Chem. Chem. Technol., 2022,
Vol. 16, No. 2, pp. 284–294

Chemical Technology

PREPARATION AND APPLICATION OF COUMARONE-INDENE-CARBAZOLE RESIN AS A MODIFIER OF ROAD PETROLEUM BITUMEN 1. INFLUENCE OF CARBAZOLE:RAW MATERIALS RATIO

Yuriy Prysiazhnyi[1, *]***, Guri Isaiah Borbeyiyong***[1]***, Serhiy Pyshyev***[1]

https://doi.org/10.23939/chcht16.02.284

Abstract. The possibility of effectively using carbazole as an improver of coumarone-indene resin for use as a modifier of petroleum bitumens is studied. All starting materials for the production of coumarone-indene-carbazole resin (CICR) were obtained from various products of the coal coking process. The influence of raw material composition (amount of carbazole added to an industrial indene-coumarone fraction) on resin yield and its modifying properties was studied. The optimal amounts of carbazole in the raw material were established, and it is recommended to use CICR as an adhesive additive to bitumen.[1]

Keywords: coumarone, indene, carbazole, modifier, bitumen.

1. Introduction

Road construction and road bitumen production are interrelated processes. Even a tiny change in various parameters of one of them immediately leads to the need to change specific parameters of the other. The causal relationship between these processes and their respective industries is represented in Fig. 1.

The result of this relationship today is a vast range of polymers,[1,2] which are used to improve specific qualitative indicators of road petroleum bitumen, which, in turn, is a determining factor for the long-term operation of roads.

At present, the nature of modifiers of road petroleum bitumens and their impact on the qualitative characteristics of bituminous material is well-studied and well-known.[1,2] It is also known that the main disadvantage of the vast majority of industrial modifiers is their high cost.

Based on the existence of the above problem, the Department of Chemical Technology of Oil and Gas Processing of Lviv Polytechnic National University for the last 5-10 years conducted experimental research on the development of new, relatively cheap modifiers of road petroleum bitumen.[3,4] In particular,[7] the possibility of obtaining a polymer product (resin) from inexpensive by-products of coal coking with the addition of carbazole was shown. The latter is a heterocycle containing a pyrrole ring and, consequently, a –NH– group, which, according to the authors, improves the modifying ability of the synthesized polymer. Since the main reactive components of the used by-products of coal coking are coumarone and indene, the resulting resin was named - coumarone-indene-carbazole resin (CICR).

The process of obtaining coumarone-indene-carbazole resin, as well as coumarone-indene resin[8] or any other polymer, depends on certain factors (parameters), which includes: the depth (degree) of conversion of raw materials, quantity and quality of the target product, energy and material costs, etc.

The coumarone-indene-carbazole resin was obtained by considering the following factors:

– composition of raw materials (primarily, consumption (amount) of carbazole in the reaction medium);

– flow rate (amount) of catalyst in the reaction medium;

– temperature;

– duration.

This article is the first in a series of scientific publications devoted to studying the above factors. It describes the effect of the composition of the raw

[1] Lviv Polytechnic National University
12, S. Bandery Str., Lviv, 79013, Ukraine
* *yurii.v.prysiazhnyi@lpnu.ua*

material (the amount of carbazole in the reaction mixture) on the yield, thermoplastic and adhesive properties of the coumarone-indene-carbazole modifier of road petroleum bitumen.

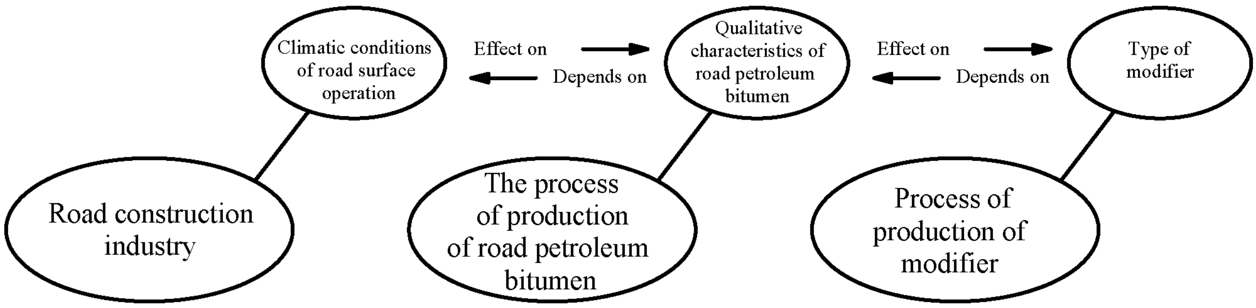


Fig. 1. The relationship between the road construction field and the process of production of road petroleum bitumen modifiers

