PHYSICS AND CHEMISTRY OF SOLIDSTATE
V. 19, № 4 (2018) P. 345-351
DOI: 10.15330/pcss.19.4.345-351

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 19, № 4 (2018) С. 345-351

UDK: 621:88+621.893+621.892.09906+665.521 ISSN 1729-4428

H.O. Sirenko[1], M.I. Martynyuk[1], V.P. Svidersky[2] ,N.V. Shmaltser[1], O.V. Kuzyshyn[1]

Problem of Selection of Lubricants for ethelene High-Pressure Compressors. 2.Characteristic of object of investigation (review)

[1]Vasyl Stefanyk Precarpathian National University, 57, Shevchenko Str., Ivano-Frankivsk, 76018, Ukraine,
mar.martinyuk2904@gmail.com
[2]Khmelnytsky National University, 11, Instytutska Str., Khmelnytsky, 29016, Ukraine

Technology of obtaining and properties of ethylene compositions with different content of oils inside are researched. The antifriction properties of naphtene and polyglicol oils have been studied. Polyethyleneglycol and polypropyleneglycol-products of condensation accordingly of ethyleneglycol and propyleneglycol have today the practical interest as lubricants. It is shown viscous-mechanical properties of polyethylene during addition of different amount of lubricants.

Key words: polyethylene, oils, composition, polyglycol, dielectrical properties,thermooxidants, compressors.

Article acted received 28.09.2018; accepted for publication 15.12.2018.

Introduction

Properties and nature of oils determine quality indicators of polyethylene and reliability of work of seal pistons and plungers of ethylene compressors. For lubrication of friction pair of these compressors mineral (naphthene - «white» oils), polybutene and polyglycol oils are used.

These oils are:

- lowmolecular Orites-88 (ELF, France);
- highmolecular Ontes-270 DS (ELF, France) with ratio of ethylene and propylene oxides 72,8:27,2 (analogue of this oil Laprol 2502-2-70);
- Breox CL 1300, Breox CL 1400, Breox CL 6601, Breox PC 1314, Breox PC 1315, Breox PC 1316 (British Petroleum Co.);
- Syntheso D 201, Syntheso D 201 N(with npncaAKOio), Syntheso D 202 (Bochaco, Klüber, Duetschland);
- lowviscous Ucon 75 H1400, Ucon PE-159 and highviscous Ucon PE-320, Ucon PE-350 (Union Carbide);
- EXD 62/152H, EHD62/152 H with ratio of ethylene and propylene oxides 48:52 (Mobiol-Oil);
- highviscous Polyol LG-56.

I. Results and discussion

Polyalkylenglicols or polyglycols are the products of condensation of twoatom glycols. They are polyethers with long chains molecules of which contain two OH-groups. Polyethyleneglycol and polypropyleneglycol-products of condensation accordingly of ethyleneglycol and propyleneglycol have today the practical interest as lubricants.

II. Polyglycols

2.1.Polyethyleneglycol

$$HO\text{-}[\text{-}CH_2\text{-}CH_2\text{-}O\text{-}]_n\text{-}H \quad (1)$$

Average molecular mass 200-6000; n≈4-136.

PEG-200 (f), M=200; n≈4-5
PEG-400 (f), M=400; n≈9
PEG-600 (f), M=600; n≈13-14
PEG-1500 (s), M=1500; n≈34; $T_{cr.}$=318-324K
PEG-2000 (s), M=2000; n≈45-46; $T_{cr.}$=326-333K
PEG-4000 (s), M=4000; n≈90-91; $T_{cr.}$=328-333K
PEG-6000 (s), M=6000; n≈136; $T_{cr.}$=330-334K

Quality indexes of polyethyleneglycols produced by “Barva” are adduced in Tabl.1

Table 1

Quality indexes of polyethyleneglycols

Indexes	PEG-2000	PEG-1500	PEG-2000	PEG-4000	PEG-6000
Alkali number, mg KOH/g	-	65.0	51.9	26.01	18.4
T_{cryst}, K	-	318	321.5	326	327.5
pH 5% of watery solution	6.60	6.80	6.05	5.65	5.3
mass fraction of ashes, %	0.04	0.10	0.08	0.07	0.08
mass fraction of water, %	0.44	0.17	0.80	0.45	0.35

