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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Preparation of Flame-Resistant Liquids Based on Mixed Tri(phenyl, *p-tert*-butylphenyl) Phosphates by Transesterification of Triphenyl Phosphate with *p-tert*-Butylphenol

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Abstract—The possibility of controlling the composition of a mixture of triphenyl phosphate, p-*tert*-butylphenyl diphenyl phosphate, di(p-*tert*-butylphenyl)phenyl phosphate, and tri(*p-tert*-butylphenyl) phosphate, formed by transesterification of triphenyl phosphate with *p-tert*-butylphenol, was demonstrated. The amount of *p-tert*-butylphenol necessary for transesterification of triphenyl phosphate to yield a mixture of phosphates of required composition was determined. If necessary, the composition of the phosphates can be adjusted by selective distillation of triphenyl phosphate in a vacuum.

Keywords: transesterification, triphenyl phosphate, *p-tert*-butylphenol, flame-resistant liquids

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Low-toxic biodegradable flame-resistant oil based on mixed *p-tert*-butylphenyl phenyl phosphates is widely used as an additive to polymers and lubricants; it is the base of the majority of liquids for hydraulic systems and working lubricating liquids, ensuring accident-free operation of turbines with high parameters of the working medium, including power facilities of nuclear power plants [1–3].

Wide range of functionalized phosphates, phosphonates, and phosphinates can be prepared by catalytic esterification of compounds containing P(O)–OH groups with diaryliodonium triflates [4], with phenols in the presence of silicon chlorides as catalysts [5], and when using as phosphorylating agents white phosphorus [6], phosphorus pentoxide [7], and phosphorylpyridine derivatives [8]. Singh and Nolan [9] reported preparation of phosphates by transesterification in the presence of N-heterocyclic carbenes. However, the process that is widely used for commercial synthesis of triaryl phosphates is based on the reaction of phenols with phosphorus oxychloride:

$$O{=}PCl_3 + 3ArOH \rightarrow (ArO)_3P{=}O + 3HCl. \qquad (1)$$

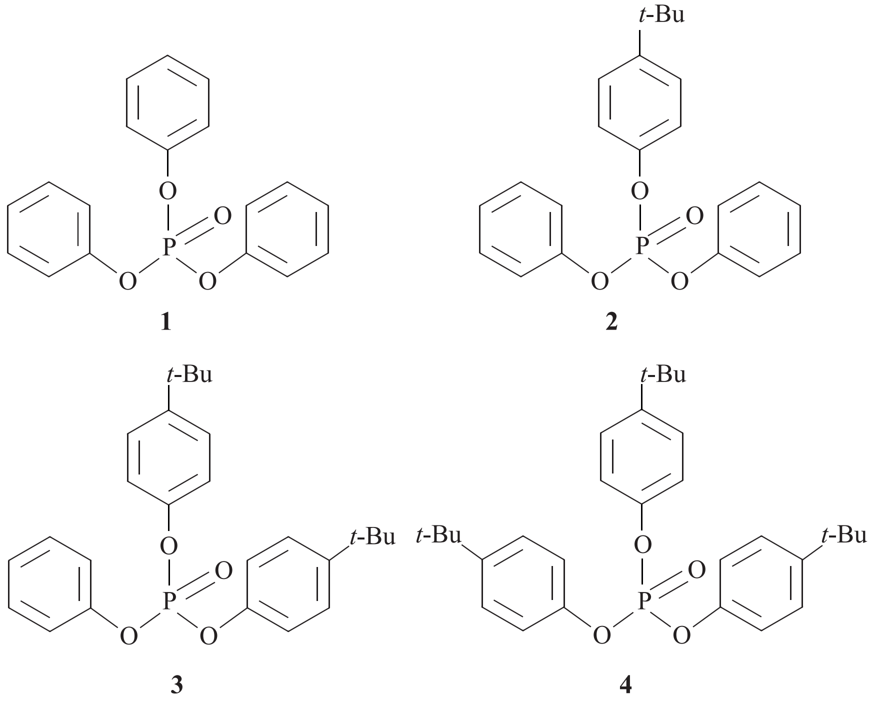
Synthetic flame-resistant butylated oil is prepared using a mixture of phenol and *p-tert*-butylphenol (BP). The reaction yields an equilibrium mixture of esters **1–4** (Scheme 1) with statistical distribution of components, usually containing 15–30% **1** (in some cases, up to 50%) [1–3, 10].

