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*R.O. Subtelnyy, D.B. Kichura, B.O. Dzinyak***SYNTHESIS OF PETROLEUM RESINS IN THE PRESENCE OF ALIPHATIC AMINOPEROXIDES****Lviv Polytechnic National University, Lviv, Ukraine**

Synthesis of petroleum resins in the presence of aliphatic N-substituted aminoperoxides of general formula $C(CH_3)_3-O-O-CH_2-N-R_1R_2$ was investigated in this communication. The effects of reaction temperature (393–493 K), reaction time (240–480 min) and aminoperoxide concentration (0.032–0.096 mol/l) on the yield and characteristics of the petroleum resins were studied. The correlation index (0.85–0.92, absolute value) for the pair «yield–bromine number» confirmed that the oligomerization reaction proceeded on monomer's unsaturated bonds. It was found that the obtained resins were mainly styrene-cyclopentadiene cooligomers. Depending on the initiator used, they contained 38.8–40.41% styrene and 31.1–33.04% cyclopentadiene. The analysis of the experimental results demonstrated that the most significant effect (correlation index of 0.75–0.88) on the yield of petroleum resins had the reaction temperature. Compared with thermal oligomerization (without initiator), the use of aminoperoxides allowed increasing the product yield (453 K, 360 min, 0.064 mol/l) by 4.6–18.3%. The yield of petroleum resins did not correlate with the reaction time. Blending the obtained resins with petroleum bitumen increased the composition stability in aggressive environments.

Keywords: C9 fraction, petroleum resin, initiator, styrene, aminoperoxide, oligomerization.

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Introduction

A significant number of liquid by-products (about 35%) are produced in the process of ethylene synthesis by diesel fuel pyrolysis. The following pyrolysis fractions are used as raw materials for oligomers (petroleum resins) production [1,2]:

- C4 fraction containing olefins to produce polybutene resins;
- C5 fraction containing linear and cyclic olefins to produce aliphatic resins (aliphatic petroleum resins);
- C9 (C8/C9) fraction contains unsaturated aromatics (styrenes and indenenes) to produce aromatic oligomers.

Aromatic oligomers are also known as petroleum resins or hydrocarbon resins [3,4]. Due to their excellent performance characteristics, these products are applied in various industries as substitutes for products of natural origin such as oils, rosin and albumin as film-forming agents in lacquer paint and

anticorrosive coatings [4,5] and bitumen modification [6,7].

The petroleum resins can be obtained by ionic, radical initiated, and radical thermal oligomerization methods. Ion oligomerization is carried out at low temperatures. Its disadvantage is a high color index and an additional technological energy-consuming stage of the catalyst separation from the reaction mixture. Oligomerization using peroxide initiators is widely used in the industry. It allows obtaining oligomers (petroleum resins) with a high yield and good properties. The petroleum resins are separated by distillation from a solution of unpolymerized fraction components. The aromatic petroleum resins obtained based on the C9 fraction mainly consist of styrene-cyclopentadiene cooligomers [2,4].

Catalytic oligomerization was investigated using bentonite clay [8] and aluminum chloride [9]. The main disadvantage of catalytic oligomerization is the high color ratio and the need to separate the heterogeneous catalyst.

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It was proposed to use the low-temperature emulsion oligomerization of unsaturated hydrocarbons of C9 fraction of diesel pyrolysis liquid by-products [10,11]. It produces light hydrocarbon resins, but the dicyclopentadiene in fraction C9 is not involved in the reaction.

In several previous works [4,12,13], highly thermostable initiators were used to initiate the C5 and C9 hydrocarbon fractions oligomerization.

The polymerization process temperature has an essential influence on the stage of initiation of the macroradical and the termination of the polymer chain. As the polymerization temperature increases, the polymerization rate increases, but at the same time, the molecular weight decreases, and the color of the cooligomer deteriorates [2,4].

Aminoperoxides, due to low decomposition temperature, allow initiation of the process at low temperatures, so their usage should enable the production of cooligomers with higher molecular weight and better color index. The search for effective initiators of the process providing the high yield of the target product and improving performance characteristics of petroleum resins production is an urgent problem. The relationship between the oligomerization parameters of the C9 fraction and the characteristics of hydrocarbon resins have been determined in this work. This will optimize the production of hydrocarbon resins and reduce their cost.

