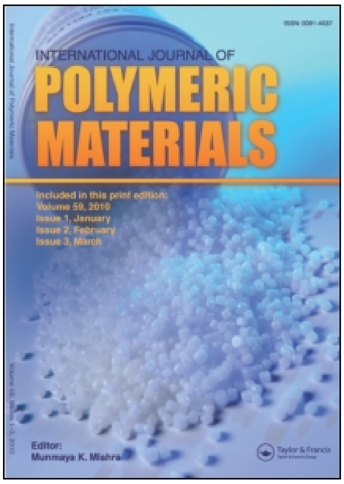

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Some Aspects of Stabilization of White and Coloured Rubbers

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Some Aspects of Stabilization of White and Coloured Rubbers

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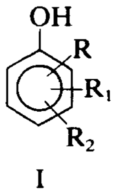
As a result of the systematic physical-chemical research (X-ray, PMR, IR-spectra etc.) of the molecular structure, reactivity and efficiency of phenolic stabilizers it was proved, that the most basic structural factors, which influence on the efficiency are: 1—the type of the space conformation in bisphenols and trisphenols; 2—close distance between two OH-groups in methylenebisphenols; 3—the energy of the intramolecular hydrogen bonds in thiobisphenols.

KEYWORDS: Stabilization, white and colored rubbers, ozone, oxiden, stabilizers, structure

In spite of the development of some new polymer materials, elastomers based on rubbers will continue to remain for a long time an important construction material at working out new articles for various purposes.

Consumer, sport and medical goods are usually manufactured from white and coloured rubbers protected ageing by phenol derivatives. Phenol stabilizers for rubbers are referred to a class of mononuclear phenols (1), bisphenols (II) and trisphenols (III):



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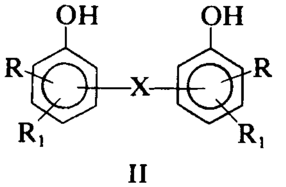
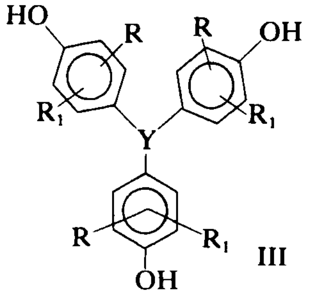


II



III

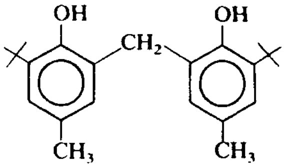
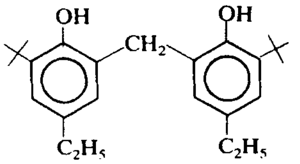
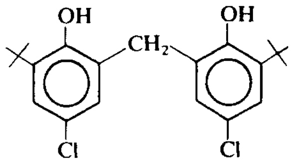
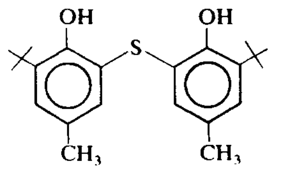
Bisphenols, compounds, in which two fragments with space-hindered phenolic hydroxyls are connected by bridge, take an important place among them.

In the class of bisphenols structure of 2,2′-methylenebis-(4-methyl-6-tert-butylphenol)—Agidol 2, antioxidant 2246, is the optimal in antioxidative activity (compound 1, Table I).

Introduction of C_2H_5 group and Cl atom to aromatic ring instead of CH_3 group in para-position to hydroxyl (compound 2 and 3), substitution of methylene

TABLE I

IR-spectra and antioxidative activity of bisphenols

NN	Bisphenol	*D*,* cm^{-1}	*E*, mV	τ, min	AF
1	 Agidol 2	3400 3600	180	220	0.96
2	 Agidol 7	3530	220	160	0.87
3	 AO-30	3562	230	130	0.82
4	 Agidol 32	3486	245	140	0.76
	Without stabilizer			20	0.30

* Notes:

D—band frequency (in max) in IR-spectra of crystals in the region of valence vibrations of OH-group;

E—potential of anodic oxidation on graphite in acetate buffer solution at pH = 6;

τ—induction period of initiated oxidation of model systems based on polypropylene;

AF—ageing factor based on tensile strength of white rubber (24 h at 90°C).

bridge for sulfur atom (compound 4) is accompanied by lowering of antioxidative activity.

Investigation of IR-spectra of crystals of these bisphenols showed that cis-conformation of molecules took place in crystals of Agidol 2 and trans-conformation—in crystals of other bisphenols studied.

