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# PRODUCTION OF INDENE-COUMARONE RESINS AS BITUMEN MODIFIERS

Serhiy Pyshyev[1], Yuriy Grytsenko[1*], Nazar Danyliv[1], Halyna Bilushak[2], Roksolana Pyshyeva[3]

*[1]Institute of Chemistry and Chemical Technology, Lviv Polytecnic National University, St. Bandery 12, 79013 Lviv, Ukraine ; [2]Institute of Applied Mathematics and Fundamental Sciences, Lviv Polytecnic National University, St. Bandery 12, 79013 Lviv, Ukraine; [3]Institute of Computer Science and Information Technologies, Lviv Polytecnic National Universit, St. Bandery 12, 79013 Lviv, Ukraine*
*[*]Corresponding author. E-mail address: grytsenko.yura@ukr.net (Yuriy GRYTSENKO)*

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**Abstract**

It has been proved that indene-coumarone resins (ICR) should be used for the road bitumen modification. Kinetic regularities of ICR production have been investigated. The experimental statistical mathematical (ESM) model of the process has been developed. The optimum conditions of ICR production have been determined on its basis providing resins high yield and softening temperature. The efficiencies of kinetic and ESM models have been compared. Bitumen was produced on the basis of ICR obtained under optimum conditions. It was modified by polymers with good adhesive properties.

***Keywords:*** indene-coumarone resin; optimum conditions; bitumen; modifier; kinetic model; experimental statistical model.

## 1. Introduction

Petroleum bitumen is one of the most widely used binding materials in the road and industrial building, as well as for the production of roofing and insulating materials. Its part in the refineries output achieves 10 %, and road bitumen is the most demanded one. Thus, cost price of road binding materials produced at the refineries and their sale price considerably affect the performance characteristics of the enterprise on the whole. In connection with all above-mentioned a great number of scientific researches are dedicated to the problem of road bitumen modification and improvement of its production method [1-4].

On the other hand, modern roadways are overloaded by motor transport. As a result it is necessary to use bitumen modified by polymers (BMP), especially while building upper layers of roadway coverings [5]. However, the usage of bitumen additives which improve its elastic, low-temperature and adhesive properties is limited by high cost of bitumen modifiers. The average price of road bitumen is 500-600$/ton [7-8] and price of the modified bitumen is 1300-1600$/ton [6]. Considering modifier maximum amount of 5 % in the mixture with bitumen and taking into account above-mentioned prices, the price of modifiers would be 15000-18000 $. Therefore the search of new cheaper materials capable to improve bitumen operational characteristics is very urgent problem.

One of the reasons of bitumen modification by polymers is its low adhesive properties. Indene-coumarone resins (ICR) may improve them [9-10]. Our scientific investigations [11] confirm that while using this modifier the significant improvement of adhesive properties is observed for the road oxidized petroleum bitumen.

Indene-coumarone fraction (ICF) which is called "heavy" benzene is the main raw material used for ICR production. ICF is obtained during the processing of coking volatile products, namely distillation of gasoline fractions ("crude" benzene). Its amount is only 0.1 wt % relative to the initial coal [12]. Whereas the typical capacity of world by-product-coke plants is 1.2 billion tons per year [13], the annual amount of ICF may be at least 1200 thousands tons.

According to the present information the ICR production is reduced (is suspended in Ukraine), because the main consumer – varnish and paint industry – turns to cheaper and more effective thickening and film-forming agents. Taking into account the above-mentioned and the fact that average price of ICR (600-850$/ton [14]) is at the level of road bitumen we may assert the urgency of these resins application for BMP. Moreover, such approach will favor qualified utilization of waste products produced at by-product-coke plants.

A lot of ICR production methods, chemism and mechanism of their obtaining in the presence of acidic catalysts are described in the literature [15-16]. While copolymerization of ICF taken from JSC "Yasynovsky by-product-coke plant" (Ukraine) the titanium tetrachloride exhibits high activity and efficiency as a catalyst [11]. Therefore we used this substance for our experiments.

It is known [17] that commercial ICR differ by their softening temperatures ($T_s$). It is logically to use resins with high $T_s$ with the aim of the modifier amount decrease and achievement of necessary softening temperature for BMP. However it is unknown how softening temperature of indene-coumarone resins affects the adhesive properties of the modified bitumen. Moreover, the analysis of scientific researches and patents demonstrates the absence of clear recommendations concerning the dependence between copolymerization parameters and initial ICF characteristics that allow to obtain ICR with definite softening temperature.

Therefore the aims of our studies were:

- to examine the effect of ICR softening temperature on the adhesive properties of bitumen modified by them;
- to develop experimental statistical mathematical and kinetic models describing the effect of ICF copolymerization parameters on resin yield and $T_s$;
- to establish the conditions under which ICR with certain $T_s$ is obtained, to synthesize the resin and to confirm its modifying ability using typical oxidized bitumen.

## 2. Experimental

### 2.1 Initial materials

To obtain ICR we used indene-coumarone fraction taken from JSC "Yasynovsky by-product-coke plant" (Ukraine). Its characteristic is given in Table 1.