Table 2

Trademarks of lubricants of linear polypropyleneglycols

	Average molecular mass	OH, %	pH	η_{298K}	Acid number, mg KOH/g
Laprol 202	200	16.75	5.25	58	0.08
Laprol 602	600	5.55	5.60	86	0.08
Laprol 1002	1000	3.13	6.30	156	0.03
Laprol 2002	2000	1.50	5.85	316	0.07

Table 3

Trademarks of lubricants of statistic copolymers of propylene and ethylene oxides

	Average molecular mass	OH, %	pH	η_{298K}	Acid number, mg KOH/g
Laprol 1502	1500	2.20	5.5	260	0.05
Laprol 2502	2500	1.37	6.6	504	0.03
	T, K		η, cp	ρ, kg/m^3	ν, cs
Orites-270-DS	303 323		423 181	1080 1065	390 170

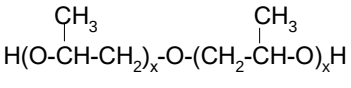
Table 4

Indexes of synthetic oils, produced by IPChl Baku

Index	Indenter 1	Indenter 2	Indenter 3	Indenter 4
Viscosity, cSt: at 373 K at 323 K	 35.75 234.48	 7.56 29.04	 36.05 208.44	 39.07 257.46
Index of viscosity:	115	135	131	120
Temperature. K: flashing solidification	 579 269	 495 251	 527 255	 513 250
Density at 293K. kg/m^3	869.6	841.0	848.1	871.8

Indenter 1 - poly-a-olefine oil; *indenter 2* - copolymer of ethylene and propylene; *indenter 3* - copolymer of ethylene and propylene; indenter 4 - poly-a-olefine oil. thickened with polymer (SKEP).

2.2. Linear polypropyleneglycols:

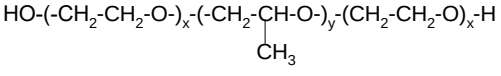


(2)

These are twobased homopolymers of propylene oxide. Content of active final OH-groups is increasing when molecular mass of olygomers decreases. Trademarks of lubricants of this group are adduced in Tabl.2

Laprol 2002 is homopolymer of propylene oxides (molecular mass 2000), production of «Sumhaitchimprom», kinematic viscosity (298K~400 cs)[1-5].

2.3. Statistic copolymers of propylene and ethylene oxides:



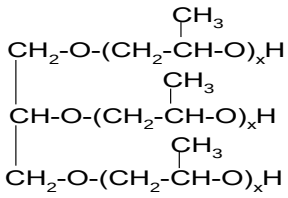
(3)

Trademarks of lubricants of this group are adduced [10-15]:

Laprol 1502-2-70 (M=1500, 70% of oxiethyl groups).
Laprol 2502-2-70 (M=2500, 70% of oxiethyl groups, kinematic viscosity at 303 K ~ 400-500 cs).
KSM (M=2500, 70% of oxiethyl groups).
Orites 125 DS (M=l 150, 72,8% of oxiethyl groups).
Orites 270 DS (M=2400, 72,8% of oxiethyl groups).
EHD 62/152 H (M=?; 48% of oxiethyl groups).
Breox CL-660 (the same polyglycol, but with additives).
Breox CL-1300 (the same polyglycol, but with additives).
Breox CL-1400 (the same polyglycol, but with additives).
Hydropol-200 (f)- is statistic copolymer of ethylene and propylene oxides. M=7000-8000.

Trademarks of lubricants of this group are adduced in Tabl. 3.

2.4. Ramified polypropylene on the base of glycerine:

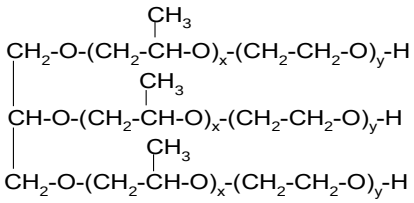


(4)

General formula:
Laprol 503:
Average molecular massM= 00, OH%=1,54; pH=6,4; η_{298K}=670 cp.; acid number, mg KOH/g=0,12[6-8].
To this group belong as well oils Laprol-3003, 6003, Polyol LG-56 (M=3000) [6-8].

