Preparation of Oligo (Hexene-1-So-Indenes) and Investigation of Its Products as Additives to Oils

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Abstract**—** *It has been carried out the copolymerization reactions of hexene-1 and indene with participation of* $BF_3{\cdot}O(C_2H_5)_2$ *as the catalyst, the yield, the composition, the structure, the copolymerization constant and the average molecular weight values depending on cooligomerization condition have been determined. It has been shown that a location of links in the prepared cooligomers has a statistic character, but the blocks organized by molecules of hexene-1 may be included. Thermal stability of the synthesized cooligomers of hexene-1-indene has been investigated both individually and in fatty solution and it has been elucidated that an increase of a quantity of indene links in cooligomer composition leads to increase of thermal stability and an increase of the molecular weight decreases a thermal stability. An inclusion of the synthesized cooligomers in composition of M-6 oil as synthetic component increases a viscosity index value and gives it anticorrosion property.*

Keywords**— *hexene-1, indene, viscosity-temperature additives.***

I. INTRODUCTION

Using the oligomer and cooligomer as synthetic component in the composition of the oils one can prepare the oils with high viscosity index [1-3]. Most of the oils intended for surface technique are prepared by this method, so they are mixed with 1-alkene oligomers and cooligomers at various ratios.

The numerous investigations have been carried out in the direction of use of cooligo- and copolymers of 1-alkenes with a number of vinyl monomers and dicyclopentadiene as additives to petroleum oils [4-8]. At the same time a use of hexene-1 as a basic monomer and also its copolymers with indene as viscous additives for oils is also of interest. It was known that an introduction of the aromatic fragments in polymer chain increases their stability to actions, and an introduction of dicyclopentadiene fragments leads to that the prepared macromolecular compounds show anticorrosion and depressor properties in the composition of lubricating oils. The indene molecule combines both aromatic and carbocyclic fragment, therefore it is subjected to cooligomerization with hexene-1.

II. EXPERIMENTAL

For cooligomerization it was used freshly distilled hexene-1 and indene, as the catalyst – $BF_3{\cdot}O(C_2H_5)_2$. The process is carried out methodologically as follows. After addition of the calculated quantity of monomer mixture of hexene-1-indene and hexane or heptane as a solvent to a flask equipped with mixer, thermometer and drop funnel the mixer is activated and the reaction temperature in the flask is created by cooling bath. The catalyst $BF_3{\cdot}OEt_2$ is introduced into the system as a solution through the drop funnel. The catalyst feed rate is adjusted so that the temperature in the flask should not be higher 415K. After the temperature rise, the reaction mass is additionally stirred for 1 h to complete the reaction, so that the reaction should be completed. Then the catalyst complex is decomposed by 2-3% alkaline solution, washed with water-isopropyl alcohol (not to form emulsion) to neutral medium, filtered, the solvent and easy part is distilled, a yield of the prepared oligomer compound, kinematic viscosity and molecular weight value is determined.

The composition and structure of the synthesized compounds have been investigated by methods of IR- and NMR-spectroscopy, elemental analysis (determination of composition on carbon) and fractional composition. The IR-spectra have been taken on Varian 640 IR FTIR spectrometer, Specord M 80 (Carl Zeiss Jena) and Spectroscopy FTIR Nicolet is 10 devices. The NMR-spectra have been taken on the device 300 MHz "Bruker" using CCl_4. For investigation of some points it has been used the device 90 MHz “Perkinq Elmer”.

The thermal analysis of hexene-1-indene cooligomers has been carried out in nitrogen atmosphere in derivatography of OD-102T type (Paulic-Paulic-Erdey system) at temperature of 293÷773K, at dynamic regime by quickly heating for 5K/min. The aluminum oxide was used as a standard and a quantity of the sample was 0.100g, the temperature rise rate was 5 K/min. For each sample DTA, TQA, and DTQ curves were obtained, the thermal or thermal-oxidative destruction of the sample was mainly estimated on the temperature corresponding to the mass loss of 5, 10 and 50% of the TGA and DTA curves.

III. RESULTS AND DISCUSSION

The study of influence of temperature showed that (cooligomerization is carried out in the condition when hexene-1-indene ratio – 0.9:0.1 (mol.p.), a quantity of the catalyst – 0.5%) with its decrease from 313K to 228 K a yield of cooligomer is changed in the range of 95.4÷98.8%, i.e. as the ions are stable at low temperature, a decrease of temperature leads to increase of both yield and molecular weight of the prepared oligomer product, which is the characteristic peculiarity of the ionic polymerization.