2. Experimental

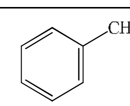
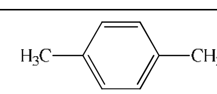
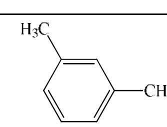
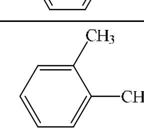
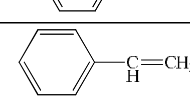
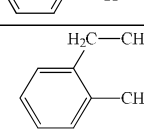
2.1. Materials

The raw material for the production of coumarone-indene-carbazole resin is a narrow coumarone-indene fraction (NCIF) with a boiling point of 413-473 K. It was isolated by atmospheric distillation from a wide coumarone-indene fraction ("heavy benzene"), from now on – WCIF. The boiling point of WCIF is 393-473 K. It is obtained from PJSC "YUZHKOKS" (Kamyanske, Ukraine).

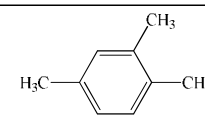
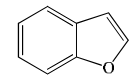
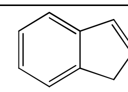
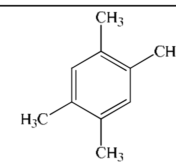
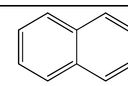
The temperature limits of WCIF selection are determined by the boiling points of the reactive components of the raw material required for the Synthesis of coumarone-indene resins, namely:boiling point of coumarone = 443,9 K; boiling point of indene = 455,8 K; boiling point of styrene = 418 K.

Qualitative and quantitative characteristics of the narrow coumarone-indene fraction are given in Table 1.

Table 1. Qualitative and quantitative characteristics of the narrow coumarone-indene fraction

Component	Structural formula	content, % wt.
1	2	3
Toluene		7.34
p-xylene		39.40
m-xylene		
o-xylene		8.26
Styrene		**3.86**
1-methyl-2-ethylbenzene		2.11

Continuation of Table 1

1	2	3
1,2,4-trimethylbenzene (Pseudocumene)		2.69
Coumarone		**2.69**
Indene		**27.24**
1,2,4,5-tetramethylbenzene (Durene)		1.11
Naphthalene		3.54
Other hydrocarbons[a] and unidentified substances	–	1.76
Total	–	100.00
Content of resin-forming[b] components, % wt.	–	**33.79**
Content of styrene in the resin-forming[b] components, % wt.	–	**11.42**
Content of coumarone in resin-forming[b] components, % wt.	–	**7.96**
Content of indene in the resin-forming[b] components, % wt.	–	**80.62**

[a] Components, the content of which in all samples did not exceed 1.0 %;
[b] Styrene, coumarone, indene.

This fraction was chosen as the most optimal raw material from several samples used in previous studies to obtain coumarone-indene resins.[3,7,8] This is because it is considered[9-11] that the optimal content of reactive components in terms of getting quality resin is 30.0–35.0 % wt., among which indene was the most preferable because it plays a vital role in the polymerization processes for the synthesis of coumarone-indene resin. Analyzing the data given in Table 1 shows that the raw material used is ideal for the production of polymeric products of this type.

The second component of the raw material (modifying agent), apart from the narrow coumarone-indene fraction used to obtain coumarone-indene-carbazole resin, is carbazole, characteristics of which are given in Table 2.[12]

Titanium tetrachloride ($TiCl_4$), a colorless (sometimes yellowish or greenish-yellow) clear liquid with a density of 1.70 g/cm^3, was used as a catalyst to obtain coumarone-indene-carbazole resin (CICR).

Oxidized petroleum road bitumen brand BND 70/100, selected at PJSC "Ukrnafta" (Kremenchuk, Ukraine), is used as a modification material. Its thermoplastic and adhesive characteristics are shown in Table 3.

The degree of adhesion between bitumen and stone material largely depends on their chemical nature.According to its chemical composition, bitumen is characterized by low polarity, acidic properties, and a slight negative charge. Stone material can be acidic (with a tendency to have a negative surface charge) and alkaline (with a tendency to have a positive surface charge). Acidic stone materials are those with a high content of silicon, and alkaline stone materials contain carbonates. Therefore, the problem of poor adhesion is usually in the case of the use of acidic (negatively charged) stone materials.[14]

