UDC 547.431.5:621.892

SYNTHESIS OF COMPLEX OLIGOESTERS OF CYCLIC POLYOLS AND INVESTIGATION OF THEM AS HIGH-TEMPERATURE LUBRICATING OILS

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A series of complex oligoesters of 2,2,5,5 tetramethylolcyclopentanol was synthesized, their physico-chemical, viscosity-temperature, thermal-oxidative and lubricating properties were studied. It was found that they have good performance characteristics and can be offered as the basis for high-temperature lubricating oils, dispersion medium of high-temperature plastic lubricants, thickening lubricant components, and anti-wear and anti-seize additives for lubricanting oils.

Keywords: *complex oligoesters, lubricating oils, performance properties, high-temperature properties, anti-wear and anti-seize additives*

Under the operating conditions of lubricating oils under severe conditions — high temperature and pressure, their operational properties become unsatisfactory. Therefore, the creation of new high-quality lubricants, including polyester, with high viscosity-temperature, thermal-oxidative and lubricating characteristics is very actual and perspectival [1-3].

However, with an increase in operating temperature $\geq 250^0$C, the viscosity, thermal-oxidative and lubricating properties of the complex esters of aliphatic neopolyols become unsatisfactory, which is due to the structural feature of these esters[4-5].

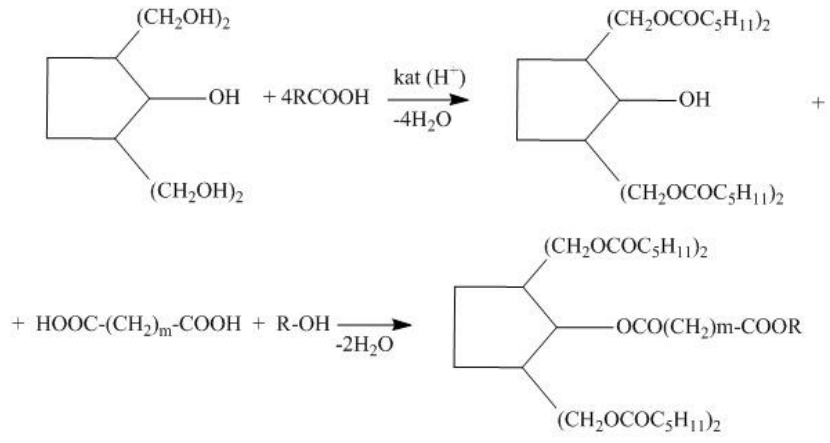
In this aspect, the obtained oligoesters on the basis of 2,2,5,5 tetramethylolcyclopentanol (TMCP) having many polar ether groups, cyclic fragments, a quaternary carbon atom not having β-hydrogen and researching them as new lubricants has a certain scientific and practical interest .

Experimental part

In the present work, the properties of complex oligoesters of 2,2,5,5 tetramethylolcyclopentanol (TMCP) with caproic, glutaric, pimelic, azelaic acids, methyl, hexyl and 2-ethyl hexyl alcohols were obtained and investigated.

The esterification reaction of TMCP was carried out in several stages in the presence of a catalyst of para-toluenesulfonic acid (PTSA) (1% load at each stage) and toluene as an azeotropic agent at a temperature of 160-180^{0}C. At the first stage, etherification was carried out to obtain a tetraester of TMCP with caproic acid, then the remaining hydroxyl group in the second stage was esterified with dicarboxylic acid into the third free carboxylic acid group of the dicarboxylic acid to esterify with mono alcohol.

The reaction of obtaining complex esters can be represented as follows:



where: m=3 m=5 m=7

R= $-CH_3$ (I) R= $-CH_3$ (IV) R= $-CH_3$ (VII)

$-C_6H_{13}$ (II) $-C_6H_{13}$ (V) $-C_6H_{13}$ (VIII)

$-C_8H_{17}$ (III) $-C_8H_{17}$ (VI) $-C_8H_{17}$ (IX)

The esterification was washed with 5% NaOH solution and water until neutral. After toluene was distilled off and the easy volatile products of the reaction were removed, the esters were evacuated at a residual pressure of 1-2 mm Hg and temperatures up to 210-250^{0}C.