The quantitative composition of a mixture of esters **1–4** strongly influences the physicochemical and operation properties of the mixture (viscosity–temperature characteristics, pour point, lubricating properties, resistance to hydrolysis and oxidation, deaeration, etc.) and its toxicological characteristics. The composition is usually optimized to impart to the oil the properties meeting the specific requirements.

The major components of the oil used for turbine systems are unsymmetrical esters **2** and **3** at minimal content of symmetrical phosphates **1** and **4** [1–3, 10].

This is due, in particular, to the fact that triphenyl phosphate exhibits low resistance to hydrolysis. Its presence accelerates the degradation of phosphate esters under the action of moisture [1–3] and causes undesirable increase in the deaeration time of the

Scheme 1. Components of butylated oil.



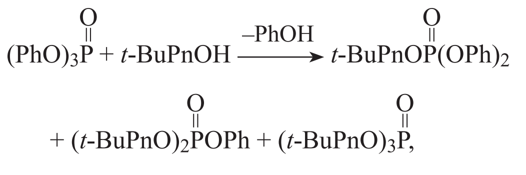
(**1**) Triphenyl phosphate, (**2**) *p-tert*-butylphenyl diphenyl phosphate, (**3**) di(*p-tert*-butylphenyl) phenyl phosphate, and (**4**) tri(*p-tert*-butylphenyl) phosphate.

resulting oil [10]. On the other hand, increased concentrations of **3** and **4** lead to an increase in the viscosity of the mixture [11].

The content of triphenyl phosphate in a quaternary mixture of **1–4** is decreased to a residual concentration of ~2% by distillation using a film evaporator; in the process, 5–30 wt % of the initial mixture is lost [12].

In addition, the concentration of **1** can be reduced to <5% by using as a phosphorylating agent diphenyl phosphorochloridate and/or phenyl phosphorodichloridate [10]. However, implementation of this procedure is complicated by difficult availability of the phosphorochloridates and their easy hydrolysis.

In this study, we examined the possibility of controlling the content of the components in a mixture of triaryl phosphates formed by transesterification:



$$(PhO)_3\overset{O}{\overset{\|}{P}} + t\text{-BuPnOH} \xrightarrow{-PhOH} t\text{-BuPnO}\overset{O}{\overset{\|}{P}}(OPh)_2 + (t\text{-BuPnO})_2\overset{O}{\overset{\|}{P}}OPh + (t\text{-BuPnO})_3\overset{O}{\overset{\|}{P}}, \quad (2)$$

where Ph is phenyl; Pn, phenylene; and *t*-Bu, *tert*-butyl.

EXPERIMENTAL

Triphenyl phosphate (>99%) was prepared at the Rosneft Research and Development Center according to [13]. *p-tert*-Butylphenol (99.5%, Novokuibyshevsk Petrochemical Company, Russia) was used without additional purification. Potassium carbonate (99%, Acros Organics) was preliminarily calcined to constant weight at 200°C. Hydrochloric acid (35–38%, NevaReaktiv, Russia) was used for neutralizing reaction mixtures. The quantitative composition of triaryl phosphate mixtures was determined by gas chromatography with a Thermo Finnigan Focus GC device equipped with a flame ionization detector and a ZB 5HT Inferno capillary column (30 m × 0.32 mm × 0.25 μm) under the following conditions: vaporizer temperature 350°C; carrier gas helium, column inlet pressure 130 kPa, flow rate before splitting 80 mL^{-1}, detector temperature 350°C; flow rates through detector, mL min^{-1}: air 350, hydrogen 40, helium 30; column temperature schedule: initial temperature 60°C, 6 min; heating to 340°C at a rate of 15 deg min^{-1}; 340°C, 10 min.