Table 2. The main characteristics of carbazole

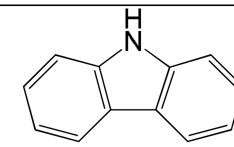
Indicator	Dimension	Value
General data		
Name	–	Carbazole 9-ozo-fluorene
Molecular formula	–	$C_{12}H_9N$
Structural Formula	–	
Physico-chemical properties		
Physical State	–	Solid (powder)
Color	–	Colorless (possibly white or beige)
Smell	–	Odorless
Molar Mass	g/mole	167.2
Boiling Point	K	628
Melting Point	K	518
Solubility in water (at 298 K)	Mg/L	0.91
Solubility in acetone (at 303 K)	g/L	111
Solubility in benzene (at 323 K)	g/L	53
Solubility in ethanol (at 303 K)	g/L	9.2
Stability and Reactivity		
Reactivity	–	When heated, vapors may form explosive mixtures with air
Chemical Stability	–	Stable under normal atmospheric conditions
Possibility of dangerous reactions	–	Strong reaction with alkali (may cause fire or explosion); strong oxidant
Toxicity		
Toxic effects on humans	–	Not classified as a highly toxic substance
Toxic effects on the aquatic environment	–	Toxic to aquatic flora and fauna
Carcinogenic effects on humans	–	It is not classified as carcinogenic.
Possibility of irritating to the skin, eyes, respiratory tract	–	It is not classified as a severe irritant to the skin, eyes, respiratory tract, or allergen.

Table 3. Thermoplastic and adhesive characteristics of bitumen

Indicator	Dimension	Value	Standard for BND 70/100 according to[13]
Depth of needle permeability (penetration) at 298 K	0.1 mm	71	From 71 to 100 inclusive
Softening Point	K	319	From 318 to 324 inclusive
Ductility at 298 K	Cm	91	≥ 60
Adhesion to the glass surface	%	39	≥ 18
Adhesion to the gravel surface	Points	2.5	Non-standardized[a]

[a] Determined for the original bitumen because this figure is normalized for bitumen modified with various additives.

Given the above, to determine the adhesion of the oxidized and modified bitumens to gravel, dense crushed granite from natural stone of erupted rocks (fr. 5–20 mm, fr. 20–40 mm), selected from LLC "Mokryansky stone quarry No. 3" (Zaporizhzhia, Ukraine) was used.

The elemental and oxidized composition of the stone material is given in Tables 4 and 5.

The above analysis of the crushed stone used shows that it belongs to the stone material of the acid type (with silicon content 27.01 %), which means that the bitumen has low adhesion to it. Thus, to determine the adhesion between bitumen and stone material, the "worst" version of crushed stone was chosen, which allowed to model the evaluation of the adhesive properties of bitumen in the most severe conditions.

Table 4. Elemental composition of stone material

Atomic Number	Element	Series	Intensity	Concentration, %
13	Al	K	302097	6.16
14	Si	K	3167423	27.01
19	K	K	62447	14.47
20	Ca	K	20510	3.91
22	Ti	K	6153	0.44
25	Mn	K	4516	0.08
26	Fe	K	428114	4.66
30	Zn	K	6161	0.02
31	Ga	K	4395	0.01
38	Sr	K	129299	0.07
40	Zr	K	52632	0.02
82	Pb	L	10160	0.02

Table 5. Oxidized composition of stone material

Atomic Number	Element	Series	Intensity	Concentration, %
13	Al_2O_3	K	302097	11,64
14	SiO_2	K	3167423	57,79
19	K_2O	K	62447	17,44
20	CaO	K	20510	5,48
22	TiO_2	K	6153	0,73
25	MnO	K	4516	0,10
26	Fe_2O_3	K	428114	6,66
30	ZnO	K	6161	0,02
31	Ga_2O_3	K	4395	0,01
38	SrO	K	129299	0,08
40	ZrO_2	K	52632	0,03
82	PbO	L	10160	0,02

2.2. ExperimentalProcedure

2.2.1. Synthesis of coumarone-indene-carbazole resin

The Synthesis of coumarone-indene resin modified with carbazole was carried out by ion cooligomerization according to the following algorithm:

– the raw material (narrow coumarone-indene fraction (NCIF)) was dried, and pyridine bases were removed by mixing it with 72 % sulfuric acid.

– the raw mixture (NCIF + carbazole) was fed into the reactor;

– the mixer was switched on, and a constant number of revolutions of the stirrer was fixed;

– the reaction medium was heated to a given temperature (taking into account the exoeffect of the process), adding a certain amount of catalyst, fixing the initial time of the process;

– when the synthesis time elapses, the obtained polymer is washed with water until the reaction is neutralized;

– separation of unreacted raw materials from coumarone-indene-carbazole resin (CICR) by vacuum distillation;

– according to the results of the weighed raw materials, carbazole and coumarone-indene-carbazole resin (CICR), the latter's yield is determined.

Fig. 2 shows a diagram of the laboratory installation for the synthesis of coumarone-indene-carbazole resin.