The molecular structure of these compounds was investigated by X-ray diffraction analysis. Figures 1–4 give the result of these studies. As it is seen from Figure 1, Agidol 2 actually exists as cis-conformer: both hydroxyl groups are

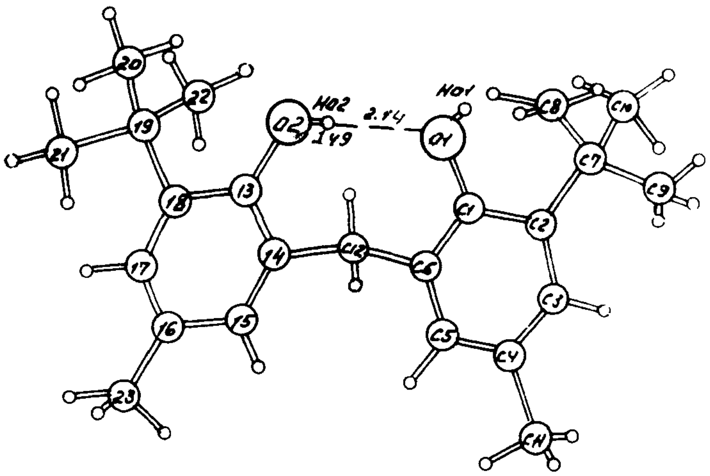


FIGURE 1 Molecular structure of 2,2′-methylenebis(4-methyl-6-tert-butylphenol) with thermal ellipsoids of the non-hydrogen atoms (X-ray diffraction analysis).

arranged on one side of the plane passing through methylene bridge and two carbon atoms linked with it. Intramolecular hydrogen bond OH···O takes place in the molecule, the geometry of such bond is given in Table II.

In contrast, compounds 2–4 have obtained trans conformation with intramolecular hydrogen bonds OH···π (compounds 2 and 3) and OH···S (compound 4). The presence of cis-conformation allows bisphenol to act more efficiently as an antioxidant due to the fact that in this case hydroxyl groups are arranged closely to each other and possibility of simultaneous in "cell" deactivation of two radicals formed at destruction of molecule of hydrogen peroxide is more favourable than at trans-conformation. This corresponds to idea of "cell" mechanism of antioxidant action developed by the school of academician N. M. Emanuel and in particular by professor Ya. A. Shlyapnikov.

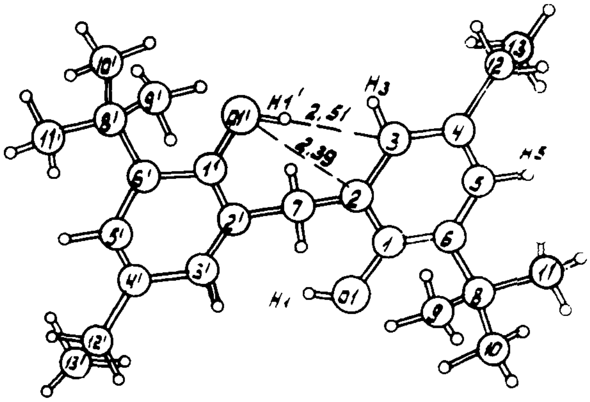


FIGURE 2 Molecular structure of 2,2′-methylenebis(4-ethyl-6-tert-butylphenol) with thermal ellipsoids of non-hydrogen atoms (X-ray diffraction analysis).

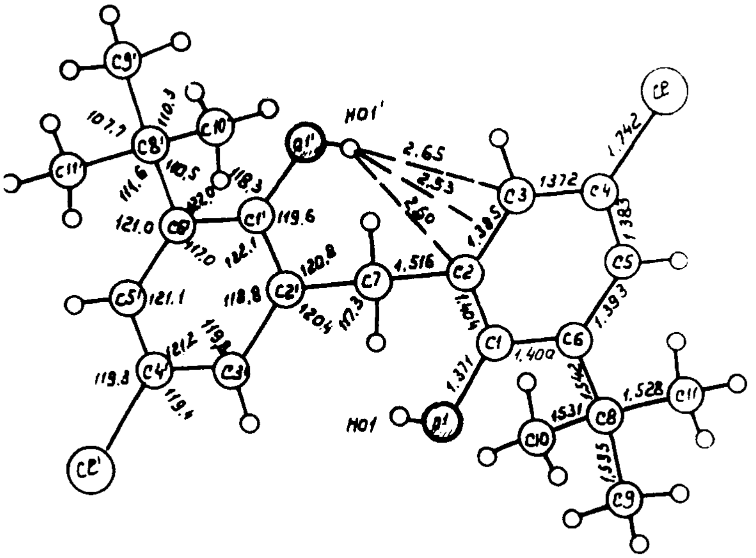


FIGURE 3 X-ray diffraction analysis of molecular structure of 2,2′-methylenebis(4-chloro-6-tert-butylphenol).