Experimental

Hydrocarbon fraction C9 of diesel pyrolysis liquid by-products was used as a raw material for the petroleum resins production. It has the following characteristics: density of 915 kg/m³; bromine number of 115 g Br₂/100 g; molecular weight of 102; content of unsaturated compounds of up to 45%, including 17.85% styrene, 6.99% vinyltoluene, 18.00% dicyclopentadiene and 1.25% indene.

Oligomerization of unsaturated hydrocarbons of fraction C9 was carried out in thermostatic stainless steel ampoules (100 ml). The raw material (fraction C9) in the amount of 50 ml was mixed with the

calculated amount of initiator and loaded into pre-purged inert gas ampoules. After that, the ampoules were sealed, placed in a thermostat, and oligomerization was performed at the desired temperature. Unreacted hydrocarbons were removed by atmospheric distillation (pressure of 0.11 MPa and temperature of 423 K); high-boiling hydrocarbons and liquid oligomers were separated using vacuum distillation (pressure of 3 hPa and temperature of 453 K). In this case, the petroleum resins were obtained with a softening temperature in the range of 347–354 K.

The yield of the hydrocarbon resin was determined by recalculating for the C9 fraction. The bromide-bromate method allowed determining the unsaturation (bromine number) of hydrocarbon resins. Molecular weight was determined by the cryoscopy method involving a benzene solvent. The coloration of hydrocarbon resin was determined visually by comparing the coloration of 10% of the solution in benzene to the reference iodometric scale. The softening temperature was determined according to the «ring and ball» method.

Aminoperoxides of general formula C(CH₃)₃-O-O-CH₂-N-R₁R₂ (Fig. 1) were obtained by condensation of the respective primary and secondary aliphatic amines with tert-butylperoxymethanol (oxymethyl tert-butylperoxide) when cooled to 268–263 K [14].

The thermodynamic properties of the synthesized aminoperoxides were investigated using the methods of thermogravimetry (TG) and differential thermal analysis (DTA). Studies of the thermal stability of aminoperoxides were performed on a derivatograph «Derivatograph-1500 D» (Paulik-Paulik-Erday system). Heating rate was 0.6 K/min, and sample weight was 200 mg. Calcined alumina was used as a standard. Heating was performed up to 523 K. Sensitivity on the scale of thermogravimetry was up to 200 mg, and sensitivity on the scale of differential thermal analysis was 100 μV.

Studies of water and chemical resistance were performed by studying a two-component mixture of

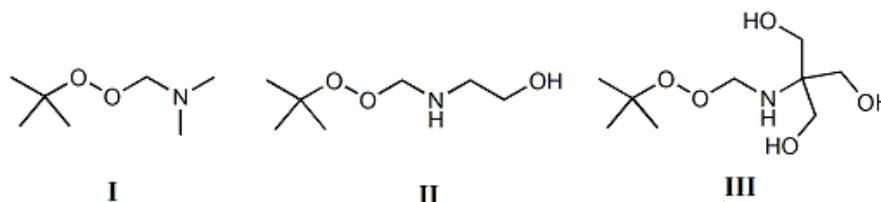


Fig. 1. The structures of N-substituted aliphatic aminoperoxides. I – N-*tert*-butylperoxymethylene-N,N-dimethylamine (active oxygen 10.88%); II – N-*tert*-butylperoxymethylene-1-amino-2-hydroxyethane (active oxygen 9.81%); and III – 2-(*tert*-butylperoxymethylamino)-2-hydroxymethyl-1,3-propanediol (active oxygen 7.17%)

bitumen: petroleum resin (10:1) in neutral and aggressive environments. The coatings were formed on glass plates pre-weighed on analytical balances to the nearest 0.0002 g. These operations were performed before the establishment of sorption equilibrium. Then the samples were dried to constant weight in a vacuum thermostat. The studies were carried out in distilled water and 10% aqueous solutions of hydrochloric acid and potassium hydroxide.

Results and discussion

Analysis of TG and DTA curves shows (Fig. 2) that the decomposition of the test compounds I and II occurs via two stages and is accompanied by the appearance of a pronounced exothermic effect on the DTA curve. Using the DTA curve, the thermal effects that accompany the thermal decomposition of the substance were determined. Based on the TG curve data, the kinetic parameters of its destruction at individual stages were established.

The kinetic characteristics of thermolysis were found according to the TG curve based on the least-squares method.

