Chem. Chem. Technol., 2023,
Vol. 17, No. 2, pp. 450–459

Chemical Technology

OBTAINING AND USE OF COUMARONE-INDENE-CARBAZOLE RESIN AS A MODIFIER OF ROAD PETROLEUM BITUMEN. 2. SETTING THE TYPE AND AMOUNT OF CATALYST

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https://doi.org/10.23939/chcht17.02.450

Abstract. In the presence of various catalysts ($TiCl_4$, $AlCl_3$, H_2SO_4), the process of obtaining a coumarone-indene-carbazole resin (CICR), which is produced from liquid products of coal coking, and its subsequent use for bitumen modification was investigated. The influence of the catalyst type on the yield and modifying properties of CICR (change in thermoplastic and adhesive properties of bitumen after adding the obtained resins to them) was studied. The effect of catalyst amount on the resin synthesis and subsequent modification of bitumen with the synthesized product was determined. According to the results, the optimal type and amount of the catalyst for obtaining CICR were chosen. The determined optimal amount of coumarone-indene-carbazole resin synthesized using the selected type of catalyst was found to have the most positive effect on the adhesive characteristics of road bitumen.

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

1. Introduction

Modifying road petroleum bitumen has been the primary trend of the last few decades to improve the quality of binders. In this regard, the share of modified bitumen is constantly increasing, and that of unmodified bitumen is decreasing. This is evidenced by the data given by several sources.[1-4] For example, in the European Union, the share of modified bitumen from the total volume of binders used in road construction during 2016-2020 increased from 18-20 % to 27-30 %. It is expected[1-3] that the consumption of modified bitumen will grow at least by 4% during 2022-2027. This is primarily due to the increase in the volume of road construction and repair work throughout the world. In monetary terms, the modified bitumen market will grow from \$11.8 billion in 2021 to \$16.3 billion in 2028.[1-3]

One can see from Fig. 1, the leading producers and consumers of modified bitumen are the USA, Canada, Mexico, the European Union, China, India, Japan, and Australia. At the same time, road bitumen accounts for the leading share of modified bitumen.[1-3] (Fig. 2).

It is worth noting that in terms of production and consumption of modified road bitumen, Ukraine follows global trends:

– the main part of road bitumen used by Ukraine is imported (mainly from the European Union);[5-7] accordingly, the quality of bitumen in Ukraine is equal to the quality of bitumen in Europe;

– for the past 5-10 years, the construction and repair of highways in Ukraine have been carried out according to modern world technologies.[8] Accordingly, the quality of bitumen must meet the requirements of these technologies.

Market analysis[1-3] shows that the most used modifiers in the world are polyethylene, polypropylene, styrene-butadiene-styrene (SBS), atactic polypropylene, rubber-based compounds, various amines, and amides. For example, in 2020, the worldwide volume of SBS production was 1.8 million tons.[9] By 2027, the figure is projected to be 2.2 million tons, 788,000 tons of which will be used for bitumen modification.

The only major drawback of almost all existing industrial modifiers is their relatively high cost. Therefore, with further implementation into the industry, constant research is being conducted in the scientific field, the purpose of which is to search for alternative cheap raw materials and ways to create modifiers of road petroleum bitumen.

Research on obtaining modifiers of road bitumen from non-target products of coal thermal processing, particularly coumarone-indene-carbazole resin (CICR), deserves special attention. Such a modifier primarily has improved adhesive properties. Accordingly, bitumen has a decisive effect on the adhesion of the latter to the mineral material.

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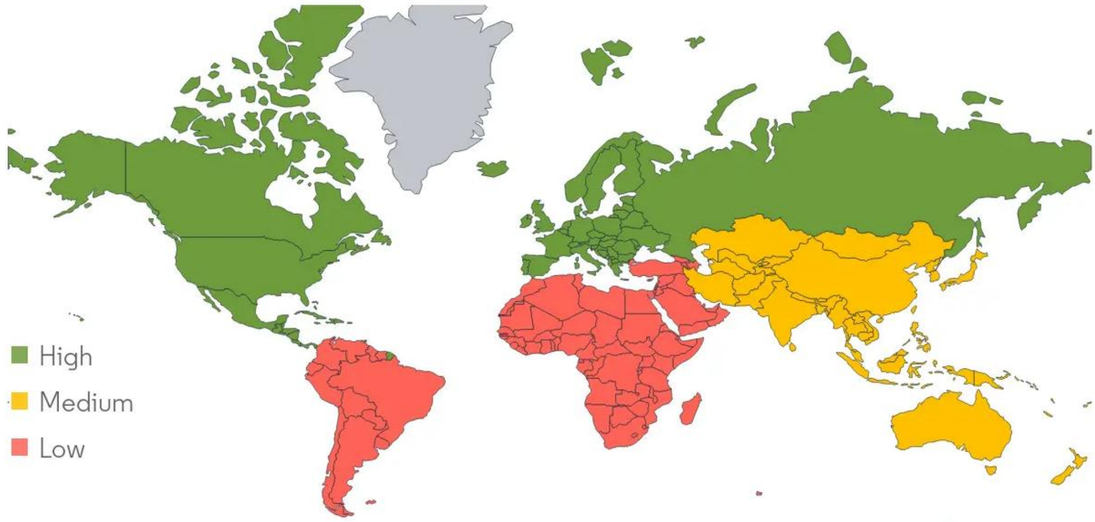

