COMPARATIVE STUDY OF THE PROPERTIES OF OXIDIZED AND DISTILLED ROAD BITUMENS AND POLYMER BITUMENS BASED ON THEM

Victor Zolotarev, Jan Pirig, Andrey Galkin, Svetlana Kudriavtseva Valdes
Kharkov national automobile and highway university

ABSTRACT

This work analyzes the results of research into two types of bitumen: a series of four oxidized bitumens with penetrations at 25 °C of 50, 75, 105, and 172 × 0.1mm, and a series of four distilled bitumens (from NYNAS) with penetrations of 52, 79, 118, and 182 × 0.1mm.
In addition to the usual properties studied, we determined their adhesion to a hard substrate, and their cohesion according to plane-shear measurements.
Significant differences were shown in the different bitumens in terms of their softening and fragility temperatures, tensile strengths at 0 and 25 °C, and passive adhesion to hard substrates. A correlation was found between cohesion and penetration for both types of bitumen, whereas a significant difference was observed in their aging resistance.
To evaluate the effectiveness of using SBS-type polymers in relation to the properties of PMBs, we used two bitumens from each series. The addition of an equal amount of polymer had a different effect on the strength of the two types of bitumen obtained by the different technologies. Besides the usual changes occurring upon bitumen modification, the polymer had beneficial effects on the tensile strength at 0 °C and the cohesion of the distilled bitumens, and on the aging resistance of the oxidized bitumens.

Keywords: oxidized and distilled road bitumens, properties, polymer bitumens, tensile strengths

1. INTRODUCTION

Interest in the quality of bitumens has increased in connection with increased road construction and especially with the building of main highways in Russia and Ukraine. In these countries, the feasibility of using distilled bitumens is under active discussion.

With this background in mind, this work aims to compare:

1) The properties of oxidized and distilled bitumens with similar penetration values;
2) The properties of pure bitumens and polymer-modified bitumens (PMBs);
3) PMBs and pure bitumens with similar penetrations;
4) PMBs with similar penetrations that are based on oxidized and distilled bitumens.

Four kinds of distilled bitumen produced by the firm "Nynas" were presented to the department of technology of road-building materials by the company Akzo Nobel (Sweden). Ukrainian oxidized bitumens were obtained from the Lisichansk refinery (TNK-BP). The properties of the bitumens from both series were compared using standard methods adopted in Ukraine and Russia. In addition, using techniques devised at Kharkiv National Automobile University (KHNADU), the adhesion of bitumen films to glass surfaces in water [1], the cohesion [2], and the stability of the adhesion of the studied binders after heating were determined.

2. RESULTS AND DISCUSSION

The index of adhesion according to the KHNADU method is taken as the fraction of the surface area remaining on the glass after heating for 25 min at 75°C for the pure bitumens, or at 85°C for bitumens with surfactant additives.

The cohesion according to the KHNADU method is determined as the in-plane shear strength of a film of binder of thickness 200 μm at a given temperature and a shear rate of 1 s^{-1}.

The adhesion stability under the influence of heating is defined by the results of experiments on the bitumen with surfactant after thermostatic heating of a thin layer at 163°C and of the bulk at 180°C for 5 hours.

The results of the experiments with distilled and oxidized bitumens are presented in Table 1. They show the following: the bitumens from different manufacturers of respective brands have very similar penetrations at 25°C. Each of the oxidized bitumens conforms to the requirements of the Ukrainian standard DSTU 4044 for the relevant brand. The same is true for the distilled bitumens in relation to the requirements of the EN 12591 standard.