In increase of a quantity of the indene from 0.05 mol.p to 0.10 mol.p (temperature 273 K and quantity of the catalyst 0.5%) in the monomer mixture the average molecular weight of the prepared cooligomer is increased from 830 to 1130. Further increase of a quantity of indene (0.20 mol.p.) leads to the decrease of the molecular weight to 950. As the indene is the monomer of the aromatic nature its small quantity facilitates the oligomerization showing positive influence on catalyst activity. In further increase of its quantity along with cooligomerization it can be taken place a dimerization and also alkylation of indene, which leads to the decrease of the average molecular weight of cooligomer (Table 1).

The results of cooligomerization are presented in Table 1.

TABLE 1

CONDITION OF COOLIGOMERIZATION OF HEXENE-1(M_1) WITH INDENE (M_2), YIELD AND SOME INDICES OF COOLIGOMERS

Condition of cooliogomerization			Yield, %	Characteristics of cooligomers	
Temperature, K	M_1:M_2. mol.p.	Quantity of the catalyst, %		Viscosity at 373K, mm^2/s	Average molecular weight
278	0.80:0.20	0.50	88.3	72.5	950
283	0.80:0.20	0.50	82.6	65.1	890
293	0.80:0.20	0.50	65.4	53.5	810
278	0.90:0.10	0.50	98.3	87.3	1180
283	0.90:0.10	0.50	96.8	55.2	1090
283	0.90:0.10	0.35	77.0	82.2	1000
283	0.90:0.10	0.50	97.3	85.6	880
313	0.90:0.10	0.50	95.4	56.5	820
278	0.90:0.10	0.17	58.2	63.7	890
278	0.95:0.05	0.50	84.1	62.6	870
313	0.95:0.05	0.17	52.0	55.7	830
313	0.95:0.05	0.50	75.3	51.8	790

For elucidation of distribution of the monomer links in oligomer chain the copolymerization constants of the investigated pairs of monomer have been determined by Fayneman-Ross method and the following values have been obtained:

for hexene-1	r_1=1.35±0,05
for indene	r_2=0.23±0,01

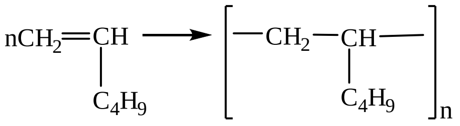
The constant values r_1 and r_2 show that the end carbocations of both alkene and indene are more inclined to connect the molecules of hexene-1, i.e. during cooligomerization it is high a probability of the formation of macromolecules of real cooligomers enriched with hexene-1 links**.** Indeed, the prepared oligomers are enriched with hexene-1 links and there is a possibility of formation of hexene-1 homopolymer. However, it should be noted that the formation of homooligomer of hexene-1 in this system doesn’t show a negative influence on results of the process, as it well dissolves in the petroleum oils. But the indene molecule is inclined to connection to the active center formed from hexene-1, i.e. a probability of being of long-chain blocks, which can be created from indene homooligomer and residue of indene in cooligomer chain in the system is very small.

The composition and structures of the synthesized compounds have been studied by methods of the IR- and NMR-spectroscopy. The absorption bands in the IR-spectrum at 1576, 1588 and 1608 cm^{-1} characterize the aromatic C=C bonds (fig1). The absorption band at 728 cm^{-1} corresponds to 1,2-substituted benzene ring (indene link).

In the NMR-spectrum there are signals characterizing indene links – 2,06; 2,17 and 7,11 mln^{-1} signals correspond to chemical substituent.