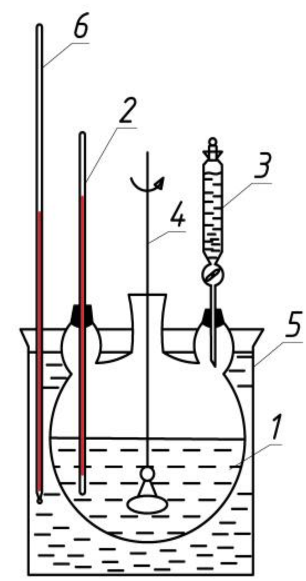


Fig. 2. Scheme of the laboratory installation for the synthesis of coumarone-indene-carbazole resin
1 – three-neck round-bottom flask;
2, 6 – thermometers;
3 – separating funnel;
4 – mixing apparatus;
5 – thermostat.

Given the purpose of the experimental studies described in this article, each subsequent sample of CICR was synthesized by increasing the content of carbazole in the raw material mixture (the amount of carbazole was calculated on the resin-forming components of raw materials - styrene, coumarone, indene). All other conditions and factors of this process were fixed and selected on the basis of literature[2,3,5,6] and are given in Table. 6.

Table 6. Conditions for the synthesis of coumarone-indene-carbazole resin

Catalyst consumption, % wt. on raw materials	3.0
Temperature, K	373
Time, min.	40.0
The upper-temperature limit of distillation[a] of unreacted raw materials from the polymer, K	423

[a] Distillation was carried out under vacuum; excess pressure was – 25 mm Hg.

The yield of coumarone-indene-carbazole resin was calculated using the formula 1:

$$X_{CICR} = \frac{m_{CICR}}{m_{fraction} + m_{carbazole}} \times 100 \qquad (1)$$

where X_{CICR} – the yield of coumarone-indene-carbazole resin, % wt. on the raw material; m_{CICR} – mass of coumarone-indene-carbazole resin, g; $m_{fraction}$ – mass of pre-treated narrow coumarone-indene fraction, g; $m_{carbazole}$ – mass of carbazole, g.

2.2.2. Obtaining modified bitumen

Modification of bitumen with coumarone-indene-carbazole resin (CICR) was carried out according to the following method:

– heating a given amount of bitumen to the modification temperature;

– switching on the mixer and fixing a constant number of revolutions of the stirrer;

– adding a given amount of the modifier (CICR) to the heated bitumen, setting the beginning of the process;

– switching off the heating and stirring after fixing the end of the process;

– qualitative analysis of the modified bitumen.

Based on the definition of quality indicators of the obtained product, it was concluded that it meets the requirements of regulatory documents in the field of bituminous road construction materials.

The laboratory installation for obtaining modified bitumens is given in Fig. 3.

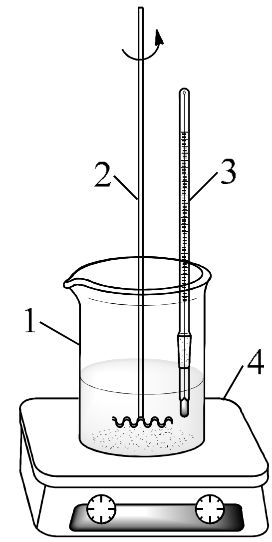


Fig. 3. Laboratory installation for obtaining modified bitumen
1 – cylindrical capacity;
2 – mixing device;
3 – thermometer;
4 – electric heater

2.3. Methods of Analysis

2.3.1. Physico-technological characteristics

Determination of physico-technological parameters of oxidized and modified bitumen was carried out following methods given in the relevant regulations:

– depth of needle permeability (penetration) at 298 K;[15]

– softening temperature;[16]

– ductility at 298 K;[17]

– adhesion to glass surface;[18]

– adhesion to gravel surface.[19]

2.3.2. Spectral analysis

X-ray fluorescence spectroscopy, XRF of the stone material was performed at the Center for collective use of scientific equipment "Laboratory of advanced technologies for the creation and Physico-chemical analysis of new substances and functional materials" (Lviv Polytechnic National University) using ElvaX Light SDD spectrometer software developed by Elvatech.

The spectra were decoded manually by localizing the electron transition peaks that emit maximum energy (for light elements) or the presence of all maxima of the characteristic transitions (for heavy elements).

Estimation of qualitative composition of the samples based on the results of spectrum decoding was performed using software that can drive the ratios of the peak areas between each element to the total peak area of all elements by an algorithm of fundamental parameters.

2.3.3. Chromatographic analysis

Qualitative and quantitative analysis of the narrow coumarone indene fraction was performed using developing gas-adsorption chromatography (chromatograph – "Chromatec crystal 5000.2"; a sensitive device with a flame ionization detector). The separation of the components was carried out on a capillary column 50 m long with the applied liquid phase designated "PONA" (Paraffins, Olefins, Naphthenes, Aromatics). Gas carrier – Helium. Programmed temperature – from 313 to 453 K (the device is calibrated for the analysis of gasoline). The error is 0.01 % vol. Chromatograms were analyzed using the software "Chromatec-analyst 1.5" and "Chromatec-gasoline".