Table 1 : Properties of oxidized and distilled bitumens

Index		Bitumen Nynas from firm Akzo Nobel				Bitumens from Lisichansk refinery			
		AN1	AN2	AN3	AN4	LB1	LB2	LB3	LB4
Penetration at 25 ºC, 0.1 mm		52	79	118	182	50	75	105	172
Penetration at 0 ºC, 0.1 mm		12	22	39	51	18	24	33	51
Softening temperature, ºC		48.3	44.7	40.8	37.3	53.8	49.5	47.0	42.6
Fragility temperature, ºC		-9	-10	-13	-15	-14	-15,5	-18	-20
Flash point, ºC		296	285	276	271	286	283	281	262
Ductility at 25 ºC, cm		>100	>100	>100	>100	74	>100	>100	>100
Ductility at 0 ºC, cm		-	-	0.4	95.0	0.8	3.2	4.0	8.6
Penetration index		-1.54	-1.55	-1.74	-1.70	-0.29	-0.32	-0.01	0.36
Adhesion with glass at T = 85 ºC, %		7	7	6	5	17	8	10	6
Adhesion with glass at T = 75 ºC, %		9	10	8	6	20	13	11	8
Plasticity range, ºC		57.3	54.7	53.8	52.3	67.8	65.0	65.0	62.6
Changes in properties after heating a thin layer at 163 °C	Residual penetration, %	81	76	87	72	76	59	62	66
	Change in softening temperature,°C	3.7	4.5	4.6	4.0	6.3	5.7	4.3	4.5
	Change in mass, %	+0.57	+0.55	+0.42	+0.44	-0.08	-0.05	-0.08	-0.1

NB: The oxidized bitumens from Lisichansk refinery are denoted by the abbreviation LB, and the distilled bitumens of Akzo Nobel are denoted by AN.

At the same time, differences in raw materials and manufacturing technologies result in the production of bitumens that differ in many other properties. The oxidized bitumens have a higher softening temperature (by 5–6°C) than distilled bitumens, as well as a lower fragility temperature (by 5–6°C), a probable lower tensile strength at 25°C (ductility determined on a ductilometer with test length of 100 cm), a higher ductility at 0°C (except for bitumen AN4), a slightly lower flash point, a slightly better adhesion index, a wider plasticity range (by 10–11°C), and a higher penetration index.

Upon heating of a thin layer at 163°C for 5 hours, the oxidized bitumens differ from the distilled bitumens, showing a smaller residual penetration and a slightly larger change in softening temperature.

The dependences of softening temperature and fragility temperature on the penetration of oxidized and distilled bitumens (Fig. 1) show curves that are shifted almost in parallel relative to each other; this is consistent with the results of a comparison of the regulatory requirements for these properties included in the European and Ukrainian standards [3].

