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Problem of Selection and Properties of Lubricants for Ethelene High-Pressure Compressors. 5. Compatibility of Oils with Polyethylene

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Technology of obtaining and properties of ethylene compositions with different content of oils inside is researched. It is shown viscous-mechanical properties of polyethylene during addition of different quantity of lubricants. The results of researches of physics-mechanics and dielectric properties of polyethylene, synthesized during ingress of naphtene, with addition of 0,15% of different oils and thermooxidants.

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

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Introduction

About 60 % of high-pressure polyethylene is used for making products by method of moulding and pressurization-containers for food industry, products of domestic chemistry and children's toys, 20 %- for making special films, which are stable to thermo- and photooxidation, films of capacitors and cable isolation with the heightened demands to the thermal aging and dielectric properties [14].

One of the most important problems of the making is choosing the high lubrication gaskets of the cylinders or shafts of ethylene compressor. Delivering fluid lubricant to the friction pair is realized either by injection it in to the gas (phase of the suction- when use gaskets with the pistons rings) or by feeding it through the openings of drilling of gasket's element (when use glad gaskets) [1, 3].

According to [1], in compressors at the compression up to 22 - 40 MPaspecific loadings of the gasket's elements reaches 7 – 10 MPa. In ethylene compressors gas compresses from 25 up to 110 – 120 MPa (on the first degree) and from 110 – 120 MPa up to 180 - 250 (and even to 350) MPa (on the second degree). There fore, gasket elements of compressors experience during lubrication influence of the limit specific loadings from the hydrodynamic to limit regime and even to seizure [2; 14].

In ethylene compressors friction pair are used:

– piunger made from the nitrided steel 38 ХМЮА or with coating of Wolfram carbide ; gasket elements from the bronze Бр ОСН 7-13-1;

– bush of the cylinder from the carbide of Wolfram (type БК-6), gasket rings from the special alloyed cast iron or from the bronze Бр ОФ > 10-1.

And also indexes of flow of plastics (g for 10 mm.), changes of bound of strength and flow during tension, relative extension during breakage ought to be found.

Demands to physic-and-chemical properties of polyethylene are determined by STATE STANDARD 16337-77 (for polyethylene) and STATE STANDARD 16336-77 (for compositions of polyethylene). Dialectical properties of polyethylene and its composition are determined by [11-14]:

– tangent of angle of dialectical loss – STATE STANDARD 22372-77;

– electrical strength at variable voltage (frequency 50 hertz) – STATE STANDARD 64333-71;

– dialectical penetrability (frequency 10^6 hertz) – STATE STANDARD 22372-71;

– resistance to thermal aging – STATE

STANDARD 16336-77.

Block-effect (sticking together films) and content of extraction substances which are in initial polyethylene and which educe from it during secondary processing relate to quality indicators of polyethylene too. Content of these substances is estimated by excess of organic substance during lubrication of ethylene compressors with mineral oil and by using light mineral oils as solvents during peroxidative initiation of polymerization of ethylene [12-14].

Feasibility study of supplying of lubrication of seal elements relates not only to quality of polyethylene but to time wasted of compressor's equipment for repair (up to 2 – 7 days for a year), which for high productivity producers (synthesis of polyethylene) turns as substantial economical losses. More over it is necessary to add that after every seal replacement necessity (100 - 300 hours) of feeding through lubricators excess of oil (for running-in of friction pair) comes into existence. Polyethylene made in this period contents of substantial quantity of oil that is not up to the requirements (for cable isolation) [6-7].

I. Materials

The demands to wear resistance of surfaces are: intensity of wearing counterface from alloy BK-6 is ought to be not higher than 0.02 μm/hour or 0.05 mm for 2500 hours of compressor work.

Pressure of pumping is 200 – 300 MPa, temperature of gas at the end of process reaches 373 K, average velocity of piston – up to 2.5 m/s. Consumption of the oil for 1 t final product – polyethylene for different compressors is from 0.7 - 0.9 to 4.7 - 6.5 kg.