The quantitative composition of the mixtures was calculated by the equation

$$c_{w_i} = \frac{S_i K_i}{\sum_{i=1}^{n}(S_i K_i)} \times 100, \qquad (3)$$

where c_{wi} is the weight fraction of *i*th component in the mixture; *n*, number of components; S_i, peak area of *i*th component; K_i, relative response factor of *i*th component.

Response factors K_i: phenol 0.868, *p-tert*-butylphenol 0.831, **1** 1.000, **2** 0.960, **3** 0.930, and **4** 0.910. A typical chromatogram of the triaryl phosphate mixture is shown in Fig. 1.

The transesterification of triphenyl phosphate was performed on a laboratory installation consisting of a three-necked flask as a still pot and a heated packed column *d* 40 × 360 mm (spiral packing *d* 3.5 × 3 mm made of wire *d* 0.5 mm; steel 12Cr18Ni10Ti). The still pot was heated with a CMUA2000/CE Electrothermal flask heater–stirrer. The temperatures of the still pot, column, and distilled phenol vapor were monitored with thermoelectric sensors. The vacuum was made with a Vacuubrand pump (Germany).

In a typical experiment, the still pot was charged with 1532.70 g (4.67 mol) of triphenyl phosphate, 328.45 g (2.186 mol) of *p-tert*-butylphenol, and 15.18 g (0.110 mol) of anhydrous potassium carbonate as a catalyst (1 wt % based on triphenyl phosphate). The transesterification was performed at a residual pressure of 10 mmHg with continuous distillation of phenol through the packed column. The still pot temperature was increased from 130 to 220°C at such a rate that the column temperature did not exceed the phenol boiling point at a residual pressure of 10 mmHg (about 90°C). After separation of the major fraction of phenol, the column temperature was elevated to 250°C by electric heating for more complete removal of residual phenol from the packing, and the still pot was kept at 220°C for 20 min to stabilize the equilibrium between esters **1**–**4**. After the completion of the phenol distillation, the reaction mixture was cooled to 40–50°C, hydrochloric acid was added for neutralization (2 mol per mole of potassium carbonate taken into the reaction), and the mixture was stirred for 4 h. The KCl precipitate was filtered off, and the reaction mixture composition was determined by gas chromatography.

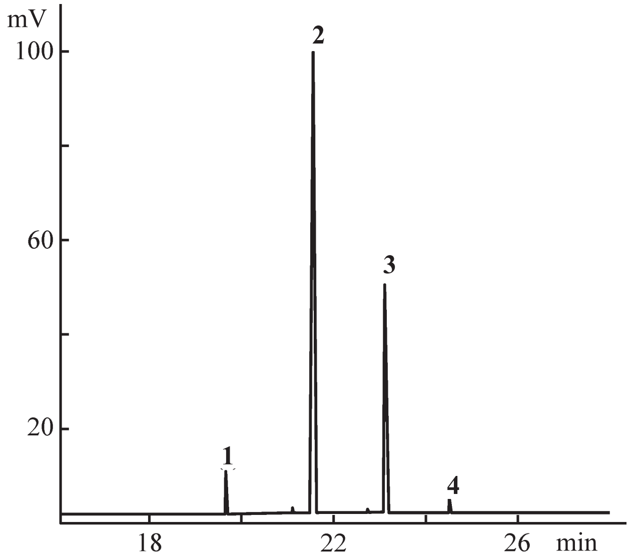


Fig. 1. Typical chromatogram of a mixture of aryl phosphate esters. (**1**) Triphenyl phosphate, (**2**) *p-tert*-butylphenyl diphenyl phosphate, (**3**) di(*p-tert*-butylphenyl) phenyl phosphate, and (**4**) tri(*p-tert*-butylphenyl) phosphate.