Fig. 1. The structure of the production and consumption of modified bitumen in the world

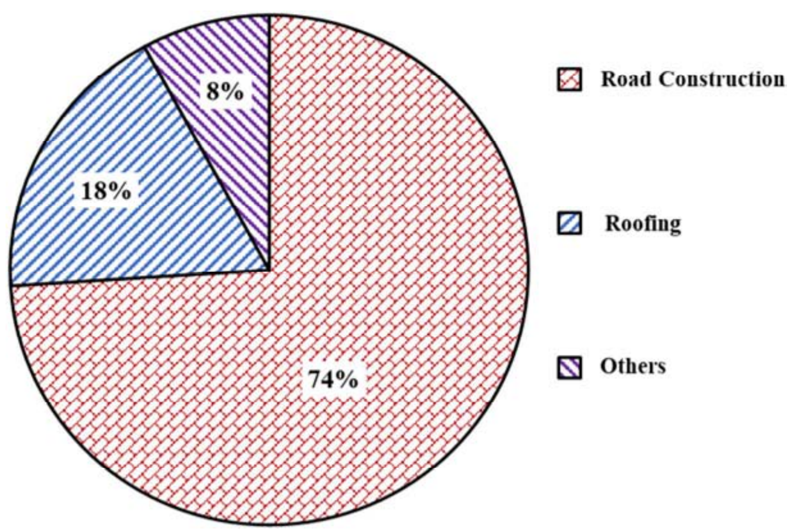

Fig. 2. Areas of modified bitumen consumption

As it was mentioned earlier,[10] the process of obtaining coumarone-indene-carbazole resin is influenced by certain factors that determine the depth (degree) of raw materials conversion, the quantity and quality of the target product, energy and material costs, etc.

Among the essential factors that influence the process of CICR obtaining, the following can be singled out: composition of raw materials (primarily, consumption (amount) of carbazole in the reaction medium); type and consumption (amount) of catalyst in the reaction medium; temperature and time.

This article is a continuation of our previous publication,[10] aimed to study the influence of some above-mentioned factors on the process.

2. Experimental

2.1. Materials

The raw material for obtaining coumarone-indene-carbazole resin is a narrow coumarone-indene fraction (NCIF) with a boiling temperature range of 413-473 K. It is separated from a wide coumarone indene fraction ("heavy benzene") and henceforth referred to as WCIF. The boiling temperature range of WCIF is 393-473 K. WCIF originates from PJSC Yuzhkoks (Kamianske, Ukraine). The choice of NCIF temperature range was substantiated by the boiling points of the reactive raw materials necessary for the synthesis of coumarone-indene-carbazole resins, namely: coumarone (443.9 K), indene (455.8 K), and styrene (418 K).

The qualitative and quantitative characteristics of the narrow coumarone-indene fraction are described earlier.[10]

The second component of the raw materials (modifying agent), besides the narrow coumarone-indene fraction used to obtain coumarone-indene-carbazole resin, is carbazole.[10, 11, 13]

The following substances are used as a catalyst to obtain coumarone-indene-carbazole resin:

– Titanium tetrachloride ($TiCl_4$) – colorless (sometimes with a yellowish or greenish-yellow tint) transparent liquid, density 1.70 g/cm^3;

– anhydrous aluminum chloride ($AlCl_3$) – white crystalline powder, density 2.47 g/cm^3;

– concentrated sulfuric acid (H_2SO_4) of reagent grade, colorless oily liquid, density 1.83 g/cm^3.

Two samples of oxidized petroleum road bitumen of the BND 70/100 brand, selected at PJSC "Ukrtatnafta" (Kremenchuk, Ukraine) in 2020, BND-1 and BND-2, respectively, were used as the modification material.

The reasons for using two samples of road bitumen of the same brand are as follows:

– BND-1 sample was used at the first stage of research, setting the type of catalyst for the synthesis of coumarone-indene-carbazole resin;

– BND-2 sample was used in the second research stage to determine the optimal amount of catalyst in the reaction medium. Since coumarone-indene-carbazole resin is mostly a modifier of adhesion, it was decided to conduct the research with bitumen, which is characterized by extremely poor adhesion to mineral material (adhesion of BND-2 to a glass surface is 39 % *vs.* 44 % for BND-1).

