

UDC 547.593.222:621.892

Petrochemicals

THE SYNTHESIS OF VICINAL SUBSTITUTING CYCLOHEXANE DIOL ETHER COMPLEXES AND THEIR STUDY AS LUBRICANTS MEETING MODERN REQUIREMENTS

Academician of NAS of Azerbaijan M.A.Mamedyarov, H.N.Gurbanov, E.M.Guliyeva,
G.T.Suleymanova, F.A.Gulu-zadeh

Nylon, adipic, sebacic acids, complex esters with alcohols methyl and 2-ethyl of vicinal substituted cyclohexane diols have been synthesized. Their physical and chemical, lubricant properties, the temperature of viscosity, thermal stability have been studied. It has been found that due to the high exploitation properties these esters are recommended as a basis and components for new lubricating oils.

Keywords: diols cyclic ethers, lubricants, thermal stability, exploitation properties

The synthesis and the study of aliphatic (pentaerythritol, trimethylolpropane, neopentyl glycol) and cyclic polyols based on – 2,2,5,5-tetrametilol TMCP cyclopentanol and cyclohexanol 2,2,6,6-tetrametilol TMCH have already been known. There is information about the using of these esters as a plastic lubricant in a dispersion medium as a component and an additive to aviation and motor oils. [1-3]

The indications of poor viscosity temperature, relatively high freezing temperature, the mismatch of thermal oxidative stability of present-day conditions of the above esters limits their using.

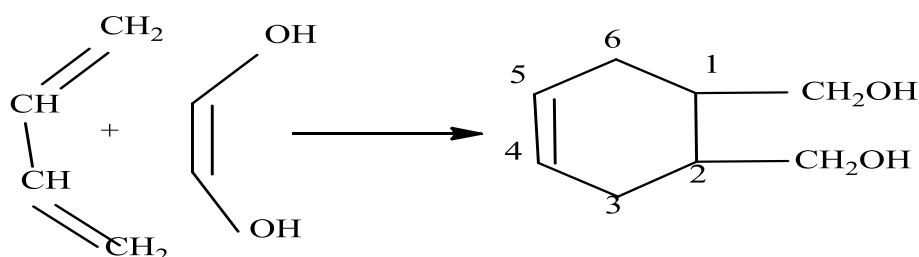
At the moment, due to a significant increase in the requirements for used lubricating oils it becomes necessary to create high-quality lubricants

that meet the new requirements. Based vitsinal substituted cyclohexane diols obtaining new ether complexes and their investigation as lubricants has special significance.

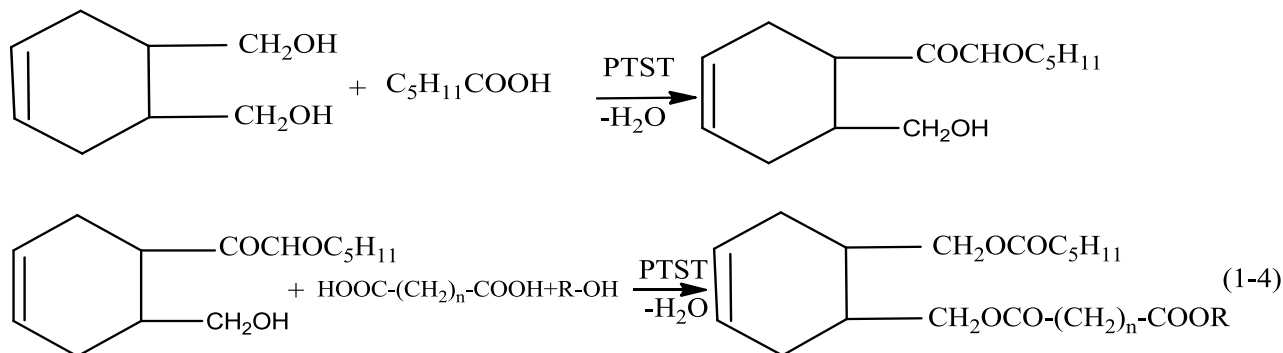
Keeping in its composition a large number of ether groups, normal iso-textured radicals, alicyclic rings, functional groups of different nature by creating a new type of active centers, obtaining high-quality lubricants has a specific scientific and practical importance.

