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## Oligomerization of dicyclopentadiene fraction using monosubstituted titanium chloride as a catalyst

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### Abstract

The purpose of this study is to investigate the dicyclopentadiene fraction of liquid pyrolysis product oligomerization with the use of the modified catalytic system based on titanium alkoxides. The choice of reaction catalyst is specified by searching the ways of obtaining petroleum resins with the improved performance characteristics and the possibility of low-temperature polymerization. The use of monosubstituted titanium chloride as a catalyst allows obtaining light resins, films on the base of which are smooth, glossy and have good technical characteristics: adhesion 1 point, resilience <1 mm, impact resistance >10 cm.

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*Keywords:* oligomerization; petroleum resins; dicyclopentadiene fraction.

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### 1. Introduction

Currently, one of the most common ways of obtaining the lower olefins is the pyrolysis of hydrocarbon raw material of different origin. Along with the main products (ethylene, propylene) in the pyrolysis, a large amount of side products (20-40 %) with higher molecular weight are formed. Skilled use of pyrolysis side products is the basic task that can greatly affect the profitability of the main products and also of products of deeper processing.

There are several variants of pyrolysis liquid products (PLP) processing: shallow hydrogenation of unsaturated hydrocarbons with the continued use of hydrogenates as high-octane components of motor fuels, the raw material for benzene, to obtain a broad range of organic products; thermal processing to synthesize the technical carbon;

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polymerization cleaning to obtain the solvents, white spirits and individual aromatic solvents. Also one of the options of PLP processing is the oligomerization to obtain the petroleum resins (PR).

Petroleum resins are prepared from thermal or catalytic polymerization of fraction unsaturated components. Nowadays, catalytic polymerization is more often used, than thermal type<sup>1,2</sup>. Hydrocarbon resins are conventionally produced by adding  $\text{AlCl}_3$ ,  $\text{BF}_3$  or other Friedel-Crafts acids to a particular feedstock<sup>3,4</sup>.

Petroleum polymeric resins are today one of the most promising and cheapest synthetic substitutes of vegetable oils and rosins. These products are widely used in production of synthetic drying oils, oil-resin lacquers, and components of various paint-and-varnish, adhesive, rubber and other formulations<sup>5</sup>.

Powder paint compositions that can form a coating film having high corrosion resistance and excellent appearance even on a metal substrate<sup>6</sup>, antifouling coating compositions<sup>7</sup>, compositions for waterproofing a surface<sup>8</sup> comprise a petroleum resin. Iron oxide red, talk, zinc oxygen are used as pigments.

In the production of EP-300, there is a possibility to realize the process of obtaining the PR by choosing and using the bottom products of the rectification column K-27 as the raw materials base. By changing the column work of higher boiling fractions of PLP, it is possible to obtain the boiler products which are enriched with DCPD<sup>9</sup>.

During the preparation of the fraction for polymerization with distillation the high-molecular compounds, the oxidation products and different antioxidants, which enter the process by the movement of PLP in the technological streams of the process are to be removed. As the result of distillation the DCPD partially or completely decomposes with the formation of the reactive cyclopentadien (CPD).

The presence of CPD in the fraction can be the reason of the low-temperature catalytic process of the polymerization with obtaining modifiable high-unsaturated oligomeric products. According to the distillation regimes and the period of saving, the fraction may have the different content of CPD, which can define its reactivity and create the difficulties in selecting a catalytic system for the polymerization.

Thus, the use of  $\text{TiCl}_4$  as a catalyst of the oligomerization fraction with the high content of active monomer even at low temperatures leads to the rapid gelling and insoluble products obtaining. That is why, in order to control the process the oligomerization DCPC fraction is investigated using the modified catalyst system.

## 2. Experimental

The object of investigation is the fraction PLP EP-300 "Tomskneftekhim" containing more than 50 % of dicyclopentadiene – DCPD fraction.

Oligomerization catalyst systems based on titanium alkoxides and diethylaluminumchloride are used as catalysts for DCPD fraction. The choice of the catalyst is based on its availability and necessity of the oligomerization process control of the highly reactive fraction and possibility to obtain the oligomeric products with a wide range of properties. Monosubstituted titanium chloride was prepared by reacting  $\text{TiCl}_4$  and oxide propylene (OP) or isopropylene alcohol (iso-PA) at a molar ratio of components 1 : 1.

The composition of DCPD fraction prepared for the oligomerization was examined with the method of gas-liquid chromatography (GLC). Method of  $^1\text{H}$  NMR spectroscopy was used to study the oligomerization process, as well as to study the structure of the catalyst.

## 3. Results and discussion

The composition of DCPD is presented in the table 1. Besides the DCPD, other monomers in different quantity, mainly of aromatic character: styrol, vinyl toluenes,  $\alpha$ -methylstyrole, indene and other monomers are included in the hydrocarbon composition systems.

