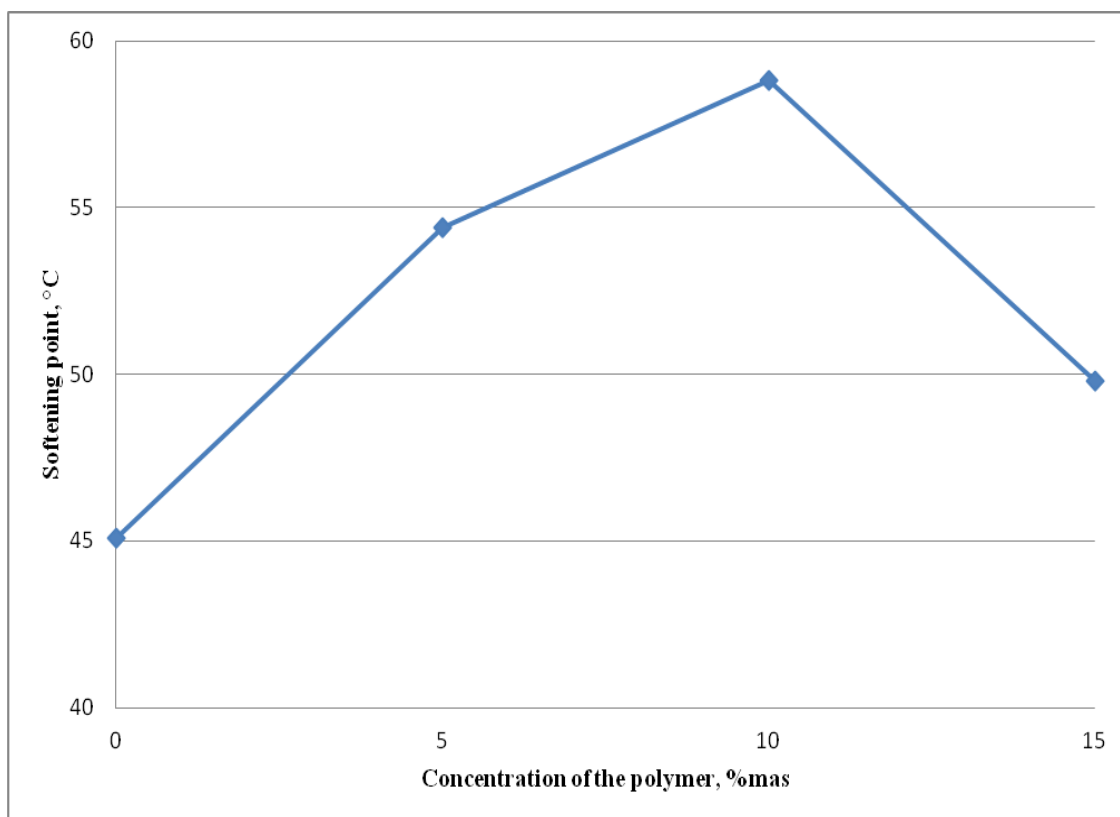


Figure 2. Relation between softening point and polymer concentration in polymer-bitumen binder

These behaviors are apparently explained by the formation of a polymer grid in the PBB. Then some stabilization and decay take place. Firstly, butadiene- $\alpha$ -methylstyrenated-copolymer acts as a filler with simultaneous increase of softening point and viscosity. Then, when the critical concentration of structure formation is reached, the peak of softening point due to the polymer saturation of the mixture is observed. The later increase of the concentration leads to the oversaturation of the bitumen by the high-molecular compound and the decay of softening point takes place.

Table 1. Physical-mechanical properties of the produced polymer-bitumen binders

	Component content in PBB,%mas								GOST R 52056- 2003
	100	95	90	85	95	93	90	85	
Bitumen	100	95	90	85	95	93	90	85	
Polymer	0	5	10	15	0	5	5	5	
Waste of PEPA	0	0	0	0	5	2	5	10	
Name of parameter									
Penetration at 25 °C, 0.1 mm	85	92	112	114	122	106	111	130	91-130
Softening point, °C	45.1	54.4	58.8	49.8	49.8	64.8	54.1	50.7	50
Breaking point, °C	-14	-32.9	-34.7	-30.7	-30.9	-37.8	-34.5	-30.4	-30
Ductility at 25 °C, sm	>100	>150	>150	>150	103	>150	>150	>150	>30
Plasticity range, °C	59.1	97.3	103.5	80.5	80.7	106.6	92.6	84.1	-
Binding with mineral filler	№3	№2	№1	№2	№2	№1	№1	№2	Agreed to sample №2

As it is seen from table 1, addition of the modifier to the base bitumen leads to improvement of the main parameters. First of all, a substantial increase of the temperature serviceability range (plasticity range) should be noted. The bitumens with a high plasticity range have a higher deformation strength evoking an increase of the resistance to cracking at low temperatures and the shearing strength of the surface at increased temperatures. The introduction of polymers into bitumens leads to improvement of the basic parameter, characterizing the binder cracking resistance – the breaking point – the lowest point of temperature serviceability range of the binder (table 1).