Thermoplastic and adhesive characteristics of the investigated BND-1 and BND-2 oxidized petroleum road bitumen are represented in Table 1.

Table 1. Thermoplastic and adhesive properties of bitumen

Indicator	Units	BND-1	BND-2	The standard for BND 70/100[12]
Depth of needle penetration (penetration) at 298 K	0,1mm	76	71	From 71 to 100 inclusive
Softening point	K	321	319	From 45 to 51 inclusive
Ductility at 298 K	Cm	69	91	≥ 60
Adhesion to a glass surface	%	44	39	≥ 18
Adhesion to a crushed stone surface	Point	2.5	2.5	Not normalized *

* It was determined for the original bitumen since this indicator is normalized for bitumen modified with various additives

To determine the adhesion of the original and modified bitumen to crushed stone, we used dense granite crushed stone made of natural stone of igneous rocks (fractions 5–20 and 20-40 mm)[10] selected at "Mokryansky stone quarry No. 3" LLC (Zaporizhzhia, Ukraine). This type of stone material belongs to the acidic type[14]. Bitumen also exhibits acidic properties due to its chemical composition. Thus, the “sticking” of bitumen particles to crushed stone will be the worst. Therefore, this particular selection of a stone material allowed to assess the adhesive properties of CICR and road bitumen modified with CICR.

2.2. Experimental Procedure

2.2.1. Synthesis of Coumarone-Indene-Carbazole Resin

The coumarone-indene resin, modified with carbazole, was synthesized *via* the earlier described[10] ionic co-oligomerization method.

Fig. 3 shows a scheme of the laboratory setup for the synthesis of coumarone-indene-carbazole resin.

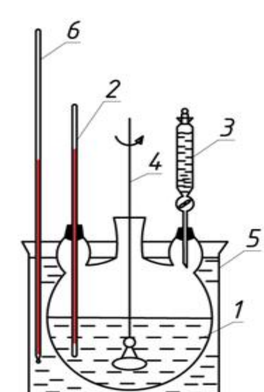

Fig 3. Scheme of the laboratory setup for the synthesis of coumarone-indene-carbazole resin
1 – round-bottomed three-necked flask; 2, 6 – thermometer; 3 – separating funnel; 4 – mixing device; 5 – thermostat

The yield of coumarone-indene-carbazole resin was calculated according to the formula (1):

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

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

2.2.2. Obtaining Modified Bitumen

Bitumen was modified with CICR according to the method described in earlier publications.[10] Quality indicators of the resulting product allows making a conclusion about its compliance with the requirements of regulatory documents in the bituminous road construction materials field.

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 penetration (penetration) at 298 K;[19]
– softening temperature;[20]
– ductility at 298 K;[21]
– adhesion to a glass surface;[22]
– adhesion to a crushed stone surface.[23]

3. Results and Discussion

3.1. Setting the Catalyst Type

It is known that the type of catalyst significantly affects the polymerization processes of any "unsaturated" raw material, particularly coumarone-indene fractions.[24-26] The catalyst significantly affects the quantity and quality of the polymerization products and, as a result, other ways of their application, including usage as modifiers of road petroleum bitumen.

Data from literary sources indicate that the unsaturated components of indene-coumarone fractions can be co-oligomerized both by a radical (thermal[24,25] and initiated[27-29] co-oligomerization) and by an ionic mechanism (acid catalysis). In industrial practice, as a rule, the last option is used. At the same time, Lewis and Brønsted acids and their mixtures are used as catalysts. In the literature, different methods of obtaining ICR by this method are described, and the chemistry and mechanism of their preparation were studied by several authors.[24,25] The most common catalysts in the industry used to obtain coumarone-indene resins from raw materials of similar origin, nature, and composition included H_2SO_4, $AlCl_3$, a complex based on aluminum chloride $AlCl_3$/EA/KC, and $TiCl_4$.[30-32] As the research results showed, when using concentrated H_2SO_4 (97 %), it is impossible to obtain a resin with a high softening temperature, which is necessary for obtaining high-quality modified bitumen. $AlCl_3$, a complex based on it, and $TiCl_4$ make it possible to obtain ICR with a softening temperature of 283–253 K, which is higher than when using sulfuric acid. Taking into account the high hygroscopicity of $AlCl_3$ (a watered catalyst sharply loses its activity) and the relative complexity of preparing the $AlCl_3$/EA/KC complex, titanium tetrachloride was selected as the optimal catalyst among the tested ones.