Table 1 Fractional composition of indene-coumarone fraction

| Indexes | Values | Standard |
|---|---|---|
| Distillation (°C): | | |
| Beginning temperature of boiling | 125 | GOST 2177-82 |
| 10 % distilled at the temperature | 137 | |
| 20 % distilled at the temperature | 141 | |
| 30 % distilled at the temperature | 143 | |
| 40 % distilled at the temperature | 145 | |
| 50 % distilled at the temperature | 149 | |
| 60 % distilled at the temperature | 153 | |
| 70 % distilled at the temperature | 158 | |
| 80 % distilled at the temperature | 170 | |
| 90 % distilled at the temperature | 180 | |
| 95 % distilled at the temperature | 195 | |
| End temperature of boiling | 210 | |
| Bromine number (g $Br_2$/100 g product) | 56,24 | GOST 8997-89 |
| Content of unsaturated compounds (wt.%)[1] | 48,51 | |

[1] *Average molecular mass of unsaturated compounds present in ICF was equal to 138*

For ICR production we used narrow indene-coumarone fraction boiled within 140–190°C. Its characteristics are given in Table 2. The characteristics of obtained ICR are represented in the Section «Results and Discussion» (except resins described in Table 4).

One can see from the experimental results that using narrower fraction (140-190°C in this case) we may increase the content of unsaturated compounds in the raw material in 1.3 times and thus ICR with higher softening temperature is produced [18].

Table 2 Characteristics of indene-coumarone fraction boiled within 140-190°C

| Indexes | Values | Procedure |
|---|---|---|
| Distillation (°C): | | |
| Beginning temperature of boiling | 139 | GOST 2177-82 |
| 10 % distilled at the temperature | 140 | |
| 20 % distilled at the temperature | 140 | |
| 30 % distilled at the temperature | 141 | |
| 40 % distilled at the temperature | 142 | |
| 50 % distilled at the temperature | 146 | |
| 60 % distilled at the temperature | 150 | |
| 70 % distilled at the temperature | 155 | |
| 80 % distilled at the temperature | 160 | |
| 90 % distilled at the temperature | 168 | |
| 95 % distilled at the temperature | 180 | |
| End temperature of boiling | 205 | |
| Bromine number (g $Br_2$/100 g product) | 74,12 | GOST 8997-89 |
| Content of unsaturated compounds (wt.%)[1] | 63,47 | |

*[1] Average molecular mass of unsaturated compounds present in the fraction boiled within 140-190°C was equal to 138*

To obtain BMP we used road petroleum bitumen BND 60/90, the characteristic of which is given in Table 3. Bitumen meets the requirements of standards excluding residual penetration value.

Table 3 Characteristic of road petroleum bitumen BND 60/90

| Index | Actual value | Standard according to DSTU 4044-2001 (EN 12591-1999) | Procedure |
|---|---|---|---|
| 1 Penetration at 25 $^{O}$C (m×$10^{-4}$) | 62 | 61 to 90 | GOST 11501-78 |
| 2 Softening temperature (ring&ball method) ($^{O}$C) | 47 | 47 to 53 | GOST 11506-73 |
| 3 Ductility (m×$10^{-2}$) | - | - | GOST 11505-75 |
| 3.1 at 0 $^{O}$C | 6 | ≥ 3 | |
| 3.2 at 25 $^{O}$C | 75 | ≥ 55 | |
| 4 Change of properties after heating: | - | - | - |
| 4.1 Change of weight after heating (wt.%) | 0.2 | ≤ 0.8 | GOST 18180 supplement according to point 8.3 DSTU 4044-2001 |
| 4.2 Residual penetration (%) | 50 | ≥ 60 | GOST 11501 supplement according to point 8.4 DSTU 4044-2001 |
| 4.3 Change of softening temperature ($^{O}$C) | 4 | ≤ 6.0 | GOST 11506 supplement according to point 8.5 DSTU 4044-2001 |
| 5 Brittleness temperature ($^{O}$C) | - | ≤ -12 | GOST 11507-78 |
| 6 Flash point determined in open firepot ($^{O}$C) | 235 | ≥ 230 | GOST 4333-87 |
| 7 Adhesion to glass (%) | 46 | Non standardize | DSTU B V.2.7 – 81 supplement according to point 8.6 DSTU 4044-2001 |
| 8 Low-temperature adhesion (%) | 38 | Non standardize | Equation (1) |
| 9 Mass part of paraffins (wt.%) | 3.4 | Non standardize | GOST 17789 |
| 10 Solubility in organic solvents (%) | 99.9 | ≥ 99.00 | GOST 20739-75 |
| 11 Penetration index | -1.0 | -2.0 ÷+1.0 | DSTU 4044-2001 |

## 2.2. Procedure of ICR synthesis

The raw material was pretreated via drying and removing pyridine bases using 72% sulfuric acid. Such procedure allows to decrease catalyst amount and increase ICR yield and softening temperature. Then the ready raw material was loaded into a reactor and set the reaction conditions (time, temperature, catalyst amount). Polymerization was carried out under stirring. The obtained product was washed by water till the reaction became neutral. Unreacted material was distilled from ICR under vacuum. Copolymerization product yield was determined by weighing raw material and ICR.

## 2.3. Procedure of BMP preparation

Definite amount of bitumen was heated to the set temperature, then a modifier was added and stirring was switched on (Re = 1200). The modification was carried out for 1 hr. Polymer amount was determined by the experiments taking into account that necessary softening temperature of BMP should be 52-54°C (according to DSTU B V.2.7-135:2007 for bitumen modified by polymers, grade BMP 60/90-52 it must be not less than 52°C).

## 2.4. Determination of adhesive properties at low temperatures

Bitumen adhesive properties may vary at the decrease of ambient temperature. There is a series of methods to determine bitumen adhesion at low temperatures. But they are complicated and laborious. We developed relatively simple procedure which allows to obtain reproducible results characterizing dependence of BMP adhesive properties on ambient temperature.