I – thermolysis occurs in 2 stages. Stage 1: 309–366 K, weight loss is 64.45%, $k_{ef}=1.6 \cdot 10^{-2}$, activation energy is 50 kJ/mol, preexponential factor is $8.9 \cdot 10^5$; stage 2: 367–405 K, weight loss is 29.55%,

$k_{ef}=2.2 \cdot 10^{-2}$, activation energy is 29 kJ/mol, preexponential factor is $1.9 \cdot 10^2$.

II – thermolysis occurs in 2 stages. Stage 1: 315–371 K, weight loss is 33.15%, $k_{ef}=0.9 \cdot 10^{-2}$, activation energy is 60 kJ/mol, preexponential factor is $1.2 \cdot 10^7$; stage 2: 372–402 K, weight loss is 48.75%, $k_{ef}=3.4 \cdot 10^{-2}$, activation energy is 74 kJ/mol, preexponential factor is $1.9 \cdot 10^8$.

III – thermolysis occurs in 1 stage. 316–378 K, weight loss is 15.0%, $k_{ef}=0.9 \cdot 10^{-2}$, activation energy is 39 kJ/mol, preexponential factor is $6.6 \cdot 10^3$.

The decomposition of peroxides into free radicals in the feedstock (hydrocarbon fractions) and subsequent free radical reactions with their participation depend significantly on the feedstock composition. In the study of the influence of the nature of medium on the kinetics of decomposition of nitrogen-containing peroxides with a *tert*-alkyl radical, it was found [15] that as the polarity of the medium increases, the rate constants of peroxide decomposition increase accordingly. It was established that the nature of the solvent significantly affects the value of the preexponential factor, which varies widely.

The investigated raw material for oligomerization (fraction C9) contains mainly non-polar solvents (benzene, allylbenzene,

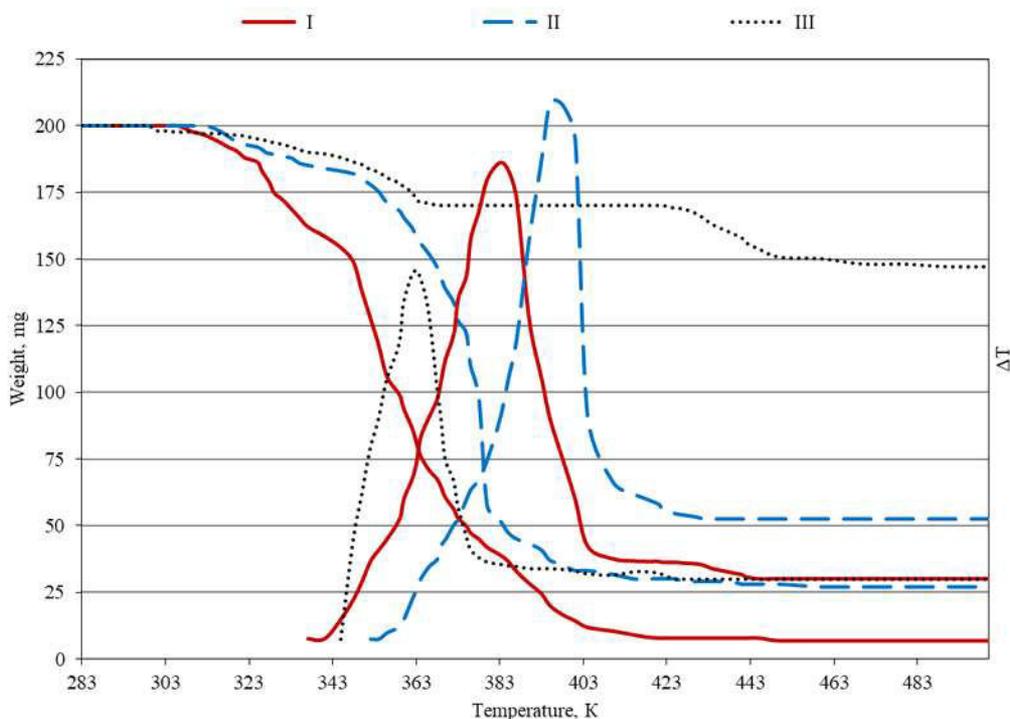


Fig. 2. Curves of thermogravimetry and differential thermal analysis of aliphatic aminoperoxides under study

trimethylbenzenes, etc.). We consider it acceptable to use the results obtained on the kinetics of decomposition of aminoperoxide initiators in further studies.