2.5. Blockcopolymers on the base of propylene and ethylene oxides on the base of glycerine with the placing of oxiethyl groups in the end of chain:

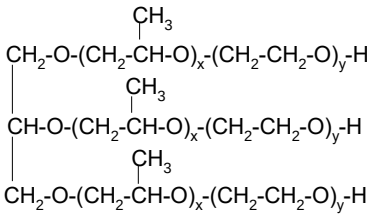
Laprol-3503-2-B 6 (M-3500, 6% of oxiethyl groups);
Laprol 5003-2B-10 (M=5000, 10% of oxiethyl groups);
Laprol 5003-2B-12 (M=5000, 12% of oxiethyl groups);
Laprol 6503-2B-18 (M=6500, 18% of oxiethyl groups);
Laprol 5003: Average molecular mass M=5000;
OH%=1,07; pH=6,45; η_{298K}=830 cp.; acid number, mg KOH/g=0,0;
Proxanol CL-3 (f). Blockcopolymer of propylene and ethylene oxides (M=3600). Proxanol-268 (s). Blockcopolymer of propylene and ethylene oxides



x>y (5)

(M = 14000)[8-15].

2.6. Statistic copolymersof propylene and ethylene oxides on the base of glycerin



y>x(6)

Laprol 3503-2-70 (analogue Syntheso D-201) - statistic copolymer on the base of glycerin and ethylene oxide (70% of ethylene oxide): OH%=1,54; pH=6,4; η_{298K}=670 cp.[6-8];
Laprol 3503-2-B5 – on the base of glycerine, the same molecular mass, but 65% of ethylene oxide and oxiethyl links are placed in the and of the chain:OH%=1,45; pH=6,3; η_{298K}=557 cp.;
Laprol 10003-2-70 -is statistic copolymer on the base of glycerin and ethylene oxide (70% of ethylene oxide): molecular mass 10000;OH%=0,47; pH=7,4; η_{298K}=6800 cp.;
Syntheso D-202 - statistic copolymer on the base of glycerin and ethylene oxide: density ρ (293 K)~1080 kg/m^3;
kinematic viscosity at 293 K~ 800 cs;
313 K~ 300 cs;
323 K~ 200 cs;
373 K~ 52 cs;
index of viscosity ~ 230; flash temperature $t_{fl.}$ > 523K; temperature of solidification $t_{sol.}$ < 293K .
Syntheso D-201 (70% oxiethyl groups).

Indexes of quality of synthetic oils produced by IPChl (Baku, Azerbaijan) adduced in Tabl.4. [15-20];

Lubricating properties of different groups of polyglycols are adduced in Tabl.5, 6[15-20]. Influences of final groups of polyglycol oils on the indexes of quality are adduced in Tabl. 7.[20-24];

Table 5

Lubricating properties of polyglycol oils

Oil	Molecular mass	Kinematic viscosity		
		at 313 K, cs	at 318 K, cs	at 353 K, cs
Linear polypropyleneglycols	200	25.8	19.8	4.3
	600	43.7	35.3	8.4
	1000	77.7	-	15.3
	2000	197.6	163.3	40.5
Ramified polypropyleneglycols on base of glycerin	500	110.4	76.6	12.3
	3000	265.8	-	45.8
	3000*	224.2	175.5	41.8
	3503	330.1	-	76.7
	3500**	300.0	-	52.0
Blockopolymer of ethylene and propylene oxides on the base of glycerin	5000	559.3	-	101.2
Statistic copolymers of propylene and ethylene oxides	1500	132.3	-	31
	2500	268.9	230.0	60
	2500***	-	237.3	59

* - Polyol LG-56, ** - Syntheso D201, *** - Orites-270 DS.

