

THE SELECTION OF RAW MATERIALS FOR THE PRODUCTION OF ROAD BITUMEN MODIFIED BY PHENOL-CRESOL-FORMALDEHYDE RESINS

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Abstract

Resins obtained from the phenolic fraction of coal tar have been synthesized by the method of formaldehyde condensation polymerization. The phenol-cresol-formaldehyde resins have been derived from the following types of starting materials: a wide phenolic fraction, narrow fractions sampled before and after 185 °C (fraction: IBP – 185 and 185 – EBP °C) coupled with the so called raw (technical) phenols that had been separated from these fractions.

The capability of utilizing resins obtained as a modifier of distilled (residual) and oxidized petroleum road bitumens has been determined. It has been shown that adding these resins increases the softening point and essentially boosts the adhesion of petroleum-based bitumens for roads.

Keywords: bitumen; phenol; cresol; formaldehyde; bitumen modifier.

1. Introduction

Data in 2011 [1] say that yearly about 102 million tons of bitumen are consumed worldwide. Nearly 85 % of all the bitumen is used as a binder in various types of paving asphalt: pavements for pedestrians and roads, airports, etc. [1-2]. Thus, more than 90 % of 5.2 million km of European motorways are estimated [3] to be covered with the asphalt whose main binder while produced is petroleum-derived bitumen for roads.

While utilizing road bitumens, a number of problems arise. However, the most acute problem is insufficiently high stiffness and adhesive properties of finished bitumens (even if they achieve high standards of regulations) [1-2].

One of the most promising directions in raising the quality of binders as to produce road surfaces with good performances is their modification with polymeric materials [1, 2, 4].

For the modification of road bitumens, thermoplastic elastomers (primarily, block copolymers of the SBS type styrene) account for the largest use due to their ability not only to increase bitumen strength, but also to make a polymer-bitumen blend more elastic, including at low temperatures, as well as increase the adhesion of bitumen to the mineral material. The content of such polymers in modified bitumen may reach 3-10 % by weight [1-5].

The main drawback that reduces the growth rate of the production of bitumens modified by thermoplastic elastomers is their high costs (1.5 – 2.5 times higher than the cost of unmodified bitumens) [1-2]. Therefore, it is important to search for inexpensive substances that would improve bitumen performance – foremost, adhesive properties.

In the past years there have been studies into the development of relatively cheap and effective modifiers of petroleum-derived bitumens from liquid products of the coal carbonization at the Department of Chemical Technology of Oil and Gas Processing of Lviv National Polytechnic University [2, 6-9].

Phenol-formaldehyde resins are known [1, 2, 10, 11] to be quite effective modifiers of petroleum bitumens. But these pure phenol resins were not widely used as polymer modifiers and this also relates, primarily, to their high cost. On the other hand, one of the products of coking

plants is a phenolic fraction of coal tar with a core portion of phenols and cresols (approximately 65 %) concentrated in it and that are formed during the carbonization process. The price of the phenolic fraction of coal tar, which normally contains more than 30 % by phenol weight and its derivatives, is 35-40 times lower than the cost of synthetic phenol [12].

In this regard, this paper aims to open up the possibility for developing phenol-cresol-formaldehyde resins from the wide phenolic fraction (WPhF), narrow fractions sampled before and after 185°C (fraction: IBP – 185°C and 185 – EBP°C) and raw phenol separated from these fractions. Besides, the paper seeks to determine whether modifying residual and oxidized petroleum bitumens for roads that are derived from phenol-cresol-formaldehyde resins is appropriate.

2. Experimental

The wide phenolic fraction (WPhF) was sampled at Zaporizhkoks PJSC for investigations. The WPhF characteristic is given in Table 1. For the purpose of concentration (separation) of phenol and cresols, the WPhF was divided into two fractions, an initial boiling point (IBP – ~ 92°C) – 185 and 185 and end boiling point (EBP ~ 211°C)°C (the boiling point of phenol is 182°C, of cresols – 191-202°C). Table 1 lists the characteristic of fractions derived. The mass balance of distillation is shown in Table 2.