The essence of our method is to determine bitumen adhesive properties while adhesion to glass (DSTU B V.2.7–81-98) after several freezing-unfreezing cycles. The freezing was carried out at -15°C, unfreezing – at +25°C for 12 hrs. Adhesion to glass was determined after samples were taken off the refrigerator. The investigation scheme was as follows:

- preparation of necessary numbers of samples;
- determination of adhesive properties of the initial samples;
- determination of adhesive properties after one freezing-unfreezing cycle;
- determination of adhesive properties after four freezing-unfreezing cycles;
- determination of adhesive properties after four freezing-unfreezing cycles followed by sustaining at -15°C for 4 days;

The value of low-temperature adhesion was calculated according to the formula, %:

$$A_{-15} = \frac{1}{2}\left(\frac{A_1 + A_2 + A_3}{3} + A_4\right), \qquad (1)$$

where $A_{-15}$ – low-temperature adhesion (adhesion to glass at – 15 °C), %; $A_1$ – initial value of adhesion to glass, %; $A_2$ – adhesion to glass after one cycle, %; $A_3$ – adhesion to glass after four cycles, %; $A_4$ – adhesion to glass after four cycles and four days of sustaining, %.

## 3. Results and discussion

To evaluate the effect of resin indexes (softening temperature, namely) on the adhesive properties of road bitumen we prepared a series of BMP samples with the softening temperature of 52-54°C. The results are represented in Table 4.

Table 4 Dependence of BMP adhesive properties on ICR softening temperature

| Bitumen content (wt.%) | ICR content (wt.%) | Softening temperature accord. to ring and ball method (R&B) ($^{O}$C) | Adhesion to glass (%) | Low-temperature adhesion (%) |
|---|---|---|---|---|
| 88.0 | 12.0 | 97 | 77 | 70 |
| 91.9 | 8.1 | 120 | 85 | 74 |
| 92.7 | 7.3 | 128 | 100 | 97 |
| 93.3 | 6.7 | 135 | 100 | 98 |
| 93.6 | 6.4 | 140 | 100 | 100 |
| 95.0 | 5.0 | 185 | 100 | 100 |

The obtained results allow to assert that the increase in polymerization degree (softening temperature) of the resins increases BMP adhesion including that at low temperatures. To prepare BMP with good adhesive properties it is necessary to use ICR with the softening temperature higher than 130-140°C.

Taking into account the data from Table 4 and experimental results from Table 5 we developed the experimental statistical model of ICF polymerization in order to determine the process conditions under which the maximum amount of IRC with $T_s \geq 130^0C$ may be obtained. The resin yield and softening temperature according to R&B method were the main efficiency indexes of ICR obtaining (response functions). While describing the model we used the following symbols for the response functions and main parameters: $Y_1$ – softening temperature according to R&B method, °C; $Y_2$ – resin yield, mass %; $X_1$ – catalyst concentration, mass %; $X_2$ – temperature, °C; $X_3$ – time, min.

Table 5 Experimental data, calculated values of response functions, and relative errors

| № | $X_1$ (wt.%) | $X_2$ (°C) | $X_3$ (min) | $Y_1$ R&B (°C) | $Y_1^{regr}$ R&B (°C) | $Y_2$ (wt.%) | $Y_2^{regr}$ (wt.%) | Relative errors | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $\varepsilon_1$ | $\varepsilon_2$ |
| 1 | 1 | 20 | 40 | 93 | 94.41 | 13.60 | 12.45 | 0.0152 | 0.0846 |
| 2 | 3 | 20 | 40 | 135 | 133.25 | 29.27 | 28.045 | 0.013 | 0.0419 |
| 3 | 1 | 60 | 40 | 96 | 98.20 | 18.37 | 18.308 | 0.023 | 0.0034 |
| 4 | 3 | 60 | 40 | 110 | 104.39 | 45.50 | 43.511 | 0.051 | 0.0437 |
| 5 | 1 | 20 | 120 | 93 | 97.23 | 9.41 | 9.2912 | 0.0455 | 0.0126 |
| 6 | 3 | 20 | 120 | 144 | 138.97 | 32.08 | 32.868 | 0.0349 | 0.0246 |
| 7 | 1 | 60 | 120 | 97 | 101.57 | 12.62 | 15.279 | 0.0471 | 0.2107 |
| 8 | 3 | 60 | 120 | 114 | 110.66 | 45.34 | 48.464 | 0.0293 | 0.0689 |
| 9 | 2 | 40 | 120 | 120 | 113.87 | 39.3 | 36.456 | 0.0511 | 0.0724 |
| 10 | 2 | 40 | 180 | 115 | 113.51 | 38.00 | 36.875 | 0.013 | 0.0296 |
| 11 | 2 | 40 | 60 | 110 | 111.00 | 32.12 | 35.82 | 0.0091 | 0.1152 |
| 12 | 1 | 40 | 80 | 115 | 102.58 | 17.2 | 15.872 | 0.108 | 0.0772 |
| 13 | 3 | 40 | 80 | 120 | 126.55 | 41.96 | 40.262 | 0.0545 | 0.0405 |
| 14 | 2 | 20 | 80 | 110 | 114.44 | 24.70 | 28.701 | 0.0404 | 0.162 |
| 15 | 2 | 60 | 80 | 100 | 102.18 | 43.16 | 39.428 | 0.0218 | 0.0865 |
| 16 | 3 | 20 | 5 | 126 | 128.94 | 26.23 | 25.813 | 0.0233 | 0.0159 |
| 17 | 3 | 20 | 20 | 138 | 130.92 | 29.45 | 26.779 | 0.0513 | 0.0907 |
| 18 | 3 | 20 | 80 | 136 | 136.83 | 29.71 | 30.504 | 0.0061 | 0.0267 |
| 19 | 3 | 40 | 5 | 114 | 118.40 | 31.85 | 35.51 | 0.0386 | 0.1149 |
| 20 | 3 | 40 | 20 | 120 | 120.43 | 34.97 | 36.488 | 0.0036 | 0.0434 |
| 21 | 3 | 40 | 40 | 124 | 122.83 | 39.20 | 37.77 | 0.0094 | 0.0365 |
| 22 | 3 | 40 | 120 | 120 | 128.82 | 43.11 | 42.657 | 0.0735 | 0.0105 |
| Mean relative error of approximation ($\varepsilon$) | | | | | | | | 0.0347 | 0.0642 |