At the same time, it is still being determined whether the described trends are inherent in synthesizing modified coumarone-indene resins, particularly with carbazole. To study the influence of the catalyst type on the yield, thermoplastic and adhesive properties of the resin and bitumen modified with it, several samples of CICR were synthesized under the same conditions (Table 2), using the above-mentioned catalysts, except $AlCl_3$/EA/KC complex due to the complexity at preparing. Attention should be paid to the fact that the resin production temperature is much lower when using sulfuric acid compared with $AlCl_3$ and $TiCl_4$.[24-26,30-34] Therefore, for an accurate assessment of the effectiveness of one or another type of catalyst, the CICR synthesis with H_2SO_4 was carried out at a temperature of 313 K, and the CICR synthesis with $AlCl_3$ and $TiCl_4$ was carried out at a temperature of 373 K.

Table 2. Conditions of resin synthesis[24-26]

Raw material[*]	NCIF
Catalyst	H_2SO_4 $AlCl_3$ $TiCl_4$
Catalyst amount, wt.% relative to raw materials	3.0
Carbazole amount, wt.% relative to resin-forming components[**] / NCIF	20.0/6.8
Temperature, K	313 373
Time, min.	40.0
Upper temperature limit of distillation[***] of unreacted raw materials, K	423

[*]The raw material was pre-treated (drying and removal of pyridine bases using 72% sulfuric acid).

[**]Resin-forming components are styrene, coumarone, and indene.

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

The coumarone-indene-carbazole resin was synthesized according to the method described in Subsection 2.2.1. Figs. 4, 5 show the yield and basic thermoplastic characteristics (softening point) of the obtained CICR. It is worth noting that the resin yield was determined based on pre-treated raw materials (drying and removal of pyridine bases using 72 % sulfuric acid) + carbazole.

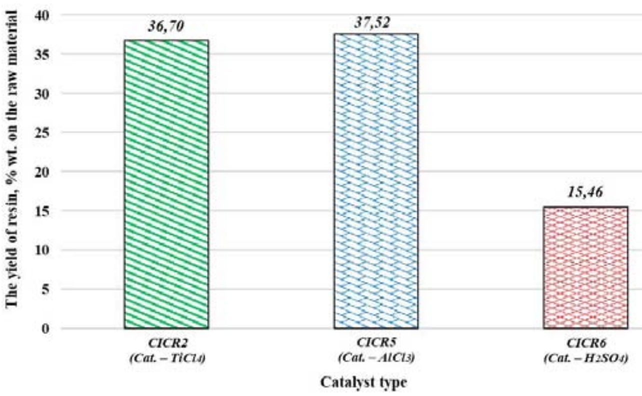

Fig. 4. Effect of catalyst type on resin yield, wt.% relative to raw materials

The qualitative and quantitative characteristics of the obtained resins (Figs. 4, 5) indicate that H_2SO_4 is the least effective catalyst in terms of the yield of the target product (CICR6) and its softening temperature. At the same time, aluminum chloride and titanium tetrachloride provide almost the exact yield of CICR2 and CICR5, with the softening temperature of CICR2 slightly higher than CICR5. Tables 3 and 4 show the modification results of oxidized road petroleum bitumen BND-1 with CICR2, CICR5, and CICR6 resins (Table 1).

Data in Tables 3 and 4 show that the resins obtained using $AlCl_3$ and $TiCl_4$ catalysts (CICR2 and CICR5) have a similar effect on the thermoplastic and adhesive properties of bitumen.

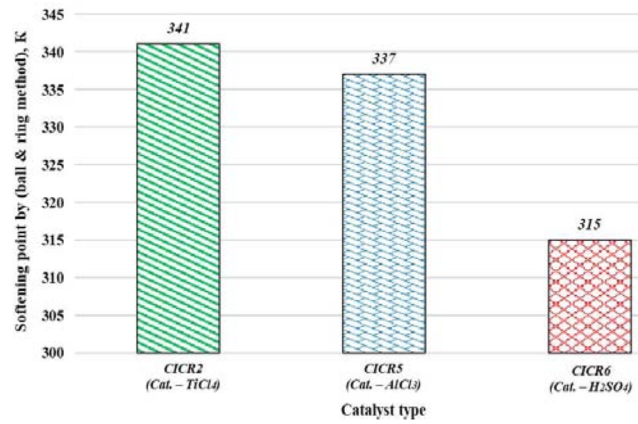

Fig. 5. Effect of catalyst type on the softening point (ball and ring method, K)

An increase in the CICR6 content (a catalyst is H_2SO_4) in bitumen (Table 3) leads to a decrease in the softening temperature and an increase in penetration (the reason is that the softening temperature of CICR6 is lower than that of BND-1). Ductility passes through a maximum: CICR6 improves the ability of bitumen to stretch up to a certain limit, after which this indicator deteriorates.

