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Bis[3-(3,5-dialkyl-4-hydroxyphenyl)propyl]mono- and Disulfides as the Sevilen Stabilizers

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Abstract—The effect of the shielding degree of the phenol hydroxy group on the hydrolytic and thermal stability of ethylene–vinyl acetate copolymer (Sevilen) was studied on a series of phenols containing one or two sulfur atoms in the aliphatic chain of the *para*-substituent. Among the synthesized compounds a group of disulfides was found with a high antioxidant efficiency, which increase the Sevilen hydrolytic stability. The most effective are the 6-*tert*-butyl-2-methylphenol derivatives.

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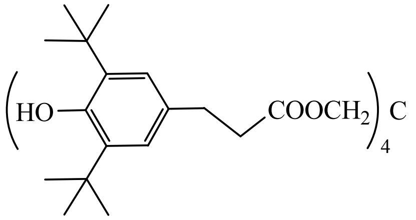
Sevilen, a copolymer of vinyl acetate with ethylene, is widely used: from the transparent goods of medical purpose, toys, and packaging, appropriate for the use in contact with the human body and food, to polymer composites used for the manufacture of the products for the technical application. The known handbooks listing the additives for polymers do not contain information on the Sevilen stabilizers.

While studying the thermal degradation of Sevilen the processes with different mechanisms have been observed, including radical and hydrolytic degradation [1]. Hence, the Sevilen stabilizers should be multifunctional, as well as non-toxic and not colorizing the copolymer. The number of such substances among those permitted for the use in polymer processing is very limited.

Sevilen differs from many polymers by its low hydrolytic stability. There is no published information of compounds improving hydrolytic stability of polymers, in particular, of Sevilen, that is essential for the creation of its compositions. By our knowledge, the set of complex antioxidant additives definitely includes a sulfur-containing stabilizer of technical purpose TAB [2], but it is not listed among the low-toxic additives.

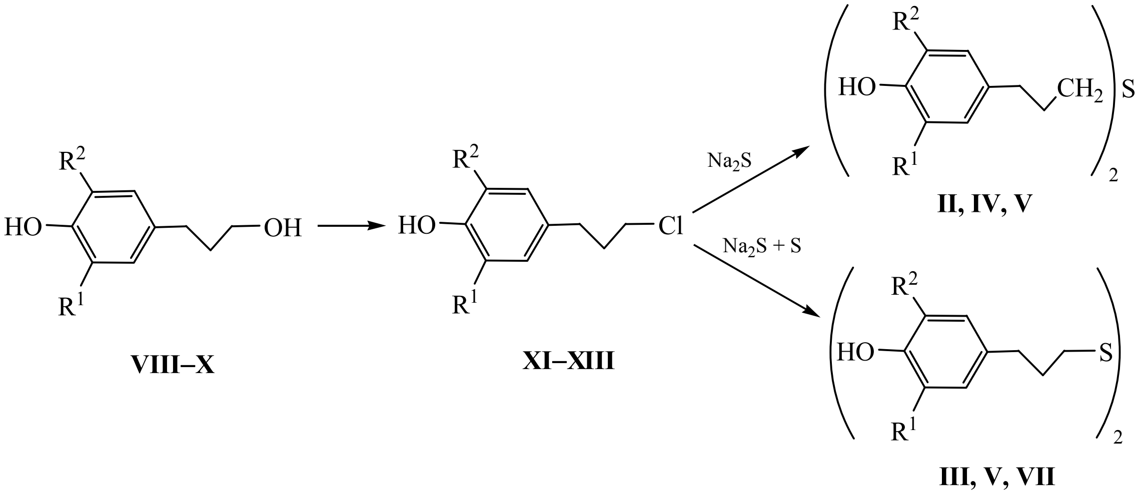
When we used the non-toxic and not colorizing phenol thermostabilizer Irganox 1010 (**I**) (also known as Phenozan-23 or Agydol-23) as a stabilizer for the Sevilen, the problems appeared related to the hydrolytic instability of both the copolymer and the antioxidant. At heating a composition stabilized with Irganox 1010 a rapid decrease occurred in the copolymer molecular mass detected by an increase in the melt flow index (MFI) (see the table). Such a stabilized polymer can be thermally processed only once. At its recycling the certified performance characteristics could not be achieved.