For the response functions we developed different dependencies on the process conditions and chose the ones that showed the best correlation with the experimental data (non-linear quadratic ones).

$$Y_1 = 69.56467 + 3.20788 \cdot X_1^2 - 0.00851 \cdot X_2^2 - 0.00042 \cdot X_3^2 - 0.34622 \cdot X_1 \cdot X_2 + 0.01167 \cdot X_1 \cdot X_3 - 0.00011 \cdot X_2 \cdot X_3 + 11.14530 \cdot X_1 + 1.02535 \cdot X_2 + 0.10877 \cdot X_3 \quad (2)$$

$$Y_2 = -23.6817 - 8.0209 \cdot X_1^2 - 0.0050 \cdot X_2^2 - 0.00001 \cdot X_3^2 + 0.1164 \cdot X_1 \cdot X_2 + 0.0480 \cdot X_1 \cdot X_3 - 0.00001 \cdot X_2 \cdot X_3 + 35.8373 \cdot X_1 + 0.4396 \cdot X_2 - 0.0763 \cdot X_3 \quad (3)$$

To estimate the adequacy of the obtained regression equations, we substituted the given experimental parameters ($X_1$–$X_3$) and found the expected (regressive) values of response functions ($Y_{ij}^{reg}$), which are represented in Table 5.

The estimation of model adequacy is conducted using the following parameters: the mean relative error of approximation ($\varepsilon_i$); the coefficient of determination ($R_i^2$); Fisher criterion ($F_i$), and criterion of statistics ($F_{r_i}$).

The value of mean relative error of approximation was calculated by the formula (4):

$$\varepsilon_i = \frac{1}{n}\sum_{j=1}^{n}\left|\frac{Y_{ij} - Y_{ij}^{reg}}{Y_{ij}}\right| \tag{4}$$

where $n$ is the amount of sampling (number of experiments); $Y_{ij}$ – values observed during the experiments; $Y_{ij}^{reg}$ – values of response functions calculated using the regression equations; $i$ is response function number, and $j$ is experiment number.

To check the adequacy of multiple-factor regressive model we used Fisher criterion. It was calculated by the formula:

$$F = \frac{S_{reg_i}^2}{S_{res_i}^2} \tag{5}$$

where $S_{reg_i}^2$ is dispersion of experimental response functions relative to their mean values and $S_{res_i}^2$ is residual dispersion of response functions.

$$S_{res_i}^2 = \frac{1}{n-1}\sum_{j=1}^{n}(Y_{ij} - \overline{Y}_i)^2 \tag{6}$$

where $\overline{Y}_i$ is average experimental value of response function.

$$S_{res_i}^2 = \frac{1}{n-m_i}\sum_{j=1}^{n}(Y_{ij}^{reg} - Y_{ij})^2 \tag{7}$$

where $m_i$ is number of coefficients in the regression equation.

In accordance with the mentioned calculations Fisher criterion should be greater than the table value at the significance level $\alpha$ and numbers of freeness ($n$-1) and ($n$ – $m_i$). In such a case it means the quantitative change of results scattering relative to the line of obtained regression equation compared with scattering relative to the mean value [19].

The coefficient of determination $R_i$ characterizing the significance of response functions dependence on the process parameters ranges from 0 to 1. It was determined using the standard procedures [20].

The criterion of statistics ($F_{r_i}$), which is a measure of statistic significance $R_i^2$, was calculated by the following formula [21]:

$$F_{r_i} = \frac{n-k_i-1}{k_i}\cdot\frac{R_i^2}{1-R_i^2}; \tag{8}$$

where $k_i$ is the number of regression equation coefficients without free term.

The calculated value $F_{r_i}$ was compared with the critical value $F_{r_{cri}}$ determined according to the tables at the level of significance $\alpha$ and numbers of freeness $k_i$ and ($n$ – $k_i$ – 1). If $F_{r_i} > F_{r_{cri}}$, then the regression is statistically significant.

Checking the adequacy of equations (2-3) we established the following regularities. The main part of $\Delta Y_{ij} = Y_{ij}^{regr} - Y_{ij}$ residues, depicted in histograms and probit-graphs (Figs. 1-4) is located around zero indicating the first essential characteristics of the resulting equations adequacy.

The mean relative approximation error is lower than 10 % ($\varepsilon_1$ = 0.0347 (3.47 %), $\varepsilon_2$ = 0.0642 (6.42 %)). Therefore, according to [21] we may certify the high compliance with the experimental data.