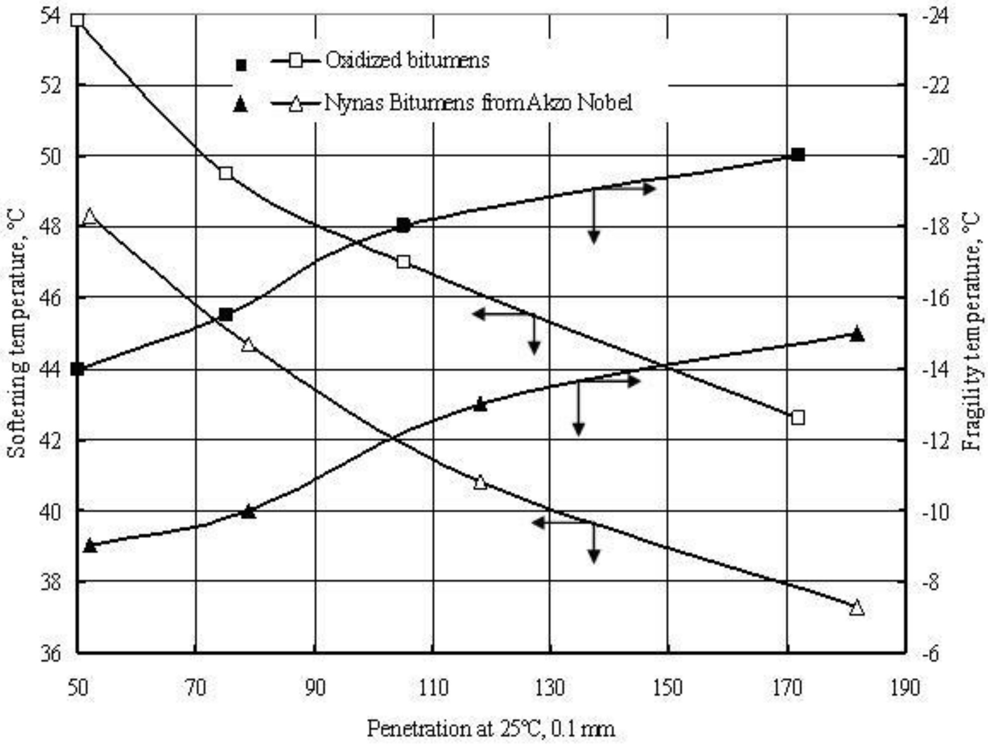

Figure 1 : Dependence of the softening temperature (Ts) and the fragility temperature (Tf) on the penetration of oxidized and distilled bitumens

At the same time, the cohesion-penetration dependences of oxidized and distilled bitumens are practically identical (Fig. 2), which fully supports the supposition that penetration is purely a characteristic of shear strength, i.e., resistance to the immersion of the indenter, and not a characteristic of the viscosity. The correct relationship between penetration and viscosity is possible only in the case of the Newtonian flow of bitumen at a constant temperature.

The compositions of bitumens of “sol-gel” type differ significantly from those of “sol” type. For example, an oxidized bitumen with a penetration of 82 (0.1 mm) contains 21% pyrobitumens, 30.3% resins, 26.8% paraffinic/naphthenic hydrocarbons, and 21.9% aromatic hydrocarbons. A distilled bitumen with a penetration of 86 (0.1 mm) contains 11.4% pyrobitumens, 43.5% resins, 13.0% paraffinic/naphthenic hydrocarbons, and 32.1% aromatic hydrocarbons. Bitumens of the “sol-gel” type also differ in their more developed coagulation structure in less homogeneous petrolene media. The greater amount of pyrobitumen in oxidized bitumens provides a higher softening temperature and better adhesion to a substrate.

The larger resin and aromatic hydrocarbon contents of the distilled bitumens give rise to better tensile strength and greater stability under heating. The greater content of paraffinic/naphthenic hydrocarbons in oxidized bitumens leads to higher crack resistance, greater penetration at 0°C, and lower stability upon heating. The higher total content of pyrobitumens and paraffinic/naphthenic hydrocarbons in oxidized bitumens gives rise to a wider plasticity range and a larger penetration index.

Although the dependences of cohesion on penetration are similar for the two groups of bitumens, the dependences of cohesion on softening temperature (Fig. 3) are represented by two curves, from which it follows that for the same softening temperature, the cohesion of the distilled bitumens is much higher: for bitumens with a low softening temperature (around 40°C) it is 2.2–2.4 times higher, and for bitumens with softening temperatures above 50°C it is 1.5–1.6 times higher.

Consequently, the softening temperature is not an objective criterion for predicting the resistance of asphalt concrete to the development of plastic deformation (rut formation) at high temperatures. For the same softening temperature, asphalt concrete made from distilled bitumen will have a much higher tensile strength than that made from oxidized bitumen. If we make such a prediction based on bitumens of both series having the same penetration values, we can expect that the resistance to rut formation will be the same.