Properties and nature of oils determine quality indicators of polyethylene and reliability of work of seal pistons and plungers of ethylene's compressors. For lubrication of friction pair of these compressors mineral (naphthene - «white» oils), polybutene and polyglycol oils are used [3; 4],

Specifications to oils are: transparence, colourlessness, absence of sediment and mechanic impurities, viscosity (not less than) approximately 450 cs at 303 K, 200 cs at 323 K, 50 cs at 373 K; temperature of flash must be higher than 293 R from the maximal allowable (373-383 K), but better not lower than 473 K; temperature of solidification – not higher than 273 K; acid number -not more than 0,4 mg KOH/g; alkali number 0 mg KOH/g; content of moisture not more than 0.1 %; ashes -0 %; point of turbidity of 1 % solution -not more than 353K [9].

According to manufacturers naphtene and polyglycol oils for the most quantity indicators satisfy these requirements (Table1).

Physic-and-chemical properties and quantity of oil which ingresses in polyethylene determine its properties and use for cable isolation, products, which contact with food etc. [8].

II. Methods of testing

Content of oil appreciably has an influence on such quality indicators as resistance (durability) to thermal aging and cracking and photooxidation processes, tangent of angle of dialectical loss, dialectical penetrability, breakdown electrical stress, sanitarian-hygienically properties. Content of oil in polyethylene is estimated by IR-spectroscopy (graduate by solution in CCl_4), tangent of angle of dielectric loss (frequency 10^3, 10^4, 10^6 hertz), dielectric penetrability (frequency 10^6

Table 1

Characteristic of properties of naphtene and polyglicol oils (information of producers)

Index	Rieslla-33	NKM-40	NKM-70	Laprol 2502-2-70	Orites-270 DS
Density,kg/m^3 at 293 K at 303 K	 884 878	 873 867	 884 878	 1078	 1080
Coefficient of refraction of light (293K)	1.4820	1.4794	1.4800	-	-
Viscosity kinematic, cs at 293 K at 303 K at 373 K	 126 42.4 8.8	 80.2 39.3 9.8	 180 70.4 12.8	 417 182 54	 462 186 46.8
Acid number, mg KOH/g	0.007	0.006	0.006	0.019	0.016
Temperature of solidification, K	255	255	260	-	≤ 270
Temperature, K in closer crucible in open crucible	 475 494	 470 488	 478 498	 489 523	 493 523
Content of water, %	0	0	0	0,1	0,1
Content of mechanic impurities, %	0	0	0	0	0

hertz) [5-7].

Were tested properties of high-pressure polyethylene (trademarkl0803-020), which was made in autoclave reactor with lubrication of compressors by naphtene oil Risella-33, and its artificial mixtures with 0.10 and 0.15 % of oils: polyglycol Orites-210 DS and Syntheso-201 N, polyvynilbutylether (PVBE) and mixture 70 % PVBE+30 % Risella-33 without or with addition of thermostabilizer and 0.1 – 0.5 % inhibitors of chain oxidation process – ionol, monox, diafen.

Artificial mixtures were got on laboratory mixer «Venbery» with mixing during 5 – 7 min. (t = 393 – 403 K). After were made tablets, which were rolled (T = 433 ± 5 K) and fiictioned 1:1.2 during 2 - 16 hours.

Were found indexes [6-9]:

– tangent of angle of dielectric losses tg δ (frequency 10^6 Hz) by STATE STANDARD 22372-77;

– electrical strength $U_{cr.}$ during variable voltage with frequency 50 Hz by STATE STANDARD 6433.3-71;

– dielectric penetrability ε(frequency 10^6 Hz) by STATE STANDARD 22372-77;

– density ρ, boundary flow σ_T, limit strength σ_B and relative elongationduring breakage γ by STATE STANDARD 16337-77;

– index of solution flow (ISF).