Table 6

Lubricating antifriction properties of polyglycol oils

Oil	Molecular mass	Boundary loading on ball, N	Diameter of wear spot, mm	Hydrodynamic effect, 10^{-14}, m^2
Linear polypropyleneglycols	200	238	0.62	0.528
	600	242	0.53	0.589
	1000	246	0.51	-
	2000	262	0.49	2.16
Ramified polypropyleneglycols on the base of glycerin	500	226	0.58	1.67
	3000	320	0.52	-
	3000*	308	0.41	1.35
	3503	-	0.71	-
	3500**	-	0.57	-
Blockopolymer of ethylene and propylene oxides on the base of glycerin	5000	349	0.49	-
Statistic copolymers of propylene and ethylene oxides	1500	361	0.73	-
	2500	402	0.68	8.09
	2500***	447	0.64	6.96

* - Polyol LG-56, ** - Syntheso D201, *** - Orites-270 DS.

Table 7

Indexes of olygoethers indenters for synthetic oils

Index	Unit of measure	Indenter №1	Indenter №2	Indenter №3
Content of OH-groups	%	1.48	0.48	1.05
Content of moisture	%	0.10	0.042	0.10
Content of K^+	mg/kg	17.2	22.3	-
Acid number	mg/g	0.117	0.365	0.02
pH		6.20	5.35	6.70
Dynamic viscosity	cs			
at 303K		405.8	290.8	456.1
at 323K		173.5	129.8	196.2
at 373 K		42.7	33.1	48.4
Turbidity point of 1% solution of polyether in water	K	>363	>363	>363

Indenter №l: olygoether L-2502-2-70 with final OH-groups; *Indenter №2*: olygoether L-2502-2-70 with final OH- and butoxygroups; *Indenter №3:* olygoether 11601-4/2-50 with final OH-group.

Table 8

Properties of naphtene oils

Oil	Density at 293K (ρ_4^{293}), kg/m^3	Kinematic viscosity at 310,8K(ν), cs	Temperature of solidification ($T_{sol.}$), K	Flash temperature ($T_{fl.}$), K
Risella-17	867	9.91	223	407
Risella-33	884	76.5	255	480
Vitorex-350	859	15.8	264	497
Esso-Christo	879-889	76.6-81.0	253	491
NKM-40	873	67.1	255	468
NKM-70	884.3	70.39 (323 K) 11.77 (373 K)	260	473
5350	880.8	43.1 (323 K) 8.37 (373 K)	249	471
KPL-201	-	68.0 (323 K) 11.8 (373 K)	-	493
NMR-12	858.3	11.9 (323 K)	228	438

Table 9

Characteristic of naphtene oils for lubrication of ethylene high-pressure compressors

Indexes	Requirements TC 38-101 434-74	Naphtene compressors oils		
		NKM-70	NKM-40	Risella-33
Density (ρ_4^{293}), kg/m^3	<880	884.3	873.0	884.2
Index of refraction (n_D^{293}),	<1480	1.4800	1.4794	1.4820
Specific dispersion (F, C)	-	97	98	98
Viscosity kinematic, cs at 323K at 373K	36-41	 70.39 11.77	 37.09 7.88	 40.96 7.69
Viscosity index	-	85	-	-
Acid number, mg KOH/g	<0,01	0.006	0.006	0.007
Temperature, K of solidfication of flashing in opened crucible	 <263 >463	 263 478	 260 468	 253 475
Colour with glass №2 on KH-51, mm	>270	270	270	270
Test of content of organic impurities	sustains	sustains	sustains	sustains
Content of water	-	-	-	-
Content of mechanical impurities	-	-	-	-

III. Naphtene oils

Properties of the naphtene oils are adduced in Tabl.8[15-20].

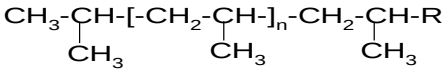
Dependence of dynamic and kinematic viscosities and density of oil Risella-33 on temperature is adduced below: T, K 303,323; η, cp 104,35,5; ρ, kg/m^3 873,861; ν, cs 120, 41,2.

Demands to the naphtene oils for ethylene compressor are adduced in Tabl.9[15-20];.

IV. Polybutene oils

Polybutene – linear polymers with the molecular mass 500-1500. Most of moleculeks of polybutene contain only one final double bond with minimal quantity of cross bonds. This polymer is stable. Polybutene do not dry, do not become like paraffin or sticky even after long-duration storing. Important properties of polybutene are as well light colour, absolute transparence and absence of smell. Polybutenes are

(7)



soluble in petroleum, in aliphatic and aromatic hydrocarbon chloride, in lubricating oils, ethers; they do not dissolve in the most of high polar solvents [1-5].