Table 1. Characteristics of a starting material

Indexes	wide phenolic fraction (WPhF)	Values		Procedure*
		Fraction IBP – 185°C	Fraction 185 – EBP°C	
Distillation (oC):				
Initial boiling point	105	92	172	GOST 2177
10 % distilled at the temperature	164	147	177	
20 % distilled at the temperature	172	156	179	
30 % distilled at the temperature	174	161	181	
40 % distilled at the temperature	177	166	183	
50 % distilled at the temperature	179	169	184	
60 % distilled at the temperature	182	172	187	
70 % distilled at the temperature	185	174	190	
80 % distilled at the temperature	197	181	200	
90 % distilled at the temperature	202	184	206	
95 % distilled at the temperature	208	189	211	
Molecular weight	136	108	167	-
Bromine number (g Br ₂ /100 g product)	81.64	81.28	75.84	GOST 8997-89

*GOST – Ukrainian national standards

Table 2. Mass balance of the WPhF distillation.

Article	Yield by weight, %
Fraction IBP – 185 °C (phenol concentrate)	50.60
Fraction 185 – EBP °C (cresols concentrate)	46.77
Distillation residue	2.63
Total	100.00

Phenol and its derivatives hereinafter called raw (technical) phenols – RPh1, RPh2 and RPh3 – were separated from the WPhF, the fraction IBP – 185 and the fraction 185 – EBP°C by using a 20% NaOH solution. The removal of phenols with the solution of NaOH was based on the fact that phenol and its derivatives form water-soluble phenolates. The latter were made into phenols by using the concentrated hydrochloric acid. The yield of raw phenols with the WPhF, the fraction IBP – 185 and the fraction 185 – EBP°C accounted for 32.3, 32.0 and 35.1 % wt, respectively.

The resins were derived from initial fractions and those raw phenols that were obtained from them by the method of formaldehyde condensation polymerization.

The scheme of the research is given in Figure 1.

