Using 2,6-Di-*tert*-butylphenol for Obtaining of bis[3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propyl]phtalate by Ecological Acceptable Industrial Method

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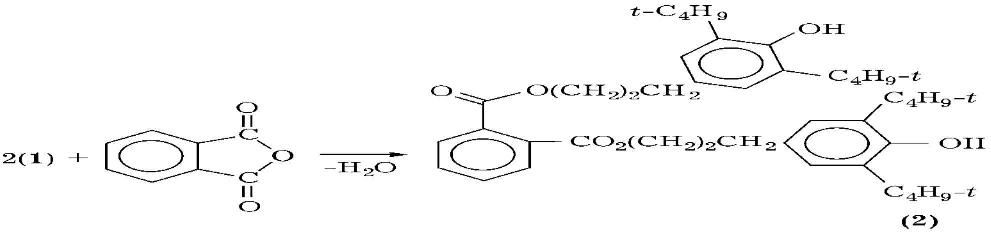
Abstract

The reaction of 2,6-di-*tert*-butylphenol with allyl alcohol resulting in the formation of 4-(3-hydroxypropyl)-2,6-di-*tert*-butylphenol is implemented on industrial scale. Condensation of the product with phthalic anhydride leads to the formation of the corresponding diphthalate, which is the final commercial product. The stability of operation at all technological stages was achieved in course of industrial practice.

Two directions have been developed for obtaining low-volatile, non-toxic and non-colouring polymer-thermostabilizing agents based on 2,6-di-*tert*-butylphenol. One of these directions is the synthesis of methyl ester of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid followed by re-esterification with alcohols; this direction has been realized in Russia in the production of phenosanes 23 and 28 [1]. Another direction is based on the use of 4-(3-hydroxypropyl)-2,6-di-*tert*-butylphenol as intermediate product; it is known as gamma-propanol. Antioxidants based on this compound are obtained by esterification using available acids or their derivatives, in particular phthalic anhydride [2, 3]. The resulting diphthalate (**2**), which is manufactured under the trademark of phenosane-43 or staphene, is efficient stabilizing agent for polymeric materials [4]. However, this direction had been long unrealized in the world industrial activities because of the absence of industrially convenient methods of obtaining compound (**1**).

We discovered [5, 6] and industrially realized a single-stage method of obtaining gamma-propanol (**1**) starting 2,6-di-*tert*-butylphenol and allyl alcohol according to scheme 1.

Laboratory experiments modeling the production of gamma-propanol (**1**) according to the indicated scheme were carried out in a



(2)

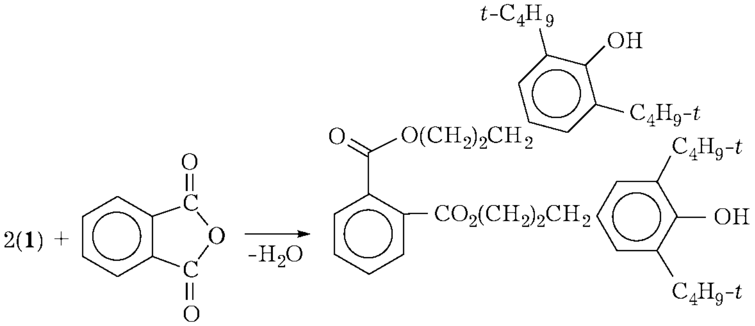
Scheme 1.

miniature steel apparatus developed at the design office of the Novosibirsk Institute of Organic Chemistry (NIOCh), SB RAS. The apparatus is 0.3 l in volume; it is equipped with a mixer with controllable frequency of rotation, heater and a filling which allows one to distillate reaction products under vacuum. This process was reproduced with an experimental installation "Orgsintez" at the experimental works of the NIOCh (Novosibirsk, Head of the Works: A. G. Khmelnitskiy).

The first successful experimental-industrial tests of the method of obtaining gamma-propanol (**1**) and diphthalate (**2**) were performed in 1979, initiated by A. I. Samokhvalov, Chief Engineer of the Moscow Oil Processing Plant (head of the works: V. A. Bulgakov). A disadvantage of the process was the presence of waste water formed in the production of gamma-propanol (**1**), which contained toxic allyl alcohol. This disadvantage was eliminated in the process described above, which produces gamma-propanol (**1**) [6] and staphene (**2**) on its basis; the process was realized at the JSC "Altaykhimprom" (Yarovoe) and introduced into industry in 1991.