Thiobisphenols, compounds with bridge sulfur atoms, are effective inhibitors of oxidation due to intramolecular synergism.

It was interesting to investigate how the increase of the number of sulfur atoms in bridge group will effect on properties of these stabilizers. Structure, reactivity

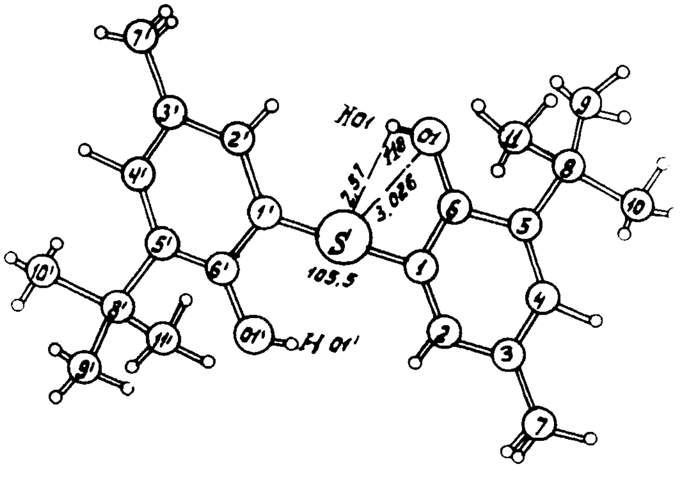


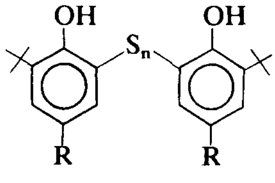
FIGURE 4 Molecular structure of 2,2′-thiobis(4-methyl-6-tert-butylphenol) with thermal ellipsoids of non-hydrogen atoms (X-ray diffraction analysis).

TABLE II

Geometric parameters of intramolecular hydrogen bonds in bisphenols

NN	Compound	Bond length, Å	Angle, degree	Sum of Van-der-Waals radii, Å
1.	Agidol 2	H···O 2.14	O—H···O 149	H + O = 2.45
2.	Agidol 7	H···C 2.39 2.51	—	H + C = 2.87
3.	AO-30	H···C 2.60 2.65 $\mathrm{H}\cdots\overset{\mathrm{C}}{\underset{\mathrm{C}}{\vert}}$ 2.53	—	H + C = 2.87
4.	Agidol 32	H···S 2.57	O—H···S 118	H + S = 3.0

and efficiency of some thiobisphenols with common formula



, where R—CH_3, C_2H_5, *n*-C_4H_9, tert-C_4H_9, Cl, Br
$n = 1 \div 4$,

were studied.

Molecular structure of di- and trithiobisphenols was determined by X-ray diffraction analysis (Figures 5 and 6). The results of spectroscopy investigations as well as structural parameters given in Table III made it possible to conclude that intramolecular hydrogen bonds O—M···S substantially effecting on reactivity of compounds studied take place in thiobisphenols.

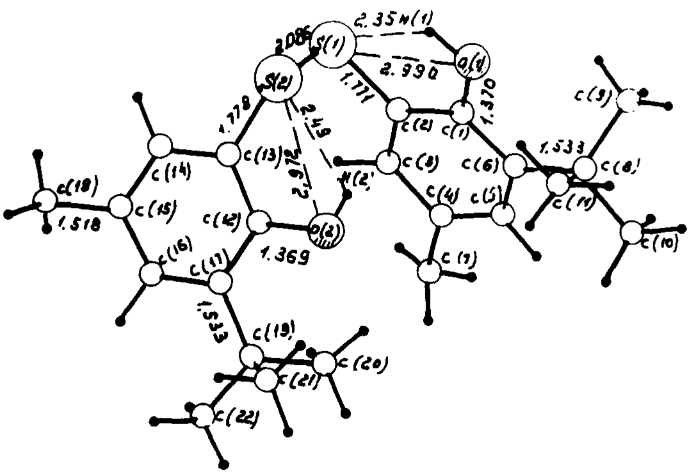


FIGURE 5 X-ray diffraction analysis of molecular structure of 2,2′-dithiobis(4-methyl-6-tert-butylphenol).