To isolate the flame-resistant oil, the neutralized reaction mixture was subjected to fractional distillation using the heated packed column. As a result, we obtained 894.60 g of the triphenyl phosphate fraction with T_b 235–244°C/10 mmHg (97 wt %) and 737.66 g of the target fraction of the flame-resistant oil with T_b 255–287°C/10 mmHg of the composition (wt %): **1** 0.45, **2** 81.48, **3** 17.01, and **4** 1.06; $T_{\text{cong}} = -18$°C; kinematic viscosity at 50°C 26 $\text{mm}^2\ \text{s}^{-1}$, *p-tert*-butylphenol conversion 99.5%. The isolated triphenyl phosphate fraction can be reused in the next cycle of flame-resistant oil preparation. The pour point was determined by method B of GOST (State Standard) 20287, Petroleum Products. Methods for Determining the Flow and Pour Points, and the kinematic viscosity, by the ASTM D445 method, Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity).

RESULTS AND DISCUSSION

Requirements to flame-resistant turbine oils concern a number of parameters. According to [1–3], to ensure the hydrolytic stability and required deaeration level, the content of phosphate **1** in the oil should not exceed

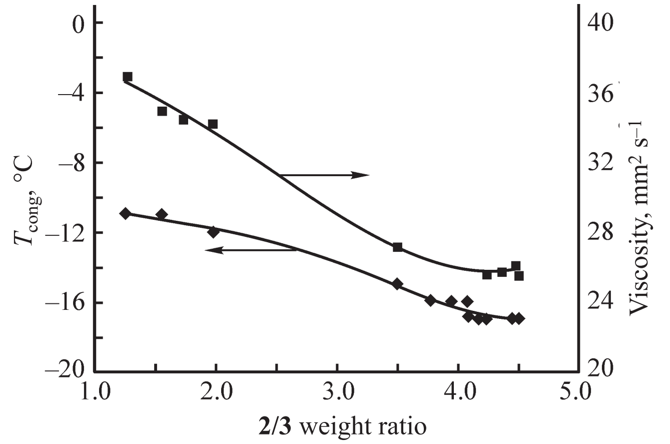
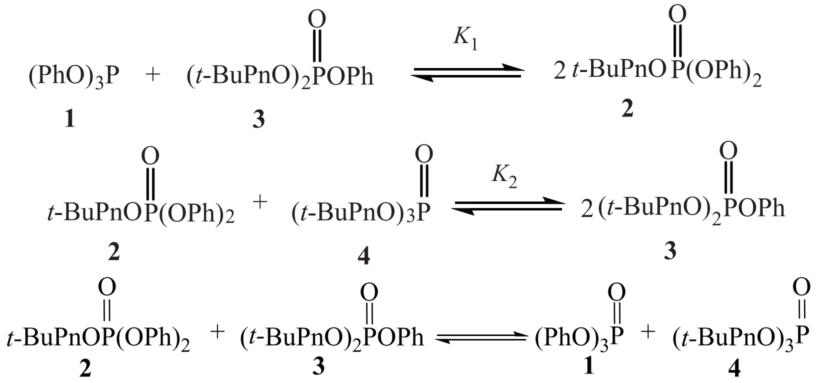


Fig. 2. Pour point and kinematic viscosity (50°C) of butylated oil consisting of esters **1–4** as functions of the **2/3** weight ratio. (**1**) Triphenyl phosphate, (**2**) *p-tert*-butylphenyl diphenyl phosphate, (**3**) di(*p-tert*-butylphenyl) phenyl phosphate, and (**4**) tri(*p-tert*-butylphenyl) phosphate. Total content of **1** + **4** 3–10 wt %.

4–5 wt %. The kinematic viscosity should be no lower than 23 mm^2 s^{-1} at 50°C, and the pour point should not exceed −17°C.[1] It has been found that these characteristics also directly correlate with the quantitative composition of the butylated oil.