Table 1. The individual composition of the fraction, %

Components	DCPD fraction
CPD	14.5
Benzene	8.5
Toluene	4.8

Ethylbenzene	1.4
p-, m- Xylols	2.0
o- Xylol, Styrol	2.2
$\alpha$ - Methylstyrol	0.8
DCPD	38.4
Indene	16.6
Non-aromatic C <sub>6</sub> -C <sub>8</sub>	5.1
Non-identified aromatic	2.5
Non-identified	3.2
Total	100.0

Reaction of the equimolar interaction of  $\text{TiCl}_4$  and OP, which produces isomeric 2-chlorine-1-propoxy titaniumtrichloride and 1-chlorine-2-propoxy-titantrichloride is shown in Figure 1.

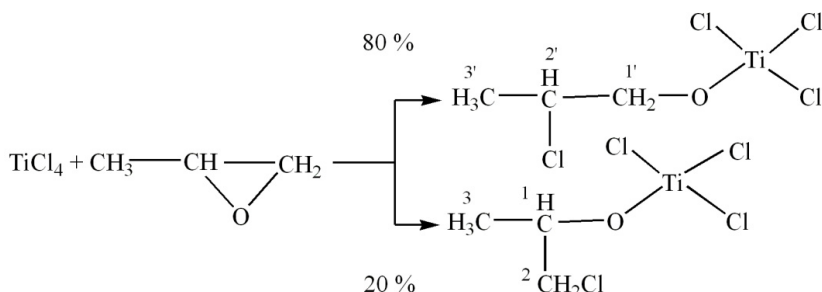


Figure 1. The interaction of  $\text{TiCl}_4$  with OP.

$^1\text{H}$  NMR -spectrum of the reaction products of  $\text{TiCl}_4$  with OP (1 : 1 mol) is a superposition of two systems of protons – of the normal and iso-structure<sup>10</sup>.

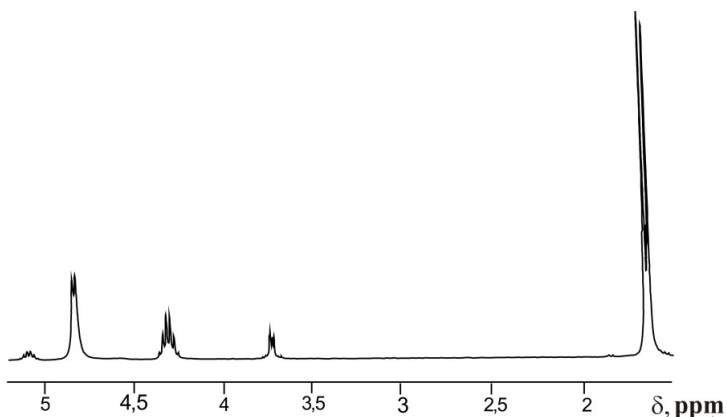


Figure 2.  $^1\text{H}$  NMR - spectra of products of the reaction of  $\text{TiCl}_4$  with OP (1 : 1 mol).

Multiplet of 5.05 ... 5.15 ppm belongs to proton 1 deputy iso-structure, doublet 4.75 ... 4.92 ppm belongs to proton 1 deputy normal structure. Multiplet 4.2 ... 4.4 ppm belongs to proton 2 deputy normal structure, doublet 3.7 ... 3.8 ppm belongs to proton 2 deputy iso-structure. Illegal multiplet 1.5 ... 1.8 ppm belongs to methyl protons of the both substituents. The possible stereoisomer linked with non-central atom of carbon in spectrums is not seen, there is no resolution of the instrument.

For the calculation of the ratio of isomeric substituents, spectra of the products interaction of OP with  $\text{TiCl}_4$  in the ratio 1 : 1, 2 : 1, 3 : 1 and 4 : 1 (mol) after 6 hours of the reaction are used.