More over were taken into account methods of finding sanitarian-hygienical, dielectric, physics-and-mechanics properties and resistance to thermooxidative aging [10; 13; 14], Polyethylene for cable isolation by STATE STANDARD16336-79 has to have such indexes:

– tangent of angle of dielectric losses tg δ (frequency 10^6 Hz) not more than

– $tg\delta \leq 3 \cdot 10^4$;

Table 2

Physics-mechanics and dielectric properties of polyethylene (trademark 10803-020), synthesized during ingress of naphtene oil Risella-33, with addition of 0.15 % of different oils and thermooxidants (recipe 01 and 02)

Recipe	Oils additives	Time of thermal aging, hours	ρ, kg/m^3	IFS, g/10 min.	tgδ,10^{-4}	σ_B, MPa	σ_T, MPa	γ,%
-	-	0	918.5	2.05	1.0	12.65	9.91	630
-	Syntheso - D201 N	0	919.2	2.16	2.11	12.75	10.30	613
0.2	Syntheso - D201 N	0	919.5	2.07	1.95	13.54	10.89	595
0.2	Syntheso - D201 N	6	-	11.6	10.95	9.32	10.89	555
0.2	Syntheso - D201 N	8	-	-	16.8	8.50	9.90	430
0.1	Syntheso - D201 N	0	920	2.15	1.95	12.96	10.3	598
0.1	Syntheso - D201 N	6	-	2.21	1.99	12.85	10.2	574
0.1	Syntheso - D201 N	8	-	2.26	4.28	11.67	10.0	563
-	PVBE	0	918.3	2.15	1.68	12.56	10.4	583
0.2	PVBE	0	918.5	2.22	1.65	13.54	11.09	608
0.2	PVBE	6	-	2.41	1.71	13.44	10.79	561
0.2	PVBE	8	-	2.51	2.5	13.34	10.59	560
0.1	PVBE	0	918.5	2.20	1.15	12.75	10.79	593
0.1	PVBE	6	-	2.22	1.52	12.16	10.20	565
0.1	PVBE	8	-	2.30	1.85	11.28	9.42	577
-	PVBE+30% Risella-33	0	918.3	2.06	1.98	12.56	9.71	600
0.2	PVBE+30% Risella-33	0	918.3	2.37	2.10	13.63	11.09	612
0.2	PVBE+30% Risella-33	6	-	2.39	2.19	12.26	10.04	555
0.2	PVBE+30% Risella-33	8	-	2.44	2.72	11.48	9.91	550
0.1	PVBE+30% Risella-33	0	918.3	2.22	1.05	13.54	10.40	603
0.1	PVBE+30% Risella-33	6	-	2.32	1.36	12.85	10.20	600
0.1	PVBE+30% Risella-33	8	-	2.35	1.44	12.36	9.91	593

Table 3

Viscous-mechanical properties of polyethylene (trademark 10803-020) during addition of different quantity of lubricants

Polyethylene trademark	Oil	Concentration of oil	ISF g/10 min	tg δ, 10^{-4}	Resistance to cracking, hours
M 10803-020	-	-	2.05	1.0	2.5
M 10803-020	Syntheso D-201 N	0.15	2.16	2.11	2.5
M 10803-020	Syntheso D-201 N	0.10	2.11	1.82	2.5
M 10803-020	PVBE	0.15	2.15	1.68	2.5
M 10803-020	PVBE	0.10	2.23	1.04	2.5
M 10803-020	PVBE (70%)+ Risella-33 (30%)	0.15	2.06	1.98	2.5
M 10803-020	PVBE (70%)+ Risella-33 (30%)	0.10	2.35	1.09	2.5

Polyethylene trademark	Oil	Mechanical properties			Density, km/m^3
		σ_1, MPa	σ_2, MPa	γ,%	
M 10803-020	-	12.65	9.91	630	918.5
M 10803-020	Syntheso D-201 N	12.75	10.3	613	919.2
M 10803-020	Syntheso D-201 N	13.04	10.69	608	919.3
M 10803-020	PVBE	12.56	10.4	583	918.3
M 10803-020	PVBE	12.94	10.49	600	918.7
M 10803-020	PVBE (70%)+ Risella-33 (30%)	12.56	99.971	600	918.3
M 10803-020	PVBE (70%)+ Risella-33 (30%)	12.26	10.11	555	918.1

– dielectric penetrability ε (frequency 10^6 Hz) not more than $\varepsilon \leq 2.3$;

– electrical strength when thickness of specimens is 1 and i variable voltage with

– frequency 50 Hz not less than $U_{cr.} \geq 40$ кВ/мм [6-10].