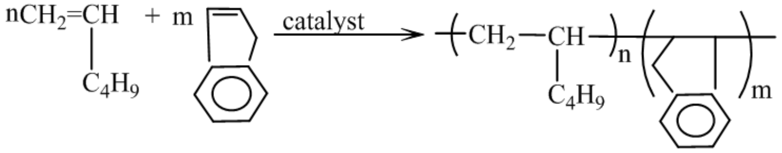
During cooligomerization of hexene-1 with indene the following reactions can be taken place:

1) homooligomerization of hexene-1:



$$nCH_2{=}\underset{C_4H_9}{\underset{|}{CH}} \longrightarrow \left[-CH_2-\underset{C_4H_9}{\underset{|}{CH}}-\right]_n$$

2) cooligomerization of hexene-1 with indene



A location of links in the composition of macromolecules of the prepared cooligomer has mainly a statistic (accidental) character. However, as it is noted, an inclusion of the blocks prepared from hexene-1 molecules in composition of cooligomer macromolecules is possible, and a probability of inclusion of indene fragments in macromolecular chain as blocks is very little and it can be only realized when a ratio of indene:hexene is very high in the monomer mixture.

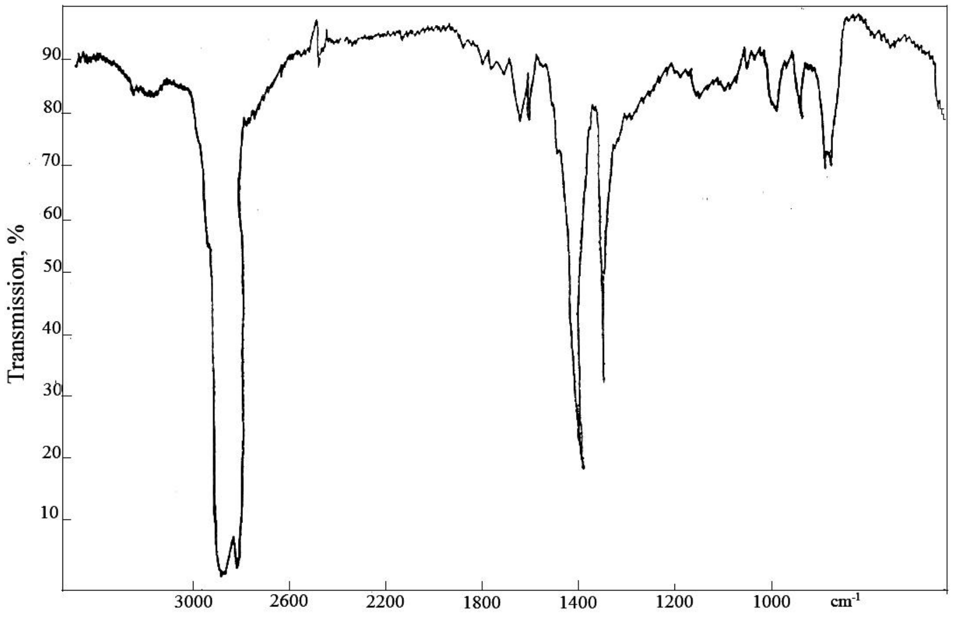


FIGURE 1 – IR-SPECTRUM OF COOLIGOMER OF HEXENE-1 WITH INDENE

The indene molecule combines the aromatic and cyclic fragments and its inclusion in macromolecular chain of hexene-1 increases the thermal stability of the prepared cooligomer. On the other hand, at cooligomerzation there are formed the interactions between aliphatic and aromatic carbons, which are stronger than interactions between aliphatic carbons and the investigation of such cooligomers as additive or component to the oils is of interest.

As the synthesized cooligomers have low molecular weight, they can present the more interesting information about stability to thermal effects individually than their destruction in the oils. Therefore, the thermal stability of the synthesized hexene-1-

indene cooligomers has been investigated by a derivatographic method and the obtained results are presented in Table 2. As is seen from Table, an increase of a quantity of the indene links in the composition of cooligomer leads to the increase of thermal stability, and an increase of the molecular weight (or viscosity) decreases thermal stability.

TABLE 2
RESULTS OF THERMOGRAVIMETRIC ANALYSIS OF HEXENE-1-INDENE BINARY COOLIGOMERS

Indices of cooligomer		Temeprature corresponding to mass loss		
Quantity of indene in cooligomer, mol.p.%	Molecular weight	$T_{5\%}$	$T_{10\%}$	$T_{50\%}$
0	700	463	493	573
0.05	660	480	503	590
0.10	600	493	513	603
0.20	540	490	518	613
0.30	500	495	543	620
0.10	700	483	513	593
0.10	810	475	505	580
0.10	1000	470	500	570

For ex., as a result of increase of a quantity of the indene links in the composition of cooligomer from 0 (oligohexene) to 0.30 mol.p the temperature corresponding to $T_{10\%}$ of mass loss of the sample rises from 493 K to 543 K. When the molecular weight value of cooligomer is increased from 610 to 1000 in the same composition (0.10 mol.p. of indene links), this temperature is decreased from 513 K to 500 K. A positive influence of increase a quantity of the indene links in the composition of cooligomer can be explained by aromatic nature of indene and creation of more stable $C_{aliph.}$- $C_{carboc.}$ bonds in the composition of cooligomer, i.e, the cooligomerization leads to the modification of macromolecule.