To perform the reaction of gamma-propanol (**1**) synthesis in the apparatus as indicated in the scheme, starting from 2,6-di-*tert*-butylphenol and aqueous alkali, initial catalyst of the process is prepared: sodium 2,6-di-*tert*-butylphenolate. After that, the calculated amounts of 2,6-di-*tert*-butylphenol and allyl alcohol are added. The reaction is conducted under mixing at a temperature of 140–170 °C; due to the exothermal process, it is rapidly completed at increased temperature. The presence of device for urgent cooling in the reactor allows smoothing down the temperature peak of the process and to perform gamma-oxypropylation of 2,6-di-*tert*-butylphenol under the pressure not higher than 3–4 atom in the apparatus. This provides the possibility to use standard equipment of any volume in the production. In practice, the process was performed in steel reactors 3 m^3 in volume. After exposure, the alcoholic fraction, which contains unreacted allyl alcohol together with methyl, ethyl and propyl alcohols formed during the reaction, is evaporated from the reactor. Then, a small amount of unreacted 2,6-di-*tert*-butylphenol mixed with 4-methyl-, 4-ethyl-, and 4-propyl-2,6-di-*tert*-butylphenols is evaporated under vacuum. Finally, the fraction of technical-grade gamma-propanol (**1**) containing the target product at a level of 95–97 % is evaporated from the reactor under vacuum. Then new portions of 2,6-di-*tert*-butylphenol and allyl alcohol are added to the bottoms which play the role of a catalyst in the process. Alkylation and evaporation stages are repeated. The bottom catalyst survives three to six cycles of this kind without adding any fresh portions of the alkaline catalyst; after that, the catalyst is unloaded and replaced with a new one. The yield of gamma-propanol (**1**) calculated per one operation is 65–75 %.

The bottoms is a fragile weakly coloured mass containing approximately equal amounts of four components: sodium 4-(3-hydroxypropyl)-2,6-di-*tert*-butylphenolate, bis- and trisphenols, gamma-propanol ester and 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid and the products of polymerization of 2,6-di-*tert*-butylphenol and allyl alcohol. It turned out to



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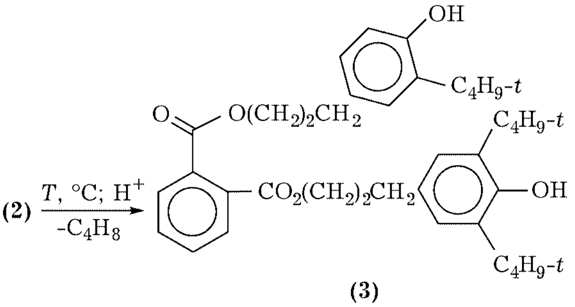
Scheme 2.



(3)

Scheme 3.

be a good stabilizing agent for polyolefins and filled plastics [7].

The final chemical stage of obtaining staphene (**2**) is performed by fusion-mixing gamma-propanol with phthalic anhydride in the molar ratio of 2 : 1 at a temperature of 140–160 °C (scheme 2). The process goes in nitrogen flow with the evaporation of water formed during reaction. After exposure, a double volume of isopropanol is added to the reaction mixture; the mixture is cooled under stirring. The precipitate is filtered, washed with isopropanol and dried. The drying stage and grinding of the product are conducted in explosion-safe and compact set-up developed and built at the Institute of Applied Physics, SB RAS (Novosibirsk) specially for this process. The yield of colourless staphene (**2**) containing 95–97 % of the target compound with melting point not lower than 94 °C is 70–80 %. The main impurity present in the filtrate and in the product turned out to be compound (**3**). This by-product is accumulated in the reaction mixture at elevated temperature and at increased exposure. Its formation was stated to be connected with mono-di-*tert*-butylation of diester (**2**) (scheme 3).

Important advantage of the final stage is the absence of waste water which was formed in the previously proposed methods of obtaining staphene (**2**) with acids [2] or bases [4] used as catalysts, which were to be neutralized after the process.

In general, the production of staphene (**2**) is performed without waste water or non-utilized waste products. The operation of experimental-industrial set-up demonstrated stability of the production at all technological stages of the process.

Recently, an information was published in the patent literature that the Japanese researchers discovered a new reaction of phenol gamma-oxypropylation for the example of obtaining gamma-propanol (**1**) from 2,6-di-*tert*-butylphenol and allyl alcohol in the presence of solvents and alkaline catalyst. The process is conducted at a temperature of 210 °C. The yield of product (**1**) is 65 % [8]. It should be noted that the indicated reaction was discovered by us in Russia 20 years ago and, as we see, it was successfully implemented till the industrial realization.

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REFERENCES

1 V. I. Paramonov, B. I. Rubinstein, L. V. Glushkova *et al.*, Tez. dokl. VIII Vsesoyuz. konf., Tambov, 1986, p. 7.
2 A. G. Khmelnitskiy, E. G. Lubenets, V. V. Aksenov *et al., Ibid.*, pp. 10–11.
3 A. P. Krysin, N. I. Nogina, V. I. Paramonov *et al., Izv. SO AN SSSR. Ser. khim. nauk,* 1 (1986) 104.
4 Inventor's Certificate 397522 SSSR, 1973.
5 Inventor's Certificate 858306 SSSR, 1981.
6 Pat. 1814807 SSSR, 1990.
7 A. M. Volkov, I. G. Ryzhikova, A. P. Krysin *et al.*, Tez. dokl. 9-go otraslevogo soveshch. "Problemy i perspektivy razvitiya Tomskogo neftekhimicheskogo kombinata", Tomsk, 1995, p. 30.
8 Pat. 64220 Japan, 2001.