Aminoperoxide-initiated oligomerization of the C9 hydrocarbon fraction was investigated under following conditions:

- the reaction temperature of 393–493 K;
- the reaction time of 240–480 min;
- the initiator concentration of 0.032–0.064 mol/l (I): 0.032 mol/l – 0.51%; 0.064 mol/l – 1.03%; 0.096 mol/l – 1.54%; (II): 0.032 mol/l – 0.57%; 0.064 mol/l – 1.14%; 0.096 mol/l – 1.71%; (III): 0.032 mol/l – 0.78%; 0.064 mol/l – 1.56%; 0.096 mol/l – 2.34%).

For comparison, thermal oligomerization (without initiator) was performed (Figs. 3–5).

The reaction temperature has the most significant effect (0.75–0.88) on the oligomers yield. An increase in the process temperature from 393 to 453 K positively affects oligomerization. At the

initiator concentration of 0.064 mol/l, such an increase in temperature provides an increase resin yield of 23.1 to 34.5%, 19.2% to 30.0%, and 16.5% to 20.8% for I, II, and III, respectively. A further increase in temperature from 453 to 493 K contributes to a less significant increase in the petroleum resin's yield, and the properties of the resulting product deteriorate. The molecular weight decreases (due to an increase in the share of the breakage stage and chain transfer), and the color index increases from 30 to 60 mg I₂/100 ml (Tables 1–3).

The most effective aminoperoxide that provides the highest product yield is compound I. The effect of aminoperoxide II on the course of the oligomerization process is similar, but II provides a more significant increase in the yield of the cooligomer over the entire temperature range under study. At the concentration of 0.032 mol/l with increasing the temperature from 393 to 413 K, the increase in yield is 3.5 %, and with increasing the temperature from 473 to 493 K the increase in yield

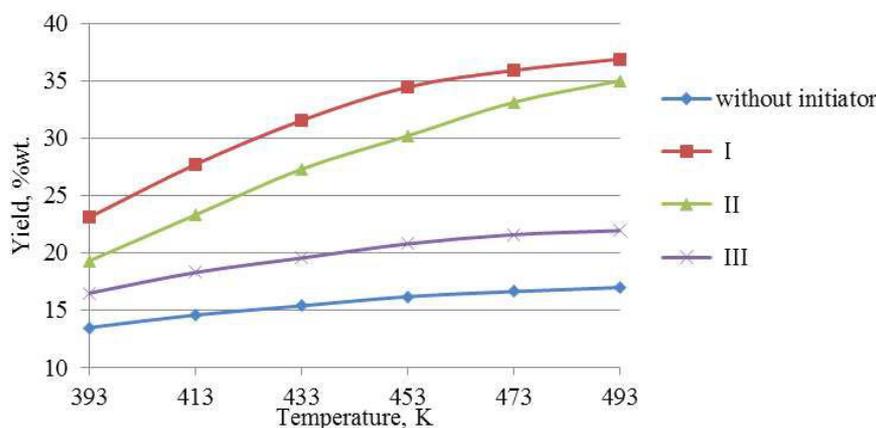


Fig. 3. The effect of reaction temperature on the yield of hydrocarbon resins (reaction time 360 min, initiator concentration 0.032 mol/l)

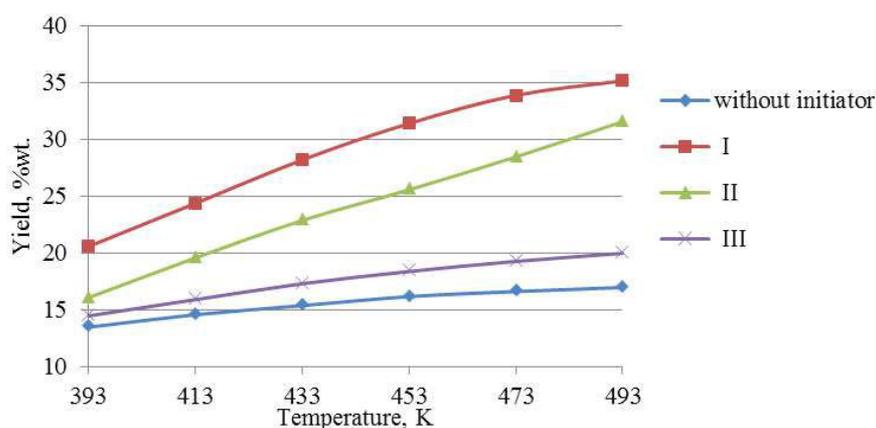


Fig. 4. The effect of reaction temperature on the yield of hydrocarbon resins (reaction time 360 min, initiator concentration 0.064 mol/l)