3. Results and Discussion

Table 6 shows the conditions for the synthesis of five samples of CICR.The amount of carbazole in the raw material mixture of each sample was different.It should be noted that previous research shows that the addition of carbazole to NCIF had a positive effect on the quality of the resin. That is, the resin in the raw material for synthesis was 0.00 % wt. Carbazole has the worst modifying effect on bitumen compared to the resin formed from the raw material due to the presence of carbazole. These studies are described in.[7]

Table 7 shows the yield and basic thermoplastic characteristics (softening point) of the obtained sample coumarone-indene-carbazole resin (CICR).

As can be seen from the data in Table 7, with an increasing amount of carbazole in the reaction mixture, the yield of resin increases. That is, this substance intensifies the polymerization processes and increases the degree of polymerization. However, when the consumption of the modifier is more than 20 % wt. (on the resin-forming components), the "effect of its excess" was observed. Thus, Fig. 4 shows photographs of the reaction mixture of samples after the polymerization process (consumption of carbazole is 30 and 40 % wt. on resin-forming components, respectively). The "white spots" are probably concentrated excess carbazole, which did not enter into chemical reactions. Comparison of the photographs in Fig. 4 shows a reaction mixture at a 5 % wt. carbazole consumption on resin-forming components, which shows that all carbazole has undergone chemical reactions ("white spots" are absent).

Table 7. The effect of carbazole consumption on the yield and softening temperature of the resin

Indicator	Value
CICR1 (carbazole consumption – 5.0/1.7[b])	
The yield of resin, % wt. on the raw material[a]	32.13
Softening point by (ball & ring method),K	366
CICR2 (carbazole consumption – 10.0/3.4[b])	
The yield of resin, % wt. on the raw material[a]	36.05
Softening point by (ball & ring method),K	352
CICR3 (carbazole consumption – 20.0/6.8[b])	
The yield of resin, % wt. on the raw material[a]	36.70
Softening point by (ball & ring method),K	341
CICR4 (carbazole consumption – 30.0/10.1[b])	
The yield of resin, % wt. on the raw material[a]	42.06
Softening point by (ball & ring method),K	327
CICR5 (carbazole consumption – 40.0/13.5[b])	
The yield of resin, % wt. on the raw material[a]	47.39
Softening point by (ball & ring method),K	333

[a] The yield of the resin was determined on pre-treated raw materials (drying and removing pyridine bases with 72 % sulfuric acid) + carbazole.

[b] Resin-forming components (styrene, coumarone, indene) / on NCIF.

a) b) c)

Fig. 4. The reaction mixture (polymer + unreacted raw material + excess carbazole) after the polymerization process:
a – consumption of carbazole – 30 % wt. on resin-forming components;
b – consumption of carbazole – 40 % of wt. on resin-forming components;
c – consumption of carbazole – 5 % wt. on resin-forming component

Later, during the distillation from the polymer of unreacted raw materials, this excess carbazole was converted into a resin, increasing its amount. However, such a product was a mixture of resin and carbazole and not pure CICR.

This negative effect of excess carbazole is confirmed by illogical values of softening Points of CICR4 and CICR5. Thus for CICR1, CICR2, and CICR3, the softening point decreases with an increasing amount of carbazole in the reaction mixture, consistent with the literature.[9,20]

Thus it is seen that the optimal consumption of carbazole relative to the raw materials of the process, given the amount of resin and the maximum value of its boiling point, is 10–20 % wt. on resin-forming components (6.8–10.1 % wt. on NCIF).

Tables 8 and 9 show the addition of CICR1, CICR2, and CICR3 to oxidized road petroleum bitumen. Table 3 shows the effect of the amount of carbazole in the reaction medium on the thermoplastic and adhesive properties of the resin and, consequently, modified bitumen. However, because the resins CICR4 and CICR5 were mixtures of pure coumarone-indene-carbazole resin with unreacted carbazole, BND modified with the given CICR was not performed.

Table 8. Effect of carbazole consumption on thermoplastic properties of the resin

Qualitative indicator on which the thermoplastic properties of the resin were concluded on. / Resin content in modified bitumen[a], % wt.	0.0[c]	0.5	1.0	2.0	3.0
CICR1(carbazole consumption – 5.0/1.7[b])					
Softening point by (ball & ring method), K	319	320	321	323	324
Penetration at 298 K, $m\cdot10^{-4}$ (0.1 mm)	71	69	66	60	54
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	88	83	79	73
CICR2(carbazole consumption – 10.0/3.4[b])					
Softening point by (ball & ring method), K	319	319	320	321	322
Penetration at 298 K, $m\cdot10^{-4}$ (0,1 mm)	71	70	68	64	57
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	87	84	82	74
CICR3(carbazole consumption – 20.0/6.8[b])					
Softening point by (ball & ring method), K	319	319	319	321	322
Penetration at 298 K, $m\cdot10^{-4}$ (0,1 mm)	71	71	70	65	59
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	89	87	82	75

[a] Conditions for mixing resin with bitumen are as follows: temperature – 463 K; duration – 60 minutes; the number of revolutions of the stirrer per minute – 300.