Experimental part

Given the above, based on cyclic diols consisting of 1,2-dimethylol cyclohexane -4 (DMCH) new complexes esters have been synthesized and investigated as lubricant oils. The aforementioned diol is obtained from the interaction of 2-butene to 1,4 diol divinyl: [4]



The esterification of caproic acid with a cyclic diol in the production step of obtaining monoester in a ratio of 1: 1.2 mixture of alcohol: acid in the presence of catalyst paratoluene sulfonic acid (PTSA) (1.5 mass%) has been carried out at 130-150 °C temperature, within nitrous environment. The result was the obtaining of a monoester containing one free hydroxyl group that in the second step has been esterified with adipic and sebacic acids comprising of dicarboxylic acids. Finally in the third step the remaining free acid groups of dicarboxylic acids have been exposed esterification with aliphatic and methyl 2 ethylhexyl alcohols. Schematic representation of mentioned obtaining ether complexes is shown in the figure below: [3]



Where, $n=4; 8$, $\text{R}=-\text{CH}_3$ or $-\text{C}_8\text{H}_{17}$

The structure of the compound has been proven by IR and NMR, as well as by determining the amount of ether and acid, and molecular weight.

Toluene is used as solvent in the esterification reaction for the extraction of water from the environment. Due to the fact that extracted water forms toluene and azeotropic mixture the esterification is purified from the mixture by means of azeotropic distillation, and then is

washed with 5% alkaline solution and then is washed with water until neutral environment. The remaining part of the production distilliruyetsya under vacuum pressure of 1-2 mmHg. The yield of polyesters is 72-80% of the theoretical yield.

The Results and their discussions

The table below shows the ratio of reactants and physicochemical parameters obtaining complex ethers.

Table 1

Physicochemical parameters of ethers

Ethers	The name of the polyethers and the ratio of their components	Yield	Refractive index n_D^{20}	Density, ρ_4^{20} kg/m ³	Molecular weight
1	2	3	4	5	6
I	Adipic and caproic acids of DMCH and methyl alcohol with polyethers 1:1:1:1	80%	1,4670	1,0120	380
II	Caproic-adipic acids of DMCH and polyether with 2-ethyl hexanol 1:1:1:1	76%	1,4685	1,0170	436

1	2	3	4	5	6
III	Caproic, sebacic acids of DMCH and polyether with methyl alcohol 1:1:1:1	74%	1,4650	1,0910	474
IV	Caproic, sebacic acids of DMCH and polyether with 2-ethyl hexanol 1:1:1:1	72%	1,4668	1,0900	530
V	Caproic acids of DMCH with diether 1:2,2	90%	1,4648	0,981	335

As seen from table synthesized complex ethers in comparison with ether di caproate of DMCH have a higher molecular weight, refractive index, density, molecular weight is significantly higher.

The viscous temperature and thermal stability of complex ethers have been identified which are reflected in the following table 2.

As shown in table 2 complex ethers have good viscosity temperature (at 100⁰ C - Viscosity - 4.82 -5.46 mm²/s), low temperature freezing (minus 44 or minus 48 °C) high viscosity index (138-146 units).

The obtaining complex ethers compared with di caproate ether of TMCH have a high viscosity index, because they are high molecular compounds whose structure consists of a large

number of polyether groups. The investigated complex ethers also have high thermal and oxidation stability, and after the oxidation the amount of acid compared with di caproate ether of DMCH decreased significantly from 3.96 to 1,94-2,76 mg-KOH / g, the corrosion of electrodes AK-4 from 0.034 to 0,010-0,028 mg / cm² and the electrode SX-15 from 0.075 to 0,010-0,028 mg / cm². But the number of sediment insoluble in isooctane decreased from 0,018 to 0,006-0,010%.

All of the above proves once again that the resulting of complexe ethers compared to di caproate of DMCH ether has a high thermal oxidative stability and high viscosity index of temperature and provides an ample opportunity to these ethers [5-6].

Table 2

The viscous temperature parameters and thermal stabilities of ethers

Ethers	Viscosity, mm ² /s, at °C		Viscosity Index VI	Temperature, °C		Acid number (after oxidation)mg KOH/g	Corrosion mg/cm ²		The amount of sediment that do not solve in isooctane. % weight
	50	100		Freezing	Flash		AK-4	SX-15	
I	13,48	4,82	140	-48	228	2,76	0,028	0,046	0,010
II	14,21	4,96	138	-46	230	2,42	0,020	0,033	0,008
III	16,28	5,26	144	-46	233	2,13	0,015	0,024	0,008
IV	16,73	5,46	146	-44	236	1,94	0,010	0,020	0,006
V	6,76	2,72	134	-62	192	3,96	0,034	0,075	0,018

It was investigated and found that the lubricating properties of complex ethers have high lubricating properties; having the volume of critical load $P_k = 740-840$, circle diameter $D_i = 0,45-0,6$ mm prove their performance, and it is closely related to their structure. A large number of polar groups in the composition of these esters, asymmetric molecules of complex ether, the contents in the molecules other functional centers eventually leads to the high density of contact between the surfaces of tangency and to the formation of resistant layer of fat, which minimizes the friction between the surfaces of contact. This is a very important fact for normal and continuous operation of machines and mechanisms [7-8].