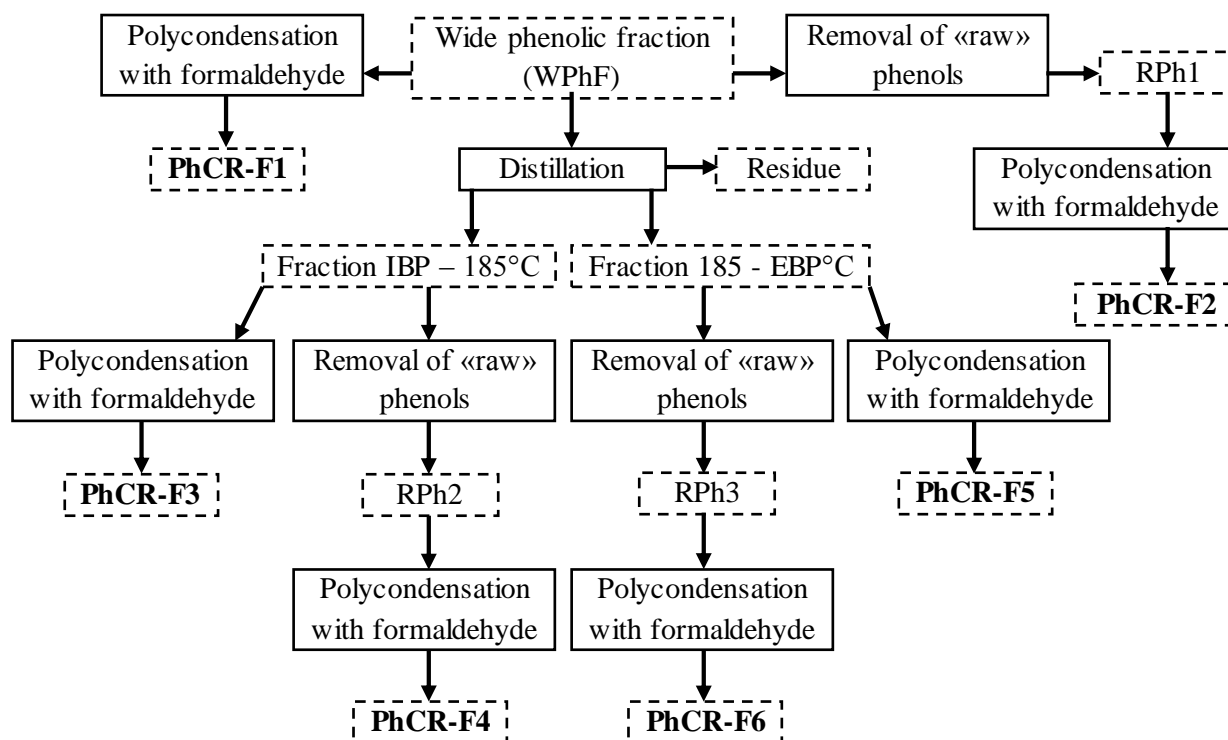


Figure 1. Scheme of the research: PhCR-F - phenol-cresol-formaldehyde resin; RPh - raw (technical) phenols

The process of formaldehyde condensation polymerization of phenols was carried out on the laboratory facility for synthesis that is depicted in Figure 2. The raw material was placed in a three-pipe reactor and heated while stirring at 100°C in a thermostat. Then, a necessary amount of formalin (a weight content of formaldehyde in formalin equaled 37 %) was added along with a concentrated hydrochloric acid (catalyst), followed by recording the start of the process that was done for 60 s. As the synthesis is over, a hot reaction mixture, obtained from raw phenols, was poured into a glass. After cooling the mixture, an aqueous phase was drained and the resin was exposed to the 3-hour drying in a vacuum dryer at 100°C. When the WPhF was used as the starting material, the fraction IBP - 185 and the fraction 185 - EBP°C, at first there was the distillation of water and unreacted constituents carried out under vacuum. After that the resulting resin was dried some more in the vacuum dryer for 3 hours at 100°C. The yield of the resins obtained was determined by the weighing of the starting material and the phenol-cresol-formaldehyde resins (PhCR-F).

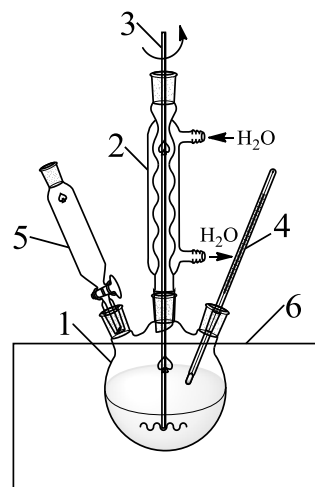


Figure 2. Laboratory facility for the synthesis of phenol-cresol-formaldehyde resins: 1 - three-pipe reactor; 2 - refrigerator; 3 - mixer; 4 - thermometer; 5 - separation funnel; 6 - thermostat

In order to obtain PMBs, the distillate (residual) petroleum-derived bitumen for roads of the BD 60/90 grade and the BND 60/90 oxidized petroleum-derived bitumen for roads were utilized. The BD 60/90 distillate (residual) petroleum road bitumen was selected at the road maintenance department of Frankivsk region (Lviv city) with its main characteristics given in Table 3.

Table 3. Main characteristics of the BD 60/90 distillate road bitumen

Index	BD 60/90	Standard for BD 60/90**	Procedure*
Penetration at 25°C (m×10 ⁻⁴)	80	61-90	GOST 11501
Softening point (ball & ring method) (°C)	43	44-52	GOST 11506
Ductility at 25°C (m×10 ⁻²)	>100	>100	GOST 11505
Adhesion to glass (%)	60	>20	DSTU B V.2.7 – 81 with supplement according to point 8.6 DSTU 4044-2001

*DSTU and GOST – Ukrainian national standards

** bitumen according to SOU 45.2-00018112-069:2011

The oxidized petroleum-derived road bitumen of the BND 60/90 grade was sampled at *Ukratnafta* PJSC (the city of Kremechuk) with its main characteristics shown in Table 4.