III. Results and discussion

Results of laboratory tests are adduced in Table 2. As we can see from Table 2, resistance to thermal aging for ethylene composition determines by oil's nature, its content in polymer and activity and content of thermostabilizer – antioxidants. For recipe with content 0.05 % of oil Orites-210DS and 0.1 - 0.2 % stabilizer nonox WSP resistance to thermal aging is 8 hours, that is up to the requirements of STATE STANDARD 16336-77, for ethylene composition with content 0.05 % of polyvynilbutylether oil is more than 14 hours.

As it is seen from the table 2, addition of 0.15 % of poly glycol Syntheso – D201 N with additive to initial and with thermoadditives (by recipe 01 and 02) of polyethylene leads to substantial changes of physics-and-chemical and dialectic properties. For recipe 02 of thermal aging during 8 hours leads to decreasing: tgδ from 1.95 to $16 \cdot 10^{-4}$, σ_B from 13.54 to 8.5 MPa, σ_T from 10.89 to 9.9 MPa, γ from 595 to 437 %, and for recipe 01 these changes smaller: tgδ from 1.95 to $4.28 \cdot 10^{-4}$, σ_B from 12.96 to 11.67 MPa, σ_T from 10.3 to 10.0 MPa, γ from 598 to 563 %.

Addition of 0.15 % of initial polyvynilbutylether or with mixtures of Risella-33 to initial and with thermoadditions polyethylene leads to small changers its properties (these changes are smaller for recipe 01 than for recipe 02) for indexes: tgδ from $1.05\text{-}2.1 \cdot 10^{-4}$ to $1.44\text{-}2.72 \cdot 10^{-4}$, σ_B from 12.75-13.63 MPa to 11.28-13.34 MPa, σ_T from 10.4-11.09 MPa to 9.42-10.59 MPa, γ from 593-612 % to 550 – 593 %. In table 3 are adduced properties of polyethylene (trademark 10803-020) during input to it of 0.1 and 0.15 % (weight) of tested oils. As is seen from the Table 3, physics-and-mechanical properties of polyethylene stay up to requirements of STATE STANDARD 16337-77.

Table 4

Properties of ethylene compositions (recipe 0,1 and 0,2) with different content of oils inside

Recipe	Oil	Concentration of oil	Thermal aging, hours	IFS, g/10 min.	Tg δ, 10^{-4}	Resistance to cracking, hours
0.2	Syntheso D-201 N	0.15	init. 5.5	2.07 11.6	1.95 10.95	2.5
0.2	Syntheso D-201 N	0.10	init. 6 8	2.19 do not sust. do not sust.	2.59 9.32 16.9	2.5
0.1	Syntheso D-201 N	0.15	init. 6 8	2.15 2.21 2.26	1.95 1.99 4.28	2.5
0.1	Syntheso D-201 N	0.10	init. 6 8	2.21 2.18 2.22	1.88 1.79 1.96	2.5
0.2	PVBE	0.10	init. 6 8	2.18 2.22 2.30	1.15 2.19 2.30	2.5
0.2	PVBE	0.15	init. 6 8	2.22 2.41 2.51	1.65 1.71 2.5	2.5
0.1	PVBE	0.10	init. 6 8	2.20 2.17 2.09	1.48 1.54 2.19	2.5
0.1	PVBE	0.15	init. 6 8	2.20 2.22 2.30	1.15 1.52 1.85	2.5
0.2	PVBE (30%)+ Risella-33 (70%)	0.15	init. 6 8	2.37 2.30 2.44	2.10 2.19 2.72	2.5
0.2	PVBE (30%)+ Risella-33 (70%)	0.10	init. 6 8	2.31 2.35 2.38	1.50 1.53 1.54	2.5
0.1	PVBE (70%)+ Risella-33 (30%)	0.10	init. 6 8	2.15 2.25 2.25	1.09 1.11 1.35	2.5
0.1	PVBE (70%)+ Risella-33 (30%)	0.15	init. 6 8	2.22 2.32 2.35	1.05 1.36 1.44	2.5