The effect of adding the obtained CICR to bitumen on its adhesive properties in all three cases is positive (Table 4). At the same time, the degree of improvement in adhesion of modified bitumen to the surface of material materials when using CICR6 (a catalyst is H_2SO_4) is much smaller than when using CICR2 and CICR5 (catalysts are $TiCl_4$ and $AlCl_3$, respectively). It is worth noting that the degree of adhesion improvement for the last two resins is almost at the same level.

Table 3. The influence of the catalyst type on the thermoplastic properties of the resin

Qualitative indicator of modified bitumen	Content of resin in modified bitumen*, wt.%				
	0.0**	0.5	1.0	2.0	3.0
CICR2 (Cat. $TiCl_4$)					
Softening temperature (ball and ring method), K	321	321	322	322	323
Penetration at 298 K, $m \cdot 10^{-4}$ (0.1 mm)	76	75	72	69	67
Ductility at 298 K, $m \cdot 10^{-2}$ (cm)	69	65	61	55	52
CICR5 (Cat. $AlCl_3$)					
Softening temperature (ball and ring method), K	321	321	322	321	323
Penetration at 298 K, $m \cdot 10^{-4}$ (0.1 mm)	76	76	74	72	68
Ductility at 298 K, $m \cdot 10^{-2}$ (cm)	69	69	66	61	54
CICR6 (Cat. H_2SO_4)					
Softening temperature (ball and ring method), K	321	321	321	320	320
Penetration at 298 K, $m \cdot 10^{-4}$ (0.1 mm)	76	76	78	81	86
Ductility at 298 K, $m \cdot 10^{-2}$ (cm)	69	69	69	70	65

* Conditions of mixing bitumen with CICR: temperature is 463 K; time is 60 min; modified Reynolds criterion is 109500.
** Pure, unmodified bitumen (characteristics are given in Subsection 2.1).

Table 4. The effect of catalyst type on the adhesive properties of the resin

Qualitative indicator of modified bitumen	Content of resin in modified bitumen*, wt.%				
	0.0**	0.5	1.0	2.0	3.0
CICR2 (Cat. $TiCl_4$)					
Adhesion of modified bitumen to a glass surface, %	44	65	88	100	100
Adhesion of modified bitumen to a crushed stone surface, point	2.5	3.5	5.0	5.0	5.0
CICR5 (Cat. $AlCl_3$)					
Adhesion of modified bitumen to a glass surface, %	44	62	84	100	100
Adhesion of modified bitumen to a crushed stone surface, point	2.5	3.5	4.5	5.0	5.0
CICR6 (Cat. H_2SO_4)					
Adhesion of modified bitumen to a glass surface, %	44	55	67	84	100
Adhesion of modified bitumen to a crushed stone surface, point	2.5	2.5	3.5	4.0	4.5

* Conditions of mixing bitumen with CICR: temperature is 463 K; time is 60 min; modified Reynolds criterion is 109500.
** Pure, unmodified bitumen (characteristics are given in Subsection 2.1).

The obtained results allow us to focus on $TiCl_4$ and $AlCl_3$ as the optimal catalysts for obtaining coumarone-indene-carbazole resin. H_2SO_4 as a catalyst provides significantly worse resin quantitative and qualitative characteristics and, as a result, the properties of the modified bitumen. In further studies, $TiCl_4$ was used as a catalyst since its increases the adhesion of the modified bitumen somewhat more than $AlCl_3$ (Table 4).

3.2. The Effect of the Catalyst Amount

Thus, among the studied catalysts for obtaining coumarone-indene-carbazole resin $TiCl_4$ was found to be the optimal one. Studying the effect of its amount on the yield, thermoplastic and adhesive properties of the resin and resin-modified bitumen we changed the raw material : $TiCl_4$ ratio (w/w). The catalyst amount was calculated relative to raw material (NCIF + carbazole).

The synthesis of coumarone-indene-carbazole resin was carried out according to the method presented in Subsection 2.2.1. The conditions of resin synthesis are given in Table 5.

Table 5. Conditions of resin synthesis

Carbazole amount, wt.% relative to resin-forming components / NCIF	20.0/6.8
Temperature, K	373
Time, min	40.0

Fig. 6 shows the yield and basic thermoplastic characteristics (softening temperature) of the obtained CICR samples.