Table 4. Main characteristics of the BND 60/90 oxidized road bitumen

Index	BD 60/90	Standard for BD 60/90**	Procedure*
Penetration at 25°C (m×10 ⁻⁴)	70	61-90	GOST 11501
Softening point (ball & ring method) (°C)	46	47-53	GOST 11506
Ductility at 25°C (m×10 ⁻²)	63	>55	GOST 11505
Adhesion to glass (%)	47	non standardized	DSTU B V.2.7 – 81 with supplement according to point 8.6 DSTU 4044-2001

*DSTU and GOST – Ukrainian national standards

** bitumen according to SOU 45.2-00018112-069:2011

The PMB has been prepared by virtue of mixing in the following sequence: a necessary amount of bitumen was heated while stirring (Re = 1200) to the temperature of modification. Then with a required amount of the modifier added, it was sustained for 1 hour.

3. Results and discussion

Novolac phenol-cresol-formaldehyde resins were obtained according to the scheme given in Figure 1 by the method of formaldehyde condensation polymerization with the WPhF, the fraction IBP – 185 C and the fraction 185 – EBP°C and from the raw phenols extracted from these fractions. Synthesis conditions for the resins were set out on the basis of [13] and are shown in Table 5. As recommended by [13], the obtaining of novolac phenol-formaldehyde resins requires maintaining the mole ratio of phenol to formaldehyde at 1.12 – 1.42, while for novolac cresol-formaldehyde resins it should equal 2.27. Considering that the raw phenols that were derived from the phenolic fraction of coal tar contain both phenols and cresols at various ratios, the syntheses were done at the mole ratio of raw phenols to formaldehydes at the value of 1.42. For calculations of reactor loading, it was assumed that the molar mass of the resulting raw phenols was 94.1 g/mole, which is equal to the molecular weight of pure

phenol. The effect of the ratio of reaction constituents on the production of resin will be looked into in further studies.

Table 5. Synthesis conditions for PhCR-F

Parameter	Value
*Mole ratio of raw phenols to formaldehyde	1.42
Weight ratio of raw phenols to formalin (formaldehyde content in formalin – 37% wt)	1.78
Catalyst weight content (concentrated HCl), % by raw phenols	1.0
Temperature, °C	100
Process duration, min	60

*The molar mass of raw phenols was proposed to be 94.1 g/mol.

The mass balance for the obtaining of phenol-cresol-formaldehyde resins is given in Table 6.

Table 6. Mass balances involved in syntheses for the obtaining of PhCR-F

Article	PhCR-F1	PhCR-F2	PhCR-F3	PhCR-F4	PhCR-F5	PhCR-F6
Loaded						
1. Starting material	WPhF	RPh1	fr. IBP-185 °C	RPh2	fr. 185-EBP °C	RPh3
g	100.00	32.30	50.60	16.19	46.80	16.43
% wt to be loaded	84.42	63.64	84.54	63.64	83.30	63.64
wt for a frond-end fraction	10.00 ¹	32.30 ¹	100.00 ²	32.00 ²	100.00 ³	35.10 ³
% wt for WPhF	100.00	32.30	50.60	16.19	46.80	16.43
2. Formalin						
g	18.13	18.13	9.09	9.09	9.22	9.22
% wt to be loaded	15.31	35.72	15.19	35.72	16.41	35.72
% wt for a frond-end fraction	18.13 ¹	18.13 ¹	17.96 ²	17.96 ²	19.70 ³	19.70 ³
% wt for WPhF	18.13	18.13	9.09	9.09	9.22	9.22
3. Concentrated HCl						
g	0.32	0.32	0.16	0.16	0.16	0.16
% wt to be loaded	0.27	0.64	0.27	0.64	0.29	0.64
% wt for a frond-end fraction	0.32 ¹	0.32 ¹	0.32 ²	0.32 ²	0.35 ³	0.35 ³
% wt for WPhF	0.32	0.32	0.16	0.16	0.16	0.16
Total, g	118.45	50.75	59.85	25.44	56.18	25.81
Results						
1. Tar						
g	18.20	29.65	8.20	13.20	9.03	14.39
% wt to be loaded	15.36	58.42	13.70	51.87	16.08	55.75
% wt for a front-end fraction	18.20 ¹	29.65 ¹	16.20 ²	26.08 ²	19.30 ³	30.75 ³
% wt for WPhF	18.20	29.65	8.20	13.20	9.03	14.39
2. Water and unreacted components						
g	100.25	21.10	51.65	12.25	47.15	11.42
% wt to be loaded	84.64	41.58	86.30	48.13	83.92	44.25
% wt for a front-end fraction	100.25 ¹	2.10 ¹	102.08 ²	24.20 ²	100.75 ³	24.40 ³
% wt for WPhF	100.25	21.10	51.65	12.25	47.15	11.42
Total, g	118.45	50.75	59.85	25.44	56.18	25.81