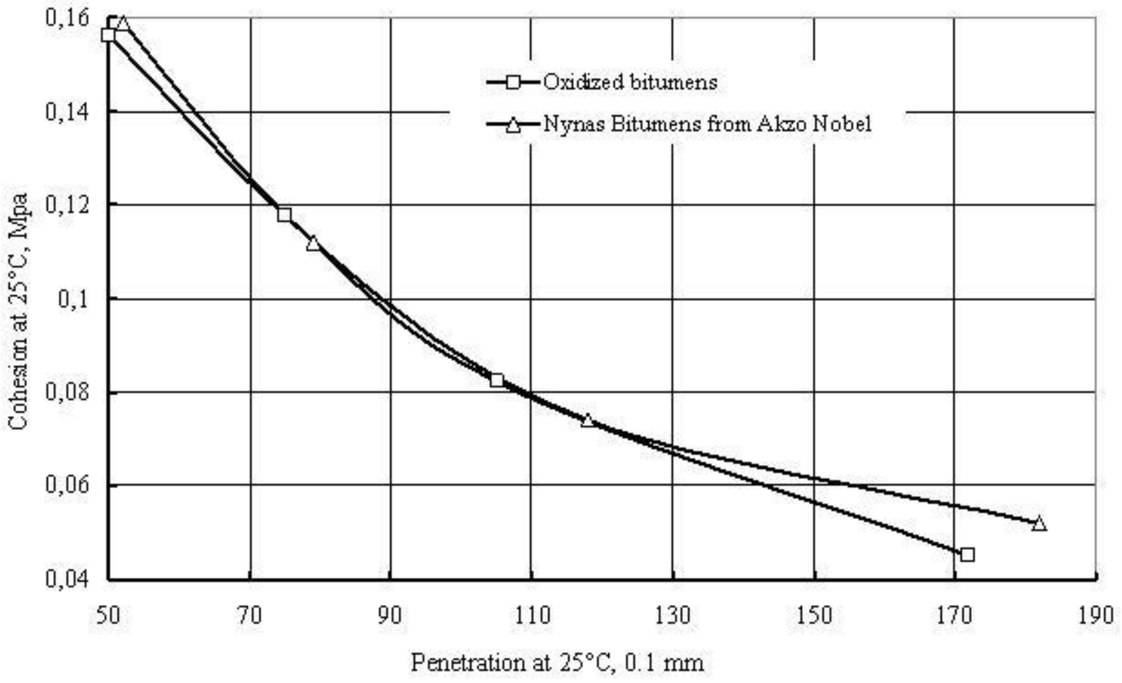

Figure 2 : Dependence of cohesion of oxidized and distilled bitumens on penetration