[b] Resin-forming components (styrene, coumarone, indene) / on NCIF.

[c] Pure, unmodified bitumen (characteristics which are given in point 2.1).

Table 9. The effect of carbazole consumption on the adhesive properties of the resin

Qualitative indicator on which the adhesive properties of the resin were concluded on. \ Resin content in modified bitumen[a], % wt.	0.0[b]	0.5	1.0	2.0	3.0
CICR1(carbazole consumption – 5.0/1.7[c])					
The adhesion of the modified bitumen to the glass surface, %	39	43	48	57	70
The adhesion of the modified bitumen to gravel surface points	2.5	2.5	2.5	3.0	3.5
CICR2(carbazole consumption – 10.0/3.4[c])					
The adhesion of the modified bitumen to the glass surface, %	39	48	64	73	90
The adhesion of the modified bitumen to gravel surface points	2.5	2.5	3.0	3.5	4.0
CICR3(carbazole consumption – 20.0/6.8[c])					
The adhesion of the modified bitumen to the glass surface, %	39	54	77	89	100[d]
The adhesion of the modified bitumen to gravel surface points	2.5	3.0	4.0	4.5	5.0

[a] Conditions for mixing resin with bitumen are as follows: temperature – 463 K; duration – 60 minutes; the number of revolutions of the stirrer per minute – 300.
[b] Pure, unmodified bitumen (characteristics which are given in point 2.1).
[c] Resin-forming components (styrene, coumarone, indene) / on NCIF.
[d] Adhesion was 95–100 %.

Analyzing the data given in Tables 8 and 9, we see that the increase in the consumption of carbazole in the reaction mixture ultimately and significantly affects the thermoplastic and adhesive properties of the bitumen modified with the corresponding coumarone-indene-carbazole resins. CICR1 has the most positive effect on the softening point of the modified product.The synthesis of which (CICR1) the smallest amount of the modifier was used (5.0/1.7 % wt.): in this case, the most significant increase in softening point is achieved. At the same time, the most significant improvement in the adhesive properties of bitumen is observed when it is modified by the sample CICR3 (consumption of carbazole– 20.0/6.8 % wt.). In any case, the values of penetration and ductility decrease slightly, which indicates a slight deterioration of the plastic properties.

Based on the requirements of regulatory documents[21,22] in the modification field of road petroleum bitumens, it can be argued that the adhesive effect of coumarone-indene-carbazole resin is superior to its thermoplastic. Therefore, CICR should be considered as an adhesive additive to road petroleum bitumens. In this case, the optimal value of the amount of carbazole in the reaction mixture should be regarded as 20.0 % wt. on resin-forming components NCIF (6.8 % wt. on NCIF). That is, the ratio of carbazole: resin-forming components should be 1:5.

Characteristically, the increase in the amount of CICR(regardless of the cost of the modifier to obtain it) in bitumen enhances the positive adhesive effect of modification (Figs. 5 and 6).

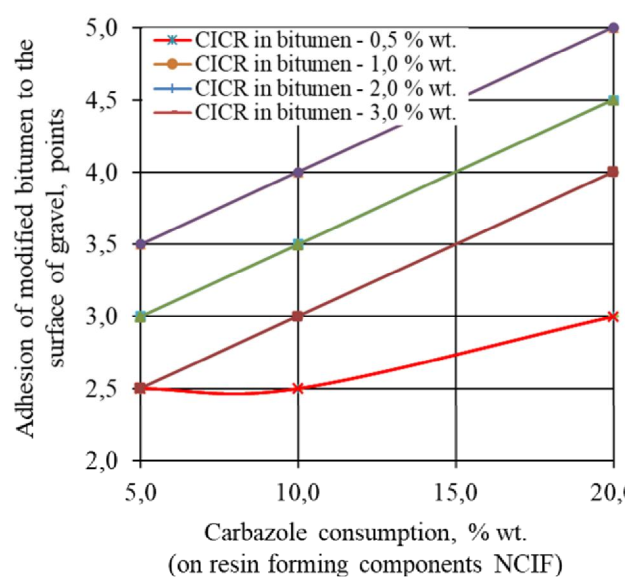


Fig. 5. The effect of carbazole consumption on the adhesion of modified bitumen to the surface of gravel