¹for the wide phenolic fraction (WPhF); ²for the fraction IBP – 185°C; ³for the fraction 185 – EBP°C

When the concentrated phenols (raw phenols) are used in the act of synthesis, the yield is observed to be higher while loading the reactor (almost fourfold increase: 51.9 – 58.4% wt against 13.7 – 16.1% wt) and for the initial fraction (nearly 2 times higher: 26.1– 30.8% wt against 16.2– 18.2% wt). So, for the obtaining of effective modifiers of petroleum bitumens,

it is mostly appropriate to carry out the synthesis not with the use of the coal tar phenolic fraction but with the raw phenols being separated from this tar.

Additionally, it is counterproductive to break up the WPhF with two narrower fractions. This is explained by that using RPh1 as the starting material produces 29.65% of the resin yield (calculated per WPhF) whereas the total resin yield if two raw phenols – RPh2 and RPh3 – are used appears to be lower: $13.20 + 14.39 = 27.59\%$.

From then on, in order to specify a temperature for bitumen modification, the BD 60/90 residual bitumen was modified with PhCR-F3 and PhCR-F4 resins derived directly from IBP – 185°C and RPh2 raw phenol, respectively, at 110°C and 190 °C temperatures. It can be stated that mechanical mixing of bitumen components occurs at 110°C while at 190°C physical and chemical interactions between them are likely to be. Characteristics of bitumen-polymer blends obtained are given in Table 7.

Table 7. Preparation conditions and main characteristics of obtained PMBs

Index	BD 60/90	Modification temperature, °C (modifier content in PMB – 2.4 % wt)			
		PhCR-F3		PhCR-F4	
		110	190	110	190
Penetration at 25 °C ($m \times 10^{-4}$)	80	78	75	–	62
Penetration decline, %	–	2.5	6.3	–	22.5
Softening point (ball & ring method) (°C)	43	44	46	–	47
Softening point increase, %	–	2.3	7.0	–	9.3
Ductility at 25 °C ($m \times 10^{-2}$)	>100	>100	>100	–	>100
Adhesion to glass (%)	60	83	82	–	88
Increase in adhesion to glass, %	–	38.3	36.7	–	46.7
Homogeneity	non standardized	homogeneous	homogeneous	not homogeneous	homogeneous

Based on the data of Table 7, it can be suggested that the addition of synthesized PhCR-F3 and PhCR-F4 (except for the case of 110°C and PhCR-F4) into bitumen leads to an increase in the softening point and, especially, in the adhesion of residual petroleum bitumen. The modification of petroleum bitumen with PhCR-F3 can be done at both 110°C and 190°C. In comparison, with PhCR-F4 – at 190°C as 110°C produces modified bitumen that does not meet requirements of homogeneity. Mixing at 190°C makes it possible to increase the softening point to a greater extent. It follows from mentioned above that further modification of petroleum-based bitumens with phenol-cresol-formaldehyde resins that were obtained from the coal tar phenolic fraction was decided to be made at 190°C.