The calculated values of Fisher criterion are: $F_1$ = 4.73; $F_2$ =13.57. In accordance with the table of Fisher criterion values [22] at the level of significance α = 0.05 the critical values are: $F_{1cr}$ = $F_{2cr}$ = $F$(0.05; 21; 12) = 2.5. They are lower than the calculated values and this fact also confirms the model adequacy.

The values of the coefficient of determination are: $R_1^2$ = 0.9377, $R_2^2$ = 0.9787. Therefore, 93.77 %, 97.87 % changes in response functions ($Y_1$, $Y_2$,) are determined by the selected factors of the process control ($X_1$–$X_3$). The fact that they are close to 1, indicates the presence of "strong" bond between $Y_1$, $Y_2$, and process parameters ($X_1$–$X_3$).

The calculated values of the criterion of statistics are: $F_{r_1}$ = 9.71, $F_{r2}$ =30.33. In accordance with the table of Fisher criterion values at the level of significance $\alpha = 0.05$ the critical values are: $F_{rcr_1} = F_{rcr2} = F(0.05;\ 9;\ 12) = 4.6$. This indicates the statistical significance of the determination coefficients $R_i^2$ ($F_{rcr_i} < F_{r_i}$).

All above-mentioned data confirm the model adequacy, statistical significance of the results and connection between the response functions and selected parameters of the process control.

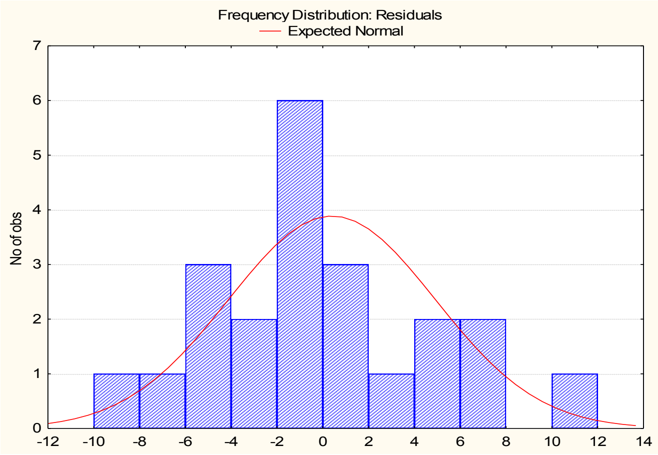

Fig. 1. Histogram of $\Delta Y_1$ residues

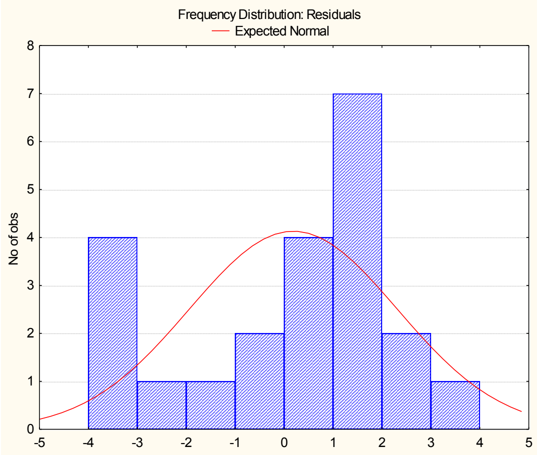

Fig. 2. Histogram of $\Delta Y_2$ residues

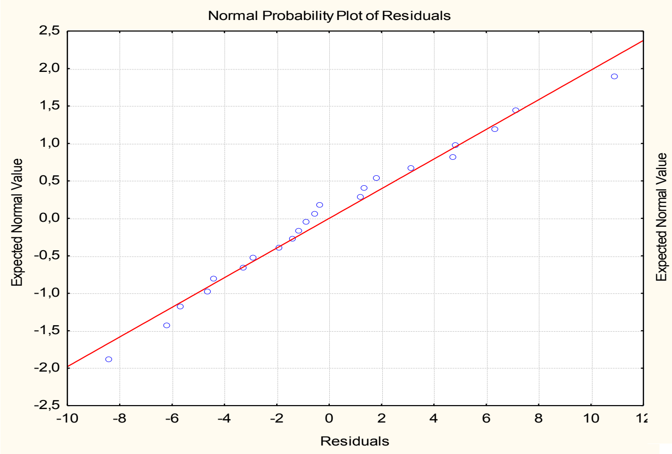

Fig. 3 Probit-graph of $\Delta Y_1$ residues

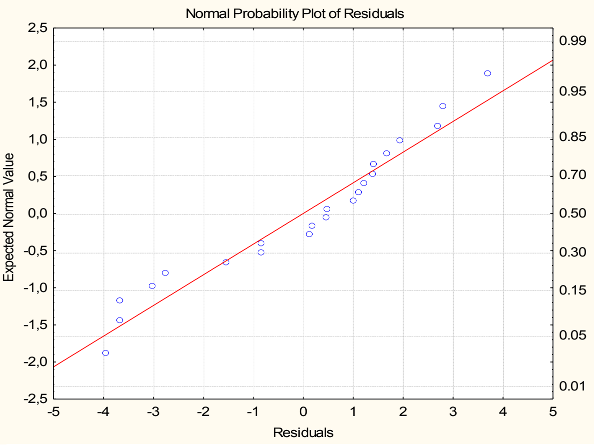

Fig. 4 Probit-graph of $\Delta Y_2$ residues

To establish the kinetic regularities of ICR obtaining reactions in the presence of $TiCl_4$ we studied the effect of time on the yield and softening temperature at 20, 40 and 60°C (catalyst concentration is 3 mass %). The results are represented in Figs. 5 and 6.