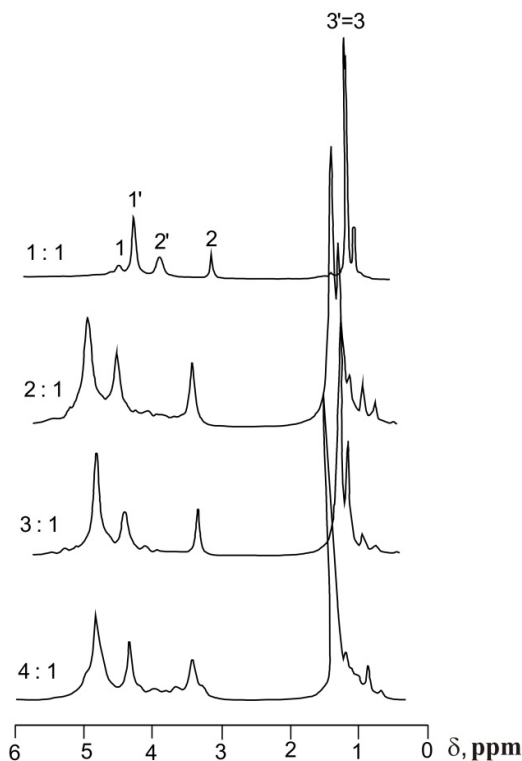


Figure 3.  $^1\text{H}$  NMR – spectra of titanium alkoxides in the different ratio of  $\text{TiCl}_4$  : OP.

The ratio of isomers for proton signals of chlormetin ( $\beta$ ) and chlormethyl ( $\beta'$ ) groups was calculated by the formula based on integral intensity of the protons. About 20 % iso- and 80 % normal isomers are created as the result of the interaction of  $\text{TiCl}_4$  and OP.

As the result of the reaction of  $\text{TiCl}_4$  and absolute iso-PA (the Figure 4) in obtaining titanium alkoxide the probability of additional protonation of cyclopentadiene and the initiation of chain appears<sup>11,12</sup>.

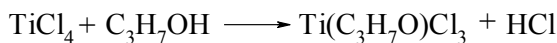


Figure 4. The interaction of  $\text{TiCl}_4$  with iso-PA.

In studying the kinetics of synthesis of  $\text{PR}_{\text{DCPDF}}$  with the use of titanium alkoxides as catalysts it was found: maximum yields of PRs are achieved during 60 min of synthesis, increasing the process temperature enhances the yield of PR.

Further synthesis of PRs was carried out using catalytic system based on titanium monoalkoxides and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  at a molar ratio of 1 : 0.5, 1 : 1, 1 : 1.5. The results of the process of oligomerization are shown in Figure 5 (at 60 °C).

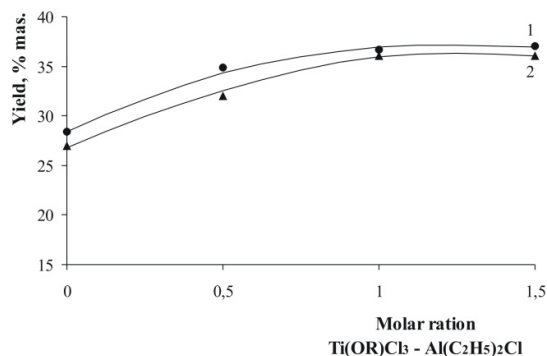


Figure 5. Influence of molar ratio of Ti(OR)Cl<sub>3</sub> – Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl on the yield of PR, 60 °C, 120 min:  
1 – OP; 2 – iso-PA.

Using components of various compounds – OP or iso-PA as catalysts insignificantly influences activity of monoalkoxy compounds during polymerization of DCPD fraction of PLP. Yield of PR<sub>DCPDF</sub> at 60 °C in case of application of Ti(OC<sub>3</sub>H<sub>6</sub>Cl)Cl<sub>3</sub> – Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl (1 : 1 mol) is 36.7, in the case of Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> – Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl (1 : 1 mol) it is 36 %. It follows from the results that at the oligomerization of DCPD fraction with the use of Ti(OR)Cl<sub>3</sub> yield of PR<sub>DCPDF</sub> is about 25 %, it is achieved at 60 – 80 °C. Addition of Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl even in small amounts by using a catalytic complex makes it possible to obtain such yields at 20 °C. Increasing the molar ratio of Ti(OR)Cl<sub>3</sub> – Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl from 1 : 0.5 to 1 : 1.5 leads to an increase in the yield of PR<sub>DCPDF</sub> of 3 – 5 % in all range of temperatures. The maximum yields of PR 36 – 38 % are achieved at the ratio of the components of the catalytic complex of 1 : 1 and temperature of 40 - 60 °C, so the increase in temperature to 80 °C and the molar ratio of 1 : 1.5 (mol) is inappropriate.

During polymerization of components of DCPD fraction with the use of monochlorpropoxytitanterchloride as a catalyst allows obtaining light (30 mg I<sub>2</sub>/100 ml KI), insoluble PR<sub>DCPDF</sub> with high bromine value (about 200 mg Br<sub>2</sub>/100 g PR), molecular weight 320-380 and softening point 70 °C.