Figure 2 shows how the pour point and kinematic viscosity depend on the oil composition (**2/3** weight ratio). As this ratio is changed from 1.2 to 4.0, the pour point decreases from −11 to −17°C, and the kinematic viscosity measured at 50°C decreases from 37 to 25 mm^2 s^{-1}. As can be seen, the **2/3** weight ratio of 4.0–4.5 in the butylated oil formula ensures the required (prescribed by regulations) levels of kinematic viscosity and pour point of the oil. Thus, ester **2** should be the major component of the oil (about 70–80 wt %).

The base-catalyzed reaction of **1** with *p-tert*-butylphenol (BP) allows preparation of products with different degrees of transesterification [Eq. (2)]. The fractions and proportions of products **2–4** depend on the ratio of **1** and BP in the loaded reactant mixture. After the completion of phenol distillation (phenol is distilled off in the equimolar amount relative to the loaded BP), an equilibrium mixture of triaryl phosphates **1–4** is formed (Scheme 1). The equilibrium between components **1–4** is considered as attained if the component concentrations do not further vary in time. The following equations of equilibrium chemical reactions correspond to the attained equilibrium in the mixture of esters **1–4**:



$$\underset{\mathbf{1}}{\mathrm{(PhO)_3P}} + \underset{\mathbf{3}}{(t\text{-}\mathrm{BuPnO})_2\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{OPh}} \xrightleftharpoons{K_1} \underset{\mathbf{2}}{2\,t\text{-}\mathrm{BuPnO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{OPh})_2} \tag{4}$$

$$\underset{\mathbf{2}}{t\text{-}\mathrm{BuPnO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{OPh})_2} + \underset{\mathbf{4}}{(t\text{-}\mathrm{BuPnO})_3\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}} \xrightleftharpoons{K_2} \underset{\mathbf{3}}{2\,(t\text{-}\mathrm{BuPnO})_2\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{OPh}} \tag{5}$$

$$\underset{\mathbf{2}}{t\text{-}\mathrm{BuPnO}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}(\mathrm{OPh})_2} + \underset{\mathbf{3}}{(t\text{-}\mathrm{BuPnO})_2\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{OPh}} \rightleftharpoons \underset{\mathbf{1}}{\mathrm{(PhO)_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}} + \underset{\mathbf{4}}{(t\text{-}\mathrm{BuPnO})_3\overset{\overset{\mathrm{O}}{\|}}{\mathrm{P}}} \tag{6}$$

where K_1 and K_2 are the equilibrium constants of reactions (4) and (5), respectively.

Equation (6) is linearly dependent [it can be obtained by summation of Eqs. (4) and (5)]; therefore, it is excluded from further consideration.

Then, the equilibrium is described by the system of Eqs. (7)–(10), where the equilibrium concentrations are given in mole fractions, and BP$_0$ and I$_0$ are the loaded amounts (moles) of *p-tert*-butylphenol and triphenyl phosphate, respectively:

$$K_1 = \frac{[\mathbf{2}]^2}{[\mathbf{1}][\mathbf{3}]}, \tag{7}$$

$$K_2 = \frac{[\mathbf{3}]^2}{[\mathbf{2}][\mathbf{4}]}, \tag{8}$$

$$\frac{\mathrm{BP}_0}{\mathrm{I}_0} = [\mathbf{2}] + 2[\mathbf{3}] + 3[\mathbf{4}], \tag{9}$$

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[1] Document RD EO 1.1.2.05.04442016: Requirements to Operation and to Organization and Procedure of Tests of Transformer and Turbine Oils at Nuclear Power Plants.

$$[\mathbf{1}]+[\mathbf{2}]+[\mathbf{3}]+[\mathbf{4}]=1 \tag{10}$$

Equation (9) reflects the molar ratio of *tert*-butylphenyl fragments (substituents) to the sum of the esters, equal to the molar ratio of BP_0 to I_0 in the reactant mixture loaded for transesterification. Equation (10) is the balance with respect to phosphate esters. Knowing the equilibrium constants K_1 and K_2, we can calculate the composition of the equilibrium mixture and determine the BP_0/I_0 ratio ensuring the required **2/3** ratio in the transesterification product mixture. To determine the equilibrium constants K_1 and K_2 under the transesterification conditions, we modeled experimentally the equilibrium mixtures with different ratios of the phosphate esters (Table 1).