I

For the creation of more stabilized Sevilen compositions we decided to use the effect of synergesis that usually occurs at the combined use of sulfur-containing compounds and sterically hindered phenols [3]. To reduce the number of additives introduced into Sevilen, we synthesized a single compound **II**, containing a fragment of 2,6-dimethylphenol and sulfur atom in the aliphatic chain of the *para*-substituent to use it instead of two substances showing synergism. Its application allowed us to reach the required stabilization of the Sevilen at producing various commodities [4]. However, a group of commodities produced from Sevilen required higher stability at their exploitation.

In this regard, for the creation of more effective stabilizers we initiated an investigation of the influence of the degree of shilding in the sterically loaded phenols on their ability to interact with the sulfur-containing fragment located in the aliphatic chain of the *para*-substituent of the same molecule. We decided to leave unchanged the distance between the sulfur atoms and the aromatic ring of phenol: three methylene groups between the sulfur and the aromatic ring. By the data of [5], this distance is optimal for the sulfur-containing polymer stabilizers both due to the availability of the methods of their synthesis, and their performance.



$R^1 = R^2 = CH_3$ (**II, III, VIII, XI**); $R^1 = CH_3$, R^2 = *t*-Bu (**IV, V, IX, XII**); $R^1 = R^2$ = *t*-Bu (**VI, VII, X, XIII**).

Effectiveness of stabilizing additives **I–VII** to Sevilen[a]

Comp. no.	Content of stabilizer in Sevilen, wt %					
	0.1		0.2		0.3	
	τ, min	MFI	τ, min	MFI	τ, min	MFI
I	–	–	40	>30	75	21
II	95	8.8	100	7.7	120	7.0
III	95	8.8	300	7.7	300	7.0
IV	70	8.8	100	7.7	150	7.0
V	105	8.7	300	7.9	330	7.0
VI	55	7.1	65	5.1	80	0.3
VII	55	8.8	90	7.7	140	7.0

[a] τ, min. specifies the induction period for each composition of the stabilized Sevilen, as defined after maintaining it at a temperature of 180°C, according to the time of its hydrolytic stability. MFI is melt flow index, determined at the end of the induction period. (MFI of the original composition is 7.0).

The derivatives of 2,6-di-*tert*-butylphenol, sulfide **VI** and disulfide **VII** (see the scheme) have been prepared by us earlier [6, 7]. The sulfur-containing derivatives of 6-*tert*-butyl-2-methylphenol, sulfide **IV** and disulfide **V**, were synthesized in this work, based on the accessible 4-(3-hydroxypropyl)-6-*tert*-butyl-2-methylphenol [8]. A new disulfide **III** was synthesized using the method of [7] based on compound **XI**.

The compounds obtained were tested at the Plastpolymer facility, Ochta Branch (St. Petersburg). For the tests the Sevilen was used of widely known brand 11306-75 that contains co-polymerized 15% of vinyl acetate and 85% of ethylene. On this basis 21 compositions were prepared containing as antioxidant a sulfide (**II, IV, VI**) or a disulfide (**III, V, VII**), or Irganox 1010 as a control, at a concentration 0.1, 0.2, or 0.3%. Table 1 shows the physico-mechanical properties measured after processing the compositions at a temperature of 180°C.

As follows from the table, any of the additives except Irganox 1010 stabilize the MFI (melt flow index) value of the composition at the content of 0.2–

0.3 wt %. Note a much higher antioxidant efficiency of disulfides **III**, **V,** and **VII** in comparison with monosulfides **II**, **IV,** and **VI**.