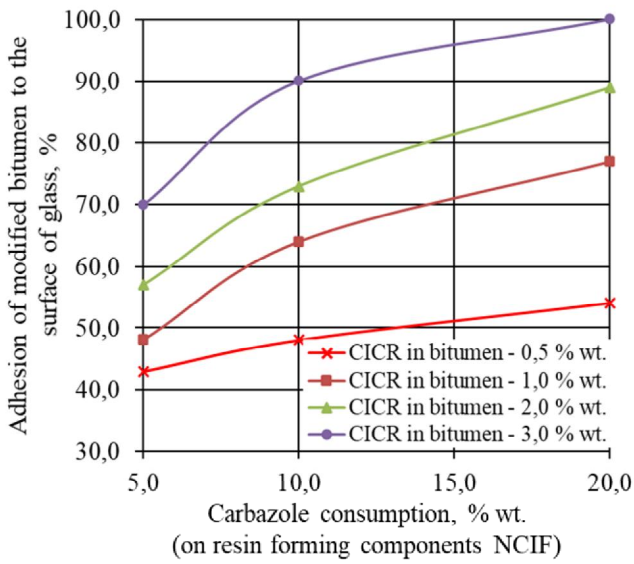


Fig. 6. The effect of carbazole consumption on the adhesion of modified bitumen to the glass surface

In order to achieve the desired effect in terms of adhesion (adhesion to glass – ≥ 75 %, with crushed stone – ≥ 4), it is enough to add 1 % CICR, which was obtained at consumption of carbazole 20 % on resin-forming components.

4. Conclusions

The above trends allow us to draw the following conclusions:

– ncreasing the amount of carbazole in the reaction mixture (from 1.7 to 13.5 % wt.) increases the yield of CICR (from 32.13 to 47.39 % wt.);

– an excessive amount of the modifier (more than 10 % wt. on raw materials) leads to oversaturation of the reaction medium;

– increasing the amount of carbazole in the reaction mixture improves the adhesive properties of the resin and, consequently, bitumen;

– increasing the amount of carbazole in the reaction mixture reduces the softening point of the resin. Consequently, a significant increase in the softening point of bitumen while improving its adhesion is difficult/impossible to achieve;

– increasing the amount of carbazole in the reaction mixture transforms CICR from the field of “thermoplastic bitumen modifiers” to the field of “adhesive additives to bitumen”;

– the optimal value of the amount of carbazole in the reaction mixture should be considered 20.0 % wt. on resin-forming components of raw materials (the ratio of carbazole: resin-forming components should be 1: 5).

References

[1] Porto, M.; Caputo, P.; Loise, V.; Eskandarsefat, S.; Teltayev, B.; Rossi, C.O. Bitumen and Bitumen Modification: A Review on Latest Advances. *Appl. Sci.* **2019**, *9*, 742. https://doi:10.3390/app9040742

[2] Pyshyev, S.; Gunka, V.; Grytsenko, Y.; Bratychak, M. Polymer Modified Bitumen: Review. *Chem. Chem. Technol.* **2016**, *10*, 631-636. https://doi.org/10.23939/chcht10.04si.631

[3] Pyshyev, S.; Prysiazhnyi, Yu.; Sidun, Iu.; Shved, M.; Borbeyiyong, G.I.; Korsh, D. Obtaining of Resins Based on Model Mixtures with Indene, Coumarone and Styrene and their Usage as Bitumen Modifiers. *Pet. Coal* **2020**, *62*, 341-346.

[4] Demchuk, Yu.; Gunka, V.; Pyshyev, S.; Sidun, Iu.; Hrynchuk, Yu.; Kucinska-Lipka, Ju.; Bratychak, M. Slurry Surfacing Mixes on the Basis of Bitumen Modified with Phenol-Cresol-Formaldehyde Resin. *Chem. Chem. Technol.* **2020**, *14*, 251-256. https://doi.org/10.23939/chcht14.02.251

[5] Pyshyev, S.; Grytsenko, Yu.; Solodkyy, S.; Sidun, Iu.; Vollis, O. Using Bitumen Emulsions Based on Oxidated, Distillation and Modified Oxidated Bitumens for Slurry Seal Production. *Chem. Chem. Technol.* **2015**, *9*, 359-366. https://doi.org/10.23939/chcht09.03.359

[6] Bratychak, M.; Gunka, V.; Prysiazhnyi, Yu.; Hrynchuk, Yu.; Sidun, Iu.; Demchuk, Yu.; Shyshchak, O. Production of Bitumen Modified with Low-Molecular Organic Compounds from Petroleum Residues. 1. Effect of Solvent Nature on the Properties of Petroleum Residues Modified with Folmaldehyde. *Chem. Chem. Technol.* **2021**, *15*, 274-283. https://doi.org/10.23939/chcht15.02.274