Increase of the butadiene- $\alpha$ -methylstyrenated copolymer concentration leads to decrease of the PBB breaking point and has an experimental character in the range 10 % mas (figure 3), with is consistent with the results, published in literature [2]. For all tested samples of PBB with different modifier contents the data, satisfying the requirements of GOST P 52056-2003, were obtained.

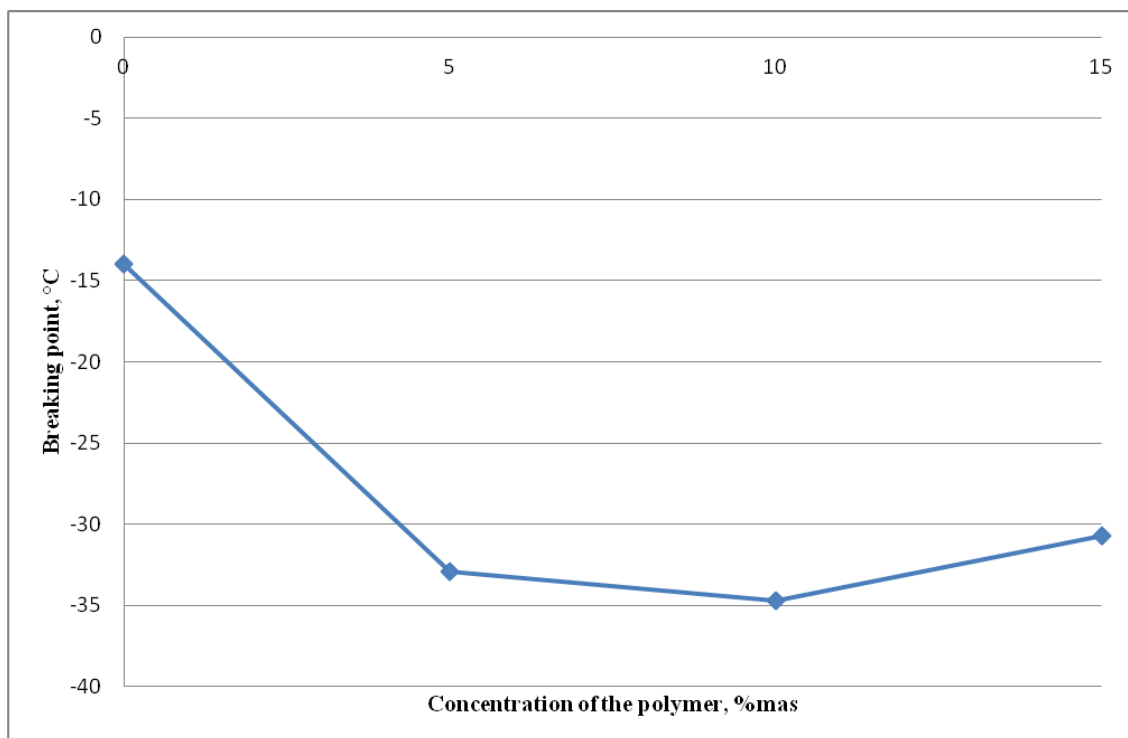


Figure 3. Relation between breaking point and polymer concentration in PBB

Taking into account the fact that nitrogen-bearing substances, including polyethylenepolyamine (PEPA), are described in scientific literature as increasing adhesion properties of PBB additives [6], we tested the waste of PEPA production. The so-called method of “passive adhesion” was chosen for our experiments. The obtained results showed that the adhesion strength with mineral material is greatly improved and agreed with the test sample № 1 at the PEPA dosage from 2 to 5 % mas (table 1), while of other parameters of the binder satisfy the GOST quality characteristics.

Together with the butadiene- $\alpha$ -methylstyrenated copolymer, the mixture of industrial oils I-20 and I-40 was introduced into the bitumen for preparing the PBB. At the basis of the data, given in table 1, the composition of PBB with the best physical-mechanical properties was chosen: 5 % mas polymer and 95 % mas bitumen. Later this relation was used for preparing the PBB with oil modifying additives. The effect of gradual increase of the oil mixture concentration (table 2) on the bitumen characteristics was studied at a fixed polymer content.