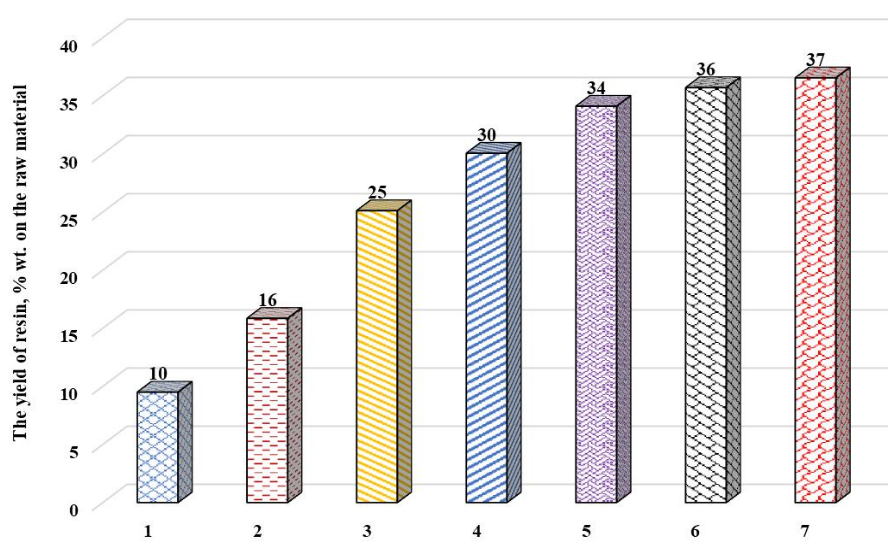

Fig. 6. The effect of catalyst amount (relative to resin-forming components/ NCIF + carbazole) on the resin yield: 1 – CICR11 (1.3/0.5); 2 – CICR12 (2.6/1.0); 3 – CICR13 (3.9/1.5); 4 – CICR14 (5.2/2.0); 5 – CICR15 (6.6/2.5); 6 – CICR2 (7.9/3.0); 7 – CICR16 (9.2/3.5)

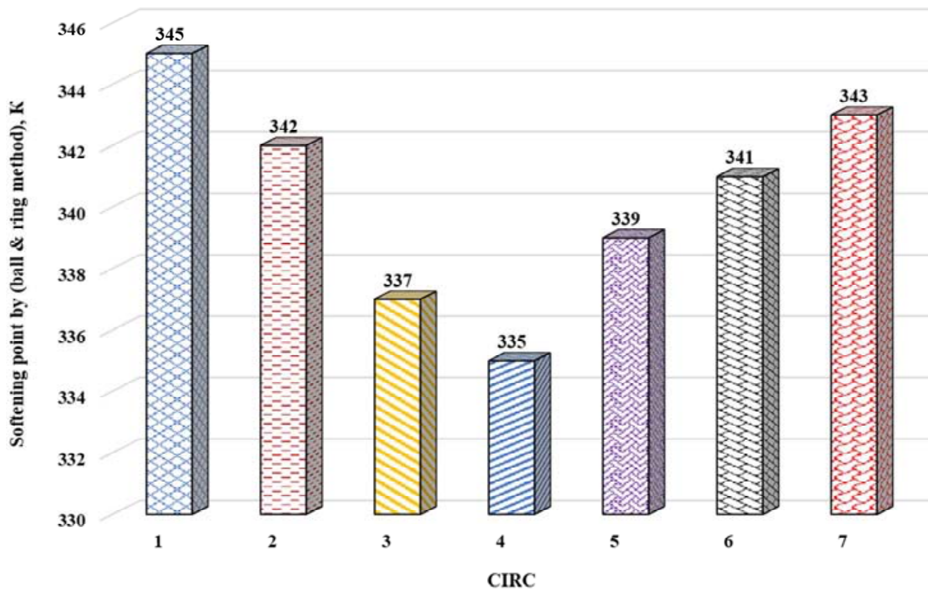

Fig. 7. The effect of catalyst amount (relative to resin-forming components/ NCIF + carbazole) on the resin softening temperature: 1 – CICR11 (1.3/0.5); 2 – CICR12 (2.6/1.0); 3 – CICR13 (3.9/1.5); 4 – CICR14 (5.2/2.0); 5 – CICR15 (6.6/2.5); 6 – CICR2 (7.9/3.0); 7 – CICR16 (9.2/3.5)

The data in Figs. 6 and 7 show that an increase in catalyst amount increases the resin yield. When the amount of $TiCl_4$ in the reaction mixture is in the range of 0.5–2.5 wt.%, the CICR yield increases rather rapidly, and at the amount of above 2.5 wt.% this trend is somewhat slowing down.