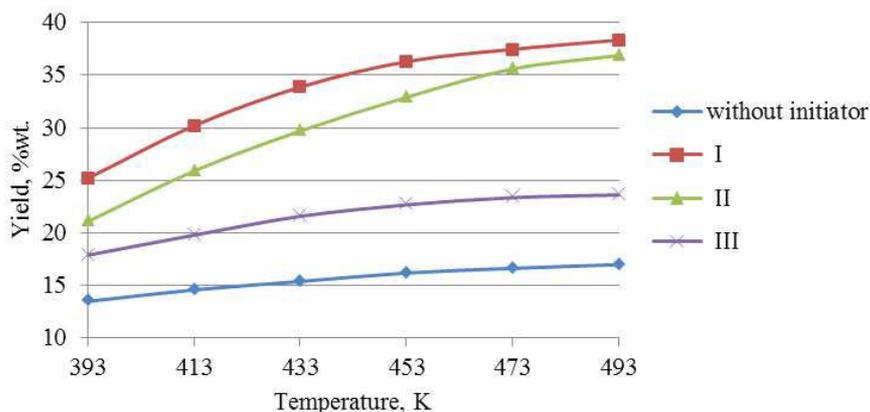


Fig. 5. The effect of reaction temperature on the yield of hydrocarbon resins (reaction time 360 min, initiator concentration 0.096 mol/l)

is 3.15%. This indicates a broader decomposition temperature range of the peroxide compound and lower values of the effective decomposition rate constant and confirms the results of thermolysis kinetic studies. Aminoperoxide III does not give oligomers with a high yield (within 14.5–23.6%). This is due to the thermal stability of III in the range of the studied temperatures. Compared with thermal oligomerization, aminoperoxides allow increasing the product yield (453 K, 0.064 mol/l) by 18.3%, 14.0%, and 4.6% for I, II, and III,

respectively. Characteristics of petroleum resins obtained in the presence of aminoperoxide initiators are shown in Tables 2–4.

The softening temperature of petroleum resins obtained using aminoperoxide I is in the range of 347 to 353 K. A slight increase in the resin color (darkening), more than 40 mg I₂/100 ml is observed when the concentration of I increases to 0.096 mol/l and the oligomerization temperature to 493 K (Table 1). Increasing the oligomerization temperature (from 393 to 493 K) and the initiator concentration (from 0.032

Table 1

Experimental data of the hydrocarbon resins characteristics obtained in the presence of N-tert-butylperoxymethylene-N,N-dimethylamine (I)

Reaction time, min	Reaction temperature, K	Initiator concentration, mol/l	Bromine number, g Br ₂ /100 g	Color index, mg I ₂ /100 ml	Softening point, K	Molecular weight
360	393	0.032	29.6	30	350	665
360		0.064	27.8	30	350	665
360		0.096	26.8	40	349	665
360	433	0.032	26.9	30	351	650
360		0.064	25.2	40	353	645
360		0.096	24.0	40	353	640
360	453	0.032	25.4	30	350	635
360		0.064	23.7	40	353	635
360		0.096	22.7	40	350	635
360	473	0.032	24.0	40	350	635
360		0.064	22.5	40	348	630
360		0.096	21.8	40	349	630
360	493	0.032	23.1	40	347	630
360		0.064	21.9	60	348	630
360		0.096	21.2	60	351	630
240	433	0.064	28.1	30	353	640
480	433	0.064	20.1	40	353	645
Correlation index						
reaction time			-0.49	0.19	0.00	0.06
reaction temperature			-0.76	0.66	-0.29	-0.94
initiator concentration			-0.38	0.45	0.27	-0.07

Table 2

Experimental data of the hydrocarbon resins characteristics obtained in the presence of N-tert-butylperoxymethylene-1-amino-2-hydroxyethane (II)