A comparison of main characteristics of obtained bitumen-polymer blends is shown in Table 8. Table 8 shows that adding all the obtained resins essentially improves the adhesive properties of bitumen. The data outlined in Table 8 indicate that the addition of the BD 60/90 resins synthesized from raw phenol (PhCR-F2, PhCR-F4 and PhCR-F6) gives rise to a larger increase in the softening point and adhesion compared to the ones synthesized from the WPhF, fraction IBP – 185, 185 – EBP°C (PhCR-F1, PhCR-F3 and PhCR-F5), but more increasingly reduces the plasticity (penetration) of the BD 60/90 residual bitumen.

With an increased content of cresols in the starting material (PhCR-F5 and PhCR-F6) compared to PhCR-F3 and PhCR-F4, the obtained modified bitumen possesses better adhesive properties (95 – 96 % against 82– 88 %, see Table 8). Nevertheless, the use of raw phenols produced from the WPhF allows almost the same adhesive properties to be obtained and the softening point to be raised as when PhCR-F5 and PhCR-F6 are used.

Table 8. Preparation conditions and main characteristics of obtained PMBs

Index	BD 60/90	Modified bitumen at 190°C (modifier content in PMB – 2.4 % wt)					
		PhCR-F1	PhCR-F2	PhCR-F3	PhCR-F4	PhCR-F5	PhCR-F6
Penetration at 25°C (m×10 ⁻⁴)	80	75	65	75	62	74	70
Penetration decline, %	–	6.3	18.8	6.3	22.5	7.5	12.5
Softening point (ball & ring method) (°C)	43	44	46	46	47	45	46
Softening point increase, %	–	2.3	7.0	7.0	9.3	4.7	7.0
Ductility at 25 °C (m×10 ⁻²)	>100	>100	>100	>100	>100	>100	>100
Adhesion to glass (%)	60	87	94	82	88	95	96
Increase in adhesion to glass, %	–	45.0	56.7	36.7	46.7	58.3	60.0
Homogeneity	non standardized	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous	homogeneous

Consequently, this results in:

- higher yield of resin if raw phenols are used for its synthesis;
- slightly better characteristics of resin-modified bitumens, which contain more cresols (PhCR-F2, PhCR-F5 and PhCR-F6);
- lack of appropriateness to break up the WPhF with two narrow fractions.
- distilled road bitumens should be preferably modified with PhCR-F2.

To confirm the possibility of modifying the resulting resins as well as the oxidized bitumens coupled with the ability to compare the effectiveness of modifying the oxidized and residual bitumens, Table 9 shows the main characteristics of these PhCR-F2 modified bitumens.

Table 9. Comparison of main characteristics between residual and oxidized PhCR-F2 modified bitumens

Index	BD 60/90	BD 60/90 + PhCR-F2 (2,4 % wt)	BND 60/90	BND 60/90 + PhCR-F2 (2,4 % wt)
Penetration at 25°C (m×10 ⁻⁴)	80	65	70	60
Penetration decline, %	–	18.8	–	14.3
Softening point (ball & ring method) (°C)	43	46	46	49
Softening point increase, %	–	7.0	–	6.5
Ductility at 25°C (m×10 ⁻²)	>100	>100	63	25
Adhesion to glass (%)	60	94	47	97
Increase in adhesion to glass, %	–	56.7	–	106.4
Homogeneity	non standardized	homogeneous	non standardized	homogeneous

Supported by data given in Table 9, it may be argued that the modification with PhCR-F2 resin raises the softening point of both distilled and oxidized road bitumens by 3°C. For the distilled bitumen, the adhesive properties of PMBs are increased by 56.7% (from 60 to 94), while the oxidized one exhibits an increase of 106.4% (from 47 to 97%). This indicates that the resin obtained can also be utilized as adhesive additives in particular for the oxidized bitumens.