Table 2. Modification of the bitumen BND 90/130 by the butadiene- $\alpha$ -methylstyrenated rubber and the mixture of mineral oils I-40 and I-20

Parameters	Component content		
	I-40 and I-20 5 mas.%	I-40 and I-20 10 mas.%	I-40 and I-20 20 mas.%
Depth of needle penetration , 0,1 mm at 25 °C at 0 °C	82	112	197
	38	31	89
Softening point, °C	56.2	56.9	45.8
Ductility, cm at 25 °C at 0 °C	>150	>150	>150
	>50	>50	>50

The analysis of concentration relations between temperature (figure 4) and penetration (figure 5) showed that the optimum dosage of industrial oil mixture amounts to 10 % mas. This quantity of plasticizer was enough for providing good dispersion of polymer in bitumen at high temperatures.

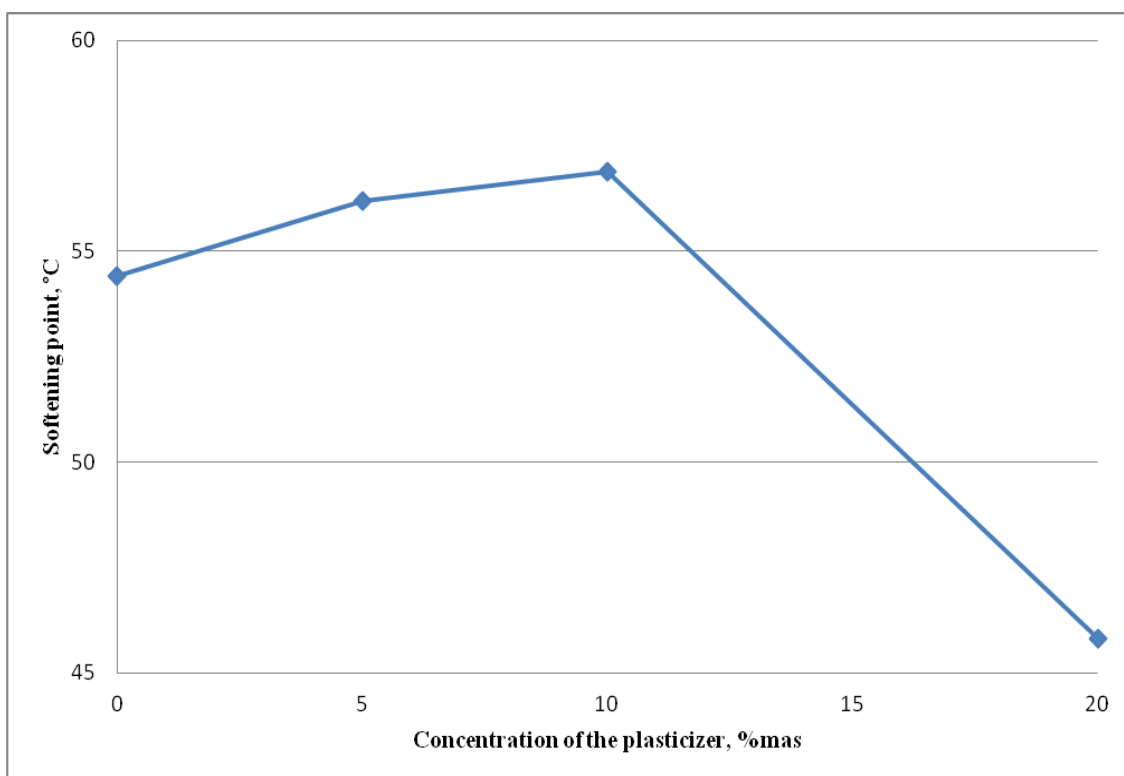


Figure 4. Relation between softening point and plasticizer concentration in the polymer-bitumen binder