Reaction time, min	Reaction temperature, K	Initiator concentration, mol/l	Bromine number, g Br ₂ /100 g	Color index, mg I ₂ /100 ml	Softening point, K	Molecular weight
360	393	0.032	29.1	40	351	660
360		0.064	27.8	40	350	655
360		0.096	26.7	60	349	655
360	433	0.032	26.1	40	349	640
360		0.064	25.3	40	353	640
360		0.096	24.3	60	350	640
360	453	0.032	24.8	40	635	635
360		0.064	23.5	60	630	630
360		0.096	22.7	60	630	630
360	473	0.032	23.3	60	351	625
360		0.064	22.4	60	350	620
360		0.096	21.6	60	349	620
360	493	0.032	22.4	60	348	620
360		0.064	21.6	60	351	620
360		0.096	20.9	60	350	615
240	433	0.064	29.2	30	351	625
480	433	0.064	20.7	40	350	640
Correlation index						
reaction time			-0.52	0.15	0.02	0.18
reaction temperature			-0.80	0.62	0.14	-0.95
initiator concentration			-0.28	0.36	0.00	-0.12

to 0.096 mol/l) leads to a decrease in the oligomer molecular weight (from 665 to 630).

Oligomers obtained in the presence of aminoperoxide I exhibit a softening temperature in the range of 348 to 352 K and a color index of 40 to 60 mg I₂/100 ml in the entire range of temperatures and concentrations of the initiator (Table 2). The oligomer's molecular weight is slightly lower than in the case of use of I. It decreases from 660 to 615 with increasing temperature from 393 to 493 K and initiator concentration from 0.032 to 0.096 mol/l. The increase in the process temperature has a more significant effect on the molecular weight. In contrast, the increase in the concentration of aminoperoxide practically does not change the product's molecular weight.

Aminoperoxide III allows obtaining oligomers, which are characterized by a softening temperature in the range of 348 to 353 K and a molecular weight of 640 to 600. There is a characteristic significant increase in the resin's color index (60–80 mg I₂/100 ml) observed at the oligomerization temperatures (473–493 K).

Prolongation of the oligomerization time above 6 hours causes in all cases an increase in the yield of resins and a slight increase in molecular weight. However, it is accompanied by an increase in color.

It should be noted that the duration has a less significant effect on the course of oligomerization than the process temperature and the initiator concentration. For comparison, thermal oligomerization (without initiator) was performed. Experimental data are shown in Table 4.

Achieving the maximum yield of the cooligomer (17.8 wt.%) requires the temperature of 493 K with the reaction time of 8 hours. The cooligomers obtained under such conditions are characterized by a low average molecular weight of 600 and a color index of 40 to 60 mg I₂/100 ml. Hydrocarbon resins obtained by thermal oligomerization than those obtained using aminoperoxides are characterized by a better color index. However, it deteriorates with increasing temperature to 473–493 K and lower molecular weight (635–600).

The yield and physicochemical properties of petroleum resins are interrelated. For example, increasing the molecular weight medium and narrowing the molecular weight distribution cause an increase in the softening temperature of the oligomers. The highest correlation index (0.85–0.92, absolute value) is observed for the yield-bromine number pair. It indicates the course of the oligomerization reaction on monomer's unsaturated

Table 3

Experimental data of the hydrocarbon resins characteristics obtained in the presence of 2-(tert-butylperoxymethylamino)-2-hydroxymethyl-1.3-propanediol (III)

Reaction time, min	Reaction temperature, K	Initiator concentration, mol/l	Bromine number, g Br ₂ /100 g	Color index, mg I ₂ /100 ml	Softening point, K	Molecular weight
360	393	0.032	29.9	40	351	640
360		0.064	29.2	40	351	630
360		0.096	27.7	40	349	630
360	433	0.032	27.4	40	349	625
360		0.064	26.2	40	352	620
360		0.096	25.0	60	350	620
360	453	0.032	26.2	40	348	620
360		0.064	25.1	40	351	615
360		0.096	23.9	60	350	610
360	473	0.032	24.9	60	349	610
360		0.064	23.9	60	350	610
360		0.096	22.9	60	353	605
360	493	0.032	24.0	60	348	605
360		0.064	23.2	80	350	605
360		0.096	22.5	80	350	600
240	433	0.064	28.3	40	349	610
480	433	0.064	23.1	60	350	625
Correlation index						
reaction time			-0.37	0.24	0.11	0.22
reaction temperature			-0.83	0.78	-0.27	-0.91
initiator concentration			-0.38	0.29	0.27	-0.21

Table 4

The hydrocarbon resins characteristics obtained by thermal oligomerization

Reaction time, min	Reaction temperature, K	Bromine number, g Br ₂ /100 g	Color index, mg I ₂ /100 ml	Softening point, K	Molecular weight
240	393	30.1	20	347	635
360		29.3	30	346	630
480		28.8	30	350	635
240	453	26.5	40	347	615
360		25.3	40	353	620
480		24.5	40	347	615
240	473	24.4	40	348	615
360		23.7	40	350	605
480		23.3	60	353	610
240	493	23.3	40	349	605
360		23.0	40	351	605
480		22.5	60	350	600
Correlation index					
reaction time		-0.21	0.41	0.40	-0.09
reaction temperature		-0.97	0.77	0.40	-0.97

bonds. Furthermore, this confirms the actual oligomerization reaction.