The increase in time leads to the increase in polymerization rate and resin yield. However the softening temperature of the obtained resin decreases with the increase in temperature. The reason is the shift of exothermal reaction equilibrium toward the initial products (copolymers with low molecular mass are formed).

It should be noted that the results represented in Figs. 5 and 6 allow to assert that ICR is produced in three stages: polymerization beginning and formation of basic part of resin (5 min.), growth of polymeric chain (5-40 min.) and process end (at polymerization time above 40 min. the reactions do not occur because the ICR yield and softening temperature are the same).

Such stages of the process are often observed while studying kinetic regulations of the polymerization process [23-24]: at the first stage the main reactions of monomers conversion into oligomers take place and the reaction rate sharply increases; at the second stage the stationary state is observed, where polymerization rate is practically constant; at the third stage the reactions attenuation occurs due to the decrease in the initial monomer amount. On the other hand, such stages are more characteristic for the initiated polymerization of the monomer which proceeds according to the radical-chain mechanism.

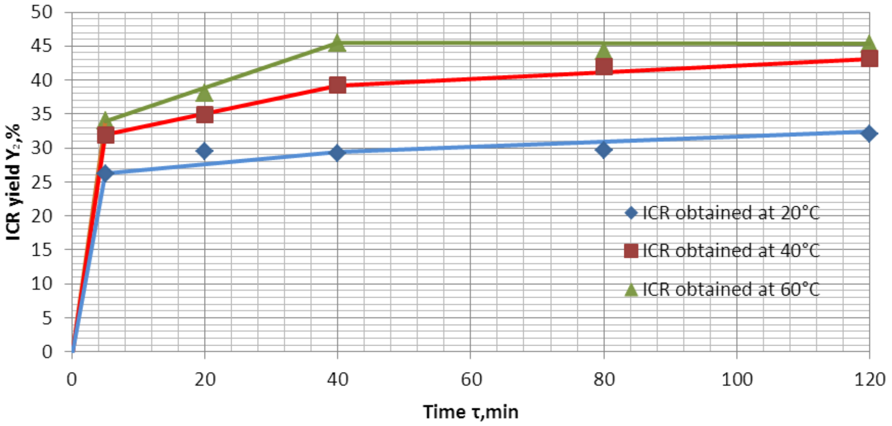

Fig.5 Effect of time on ICR yield

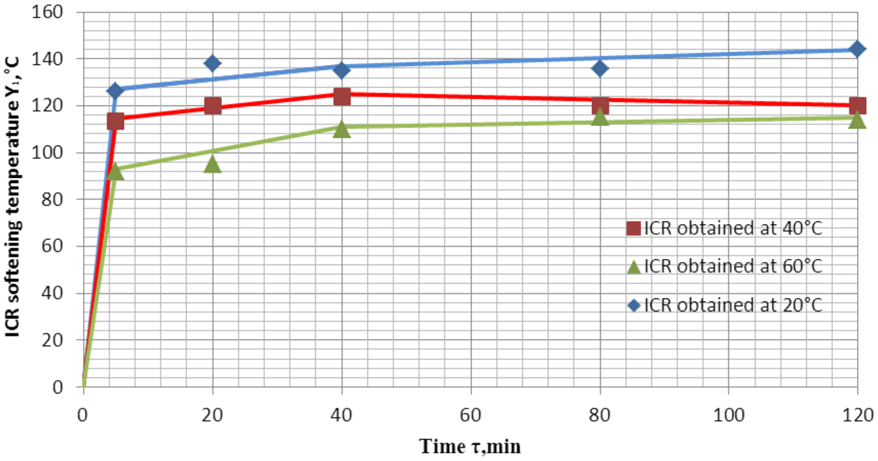

Fig. 6 Effect of time on ICR softening temperature

It also should be noted that the rate of indene polymerization which proceeds according to the carb-cation mechanism is 1,5-2 times higher than that of styrene and considerably higher than that of coumarone [15]. Moreover, the increase in polymerization degree (resin softening temperature increases) leads to the increase in its bromine number: for ICR with $T_s$ 120, 125 and 133 the bromine numbers are 21,18, 24,98 and 25,99, respectively. It means that more compounds with two double bonds participate in the resin formation with the increase in reaction time. That is why in our case the stage wise (Figs. 5 and 6) is explained by different rates of monomers polymerization.

Taking into account that ICR with necessary $T_s$ (130-140°C) may be obtained at the approximate time of 40 min., the results were treated on the basis of dependencies of the process second stage (5-40 min.).

The polymerization reactions of individual components and mixtures are described by the equations of the first, second and fractional orders [23-28]. The conversion [29], the ratio between initial and current concentration of the polymer [23], epoxy number [25], the logarithm of the inverse value to the initial monomer current concentration [27] may be accepted as the index characterizing the reaction rate (raw material conversion degree). As a measure of the reaction rate we took dimensionless value equal to the part of unconverted compounds of the raw material. It was calculated according to the formula (8):

$$C = 1 - \frac{Y_2}{100} \qquad (8)$$

where $Y_2$ - ICR yield, %.