Polybutene oil–is linear polymer with average molecular mass from 400 to several thousands. This is transparence viscous light-yellow fluid: ν_{50}= 80-200 cs; ν_{100}=15-40cs; t_{fi}. (in opened crucible)= 438; ρ (293 K)= 850-890 kg/m^3[1-5].

Lowmolecular polybutene for succynimide additives:

Molecular mass-860; Iodine number – 33,94 g of iodine/l00g of product; ν_{100} =287,6cs; t_{fl}.(in opened crucible)=417; content of moisture -absen.; content of mechanical impurities c_{mech}.=0,06 %w; content of ions Cl^- c_{Cl^-}=0,03 %w.;ρ(293K)=886 kg/m^3.

*O-Vax:*ρ(293K)=1030kg/m^3; colour-light-yellow; point of dropfalling t_{dr}.=373K ; structure-solid; acid number 10-15; alkali number 111-133 [5-15].

V. Polyvynilbutylether (PVBE)

It is viscous fluid with light-yellow colour or colourless with specific smell, does not dry. Density 903-921 kg/m^3 , index of refraction 1,450-1,457; does not dissolve in water; relative viscosity of 1% solution in toluol 0,63-0,68; molecular mass 2500-5500; chemical formula [16-24]:

Conclusions

Polyglicol oils in comparing with naphtene have advantages:

- low solubility in ethylene and npn saturation by ethylene viscosity, antiseizure and antiwear properties do not change;
- low loading ability which force to limit of ethylene plants little and

medium productivity (term of seal service 1000-4000 hours).

Moreover, according to firm Esslingen term of work of seal elements during lubrication with polyglicol oils 3-5 time bigger and increases from 1000-4000 hours fo naphtene and polybutene oils to 5000-15000 for polyglicol oil, According to firm ELF expenditure for 11 of polyethylene during transition to lubricating from naphtene oils to polyglicol Orites 270 DS decreased from 3-4 to 1 kg/t.

At the same time from 0,02 to 0,15% of oil ingress into polyethylene, which decreases durability of polyethylene to thermal aging and photooxidation processes and electroisolation roperties.

Sirenko H.O. – Professor, Doctor of Technical Sciences, Professor of Department of Chemistry;
Martynyuk M.I. – Ph.D. student of Department of Chemistry;
Svidersky V.P. – Ph.D (Tech.Sci.),Associate Professor of the Department of wear resistanceand reliability of machines;
Shmaltser N.V.– Ph.D. student of Department of Chemistry;
Kuzyshyn O.V.– Ph.D (Phys.-Math.Sci), Associate Professorof Department of Chemistry of the Environment and Chemical Educat.

[1] A. M. Zavoiko, I. I. Novikov, G. A. Sirenko G. A. and others, Chemical and Petroleum Engineering 1, 19 (1984).
[2] A. M. Zavoiko, I. I. Novikov, G. A. Sirenko, A. G. Platonov, NIIEEKHIM 1, 3 (1987).
[3] H. A. Sirenko, R. V. Grinevich, I. I. Novikov, All-Union. scientific and technical conf. "Tribonica and antifrictional material science" (NPI, Novocherkassk, 1980).
[4] G. O. Sirenko, Sci. "Bulletin of Allukr. Sciences, prof. Come on to them. M. Mikhnovsky" 9, 1 (1998).
[5] O. Gavrishov, A. M. Zavoiko, Bulletin Prikarp. un-th them Vasyl Stefanik 3, 142 (2003).
[6] O. Gavrishkov, Antifrictional Properties of Polyglycols. Tez papers Fourth Regional Conference of Young Scientists and Students on Actual Chemistry Issues. (Dnipropetrovsk, 2002).
[7] O. Gavrishkov, Antifrictional Properties of Polyglycol Oils. Tez papers Reporting scientific conference of Precarpathian University named after. Vasyl Stefanyk for the year 2002. (Ivano-Frankivsk, Prikarp, Unternehmens named after V. Stefanik, 2003).
[8] I. I. Novikov, V. P. Zakharenko, B. S. Lando, Lubricating Piston Seals in Compressors (Mechanical Engineering, Leningrad, 1985).
[9] A. A. Tarzimanov, A. V. Maryshev, Proceedings of the Kazan Chemical Technology. inst. 90(73), 3 (1976).
[10] I. R. Krichevsky, Phase equilibrium in solutions at high pressures (Goshimizdat, Moscow, 1952).
[11] T. P. Juze, Compressed gases as solvents (Science, Moscow, 1974).
[12] R. A. Shaghikmetov, Investigation of viscosity, density of oils and the effect of dissolved gas on viscosity at pressures up to 100-200 MPa. Author's abstract. Cand. dis (Kazan, 1981).
[13] H. A. Sirenko V. P. Svidersky, V. D. Gerasimov, Technique 2, 110, (1978).
[14] H. A. Sirenko, Technique 2, 179 (1985)
[15] G.O. Sirenko, Creation of antifrictional composite materials based on powders of thermoforming polymers and carbon fibers. Dis on ... doc. tech Mr. (Institute of Materials Science, NASU, 1997).