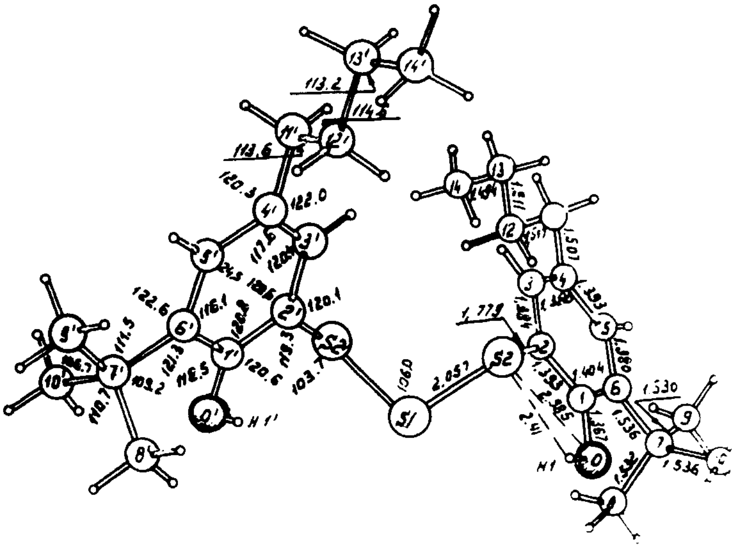
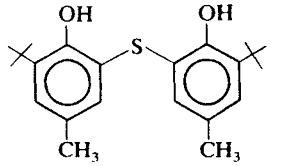
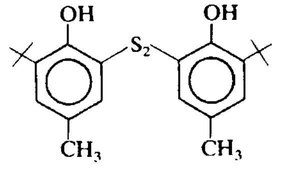
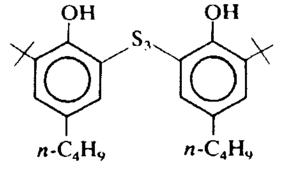


FIGURE 6 X-ray diffraction analysis of molecular structure of 2,2'-trithiobis(4-*n*-butyl-6-tert-butylphenol).

TABLE III

Geometric parameters of intramolecular hydrogen bonds in thiobisphenols

NN	Thiobisphenol	Bond length, Å	Angle, degree	Sum of Van-der-Waals radii, Å
1		S···H 2.57 S···O 3.026	O—H···S 118	S + H = 3.0 S + O = 3.13
2		S···H 2.49 S···O 2.990	O—H···S 116	S + H = 3.0 S + O = 3.13
3		S···H 2.41 S···O 2.985	O—H···S 125	S + H = 3.0 S + O = 3.13

The distances S···H and S···O are shortened in comparison with the sum of Van-der-Waals radii; such a shortening is more significant in dithiobisphenol than in monothiobisphenol and in turn in trithiobisphenol it is more considerable than in dithiobisphenol. Elongation of sulfide bridge between aromatic nuclei in thiobisphenols is accompanied with increase of reactivity and antioxidative activity of the compound (see Table IV).

Trithiobisphenols have a sulfur atom free from intramolecular hydrogen bonds. The presence of such an atom causes the increase of reactivity in model reactions and antioxidative activity in the polymer.

It may be supposed that the increase of number of sulphur atoms in the bridge up to four will result in increase of reactivity and antioxidative activity.

An attempt was made to carry out a directional synthesis with introduction of the fourth sulfur atom into trisulfide based on 4-*n*-butyl-2-tert-butylphenol. Tetrasulfide obtained under such synthesis really has higher reactivity and antioxidative activity (see Table IV).

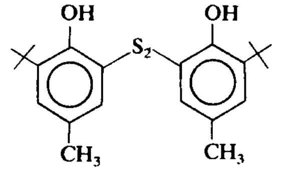
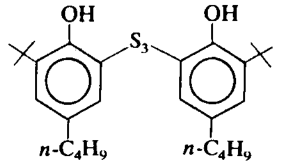
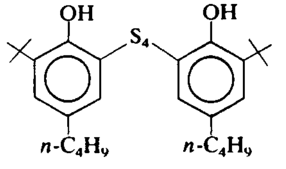
A technical mixture of mono-, di- and trithiobisphenol was synthesized and tested in rubbers. This stabilizer produced by using available technical mixture of sulfur chlorides, is more effective than individual monothiobisphenol (see Table V).