To determine the order of the oligomerization reaction of the fraction 140-190$^0$C the kinetic dependencies were plotted for the first (Fig. 7) and second (Fig. 8) order reactions on the basis of data from Fig. 5.

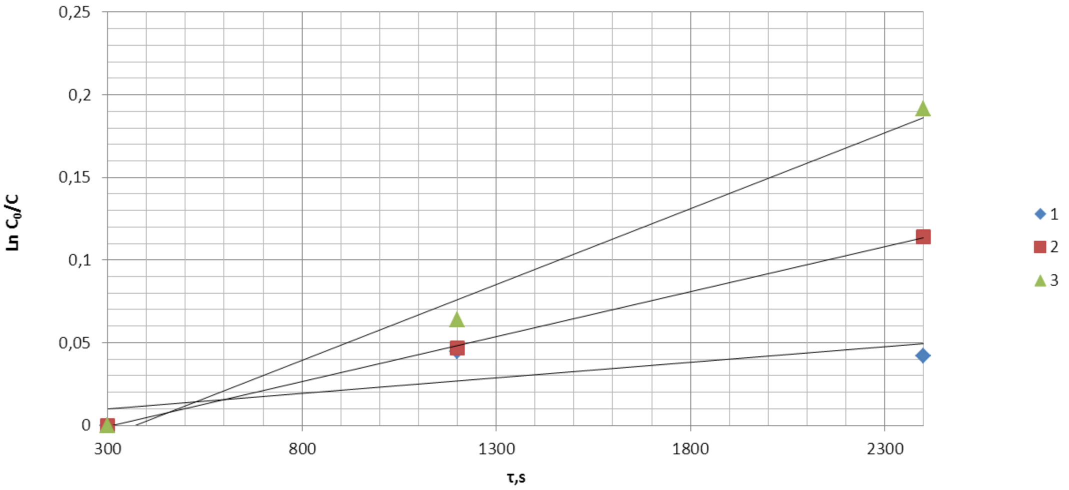

Fig. 7 Kinetic curves of polymerization process of the fraction 140-190$^o$C for the first order reaction (1 – 20°C , 2 – 40°C, 3 – 60°C).

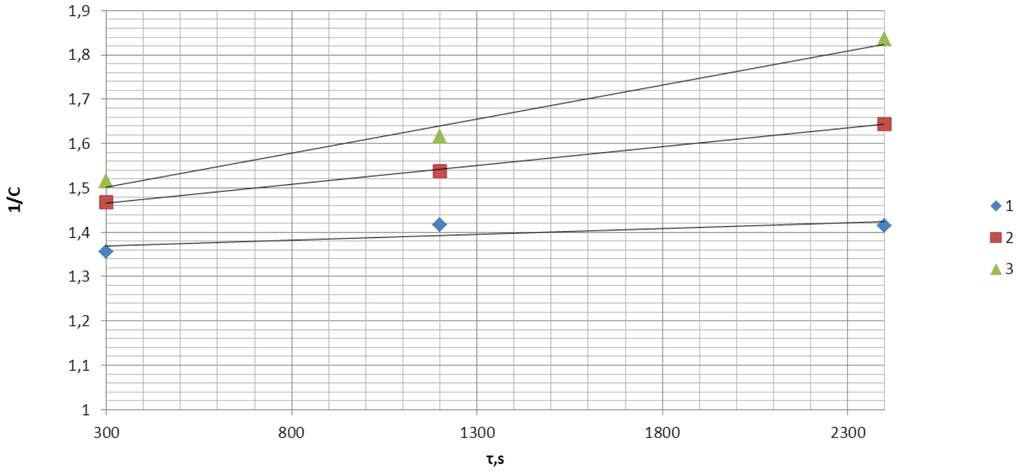

Fig. 8 Kinetic curves of polymerization process of the fraction 140-190$^o$C for the second order reaction (1 – 20°C , 2 – 40°C, 3 – 60°C).

Kinetic dependencies represented in Fig. 8 have more straightforward character, hence we may assert that the most of the oligomerization process reactions proceed by the second order.

On the basis of data from Fig. 8 and Arrhenius equation we calculated the effective activation energy (equation (9)) and preexponent factor (equation (10)) within various temperature ranges and time interval of 300 – 2400 s.

$$E = \frac{R.\ln(k_{i+1}/k_i).10^{-3}}{1/T_i - 1/T_{i+1}} \qquad (9)$$

$$k_0 = e^{\frac{ln.T_i k_i - T_{i+1}.ln k_{i+1}}{T_i - T_{i+1}}} \qquad (10)$$

where R = 8.314 J/(mol·K) – universal gas constant; $k_i$, $k_{i+1}$ – effective rate constants at the corresponding temperatures $T_i$ and $T_{i+1}$, which are equal to the slope angle (Fig. 8)

The results are represented in Table 6.

Table 6 Calculation of the kinetic parameters according to Arrhenius equation (method No.1)

| Temperature range (°C) | 20-40 | 40-60 |
|---|---|---|
| k ($s^{-1}$) | $2{,}74\times10^{-5}$;$8{,}38\times10^{-5}$ | $8{,}44\times10^{-5}$;$1{,}52\times10^{-5}$ |
| E (kJ $mol^{-1}$) | 42.52 | 25.48 |
| $k_0$ ($s^{-1}$) | 1053 | 1.52 |

Taking into account that

$$k = \frac{1/C - 1/C_0}{\tau - \tau_0} \qquad (11)$$

On the basis of Arrhenius equation and equation (8) we suggest the general view of ICR yield vs. process temperature and time.

$$Y_2 = 100.\frac{100}{\frac{1}{C_0} + k_0.(\tau - \tau_0).e^{\frac{-E}{RT}}} \qquad (12)$$

where $C_0$ - initial value of the part of unconverted compounds in the raw material at the initial time ($\tau_0$).