The yield of oligoesters was 76-88% of theoretical.

The structure of the synthesized complex esters of TMCP was confirmed by IR and NMR spectroscopy, as well as by determining the molecular weight, acid and ester numbers.

Thermal-oxidative stability (TOS) of oligoesters was determined according to GOST 23797-79 in the amount of lubricants in accordance with GOST 9450-75 on a four-ball friction machine (FFM) at 20 ± 5°C, on balls 127 mm in diameter made of steel ШХ-15, with the number of revolutions 1500mm^{-1}.

Discussion of the results

After determining the physico-chemical characteristics of the esters obtained, it was found that esters were obtained with a yield of 71-85% by weight, with high refractive index values - 1101 ÷ 1125 kg/m^3, molecular weight - 740÷894. The density of all complex esters at 20^{0}C is above 1. The density of all esters at 20^{0}C is higher than 1.

The viscosity-temperature, TOS and lubricating characteristics of oligoesters were determined. From tab. 1 shows that the obtained oligoesters have a relatively high viscosity at 100°C (14,12-19,57 mm^2/s), a high viscosity index (129-142 units), a flash point (281-337°C) and relatively low freezing point (minus 36 ÷ minus 43°C). However, all the synthesized esters compared with the individual esters of TMCP are higher molecular weight, have higher viscosity values, flash point and, importantly, a high viscosity index.

After determining the TOS of oligoesters (table 2), they were found to have small acid numbers after oxidation (2.23-3.12 mgKOH/g), a residue that is insoluble in isooctane (0.091-0.173 wt.%), evaporation (0.361-0.762% wt.), corrosion of AK-4 (0.072-0.122 mg/cm^2) and ШХ-15 (0.086-0.165 mg/cm^2).

In determining the lubricating characteristics of oligoesters of TMCP, it has been found that they have high anti-wear and anti-seize properties. As can be seen from table 3, they have a critical load, Pc,H = 840-950 and the diameter of the wear spot, Di,mm = 0.40-0.60 mm.

These esters having a relatively high molecular weight, can withstand loads at high temperatures (≥250°C), forming a strong and durable oil film between the rubbing surfaces. Since they are oligoesters, have many polar ether groups and asymmetric molecules of esters, all these factors play a large role in the lubricity of these compounds [7-8]. From table 3 it is also seen that the complex esters of TMCP in comparison with the individual esters have a high lubricity.

Table 1

Viscosity-temperature properties of complex oligoesters of TMCP

Number of esters	Molar ratio of components	Viscosity, mm^2/s, at tem. °C		Viscosity index	Temperature, °C	
		40	100		flash point	freezing point
I	TMCP, caproic, glutaric acid, methanol (1:4:1:1)	43,16	14,12	130	281	-39
II	TMCP, caproic, glutaric acid, hexanol (1:4:1:1)	51,72	16,48	133	296	-36
III	TMCP, caproic, glutaric acid, 2-ethylhexanol (1:4:1:1)	57,61	18,63	142	312	-41
IV	TMCP, caproic, pimelic acid, methanol (1:4:1:1)	49,12	15,70	129	290	-38
V	TMCP, caproic, pimelic acid, hexanol (1:4:1:1)	56,23	17,90	136	320	-37
VI	TMCP, caproic, pimelic acid, 2-ethylhexanol (1:4:1:1)	60,49	19,57	138	328	-43
VII	TMCP, caproic, azelaic acid, methanol (1:4:1:1)	53,18	17,12	140	301	-36
VIII	TMCP, caproic, azelaic acid, hexanol (1:4:1:1)	59,35	19,56	132	330	-35
IX	TMCP, caproic, azelaic acid, 2-ethyl hexanol (1:4:1:1)	71,11	22,90	135	337	-39
X	TMCP and MFA fr. C_5-C_6	31,7	7,56	121	234	-62