[16] L. M. Rogacheva, A. V. Germans, Development of technology for the production of additives based on petroleum raw materials and active elements. 5. Studying the properties of copolymers of molecular weight 2000-3500. (Kuybyshev, GOSNINP., I961).
[17] R. M. Matviyevsky, Temperature resistance of boundary lubricating layers and solid lubricants coated with friction of metals and alloys. (Moscow, Science, 1971).
[18] G. V. Vinogradov, Yu.Ya. Podolsky, M. D. Bezborodko, Use of machines with point contact of friction bodies for estimation of wear of metals, antiwear and anti-friction properties of lubricants. Methods of Testing for Wear (Moscow, USSR Academy of Sciences, 1962).
[19] H. A. Sirenko, A. S. Smirnov, Questions of the theory of friction, wear and lubrication 215, 38 (1969).
[20] H. A. Sirenko, O. V. Kuzyshyn, A. M. Zavoiko, Problems of tribology 4, 150 (2003).
[21] R. V. Grinevich, V. V. Tsasyuk, A. S. Smirnov, Specialized Friction Machines. Application of synthetic materials. (Chisinau: Kartya Moldoveniaska, 1975).
[22] H. O. Sirenko, I. V. Sulyma N. V. Shmaltser, Physics and Chemistry of Solid State 18(3), 365 (2017) (doi:10.15330/pcss.17.3.440-449).
[23] H.O. Sirenko, M.I. Martynyuk, V.P. Svidersky, I.V. Sulyma and ect., Physics and Chemistry of Solid State 18(4), 460 (2017) (doi:10.15330/pcss.18.4.466).
[24] H.O. Sirenko, M.I. Martynyuk, V.P. Svidersky, Physics and Chemistry of Solid State 19(3), 279 (2018) (doi:10.15330/pcss.18.3.365-371).

Г.О. Сіренко[1], М.І. Мартинюк[1], В.П. Свідерський[2], Н.В. Шмальцер[1], О.В. Кузишин[1]

Проблема вибору та властивостей мастильних матеріалів для етиленових компресорів надвисокого тиску. 2. Характеристика об'єкта дослідження*(огляд)*

[1]Прикарпатський національний університет імені Василя Стефаника, вул. Шевченка, 57, м. Івано-Франківськ, 76018, Україна, mar.martinyuk2904@gmail.com
[2]Хмельницький національний університет, вул. Інститутська, 11, м. Хмельницький, 29016, Україна

Досліджено технологію отримання та властивості етиленових композицій з різним вмістом мастил. Вивчено антифрикційні властивості нафтових та поліглікольних олив. Показано, що продукти конденсації відповідно етиленгліколю та пропіленгліколю мають сьогодні практичний інтерес як мастильні матеріали. Показано в'язко-механічні властивості поліетилену при додаванні різної кількості мастильних матеріалів.

Ключові слова: поліетилен, мастила, композиції, полігліколі, діелектричні властивості, термооксиданти, компресори.