Thus, the synthesis and study of 1,2-dimethylol cyclohex-4 (DMCH) of cyclic diols showed that these ethers with caproic acid of DMCH as compared with diester, the temperature of the viscous properties, thermooxidation, lubricants, have high rates, with this point of view, they can be used as a main lubricating oil and as a component of other oils [9].

REFERENCES

1. Tsvetkov O.N. Lubricating oil-base and technological progress // World oil. 2008, №2, p. 25-27.
2. Patent 2186386 Russia, 2002
3. Gurbanov G.N., Mammadyarov M.A. Complex ethers alicyclic of neopolyols - high temperature components of lubricants // ACJ, №1, 2006, p. 20-23.
4. Onishchenko AS Diene synthesis. -M: Publishing House of the USSR Academy of Sciences, 1963, 649 p.
5. Gurbanov G.N., Mammadyarov M.A., Kuli-Zade F.A. Thermal stability of cyclic ethers of many atomic alcohols // Chemistry and technology of fuels and oils. 2008, №1, p. 36-39.
6. Gurbanov G.N., Mammadyarov M.A. Synthesis of 2,3 dialkanoates (bicyclo / 2.2.1 / hept-5-ene) dimethanol and their investigation as lubricants // Petrochemicals, 2008. v 48, №6, p. 482-485.
7. US Patent 6,444,626, 2002.
8. Patent 2,261,895, Russia, 2005.
9. Gurbanov G.N., Mammadyarov M.A., Aliyev F.H. New types of ether synthetic oils // Collection of review articles Institute of Petrochemical Processes, Azerbaijan National Academy of Sciences, Baku: Elm, 2013, p. 319-409.

*Institute of Petrochemical Processes named
after acad. Yu.G.Mamedaliyev
huseynqurbanov23@rambler.ru*

VİTSİNAL ƏVƏZOLUNMUŞ TSİKLOHEKSEN DİOLLARIN KOMPLEKS EFİRLƏRİNİN SİNTEZİ VƏ ONLARIN MÜASİR TƏLƏBLƏRƏ CAVAB VERƏN SÜRTKÜ YAĞLARI KİMİ TƏDQIQI

M.A.Məmmədیارov, H.N.Qurbanov, E.M.Quliyeva, G.T.Süleymanova, F.Ə.Qulu-zadə

1,2-dimetilol tsikloheks-4-enin kapron, adipin, sebasin turşuları və metil, 2-etilheksil spirtləri ilə kompleks efirləri sintez olunmuşdur. Alınmış efirlərin fiziki-kimyəvi, özlülük-temperatur, termooksidləşmə və yağlama xassələri öyrənilmişdir. Müəyyən olunmuşdur ki, onlar yaxşı istismar xassələrinə malikdirlər və bu səbəbdən də yeni sürtkü yağlarının əsası və komponenti kimi tövsiyə olunurlar.

Açar sözlər: Tsiklik diolların efirləri, sürtkü yağları, termooksidləşmə stabilizələri, istismar xassələri

СИНТЕЗ КОМПЛЕКСНЫХ ЭФИРОВ ВИЦИНАЛЬНО-ЗАМЕЩЕННЫХ ЦИКЛОГЕКСЕН ДИОЛОВ И ИССЛЕДОВАНИЕ ИХ В КАЧЕСТВЕ СМАЗОЧНЫХ МАСЕЛ, ОТВЕЧАЮЩИХ ТРЕБОВАНИЯМ СОВРЕМЕННОЙ ТЕХНИКИ

М.А.Маммедьяров, Г.Н.Гурбанов, Э.М.Кулиева, Г.Т.Сулейманова, Ф.А.Кули-заде

Синтезирован комплекс эфиров циклогексен диолов-1,2-диметилol циклогекс-4-ена с капроновой, адипиновой, себадиновой кислотами и метиловым, 2-этилгексиловым спиртом. Определены их физико-химические, вязкостно-температурные, термоокислительные и смазывающие свойства. Найдено, что они обладают хорошими эксплуатационными свойствами. В силу этого их можно рекомендовать в качестве основы и компонента новых смазочных масел.

Ключевые слова: эфиры циклических диолов, смазочные масла, термоокислительная стабильность, эксплуатационные свойства