Analysis of results in Table 4, shows that physics-and-mechanical properties of compositions are up to requirements of STATE STANDARD 16337-77. Oil PVBE and its mixtures with oil Risella-33 provide quality of compositions of recipe 0.1 and 0.2 up to requirements of STATE STANDARD 16337-77, (and to index “resistance to thermal aging”. Oil Syntheso D-201 makes worse properties of polyethylene compositions of recipe 0.1 and 0.2, especially its resistance to thermooxidative aging [14].

Conclusions

Were tested properties of high-pressure polyethylene (trademarkl 0803-020), which was made in autoclave reactor with lubrication of compressors by naphtene oil Risella-33, and its artificial mixtures with.

It is shown resistance to thermal aging for ethylene composition determines by oil’s nature, its content in polymer and activity and content of thermostabilizer – antioxidants. As is seen, addition of 0.15 % of poly glycol Syntheso – D201 N with additive to initial and with thermoadditives (by recipe 01 and 02) of polyethylene leads to substantial changes of physics-and-chemical and dielectric properties.

Analysis of results shows that physics-and-mechanical properties of polyethylene (trademark 10803-020) during input to it of 0.1 and 0.15 % (weight) of tested oils and of compositions are up to requirements of STATE STANDARD 16337-77. Oil PVBE and its mixtures with oil Risella-33 provide quality of compositions of recipe 0.1 and 0.2 up to requirements of to index “resistance to thermal aging”. Oil Syntheso D-

Continuation Table 4

Recipe	Oil	Concentration of oil	Mechanical properties			Density, km/m^3
			σ_1, MPa	σ_1, MPa	σ_1, MPa	
0.2	Syntheso D-201	0.15	13.54 9.32	10.89 10.89	595 555	919.5
0.2	Syntheso D-201	0.10	12.76 12.36 10.40	10.39 11.18 11.48	595 594 436	920.0
0.1	Syntheso D-201	0.15	12.96 12.85 11.67	10.30 10.20 10.00	598 574 563	920.0
0.1	Syntheso D-201	0.10	12.46 12.07 11.38	10.69 10.69 10.59	610 449 448	919.5
0.2	PVBE	0.10	13.74 12.46 12.26	11.08 9.32 9.52	597 555 560	918.7
0.2	PVBE	0.15	13.54 13.44 13.34	11.09 10.79 10.59	608 561 560	918.5
0.1	PVBE	0.10	12.85 12.95 13.54	10.89 10.40 10.49	525 585 588	918.7
0.1	PVBE	0.15	12.75 12.16 11.28	10.79 10.20 9.42	593 565 577	918.5
0.2	PVBE (30%)+ Risella-33 (70%)	0.15	13.63 12.26 11.48	11.09 10.40 9.91	612 555 550	918.3
0.2	PVBE (30%)+ Risella-33 (70%)	0.10	12.36 12.46 12.75	10.11 9.91 9.91	570 563 580	918.3
0.1	PVBE (70%)+ Risella-33 (30%)	0.10	13.34 12.95 12.26	10.69 9.91 9.91	585 577 595	918.5
0.1	PVBE (70%)+ Risella-33 (30%)	0.15	13.54 12.85 12.36	10.40 10.20 9.91	603 600 593	918.3

201 makes worse properties of polyethylene compositions of recipe 0.1 and 0.2, especially its resistance to thermooxidative aging.

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Проблема вибору та властивостей мастильних матеріалів для етеленових компресорів надвисокого тиску. 5. Сумісність олив з поліетиленом

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Досліджено технологію отримання та властивості етиленових композицій з різним вмістом мастил всередині. Показано в'язко-механічні властивості поліетилену при додаванні різної кількості мастильних матеріалів. Приведені результати досліджень фізико-механічних та діелектричних властивостей поліетилену, що синтезований при надходженні нафтенового масла, з додаванням 0,15% різних мастил та термооксидантів.

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