According to the chromatographic analysis of the initial fraction C9 and the obtained distillates, the conversion of resin-forming hydrocarbons was

determined. According to these data, the approximate composition of the obtained hydrocarbon resins was established (Table 5). It was found that the obtained resins are mainly styrene-cyclopentadiene cooligomers.

Table 5

The approximate composition of hydrocarbon resins obtained by initiated cooligomerization of fraction C9 in the presence of aminoperoxides

Component	Aminoperoxide		
	I	II	III
Styrene	39.34	38.80	40.41
Allylbenzene	2.09	2.22	2.74
o. m. p-Vinyltoluene	8.32	8.62	7.72
Methylstyrenes	0.40	0.42	0.39
Cyclopentadiene	32.69	33.04	31.10
Inden	3.97	4.12	4.78

Based on the obtained experimental data, the optimal oligomerization conditions have been proposed (Table 6).

Samples of resins are entirely soluble in white spirit. The combination of resin with petroleum bitumen in a ratio of 1:10 increases the softening temperature of the composition relative to the original petroleum bitumen by 6–12 K. In aggressive environments (acidic (10% hydrochloric acid) and alkaline (10% sodium hydroxide) and in neutral,

water), the bitumen:petroleum resins compositions are relatively stable for 30 days (Fig. 6).

Bitumen:petroleum resin composition is characterized by higher stability in the studied media. In alkaline medium and water, the change in mass of the composition is 0.0072% and 0.0080% (30 days) which is 1.94 and 1.96 times less than the change in mass in bitumen (0.0139% and 0.0157%, respectively). In an acidic environment, the bitumen:petroleum resin sample changes its mass 2.83 times less than bitumen.

Conclusions

Our study has confirmed the possibility of obtaining hydrocarbon resins by oligomerization of C9 fraction initiated by N-substituted aminoperoxides. Comparing the methods of obtaining hydrocarbon resins using aminoperoxide initiators and without initiators, it should be noted that the petroleum resin yield and physicochemical properties at lower temperatures (30–50 K) are similar to industrial ones and the products of thermal oligomerization predominate in quality. The synthesized hydrocarbon oligomers meet the requirements for resin oil-based synthetic paint. It

Table 6

Optimal conditions for oligomerization of fraction C9 initiated by aliphatic aminoperoxides

Aminoperoxide	The reaction time, min	The initiator concentration, mol/l	The reaction temperature, K	Yield, wt. %
I	360	0.064	433	31.5
II	360	0.064	453	30.5
III	360	0.096	473	23.4

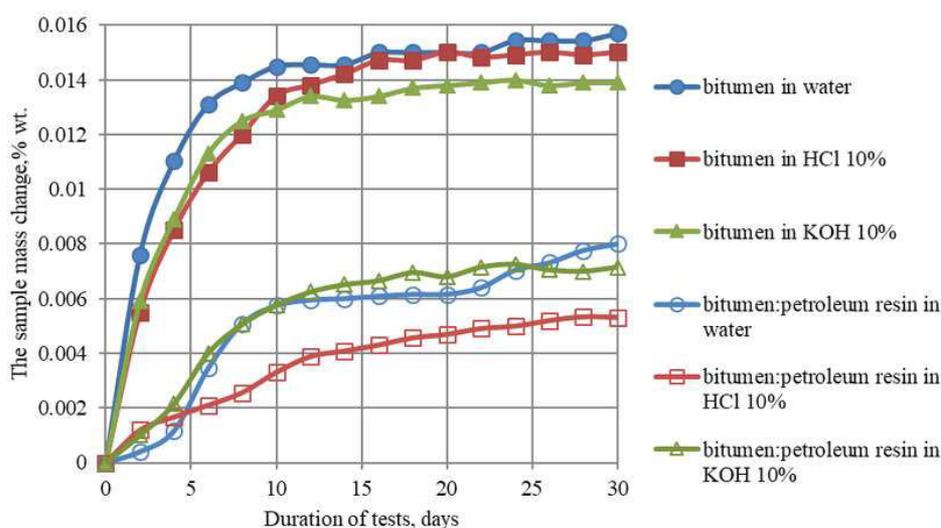


Fig 6. Resistance of bitumen and bitumen:petroleum resin compositions in different media