The most attractive for the stabilization of Sevilen is disulfide **V**. This compound is a low-toxic derivative of 2-methyl-6-*tert*-butylphenol (LD/50 = 8000 mg kg^{-1}, mice), and all other parameters at its application at the concentration up to 0.2% satisfy all the requirements for the Sevilen stabilizers. The effect-tiveness of 2,6-di-*tert*-butylphenol derivatives **I**, **VI,** and **VII** was low compared to this compound. The sulfur-containing derivatives of 2,6-dimethylphenol are more effective, but currently their use is limited by the lack of domestic production of 2,6-dimethylphenol. Nevertheless, as is seen from the data of this work, the effectiveness of non-toxic derivatives of 2,6-di-*tert*-butylphenol is not enough to stabilize the critical parts made of this polymers. Now a new basis is required for the production of non-toxic phenol-based antioxidants.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Bruker AV-300 instrument (300.13 MHz) from solutions in CCl_4. As internal references were used TMS and $CDCl_3$. The UV spectra were recorded on a Specord UV VIS instrument from 1×10^{-4} molar solutions in ethanol. The IR spectra were recorded on a Bruker Vektor-22 spectrometer from KBr pellets and 1% solutions in CCl_4. The mass spectra were obtained on a high-resolution instrument Finnigan MAT-8200, the elemental compositions were calculated from the spectra with a resolution of 10000. The melting points were measured on a Köffler device.

For the preparation of the compositions Sevilen TU 6-05-1636-97 brand 11306-75 was used, whose practical properties are listed on the site http://www.sevilen.ru/sev.html.

Bis-3-[(3,5-dimethyl-4-hydroxyphenyl)propyl]disulfide (III). A mixture of preliminary triturated sulfur (1.22 g, 0.038 mol) and 4.35 g of 74% aqueous Na_2S (0.041 mol) was loaded to the reactor containing 50 ml of isopropyl alcohol. The reaction mixture was heated to boiling and maintained at vigorous stirring for 3 h till it became transparent. Then to the reactor a solution was added of 12.99 g (0.064 mol) of compound **XI** (content of the main product 98%) in 6 ml of isopropyl alcohol, and the stirring was continued for 4 h at reflux. From the hot reaction mixture the precipitate of salt was filtered off, the solvent was evaporated from the filtrate to obtained 13.55 g of brown oil. The oil was dissolved in 10 ml of boiling chloroform, to the solution was added 10 ml of hexane, and the mixture was kept in a refrigerator for 1 h. The precipitate formed was filtered off and washed with cold hexane. White crystals of disulfide **III** (8.37 g, 67%) was isolated, mp 95.5–97.0°C. Found, %: C 66.99, H 7.68, S 16.52. $C_{22}H_{30}O_2S_2$. *m/z* 390.1691 (mass-spectrometrically). Calculated, %: C 67.45, H 7.74, S 16.42. *m/z* 390.1687.

^{1}H NMR spectrum (in $CDCl_3$) δ, ppm: 1.70–2.12 t (2H, $ArCH_2CH_2$, J = 6 Hz); 2.16 s (6H, $ArCH_3$); 2.55–2.58 m (2H, CH_2S, J = 8 Hz), 2.64–2.87 t (2H, $ArCH_2$, J = 7 Hz), 4.22 s (1H, OH); 6.66 s (2H, ArH). UV spectrum (in ethanol): λ_{max} 280 nm, log ε 3.64. IR spectrum (in CCl_4): 3625 cm^{-1} (OH).