4. Conclusions

1. By the distillation method, the wide phenolic fraction of coal tar sampled at *Zaporizhkoks* PJSC was separated into two ones, IBP (the initial boiling point – ~92°C) – 185 and 185 – EBP°C (the end boiling point ~ 211°C). From the wide phenolic fraction and narrow fractions

- that were derived by using 20% NaOH solution, raw phenols were extracted, yielding 32.3% wt, 32.0% wt and 35.1% wt, respectively, for the initial and narrow fractions.
2. Novolac phenol-cresol-formaldehyde resins were produced by the method of formaldehyde condensation polymerization and from the wide phenolic fraction, fraction IBP – 185 and 185 – EBP°C and from the raw phenols extracted from these fractions. The results achieved show that the use of raw phenols as the starting material is the most advisable for the synthesis of resins as this allows the resin yield to be increased nearly fourfold while loading the reactor (from 13.7 – 16.1% wt to 51.9 – 58.4% wt, respectively).
 3. Modification of petroleum-derived road bitumens should be performed with phenol-cresol-formaldehyde resin that was obtained from raw phenols, extracted from the wide phenolic fraction of coal tar. It is counterproductive for the obtaining of resin to break up the wide phenolic fraction with phenol concentrate (fraction IBP – 185°C) and concentrate of cresols (185 – EBP°C).
 4. It has been observed that with a content of 2.4% by weight of phenol-cresol-formaldehyde resins in distilled (residual) and oxidized petroleum-derived road bitumens, there is an increase of 3°C in the softening point and adhesive properties for the distilled bitumen by 56.7% (from 60 to 94%), for the oxidized one – by 106, 4 (from 47 to 97).

References

- [1] Zhu J, Birgisson B and Kringos N., *European Polymer Journal*, 2014; 54: 18-38
- [2] Pyshyev S, Gunka V, Grytsenko Y and Bratychak M., *Chemistry and Chemical Technology*, 2016; 10 (4s): 631-636.
- [3] Kowalski KJ, Krol J, Radziszewski P, Casado R, Blanco V, Perez D, Vinas VM, Brijse Y, Frosch V, Le DM and Wayman M., *Transportation Research Procedia*, 2016; 14: 3582-3591.
- [4] Schaur A, Unterberger S and Lackner R., *European Polymer Journal*, 2017; 96: 256-265.
- [5] Kishchynskiy SV., *Vestn. HNADU*, 2008; 40: 28-32.
- [6] Pyshyev S, Gunka V, Grytsenko Y, Shved M and Kochubei V., *International Journal of Pavement Research and Technology*, 2017; 10 (4): 289-296.
- [7] Pyshyev S, Grytsenko Y, Bilushchak H, Pyshyeva R and Danyliv N., *Pet Coal*, 2015; 57 (4): 303-314.
- [8] Pyshyev S, Hrytsenko Y, Khlibyshyn Y, Strap H and Koval T., *East-European Journal of Enterprise Technologies*, 2014; 2/11 (68): 4-8.
- [9] Pyshyev S, Hrytsenko Y, Nikulyshyn I and Hnativ Z., *Coal Chemistry Journal (Ukhlekhimicheskii Zhurnal)*, 2014; 5: 41-48.
- [10] Strap G, Astakhova O, Lazorko O, Shyshchak O and Bratychak M., *Chemistry and Chemical Technology*, 2013; 7 (3): 279-287.
- [11] Çubuk M, Gürü M, Çubuk M and Arslan D., *Journal of Materials in Civil Engineering*, 2014, 26 (6): 4014-4015.
- [12] Pavlovich LB and Solovyova NY, *Bulletin of the Siberian State Industrial University*, 2016, 1 (15): 35-39.
- [13] Toroptseva AM, Belogorodskaya KM and Bondarenko VM., *Laboratory session on chemistry and technology of high-molecular compounds; Chemistry: L.*, 1972, p. 416.

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