was established that the product yield depends on all process conditions. There is no single decisive parameter of the process. However, it is possible to identify the parameters that have the most significant impact on the reaction course. The correlation of oligomerization parameters and characteristics of hydrocarbon resins was calculated. It was found that the main factor influencing the yield of hydrocarbon resins is the reaction temperature (correlation index of 0.75–0.88). Specifically, it was established that the yield of petroleum resins does not correlate with the reaction time. In particular, the color of petroleum resins depends on the stage of isolation and drying of the product. Blending the obtained hydrocarbon resins with petroleum bitumen increases the composition stability in aggressive environments. The process conditions provide cooligomerization of hydrocarbon fraction C9 initiated by aminoperoxide I, *N*-*tert*-butylperoxymethylene-*N,N*-dimethylamine, (concentration 0.064 mol/l) at 433 K for 360 min. Under such conditions, the yield of hydrocarbon resin is 31.5%.

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СИНТЕЗ НАФТОПОЛІМЕРНИХ СМОЛ У ПРИСУТНОСТІ АЛІФАТИЧНИХ АМІНОПЕРОКСИДІВ

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В даній роботі досліджено синтез нафтополімерних смол у присутності аліфатичних *N*-замішених амінопероксидів загальної формули $C(CH_3)_3-O-O-CH_2-N-R_1R_2$. Досліджено вплив температури реакції (393–493 K), часу реакції (240–480 хв) та концентрації амінопероксиду (0,032–0,096 моль/л) на вихід і характеристики нафтополімерних смол. Показник кореляції (0,85–0,92 за модулем) пари вихід–бромне число підтверджує перебіг реакції олігомеризації за ненасиченими зв'язками мономерів. Встановлено, що одержані нафтополімерні смоли є в основному стирен-циклопентадієновими коолігомерами. Залежно від використаного ініціатора вони містять 38,8–40,41% стирену і 31,1–33,04% циклопентадієну. На підставі аналізу експериментальних даних встановлено, що найбільш істотний вплив (індекс кореляції 0,75–0,88) на вихід нафтових смол має температура реакції. У порівнянні з термічною олігомеризацією (без ініціатора) ініціювання амінопероксидами дозволяє підвищити вихід продукту (453 K, 360 хв, 0,064 моль/л) на 4,6–18,3%. Вихід нафтополімерних смол не корелює з часом реакції. Змішування одержаних смол з нафтовим бітумом підвищує стійкість складу в агресивних середовищах.

Ключові слова: фракція C9, нафтополімерна смола, ініціатор, стирол, амінопероксид, олігомеризація.

SYNTHESIS OF PETROLEUM RESINS IN THE PRESENCE OF ALIPHATIC AMINOPEROXIDES**R.O. Subtelnyy*, D.B. Kichura, B.O. Dzinyak**

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Synthesis of petroleum resins in the presence of aliphatic N-substituted aminoperoxides of general formula $C(CH_3)_3-O-O-CH_2-N-R_1R_2$ was investigated in this communication. The effects of reaction temperature (393–493 K), reaction time (240–480 min) and aminoperoxide concentration (0.032–0.096 mol/l) on the yield and characteristics of the petroleum resins were studied. The correlation index (0.85–0.92, absolute value) for the pair «yield–bromine number» confirmed that the oligomerization reaction proceeded on monomer's unsaturated bonds. It was found that the obtained resins were mainly styrene-cyclopentadiene cooligomers. Depending on the initiator used, they contained 38.8–40.41% styrene and 31.1–33.04% cyclopentadiene. The analysis of the experimental results demonstrated that the most significant effect (correlation index of 0.75–0.88) on the yield of petroleum resins had the reaction temperature. Compared with thermal oligomerization (without initiator), the use of aminoperoxides allowed increasing the product yield (453 K, 360 min, 0.064 mol/l) by 4.6–18.3%. The yield of petroleum resins did not correlate with the reaction time. Blending the obtained resins with petroleum bitumen increased the composition stability in aggressive environments.

Keywords: C9 fraction; petroleum resin; initiator; styrene; aminoperoxide; oligomerization.

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