Addition of Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl as a cocatalyst insignificantly increases the color of PR<sub>DCPDF</sub> (to 50 g I<sub>2</sub>/100 ml KI), reduces the value of the bromine number (about 170 mg of Br<sub>2</sub>/of a 100 g of PR), but increases the molecular weight (about 500) and softening point (to 120-130 °C). This dependence is observed at the increase in temperature of synthesis. Molar ratio of components of the catalyst complex 1:1, temperature 40-60 °C are the optimal synthesis parameters, which allow obtaining light PR<sub>DCPDF</sub> (30 mg I<sub>2</sub>/100 ml KI), with a molecular weight of 490-495, bromine value of 170-180 g Br<sub>2</sub>/100 g PR, a softening point of 115 °C.

The use of Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> leads to darker products (up to 80 mg ml I<sub>2</sub>/100 ml KI) with bromine numbers 130-140 g Br<sub>2</sub>/100 g PRs, the molar weight of 420 and the high softening point of 110 °C. Addition of Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl for polymerization of unsaturated components of the highly reactive fraction under the influence of the catalyst system Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> - Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl improves the color of the obtained solution of PR<sub>DCPDF</sub> (10-20 mg I<sub>2</sub>/100 ml KI) and increases the value of bromine number (up to 150 mg of Br<sub>2</sub>/100 g PR) and molar mass (430). The optimal synthesis parameters in this case are the molar ratio of components of the catalytic complex of Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> - Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl 1:1 and temperature 40-60 °C.

In order to determine the suitability of petroleum resins were obtained as film former, and the properties of obtained resin compositions with green iron oxide pigments S5605 are investigated. All iron oxides possess good tinting strength and excellent hiding power. They are also lightfast and resistant to alkalis. These properties are responsible for their versatility. Iron oxide pigments have long been used for construction materials coloring<sup>13</sup>.

Pigmented formulations were prepared by mixing the pigment with the solution of the petroleum resin in an eraser of cup. Dispersion was carried out for 3 minutes, and the degree of fineness was 5-7.5 microns. Further the composition comprising the resin obtained by using catalyst systems Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> and Ti(OC<sub>3</sub>H<sub>6</sub>Cl)Cl<sub>3</sub> were added to the amount of the oxidized vegetable oil: 5, 10, 15, 20, 25 %. Oxidized sunflower oil (OSO) is used as the vegetable oil. Using the applicator coating were obtained, and performance was investigated.

The matte, smooth pigmented coatings with the thickness of 20-25 microns and improved mechanical characteristics: elasticity <1 mm, 1 point adhesion, impact resistance of film – more than 30 cm were obtained for all the samples of PR<sub>DCPDF</sub>.

Dependence of film impact resistance on the content of oxidized vegetable oil for compositions with PR<sub>DCPDF</sub>: 1 –Ti(OC<sub>3</sub>H<sub>6</sub>Cl)Cl<sub>3</sub>, 2 –Ti(OC<sub>3</sub>H<sub>7</sub>)Cl<sub>3</sub> is shown in Figure 6.

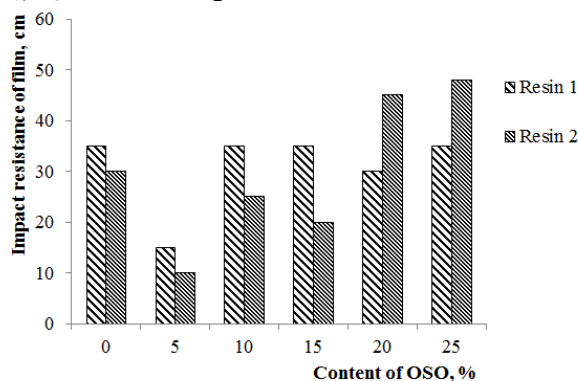


Figure 6. Dependence of film impact on the content of oxidized vegetable oil for compositions with green iron oxide.

When replacing 5-10 % resin oxidized sunflower oil, there is a sharp decrease in the impact resistance of film. Oxidation sunflower oil has polar groups in the structure, iron oxide pigments also has polar groups. Thus, the first one is adsorbed by OSO on the pigment surface. Introducing a small amount of OSO is not enough for the wet-out of the pigment surface. A part of pigment is distributed in the oil, a part – in the resin which leads to heterogeneity of the resulting composition and a sharp deterioration of the properties of the coatings. Further increase in added amount of oxidized sunflower oil results in improved impact resistance of film due to uniform distribution of oil on the surface of pigment and formation of the homogeneous system.

Storage of coatings in atmospheric conditions, leads to an increase in strength up to 75 cm of steel structure and crosslinking processes. It is caused by unsaturated resin and oxidized sunflower oil acting as binders.

Thus, the polymerization components of DCPD fraction of PLP using the catalyst system Ti(OR)Cl<sub>3</sub> – Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl leads to formation of oligomer products with the improved properties, it allows to extend their application in paint industry and also in the production of protective and anticorrosive coverings that, in turn, stipulates economic efficiency of production and application of this PR.

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