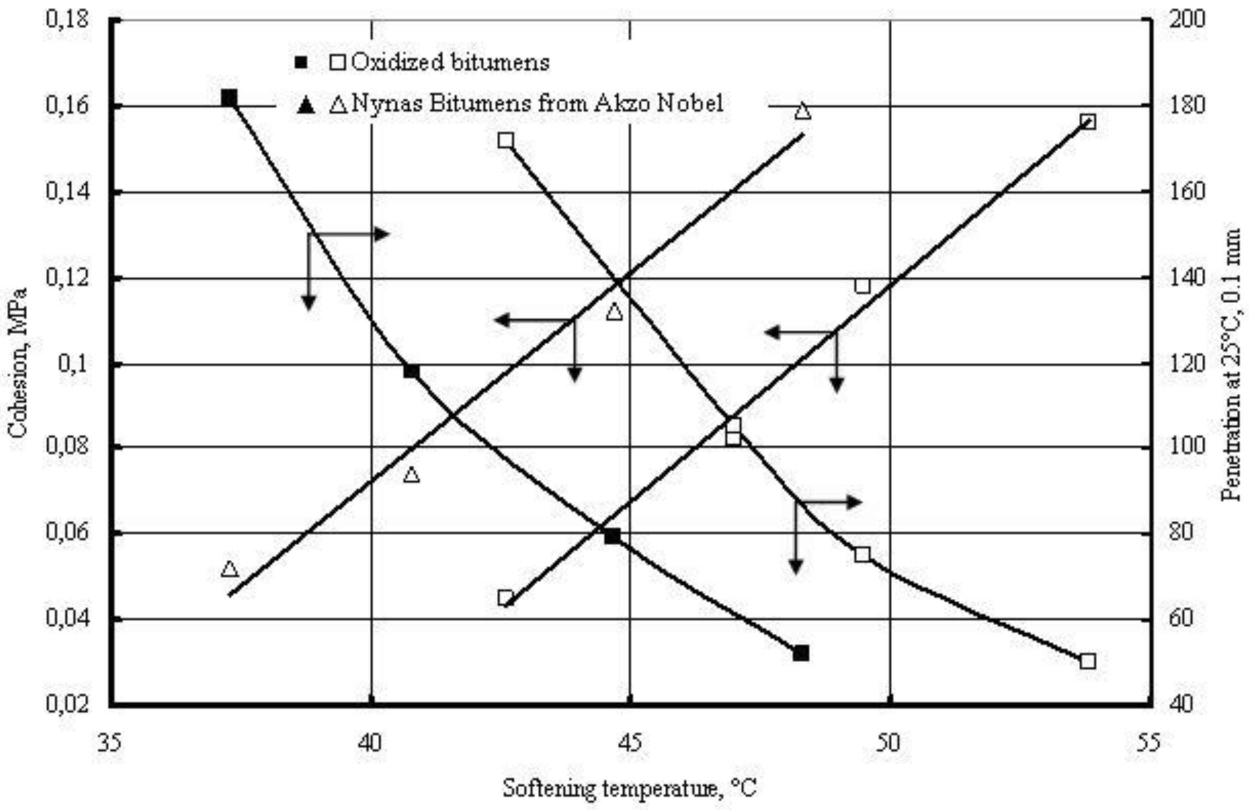

Figure 3 : Dependence of cohesion and penetration of oxidized and distilled bitumens on softening temperature

It is well known that oxidized bitumens heated at high temperatures (such as those used in their technological processes) and under the action of atmospheric oxygen have poorer resistance, which is defined in terms of the changes in the penetration and softening temperature. At the same time, the deterioration of the adhesion of the bitumen with a hard surface after heating is not so evident (Table 1).

This effect appears more pronounced in the bitumens containing surfactants (Table 2). The introduction of additive № 1 increases the adhesion of both bitumens up to about 100%. After heating, the adhesion of the oxidized bitumen with additive № 1 changed very little (90–95%), but for the distilled bitumen it fell to 20–36%. In the case of additive № 2, the adhesion of the oxidized bitumens increased to 92–94%, and that of the distilled bitumens to 37–52%. After heating, the adhesion of the oxidized bitumens decreased to 23–26%, and that of the distilled bitumens fell to 8–11%. These results show that the adhesion is the characteristic of bitumens with surfactant that is most sensitive to heating. Its impairment may be a consequence of chemical changes in the bitumen, to which the mechanical characteristics of penetration and softening temperature are less sensitive.

Table 2 : Influence of bulk heating and surfactant addition on the properties of oxidized and distilled bitumens

Property index		surfactant	%	LB1	LB2	LB3	LB4	AN1	AN2	AN3	AN4
Before heating	Penetration at 25 ºC, 0.1 mm (P_{25})		0	50	75	105	172	52	79	118	182
	Softening temperature (Ts), ºC			53.8	49.5	47	42.6	48.3	44.7	40.8	37.3
	Adhesion at 85 ºC, %			17	8	10	6	7	7	6	5
	Adhesion at 75 ºC, %			20	13	11	8	9	10	8	6
After heating	P_{25}, 0.1 mm		0	37	55	80	168	52	70	116	184
	Residual penetration, %			74	73	76	100	100	87	98	100
	Ts, ºC			54.4	50.6	47.3	43.2	47.8	44.3	41.5	36.9
	Change in Ts, ºC			0.6	1.1	0.3	0.6	-0.5	-0.4	0.7	-0.4
	Adhesion at 85 ºC, %			5	6	7	6	6	6	6	6
	Adhesion at 75 ºC, %			9	11	11	5	6	6	5	5
Before heating	P_{25}, 0.1 mm	Additive № 1	0.5	40	65	99	192	51	80	116	174
	Ts, ºC			53.3	49.7	47.0	42.9	48.9	44.7	40.3	36.6
	Adhesion at 85 ºC, %			100	100	100	100	99	100	100	100
	Adhesion at 85 ºC, %	Additive № 2	0.4	-	94	92	-	-	52	37	-
After heating	P_{25}, 0.1 mm	Additive № 1	0.5	44	63	84	204	51	77	117	166
	Residual penetration, %			110	97	85	106	100	96	100	95
	Ts, ºC			55.3	50.7	47.7	42.4	49.0	45.9	42.0	36.7
	Change in Ts, ºC			2.0	1.0	0.7	-0.5	0.1	1.2	1.7	0.1
	Adhesion at 85 ºC, %			90	92	93	95	36	32	22	20
	Adhesion at 85 ºC, %	Additive № 2	0.4	-	26	23	-	-	11	8	-