If we know values of E, $k_0$, $C_0$ and $\tau_0$ within the temperature range of 20 – 40°C and 40 – 60°C for the polymerization reactions of the fraction 140-190°C in the presence of 3 mass % $TiCl_4$ the equation (12) takes a view:

$$Y_2^{20-40} = 100 - \frac{100}{1.41 + 1053.(\tau - 300)e^{\frac{-5116}{T}}} \qquad (13)$$

$$Y_2^{40-60} = 100 - \frac{100}{1.49 + 1.52.(\tau - 300)e^{\frac{-3066}{T}}} \qquad (14)$$

It is well-known that dependence of the reaction rate on temperature within narrow temperature range is described by Van't Hoff empiric rule: while changing temperature by 10 degree the rate of most chemical reactions is changed in 2-4 times. The mathematical view of Van't Hoff rule is:

$$v_{T_2} = v_{T_1}.\gamma^{\frac{T_2 - T_1}{10}} \qquad (15)$$

where $V_{T_1}$ , $V_{T_2}$ , - rates of the chemical reactions at $T_1$ and $T_2$;

γ - temperature coefficient (Van't Hoff coefficient).

The dependence between the temperature coefficient and activation energy is as the following:

$$ln\,\gamma_T = \frac{10.E}{R.T^2} \qquad (16)$$

Thus, in the basis of data from Fig. 5 and equations (15) and (16) we calculated the effective activation energy of the polymerization process of the fraction 140-190°C in the presence of 3 mass % $TiCl_4$ within the temperature ranges of 20 – 40°C and 40 – 60°C.

At the same time the reaction rate was calculated as the ratio between changes in resin yield and time. Thus, using equations (15) and (16) we determined the activation energy according to the method No.2. The results are represented in Table 7.

Table 7Calculation of kinetic parameters according to Van't Hoff rule (method No.2)

| Temperature range (°C) | 20-40 | 40-60 |
|---|---|---|
| Reaction rate ($v_T$) | 0.0867; 0.2100 | 0.2100; 0.3282 |
| Temperature coefficient ($\gamma_T$) | 1.5564 | 1.2503 |
| E (kJ $mol^{-1}$) | 33.76 | 19.37 |

Thus, the effective activation energies of oligomerization process of the fraction 140-190°C in the presence of 3 mass % $TiCl_4$ are 19.37-42.52 kJ/mol within the temperature range of 20-60°C and time interval of 5–40 min. These values correlate with the value of cationic polymerization activation energy that does not exceed 85 kJ/mol. [30].

On the basis of regression equations (2) and (3) we established the process optimum conditions (temperature – $37^0$C, time – 40 min., catalyst concentration – 3.3 mass%) using the uniform search method of response functions. Such conditions should ensure ICR maximum yield at $T_p \geq 130^0$C. The characteristic of the obtained resin and its comparison with the characteristic predicted by experimental statistical (equations (2) and (3)) and kinetic (equation (13) models are represented in Table 7.

$$\vartheta_T = \frac{dY_2}{d\tau} \qquad (17)$$

So, the resin yield predicted by ESM is closer to the experimental value than that predicted by kinetic model (Table 8). Moreover, using ESM we may predict the yield and softening temperature of ICR depending on all three factors of the process and taking into account their mutual influence on the system.

Table 8 Predicted and experimental indexes of ICR obtained under the optimum conditions

| Index | Values | | |
|---|---|---|---|
| | Experimental | Predicted according to (2), (3) | Predicted according to (13) |
| Resin yield, $Y_2$ (wt.%) | 33.30 | 33.69 | 35.64 |
| Softening temperature ($^0$C) | 135 | 130 | – |

Based on ICR obtained under the optimum conditions and BND 60/90 bitumen (vide Table 3) we prepared bitumen modified by polymers (BMP). Its characteristic is given in Table 9.

Table 9 Properties of BMP prepared on the basis of ICR obtained under the optimum conditions

| Bitumen content (wt.%) | ICR content (wt.%) | Softening temperature (by R&B method) ($^0$C) | Adhesion to glass (%) | Low-temperature adhesion (%) |
|---|---|---|---|---|
| 93.3 | 6.7 | 52 | 100 | 97 |

Using ICR to produce BMP permits to improve the adhesion properties of bitumen (including that at low temperatures) and increase its softening temperature.

## 4. Conclusions

1. The procedure for evaluating the adhesive properties of the road bitumen at low temperatures has been developed.
2. To prepare BMP with good adhesive properties it is necessary to use ICR with the softening temperature of 130-140°C.
3. Adequate experimental statistical models have been developed for ICR obtained via oligomerization of the fraction 140-190°C, which is produced during processing coal coking volatile products.
4. Based on ESM the optimum conditions of the process have been determined: temperature 37°C, time 40 min., and catalyst ($TiCl_4$) concentration 3,3 wt.%. Such conditions ensure maximum ICR yield and softening temperature ≥ 130°C.
5. The effective activation energies of oligomerization process of the fraction 140-190°C in the presence of 3 wt.% $TiCl_4$ are 19,37-42,52 kJ $mol^{-1}$ within the temperature range of 20-60°C and time interval of 5–40 min.

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