From the mean values of the constants, $K_1 = 2.8639$ and $K_2 = 3.0201$, by numerical solution of Eqs. (7)–(10) we calculated the dependence of the esterification mixture composition on the BP_0/I_0 molar ratio. The calculation results are plotted in Fig. 3. The calculated dependence of the **2/3** weight ratio in the equilibrium mixture of transesterification products on BP_0/I_0 is plotted in Fig. 4.

With reasonable agreement between the calculated and experimental values (Fig. 3), at a constant amount of triphenyl phosphate loaded, an increase in the amount of the BP loaded leads to a monotonic decrease in the equilibrium concentration of **1** and to an increase in the concentrations of **3** and **4**, whereas the concentration of **2** passes through a maximum at BP_0/I_0 molar ratios in the interval 0.8–1.0. The **2/3** weight ratio of 4.0–4.4, required for obtaining the oil that meets the regulation requirements to flame-resistant turbine oils with respect to viscosity and temperature characteristics, is reached at the BP_0/I_0 molar ratio in the starting mixture of ~0.5 (Fig. 4). In this case, the concentration of **4** in the equilibrium mixture is satisfactorily low (~1 wt %), whereas the concentration of triphenyl phosphate is inadmissibly high (about 53 wt %). Decreasing the concentration of **1** by increasing the BP_0/I_0 ratio leads to undesirable distribution of components **2–4** (Table 1). Indeed, as shown in [14], at the molar ratio $BP_0/I_0 = 3$ the fraction of unchanged **1** is 11 wt %, but a large amount of **4** (19 wt %). is formed. The excess triphenyl phosphate after deactivating the transesterification catalyst can be selectively separated from a mixture of phosphates **2–4** to the preset residual content by vacuum distillation. For example, at the preset residual content of **I** of 3 wt %, the oil composition is characterized by the following component ratio (wt %): **I**, 3; **2**, 79; **3**, 17; and **4**, 1. Such oil had the pour point of –18°C and the kinematic viscosity at 50°C of 26.3 mm^2 s^{-1} [15].

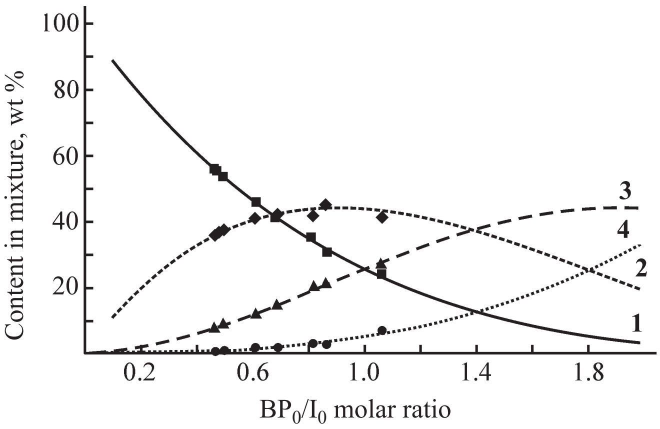

Fig. 3. Composition of the equilibrium mixture of transesterification products as a function of the BP_0/I_0 molar ratio. Points: experiment; lines: calculation by Eqs. (7)–(10). (BP_0) *p-tert*-Butylphenol, (I_0) triphenyl phosphate, (**2**) *p-tert*-butylphenyl diphenyl phosphate, (**3**) di(*p-tert*-butylphenyl)phenyl phosphate, and (**4**) tri(*p-tert*-butylphenyl) phosphate.