The values of the softening temperature of CICR2, CICR11-CICR16 pass through a minimum (Figs. 6, 7). This is probably due to the fact that with a small amount of the catalyst (0.5 wt.%), its effect extends primarily to indene, which most quickly enters the oligomerization process and the amount of which is the largest among all reactive components of the raw material.[24-26] Thus, the resulting resin (CICR11) is more of an indene than a coumarone-indene-carbazole. Moreover, as it is known[24,26] the softening temperature of CIR is higher than that of CICR. With the increase in the catalyst amount above 0.5 wt.% the number of active centers increases and other reactive compounds (coumarone, styrene, and carbazole) begin to oligomerize intensively. As a result, products of lower molecular weight are formed, which is confirmed by a decrease in the softening temperature of the resins (CICR12, CICR13). Furthermore, with an increase in the $TiCl_4$ amount in the reaction medium above 2.5 wt.% the increase in the softening temperature is observed, whereas resin yield remains almost unchanged (CICR15, CICR2, CICR16). Such an increase in the softening temperature at a constant yield is probably explained by the fact that the initially formed oligomers combine with each other, forming products of higher molecular weight with a higher softening temperature.

Therefore, it can be concluded that for the raw materials used, the amount of catalyst at the level of 2.0-2.5 wt.% is sufficient for the reactive components to almost completely enter the oligomerization processes.

Oxidized road petroleum bitumen BND-2 was modified with the obtained resin samples (CICR2 and CICR11-CICR16) (Table 1); the results are represented in Tables 6 and 7.

Comparing the results of Tables 6 and 7, one can see that the thermal stability of the modified bitumen and synthesized CICR samples changes similarly. The softening temperature of bitumen, CICR2, and CICR11-CICR16 passes through the minimum. At the same time, as the resin content in bitumen increases, its softening temperature increases. Due to the fact that the hardness of all CICR samples is higher compared with that of the original bitumen, its plasticity deteriorates, and the values of penetration and ductility decrease. This is especially evident when the CICR : bitumen ratio increases.

Table 7 shows that the increase in the amount of the catalyst relative to the raw material improves the adhesive properties of coumarone-indene-carbazole resin and resin-modified bitumen. At the same time, for CICR11-CICR15 samples (catalyst amount 0.5–2.5 wt.%), adhesive properties are rapidly improved from sample to sample. Furthermore, with 2.5–3.5 wt.% of the catalyst in the reaction medium (samples CICR15, CICR2, CICR16) adhesion increases slightly.

Table 6. The effect of the catalyst amount on the thermoplastic properties of the resin

Qualitative indicator of modified bitumen	Content of resin in modified bitumen*, % wt.				
	0.0**	0.5	1.0	2.0	3.0
CICR11 (catalyst amount*** 1.3/0.5)					
Softening temperature (ball and ring method), K	319	319	320	321	322
Penetration at 298 K, $m\cdot10^{-4}$ (0.1 mm)	71	70	67	65	58
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	88	85	83	75
CICR12 (catalyst amount*** 2.6/1.0)					
Softening temperature (ball and ring method), K	319	319	319	321	322
Penetration at 298 K, $m\cdot10^{-4}$ (0.1 mm)	71	71	68	66	59
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	90	87	83	75
CICR13 (catalyst amount*** 3.9/1.5)					
Softening temperature (ball and ring method), K	319	319	319	320	321
Penetration at 298 K, $m\cdot10^{-4}$ (0.1 mm)	71	71	71	69	66
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	91	89	87	83
CICR14 (catalyst amount*** 5.2/2.0)					
Softening temperature (ball and ring method), K	319	319	319	320	320
Penetration at 298 K, $m\cdot10^{-4}$ (0.1 mm)	71	71	71	69	67
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	91	89	87	84
CICR15 (catalyst amount*** 6.6/2.5)					
Softening temperature by ball and ring, K	319	319	319	320	321
Penetration at 298 K, $m\cdot10^{-4}$ (0,1 mm)	71	71	71	67	64
Ductility at temperature 298 K, $m\cdot10^{-2}$ (cm)	91	91	89	85	80
CICR2 (catalyst amount*** 7.9/3.0)					
Softening temperature by ball and ring, 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
CICR16 (catalyst amount*** 9.2/3.5)					
Softening temperature by ball and ring, K	319	319	319	321	322
Penetration at 298 K, $m\cdot10^{-4}$ (0,1mm)	71	71	69	65	57
Ductility at 298 K, $m\cdot10^{-2}$ (cm)	91	90	86	83	75

* Conditions of mixing bitumen with resin: temperature is 463 K; time is 60 min.; modified Reynolds criterion is 109500.
** Pure, unmodified bitumen (characteristics are given in Subsection 2.1).
*** Relative to resin-forming components (coumarone, indene, carbazole) / NCIF + carbazole.