3-(6-*tert*-Butyl-2-methyl-4-hydroxyphenyl)-1-chloropropane (XII). In a reactor with stirrer was placed 7.4 g of 96% 3-(6-*tert*-butyl-2-methyl-4-hydroxyphenyl)propanol (0.032 mol) and 4.55 g (0.0383 mol) of distilled $SOCl_2$. The mixture was heated while stirring for 3.0 h at a temperature in the reactor 80°C. Then into the reactor were injected in succession 30 ml of cold water and 30 ml of methyl *tert*-butyl ether. The organic layer was separated, washed with water, and dried over anhydrous $CaCl_2$. The desiccant was filtered off, the solvent was evaporated in a vacuum, and 7.79 g of black oil was obtained. The oil was placed in a column with 77 g of silica gel of 140–315 mesh. The product was eluted with a hexane–chloroform mixture, 2:1. Compound **XII** (5.52 g) was isolated as a yellow oil, bp 120–125°C (1–2 mm Hg) Found: *m/z* 240.1283 (mass spectrometry). $C_{14}H_{21}ClO$. Calculated: *m/z* 240.1281. IR spectrum in CCl_4: 3610 and 3650 cm^{-1} (OH). UV spectrum, λ_{max} 278 nm, log ε 3.32. ^{1}H NMR spectrum (in $CDCl_3$) δ, ppm: 1.39 s (4H, C_4H_9-*t*), 1.81–2.21 m (2H, $ArCH_2CH_2$), 2.62 t (2H, $ArCH_2$, J = 7 Hz), 3.44 t (2H, CH_2Cl, J = 6 Hz); 4.44 s (1H, OH); 6.7 and 6.9 m (2H, ArH).

Bis-[3-(2-*tert*-butyl-6-methyl-4-hydroxyphenyl)-propyl]sulfide (IV). In a three-neck flask with a stirrer and reflux condenser was mixed 1.43 g (0.013 mol) of crude 74% aqueous Na_2S, 5.6 g (0.023 mol) of chloride **XII**, and 20 ml of isopropyl alcohol, and the mixture was stirred for 7 h at 100ºC. The hot reaction mixture was filtered to remove the NaCl precipitate, and the solvent was evaporated. The resulting oil was purified by column chromatography on silica gel eluting with a mixture of hexane-chloroform, 2:1, and then with chloroform. The fractions containing sulfide **IV** were combined and evaporated. 4.32 g of oil (yield

70%) containing, according to the NMR spectrum, 97% of sulfide **IV**, was isolated. Found: *m/z* 442.2903 (mass spectrometry). $C_{22}H_{42}O_2S$. Calculated: *m/z* 442.2906. ^{1}H NMR spectrum (in $CDCl_3$) δ, ppm: 1.37 s (9H, C_4H_9-*t*), 1.56–2.06 m (C*H*$_2$CH$_2$Ar), 2.14 s (3H, CH$_3$), 2.22–2.68 m (2H, ArCH$_2$), 4.28 s (ArOH), 6.67 and 6. 84 m (2H, ArH).

Bis[3-(2-*tert*-butyl-6-methyl-4-hydroxyphenyl)-propyl]disulfide (V). A triturated mixture of 0.4 g (0.013 mol) sulfur and 1.43 g of Na_2S containing 74% of the main substance (0.013 mol) was placed in the reactor, and 20 ml of isopropyl alcohol was added. The mixture was refluxed with stirring for 4 h, until the solution became clear. Then in the reactor was added a solution of 5.6 g (0.023 mol) of chloride **XII** in 5 ml of isopropyl alcohol, and the mixture was maintained at reflux over another 4 h. The hot solution was filtered from the residue of salt, and the solvent was evaporated. The resulting oil, 5.0 g, was placed in a column with silica gel (60 g) and eluted with a hexane–chloroform mixture, 2:1. The fractions containing compound **V** were combined, and the solvent was evaporated. 3.82 g (yield 80%) of compound **V** was isolated as oil. Found: *m/z* 474.2623. $C_{28}H_{42}O_2S_2$ (mass spectrometry). Calculated: *m/z* 474.2626.

^{1}H NMR spectrum (in $CDCl_3$), δ, ppm: 1.37 s (9H, C_4H_9-*t*), 1.7–2.2 m (2H, C*H*$_2$CH$_2$S), 2.17 s (3H, ArCH$_3$), 2.4–2.7 t (Hz, 2H, ArCH$_2$, *J* = 7 Hz), 2.7–3.0 m (2H, CH$_2$S), 4.42 s (OH), 6.76 and 6.84 m (2H, ArH). UV spectrum (ethanol): λ_{max} 280 nm, log ε 3.69. IR spectrum (in CCl_4): 3610 and 3650 cm^{-1} (OH).

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