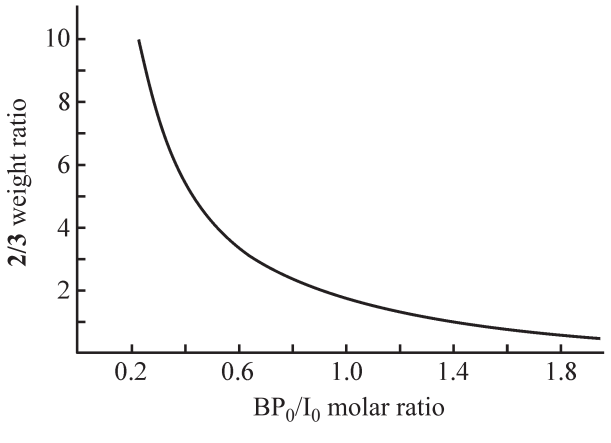

Fig. 4. Calculated dependence of the **2/3** weight ratio in the equilibrium mixture of transesterification products on the BP_0/I_0 molar ratio. (BP_0) *p-tert*-Butylphenol, (I_0) triphenyl phosphate, (**2**) *p-tert*-butylphenyl diphenyl phosphate, and (**3**) di(*p-tert*-butylphenyl) phenyl phosphate.

Thus, the equilibrium constants found and the mathematical description allow calculation of the optimum amounts of reactants loaded for transesterification to obtain the reaction mixture of

Table 1. Equilibrium composition of the phosphate mixture as a function of the molar ratio of *p-tert*-butylphenol to triphenyl phosphate and calculated equilibrium constants of reactions (4) and (5)

BP_0/I_0 molar ratio	Calculated ester mixture composition, wt %				**2**/**3**, g g^{-1}	K_1	K_2
	1	**2**	**3**	**4**			
1.060	24.43	41.36	27.12	7.09	1.53	2.5268	2.4674
0.818	35.05	41.69	20.10	3.17	2.07	2.4144	3.0094
0.864	30.99	45.23	21.25	2.54	2.13	3.0390	3.8739
0.689	41.16	42.7	14.83	1.74	2.85	2.8640	2.9446
0.613	45.65	41.02	12.13	1.20	3.38	2.9735	2.9517
0.498	53.46	37.32	8.57	0.65	4.36	2.9747	2.9543
0.497	53.52	37.27	8.57	0.65	4.35	2.9636	2.9924
0.474	55.36	36.10	7.96	0.58	4.54	2.8943	2.9583
0.464	56.00	35.87	7.61	0.52	4.71	2.9549	3.0492
0.468	55.72	36.03	7.71	0.54	4.67	2.9570	3.0295
0.478	55.01	36.40	8.01	0.58	4.54	2.9407	2.906

preset composition (preset ratio of phosphate esters **2**, **3**, and **4** in the flame-resistant oil). For example, to obtain flame-resistant butylated oil similar to commercial butylated oil Fyrquel® EHC Plus for electrohydraulic control in the turbine lubrication system (component content, wt %: **1**, 0–4; **2**, 32–78; **3**, 10–30; **4**, 0–10),[2] the calculated molar ratio of the reactants taken for transesterification, BP_0/I_0, should be in the interval 0.35–0.65 (Fig. 4). The required residual content of triphenyl phosphate is reached by removing its excess by vacuum distillation after the catalyst neutralization.

CONCLUSIONS

The possibility of controlling the composition of the triaryl phosphate mixture obtained by transesterification of triphenyl phosphate with *p-tert*-butylphenol was demonstrated. The equilibrium composition of the phosphate mixture, if necessary, can be adjusted by reducing the concentration of triphenyl phosphate by its selective vacuum distillation. The equilibrium constants K_1 and K_2 can be used for calculating the equilibrium concentrations of components **1–4** and the amount of *p-tert*-butylphenol necessary for transesterification of triphenyl phosphate to yield the required composition of the product mixture.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest requiring disclosure in this article.

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