Table 7. The effect of the catalyst amount on the adhesive properties of the resin

Qualitative indicator of modified bitumen	Content of resin in modified bitumen*, % wt.				
	0.0**	0.5	1.0	2.0	3.0
1	2	3	4	5	6
CICR11 (catalyst amount*** 1.3/0.5)					
Adhesion of modified bitumen to a glass surface, %	39	40	46	52	63
Adhesion of modified bitumen to a crushed stone surface, point	2.5	2.5	2.5	3.0	3.5
CICR12 (catalyst amount*** 2.6/1.0)					
Adhesion of modified bitumen to a glass surface, %	39	44	52	62	74
Adhesion of modified bitumen to a crushed stone surface, point	2.5	2.5	3.0	3.5	4.0
CICR13 (catalyst amount*** 3.9/1.5)					
Adhesion of modified bitumen to a glass surface, %	39	43	56	68	81
Adhesion of modified bitumen to a crushed stone surface, point	2.5	2.5	3.0	3.5	4.5
CICR14 (catalyst amount*** 5.2/2.0)					
Adhesion of modified bitumen to a glass surface, %	39	50	74	79	93
Adhesion of modified bitumen to a crushed stone surface, point	2.5	2.5	4.0	4.5	5.0
CICR15 (catalyst amount*** 6.6/2.5)					
Adhesion of modified bitumen to a glass surface, %	39	55	85	94	100

Continuation of Table 7

1	2	3	4	5	6
Adhesion of modified bitumen to a crushed stone surface, point	2.5	3.0	5.0	5.0	5.0
CICR2 (catalyst amount*** 7.9/3.0)					
Adhesion of modified bitumen to a glass surface, %	39	58	86	96	100
Adhesion of modified bitumen to a crushed stone surface, point	2.5	3.5	5.0	5.0	5.0
CICR16 (catalyst amount*** 9.2/3.5)					
Adhesion of modified bitumen to a glass surface, %	39	61	88	98	100
Adhesion of modified bitumen to a crushed stone surface, point	2.5	3.5	5.0	5.0	5.0

* Conditions of mixing bitumen with resin: temperature is 463 K; time is 60 min.; modified Reynolds criterion is 109500.
** Pure, unmodified bitumen (characteristics are given in Subsection 2.1).
*** Relative to resin-forming components (coumarone, indene, carbazole) / NCIF + carbazole.

Thus, the optimal amount of catalyst in the reaction medium can be considered in the range of 6.6/2.5–7.9/3.0 wt.% (relative to resin-forming components (coumarone, indene, carbazole) / NCIF + carbazole). Further increase in the $TiCl_4$ amount is impractical, given the slight changes in the quality of the modified bitumen.

4. Conclusions

The results of experimental studies allow us to draw the following conclusions:

– the optimal catalyst for the synthesis of CICR is $TiCl_4$;

– when using $TiCl_4$ as a catalyst, the qualitative and quantitative characteristics of the synthesized CICR improved compared to the use of H_2SO_4 and $AlCl_3$; the yield of CICR is 36.7 wt.% relative to raw materials, and the softening temperature is 341 K;

– an increase in the $TiCl_4$ amount from 0.5 to 2.5 wt.% leads to a rapid increase in the CICR yield and with the catalyst amount above 2.5 wt.% the yield increases slightly;

– the optimum amount of $TiCl_4$ catalyst in the reaction medium was found to be 6.6/2.5-7.9/3.0 wt.% (relative to resin-forming components (coumarone, indene, carbazole) / NCIF + carbazole). Further increase in the catalyst amount is impractical, given the minor changes in the qualitative indicators of the resin-modified bitumen;

– the use of $TiCl_4$ as a catalyst in the above-mentioned optimal amount allows obtaining CICR, which has the most positive effect on the quality characteristics of bitumen, particularly on its adhesive properties.

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Received: November 03, 2022 / Revised: December 05, 2022 / Accepted: December 20, 2022

ОДЕРЖАННЯ І ЗАСТОСУВАННЯ КУМАРОН-ІНДЕН-КАРБАЗОЛЬНОЇ СМОЛИ ЯК МОДИФІКАТОРА ДОРОЖНІХ НАФТОВИХ БІТУМІВ. 2. ВСТАНОВЛЕННЯ ТИПУ ТА КІЛЬКОСТІ КАТАЛІЗАТОРА

Анотація. *За присутності різних каталізаторів ($TiCl_4$, $AlCl_3$, H_2SO_4) досліджували одержання кумарон-інден-карбазольної смоли (КІКС), що виробляється з рідких продуктів коксування вугілля і надалі застосовується для модифікування бітумів. Вивчено вплив типу каталізатора на вихід та модифікувальні властивості КІКС (зміну термопластичних та адгезійних властивостей бітумів у разі додавання до них отриманих смол). Встановлено вплив кількості каталізатора в реакційному середовищі на синтез смоли та подальше модифікування нею бітумів. Згідно з одержаними результатами вибрано оптимальний тип та кількість каталізатора для отримання КІКС. Також встановлено, що кумарон-інден-карбазольна смола, синтезована з використанням вибраного типу каталізатора і визначеної оптимальної його кількості, максимально позитивно впливає на адгезійні характеристики дорожнього бітуму.*

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