An increase of the average molecular weight of cooligomer has been connected with increase of length of macromolecules, as a result not subjecting macromolecules to destruction their intensity of motion is decreased depending on temperature. As a result of destruction the macromolecule is divided into more small-measured analogs and its motion is facilitated. Therefore, the oligomers with low molecular weight are more stable to destructive effects.

Thermal destruction of hexene-1-indene binary cooligomers has been carried out in the oil solutions. This is carried out according to known method; 5% solution of the polymer samples in turbine “L” oil is heated for 12 h at temperature 473 K and after certain time intervals a decrease of value of the initial kinematic viscosity is observed and certain information about destruction is obtained. The prepared results are presented in Fig.2 and 3.

It is seen from Fig.2 that an increase of a quantity of the indene links from 0.05 mol.p. to 0.20 mol.p in the composition of cooligomer increases a stability of concentrated oil to thermal influence, in this time the initial viscosity of the oil is decreased from 3% to 1,2%, and as has been already noted, it is connected with stabilizing effect of the indene links. An increase of the average molecular weight value of hexene-1-indene binary cooligomers from 600 to 1000 leads to the decrease of thermal stability, in this time a viscosity value of the concentrated oil decreases from 2,3% to 3,1% (Fig. 3).

The mechanical destruction solutions of the synthesized cooligomers of hexene-1-indene in the oil have been also studied. For this purpose there have been investigated the solutions of cooligomer samples in I-12 A oil with various composition and molecular weight values by means of device UZDN-1. The obtained results are very close to the results of thermal destruction, i.e. thermomechanical stability is also determined by average molecular weight value and composition of copolymer. However, it should be noted that the mechanical destruction leads to breaking of C-C bond composing the main chain of the viscous additives. Thermal destruction can be referred to all chemical bonds and if destruction occurs in air medium, firstly thermal oxidation of molecule takes place, i.e. the process is more correct to characterize as thermooxidation destruction.

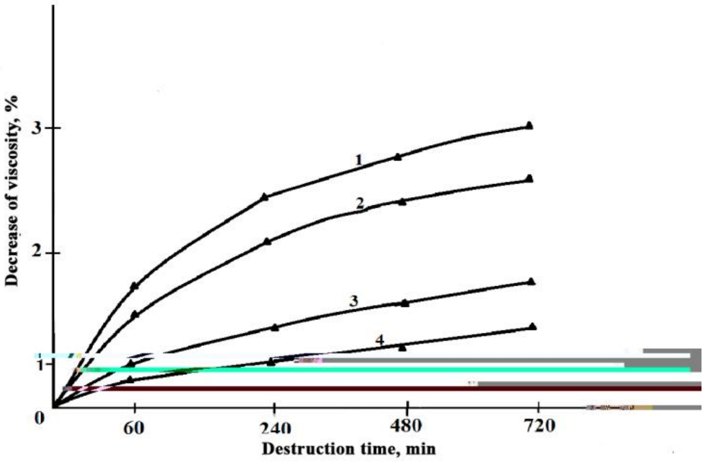


Figure 2 – Dependence of thermal stability of hexene-1-indene cooligomers on quantity of indene links. Quantity of indene links, mol.p.: 0.05 (1), 0.10 (2), 0.15 (3) and 0.20 (4).

The properties of these cooligomers have been compared with results of destruction of viscous additives used for improvement of viscosity-temperature properties of the oils. So, a decrease viscosity during thermal destruction of polyisobutylene of mark KP-10 being industrial additive is 12%, for oligohexene – 9,4%. Thus, the binary cooligomers of hexene-1-indene possess excellent indices from the point of view thermomechanical destruction stability.