[7] Pyshyev, S.; Prysiazhnyi, Yu.; Borbeyiyong, G.I.; Chervinskyy, T.; Kułażyński, M.; Grytsenko, Yu. Effect of raw material composition on the properties of road asphalt modifier obtained from liquid coal coking products. *Przemysl Chem.* **2021**, *100*, 680. https://doi.org/10.15199/62.2021.7.9

[8] Pyshyev, S.; Grytsenko, Yu.; Bilushchak, H.; Pyshyeva, R.; Danyliv, N. Production of Indene-coumarone Resins as Bitumen Modifiers. *Pet. Coal* **2015**, *57*, 303-314.

[9] Sokolov, V. *Inden-Kumaronovye Smoly*; Metalurgia: Moskva, 1978.

[10] Litvinenko, M.S. *Himicheskie produkty koksovania dlia proizvodstva polimernyh materialov*; Metalurgizdat: Harkov, 1962.

[11] Chistiakov, A.N. *Himiia i tehnologiia pererabotki kamennougolnyh smol*; Metalurgia: Cheliabinsk, 1990.

[12] Carbazole. Security passport https://www.carlroth.com/medias/SDB-9752-RU-RU.pdf?context=bWFzdGVyfHNlY3VyaXR5RGF0YXNoZWV0c3wyNjk0MDd8YXBwbGljYXRpb24vcGRmfHNlY3VyaXR5R

GF0YXNoZWV0cy9oZDEvaGRhLzg5NzMxMDQzMTY0NDYucGRmfGRkZTgxODk5ZWUxMDYzMDNkMjg3ZTgzYWRmNjFiNzRmN2RmY2I4MjFiYWI2MDRjZWJhYWJiNDUwODRmOTczMjc (accessed 2020-01-07).
[13] DSTU 4044:2019 http://online.budstandart.com/ua/catalog/doc-page.html?id_doc=84291 (accessed 2020-05-01).
[14] Rossi, C.O.; Teltayev, B.; Angelico, R. Adhesion Promoters in Bituminous Road Materials: A Review. *Appl. Sci.* **2017**, *7*, 524. https://doi.org/10.3390/app7050524
[15] DSTU EN 1426:2018 http://online.budstandart.com/ua/catalog/doc-page?id_doc=78299(accessed 2019-06-01).
[16] DSTU EN 1427:2018 http://online.budstandart.com/ua/catalog/doc-page.html?id_doc=78301(accessed 2019-06-01).
[17] DSTU 8825:2019http://online.budstandart.com/ua/catalog/doc-page.html?id_doc=82135(accessed 2020-01-01).
[18] DSTUBV.2.7-81-98http://online.budstandart.com/ua/catalog/doc-page?id_doc=4804(accessed 1999-03-01).
[19] DSTU 8787:2018http://online.budstandart.com/ua/catalog/doc-page?id_doc=77885(accessed 2019-06-01).
[20] Mildenberg, R.; Zander, M.; Collin, G. *Hydrocarbon Resins*; VCH: Weinheim, New-York, Basel, Cambridge, Tokyo, 1997.
[21] DSTUBV.2.7-135:2014http://online.budstandart.com/ua/catalog/doc-page?id_doc=58777(accessed 2015-04-01).
[22] SOU 45.2-00018112-067:2011http://online.budstandart.com/ua/catalog/doc-page.html?id_doc=69813 (accessed 2017-06-01).

Received: June 3, 2021 / Revised: July 7, 2021 / Accepted: October 26, 2021

ОДЕРЖАННЯ І ЗАСТОСУВАННЯ КУМАРОН-ІНДЕН-КАРБАЗОЛЬНОЇ СМОЛИ ЯК МОДИФІКАТОРА ДОРОЖНІХ НАФТОВИХ БІТУМІВ. 1. ВПЛИВ СПІВВІДНОШЕННЯ КАРБАЗОЛ:СИРОВИНА

Анотація*. Показано можливість ефективного застосування карбазолу як покращувала кумарон-інденової смоли, що застосовується як модифікатор нафтових бітумів. Усі вихідні речовини для отримання кумарон-інден-карбазольних смол (КІКС) можна отримувати з різних продуктів процесу коксування вугілля. Вивчено вплив складу сировини (кількості карбазолу, який додається до промислової інден-кумаронової фракції) на вихід смоли та її модифікуючі властивості. Встановлено оптимальні кількості карбазолу у вихідній сировині та рекомендовано застосовувати КІКС як адгезійну добавку до бітумів.*

Ключові слова*: кумарон, інден, карбазол, модифікатор, бітум.*