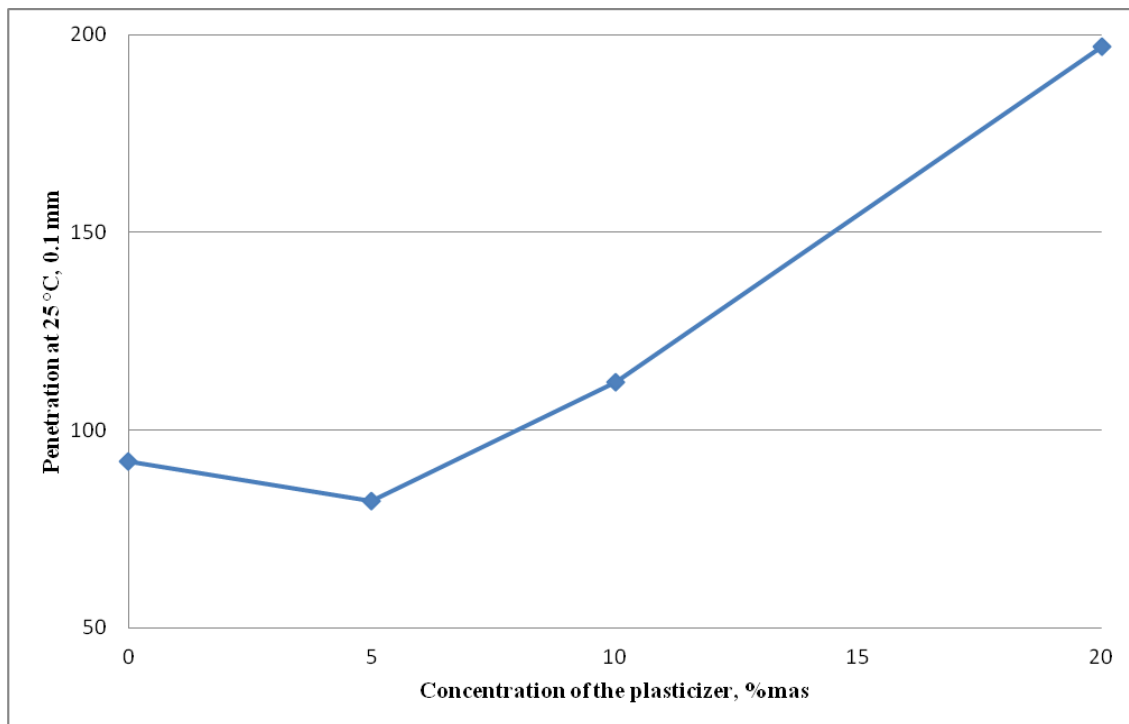


Figure 5. Relation between needle penetration depth and plasticizer concentration in PBB

The composition, % mas (bitumen BND 90/130 – 85, polymer – 5, plasticizer – 10), composed on the basis of the experimental data, makes it possible to produce the polymer-bitumen-binders, satisfying the GOST P 52056-2003 requirements and superior to the base bitumen in all characteristics. The proper selection of the polymer-bitumen composition makes it possible to avoid the deformation of road surfaces in summer and the temperature-shrinkage cracking in winter.

One of the reasons of the overdue destruction of road surfaces is the aging, taking place at durable operation periods. At this the whole complex of mechanical and physical reactions in material structure is meant, leading to deterioration of mechanical properties and decrease of surface serviceability. We studied physical-mechanical characteristics of the modified PBB, subjected to test aging. As it is seen from table 3 the ductility decreased, while the softening point increased. Probably it is connected with the reactions of oxidative dehydration of bitumen naphthenearomatic compositions, taking place in the conditions of aging, leading to the formation of polycyclic aromatic molecules and their subsequent association in asphaltenes.



Table 3. Effect of the PBB composition on the aging resistance

№	Component content, mas. %			Softening point before heating, °C	Softening point after heating, °C
	Bitumen	Polymer	PEPA		
1	100	0	0	45.1	46.5
2	95	0	5	49.8	58.0
3	93	5	2	64.8	69.1
4	90	5	5	54.1	58.9
5	85	5	10	50.7	55.5

For determination of the road surface deformation resistance we prepared the asphalt concrete mixtures of the same granulometric composition at the base of the 90/130 bitumen with various contents of modifying additives. The test results of the samples of asphalt concrete effects on the compression strength are given in table 4. The experimental data show that the strength characteristics of the asphalt concrete with PBB are greatly superior to the asphalt concrete at the base of the 90/130 bitumen.

Table 4. The compression strength limits for polymer asphalt concretes

№ number	Component content in PBB, % mas.				Compression strength limit, MPa	
	Bitumen	Polymer	Industrial oil of I-20 and I-40 grades	Waste of PEPA	0°C	50°C
GOST 9128-97	-	-	-	-	not above 12	not below 1.2
1	100	0	0	0	8.75	1.25
2	95	5	0	0	9.50	2.75
3	90	5	5	0	10.00	3.50
4	95	0	0	5	4.79	2.80
5	93	5	0	2	11.50	4.00
6	90	5	0	5	12.00	2.60
7	85	5	0	10	11.00	1.30

## Conclusion

The butadiene- $\alpha$ -methylstyrenated copolymer is offered as a modifying additive to road bitumen composition. Variation of the ratio of the bitumen, the modifying additive (butadiene- $\alpha$ -methylstyrenated copolymer) and the plasticizer permitted to choose the composition of polymer-bitumen binder with improved operation characteristics, making it possible to produce the road polymer-bitumen binders, satisfying the requirements of GOST P 52056-2003. Addition of the waste of polyethylenepolyamine production in the road polymer-bitumen binder composition increases its adhesion characteristics.

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