Table 2

Thermal-oxidative characterization of complex oligoesters of TMCP

Number of esters	Acid number mgKOH/g (after oxidation)	The precipitate is insoluble. in isooctane,% wt.	Corrosion, mg/cm^2		Evaporation % wt.
			AK-4	IIIX-15	
I	2,23	0,091	0,072	0,086	0,361
II	2,85	0,110	0,081	0,102	0,420
III	3,02	0,103	0,103	0,121	0,452
IV	2,56	0,125	0,092	0,110	0,409
V	2,91	0,141	0,110	0,133	0,507
VI	3,04	0,172	0,121	0,165	0,723
VII	2,84	0,138	0,103	0,107	0,556
VIII	2,96	0,152	0,100	0,156	0,672
IX	3,12	0,173	0,122	0,162	0,762
X	2,50	0,067	0,020	0,035	0,560

Table 3

Lubricating characteristics of some complex oligoesters of TMCP

Number of esters	Critical load, P_c,H	Wear rate Di,mm at P = 196 H
I	840	0,60
III	880	0,55
V	920	0,50
VI	930	0,50
VIII	910	0,45
IX	950	0,40
X	680	0,70

Thus, the synthesis and study of a series of complex esters of TMCP shows that they have a significant advantage in comparison with the individual esters of this series and the polyesters of aliphatic polyols, which allows them to be recommended as specialty lubricants assigning a dispersion medium of high-temperature plastic lubricants, thickening lubricant components, as well as antiwear and anti-seize additives for lubricanting oils [9-10].

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2,2,5,5 TETRAMETİLOLTSİKLOPENTANOLUN KOMPLEKS OLİQOEFİRLƏRİNİN SİNTEZİ VƏ ONLARIN YÜKSƏK TEMPERATURA DAVAMLI SÜRTGÜ MATERİALLARI KİMİ TƏDQİQİ

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2,2,5,5 tetrametiloltsiklopentanolun müxtəlif kompleks oliqoefirləri sintez olunmuş, onların fiziki-kimyəvi, özlülük-temperatur, termooksidləşmə stabilliyi və yağlama xassələri öyrənilmişdir. Müəyyən olunmuşdur ki, onlar yaxşı istismar xassələrinə malikdirlər, bu səbəbdən də yüksək temperatura davamlı sürtgü yağlarının əsası kimi, yüksək temperatura davamlı plastik yağlayıcıların dispers mühiti kimi, sürtgü yağlarına özlülük artırıcı komponent kimi, həmçinin yağlara yeyilmə və siyrilmə əleyhinə aşqar kimi tövsiyə olunur.

Açar sözləri: *kompleks oliqoefirlər, sürtgü yağları, istismar xassələri, yüksək temperatura davamlı xassələr, yeyilmə və siyrilmə əleyhinə əlavələr*

СИНТЕЗ КОМПЛЕКСНЫХ ОЛИГОЭФИРОВ 2,2,5,5 ТЕТРАМЕТИЛОЛЦИКЛОПЕНТАНОЛА И ИССЛЕДОВАНИЕ ИХ В КАЧЕСТВЕ ВЫСОКОТЕМПЕРАТУРНЫХ СМАЗОЧНЫХ МАТЕРИАЛОВ

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Синтезирован ряд сложных комплексных олигоэфиров 2,2,5,5 тетраметилолцикло-пентанола, изучены их физико-химические, вязкостно-температурные, термоокислительные и смазывающие свойства. Было установлено, что они имеют хорошие эксплуатационные характеристики и могут быть предложены в качестве основы для высокотемпературных смазочных масел, дисперсионной средой высокотемпературных пластичных смазок, загущающих компонентов смазочных масел, а также противоизносных и противозадирных присадок к смазочным маслам.

Ключевые слова: *комплексные олигоэфиры, смазочные масла, эксплуатационные характеристики, высокотемпературные свойства, противоизносных и противозадирных присадок*