It also follows that the adaptability of the same additive is not the same for different bitumens (with different compositions or produced by different technologies), either in terms of the increase in adhesion before heating or its decrease after heating.

Significant differences in the composition and properties of oxidized and distilled bitumens made it necessary to investigate the peculiarities of the influence of the polymer on them. A linear SBS-type polymer was used as the modifier. The pure bitumens and bitumens with 3% of the SBS polymer were investigated (LB2 and LB3 of the oxidized bitumens, and AN2 and AN3 of the distilled ones).

The results obtained confirmed the well-known patterns of behavior (Table 3). At the same time, attention is drawn to the degree of change in some properties. Above all, this concerns the enhancing abilities of the polymer: in the case of the oxidized bitumens LB2 and LB3, the penetrations at 25°C decrease by factors of 1.66 and 1.84, respectively, while the penetrations of the distilled bitumens AN2 and AN3 decrease by factors of 1.30 and 1.39, respectively. This is probably connected with the participation of pyrobitumens, contained in PMBs based on oxidized bitumens, in the structural formation of such PMBs. This susceptibility to polymers of bitumens with different structural types is noted in reference [4]. The degrees of the decrease in penetration at 0°C of bitumens of both series are rather similar.

The softening temperature of oxidized bitumens after modification increased by 7°C, and that of distilled bitumens by 6.5–8°C, i.e., the softening temperature was less sensitive to the action of the polymer than the penetration at 25°C. The fragility temperature in both cases stayed almost the same as that before modification. This is in agreement with the data found in many literature works, and is explained by the fact that the fragility temperature of bitumen containing a small amount of polymer is determined by the fragility temperature of the bitumen matrix. It should be taken into account that the penetration of PMB is lower than that of the source bitumen. This results in a harder binder with the fragility temperature of the softer source bitumen. The plasticity range of PMBs based on oxidized bitumens remains wider than for those based on distilled bitumens (just as for the source bitumens themselves).

The ductilities of PMBs based on the oxidized bitumens LB2 and LB3 decreased to 26 and 36 cm, respectively, and for those based on distilled bitumens to 95–100 cm. The most important fact may be considered to be the high ductility of PMBs based on distilled bitumens at 25°C, and especially, their high ductility exhibited at 0°C.

The second important point is that the stability after heating of PMBs based on oxidized bitumens reached the level of the stability of PMBs based on distilled bitumens. This is probably due to the thickening effect of the polymer with respect to the oils of the oxidized bitumens, which is expressed in the solvation of the less viscous petrolene medium by the polymer during its swelling. This agrees with the higher enhancing ability of polymers in relation to these bitumens.

The adhesion of PMBs with a hard substrate was practically the same as for source bitumens, since, with only a small (3%) polymer content, this is determined by the bitumen matrix.