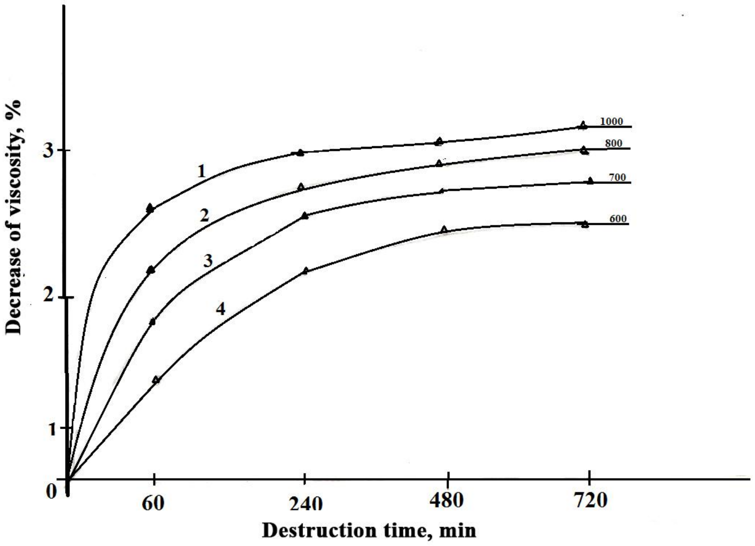


Figure 3 – Dependence of thermal stability of hexene-1-indene cooligomers on quantity of average molecular weight value. Average molecular weight of cooligomer: 1000 (1), 800 (2), 700 (3) və 600 (4).

The binary cooligomers of hexene-1-indene have been investigated as synthetic component in the composition of M-6 oil and the results are obtained in Table 3. As synthetic component it was used the cooligomer with average molecular weight – 1180, and a quantity of indene links – 0.10 mol.p.

Table 3
Influence of hexene-1-indene binary cooligomers on viscosity-temperature properties of M-6 oil.

Quantity of cooligomer in the oil	Kinematic viscosity, mm^2/s		Viscosity index	Corrosion, g/m^2
	373 K-də	313 K-də		
0	5.8	39.40	78	180
5	6.3	42.10	83	150
10	6.5	45.00	83	100
20	7.6	50.30	94	50
30	8.4	59.80	106	10
40	8.8	64.20	108	5
50	9.1	65.40	110	4

As is seen from Table that an increase of concentration of synthetic component in M-6 oil leads to improvement viscosity-temperature properties of the prepared mixture, and for preparation of base oil with kinematic viscosity 8±0,5 mm^2/c at 373 K it is enough to include 20-30% synthetic component in composition of M-6 oil. In this time a viscosity index value of M-6 oil rises from 78 to 94 ÷ 106 (norm – no less 93).

When an increase of viscosity index of M-6 oil by synthetic component in 20-30% concentration is higher, a further increase of concentration has little effect on value of this parameter. At the same time, the investigated cooligomer shows anticorrosion property in the composition of M-6 oil. So, the oxidation products create corrosion. Due to availability of indene links in the composition of the investigated compound it is more stable to oxidation. It has been elucidated that the use of 30% of oligomer in the composition of M-6 oil leads to the decrease of a quantity of precipitate forming as a result of oxidation from 3÷4% to 1,2÷1,3%. Thus, by use of synthetic component in the composition of petroleum oil it is reached an improvement of its viscosity-temperature property and stability to oxidation and anticorrosion.

IV. CONCLUSIONS

It has been carried out the copolymerization reactions of hexene-1 and indene with participation of $BF_3 \cdot O(C_2H_5)_2$ as the catalyst, and the yield, the composition, the structure, the copolymerization constant and the average molecular weight values depending on cooligomerization condition have been determined. The cooligomerization constant values (for hexene-1 – r_1=1.35±0,05, for indene – r_2=0.23±0,01) have been determined at low depth of conversion of comonomers. It has been shown that a location of links in the prepared cooligomer has a statistic character, but the blocks prepared from molecules of hexene-1 may be included.

Thermal stability of the synthesized cooligomers of hexene-1-indene has been investigated both individually and in oil solution and it has been elucidated that an increase of quantity of indene links in cooligomer composition leads to increase of thermal stability, and an increase of molecular weight decreases a thermal stability.

An inclusion of the synthesized cooligomers in a quantity of 20-30% in composition of M-6 oil as synthetic component increases a viscosity index value from 78 to 94÷106 and gives it anticorrosion property.

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