Table 3 : Properties of polymer-modified oxidized and distilled bitumens

Property index		Bitumen			PMB		Bitumen		PMB	
		LB1	**LB2**	**LB3**	**LBP2**	**LBP3**	**AN2**	**AN3**	**ANP2**	**ANP 3**
Penetration at 25 ºC, 0.1 mm		50	75	105	45	57	79	118	59	80
Penetration at 0 ºC, 0.1 mm		18	24	33	18	22	22	39	17	28
Softening temperature, ºC		53.8	49.5	47.0	56.9	54.1	44.7	40.8	51.2	49.8
Fragility temperature, ºC		-14	-15,5	-18	-14	-16.5	-10	-13	-11	-16
Flash point, ºC		286	283	281	291	276	285	276	283	270
Ductility at 25 ºC, cm		74	>100	>100	26	36	>100	>100	100	95
Ductility at 0 ºC, cm		0.8	3.2	4.0	1.0	4.8	-	0.4	10	17
Elasticity, % at 25 °C		-0.29	-0.32	-0.01	66	63	-1.55	-1.74	62	93
Glass adhesion, % (85 ºC)		17	8	10	12	9	7	6	5	8
Plasticity range, ºC		20	13	11	70.9	70.6	10	8	62.2	65.8
Cohesion at 25 ºC, MPa		67.8	65.0	65.0	0.137	0.108	54.7	53.8	0.130	0.104
After heating for 5 h at 163 ºC	Residual penetration, %	76	59	62	84	88	76	87	80	89
	Softening temperature, ºC	60.1	55.2	51.3	58.8	53.9	49.2	45.4	54.5	49.6
	Change in Ts, ºC	6.3	5.7	4.3	1.9	-0.2	4.5	4.6	3.3	-0.2
After heating for 5 h at 180 ºC	Residual penetration, %	74	73.3	76.2	93	103	89	98	90	91
	Softening temperature, ºC	54.4	50.6	47.3	60	57.6	44.3	41.5	56.7	54.8
	Change in Ts, ºC	0.6	1.1	0.3	3.1	3.5	-0.3	0.7	5.5	5.0
	Glass adhesion, % (85 ºC)	5	6	7	10	10	6	6	5	5
Storage stability	Change in Ts, ºC				42.2	40.6			32.2	39.5
	Change in P_{25}, 0.1 mm				11	4			12	12

Usually, studies of polymer-modified bitumens are limited to a comparison of the properties of the obtained PMBs and the source bitumens. Such a comparison has been presented above. However, it seems useful to clarify the extent of the differences in the properties of PMBs from bitumens of similar penetrations obtained through the same technology or from the same materials [5]. The results of studies carried out on binders allow us to do this.

Regarding the oxidized bitumens and PMBs based on them, one can compare the properties of bitumen LB1 and the average values of the property indices of the modified bitumens LBP2 and LBP3. Then, for penetrations of 50–51 (0.1 mm), we can note the following: for the PMBs, the softening temperature is 2°C higher, the fragility temperature is 2°C lower, the tensile strength at 25°C is of course lower, and at 0°C even a little higher, than for the bitumen. The residual penetration after heating at 163°C is higher for the PMBs, and the changes in softening temperature are lower. Thus, the merits of PMBs as compared to bitumens of the same penetration can be said to include the increase in ductility at 0°C and the increase in stability upon heating.

In terms of the distilled bitumens and PMBs based on them, we can compare bitumens AN2 and ANP3, since they have equal penetration values. The PMB is characterized by a slightly larger penetration at 0°C, a higher softening temperature (by 4°C), a higher fragility temperature (by 4°C), a much higher tensile strength at 0°C, a wider plasticity range, a larger residual penetration, and a smaller change in softening temperature upon heating compared to the bitumen.

Thus, the advantages of the PMB compared to the distilled bitumen of equal penetration include: the increase in softening temperature, the decrease in fragility temperature, the high ductility at 0°C, the widening of the plasticity range, and the slightly higher stability upon heating.

In order to establish the differences between PMBs of equal penetrations from bitumens made through different technologies, we can compare LBP3 (penetration at 25°C of 57, 0.1 mm) and ANP2 (penetration at 25°C of 59, 0.1 mm). The main feature of these PMBs is that LBP3 is obtained from bitumen LB3, with a penetration of 105 (0.1 mm), while ANP3 is based on bitumen AN2, having a penetration of 79 (0.1 mm). So, the PMB based on the oxidized bitumen differs from that based on the distilled bitumen in the following ways: the penetration at 0°C is higher by 15 (0.1 mm); the softening temperature is 3°C higher; the fragility temperature is 5°C lower; the flash point is 7°C lower; the tensile strength at 25°C is almost three times lower; the tensile strength at 0°C is lower by 5 cm; the elasticity is approximately the same; the plasticity range is 8°C wider; the residual penetration after heating is a little higher (by 8%); and the change in softening temperature is slightly lower.

3. CONCLUSIONS

The main differences between the oxidized and distilled bitumens studied here are due to the structural type, the former being “sol-gel” and the latter “sol”. In this regard, notable features are the high index of penetration and plasticity range for oxidized bitumens.

The advantages of oxidized bitumens include their high softening temperature and low fragility temperature. The main advantage of distilled bitumens is the stability of their properties upon heating. Bitumens with the same penetration manufactured by each of these technologies exhibit similar cohesion. At the same time, for the same softening

temperature, the cohesion of distilled bitumens is significantly higher.
Distilled and oxidized bitumens show different degrees of change in their adhesion to hard substrates after the addition of the same surfactant. This is particularly evident in the adhesion values after heating. More generally, the choice of the bitumen–surfactant pair should be made on an individual basis.
Bitumens obtained through oxidation or vacuum distillation react differently to modification with SBS-type polymers. This is due to the peculiarities in their group composition. In terms of oxidized bitumens, the polymer additive has a greater strengthening effect and increases their stability upon heating to the level of PMBs based on distilled bitumens. The introduction of polymer in distilled bitumens gives rise to a sharp increase in the ductility at 0°C.
Compared to the source bitumens with similar penetration values, PMBs based on oxidized bitumens differ in terms of their lower fragility temperature and higher softening temperature, greater ductility at 0°C, and better stability upon heating.
In the analogous case, PMBs based on distilled bitumens show a significantly higher softening temperature, lower fragility temperature, wider plasticity range, and slightly higher stability upon heating than the source bitumens of equal penetration.
The properties of PMBs based on oxidized and distilled bitumens (with similar penetration values) are correlated as follows: the former have higher softening temperatures in comparison with the latter, as well as lower fragility temperatures, lower tensile strengths at 0°C, wider plasticity ranges, similar residual penetrations and changes in softening temperature after heating, and slightly lower stabilities of properties upon storing.
The results obtained in this study show that the addition of an SBS-type polymer improves the properties of both oxidized and distilled bitumens, albeit more significantly for oxidized bitumens. The polymer compensates for the shortcomings of oxidized bitumens, and changes the composition and quality of their petrolene fractions.

REFERENCES

[1] Viscous road oil bitumens. The method to determine the index of engagement with the surface of glass and rock materials, DSTU Б В.2.7-81-98
[2] Bitumen cohesion – the basis of the temperature and temporal dependences of the strength of asphalt concrete, Zolotaryov V.A., “Highways” magazine (The Automobilnye Dorogy) 10, 25–27, 1995.
[3] Peculiarities of the standardization of viscous bitumens, Zolotaryov V.A., Autodorozhnik Ukrainy, 3, 43–46, 2002.
[4] Polymer-bitumen binder with the addition of SBS, Gokhman L.M., Trudy SoyuzdorNII (Proceedings of SoyuzdorNII Institute), Moscow, 50, 13–19, 1971.
[5]On the system of quality estimation of bitumens modified with SBS-type polymers, Zolotaryov V.A., Autodorozhnik Ukrainy, 6, 26–31, 2004.