From the stabilizers for rubber medical goods trisphenol-1,3,5-tris (3′,5′-di-tert-butyl-4′-oxybenzyl) mesithylene, Agidol 40, Ionox 330 is of great interest.

This stabilizer is characterized by such biological inertness that it is approved for application in production of baby tests.

TABLE IV

Reactivity and antioxidative activity of thiobisphenols

NN	Thiobisphenol	K,* $M^{-1} \cdot c^{-1}$	*E*, mV	*τ*, min
1		0.4	295	160
2		1.9	260	175
3		9.5	—	185

* K—rate constant of model radical reaction.

TABLE V

Testing of technical mixture of thiobisphenols as stabilizer for white rubbers (mixture composition: mono—36%; di—42%; tri—22%)

Property	Without stabilizer	Composition of thiobisphenols, 1 pbm	Agidol 32, 1 pbm	Agidol 2, 1 pbm
Tensile strength, MPa	17.3	20.3	17.6	17.9
Elongation at break, %	800	700	760	750
Ageing factor based on tensile strength at 90°C, 24 h	0.32	0.82	0.77	0.94
Fatigue strength up to destruction, 100 cycles:				
at bending	43.2	64.5	60.5	69.0
at elongation 100%	24.9	36.5	34.0	43.3

Reaction mechanism and high efficiency (τ = 240 min) of this tris-phenol can be also explained by results of X-ray diffraction analysis. Agidol 40 molecule contains four aromatic rings. In space it represents a "basket," a bottom of which is formed by mesithylene ring and walls-by three rings containing space hindered hydroxyl groups (Figure 7). The "basket" has a "pocket"-trap for entrapment of hydroperoxide radicals and their quick deactivation by OH-groups arranged at the boundary of "basket" walls.

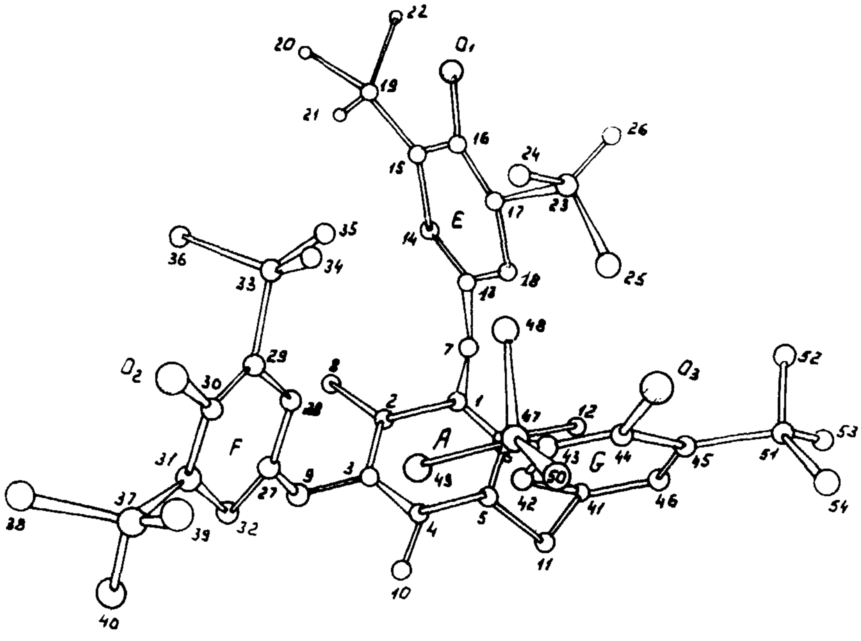


FIGURE 7 X-ray diffraction analysis of molecular structure of 1,3,5-tris(3′,5′-di-tert-butyl-4′-oxybenzyl) mesithylene.

Trisphenol based on *m*-xylol recently synthesized in our laboratory has a similar structure.

X-ray diffraction analysis of monocrystal of trisubstituted *m*-xylol allowed to obtain space group and cell dimensions, comparison of which with crystallographic parameters of Agidol 40 showed, that crystals of these two trisubstituted derivatives have isostructure. Due to this, space conformation of molecule is retained at substitution of methyl group in central ring for hydrogen atom. The existence of "basket" conformation provides high antioxidative activity of the new stabilizer ($\tau = 230$ min).

The above-mentioned data prove that it is possible to increase the assortment of effective trisphenol stabilizers using anone, based on available raw material, *m*-xylol.

X-ray diffraction analysis was carried out in Karpov Research Institute of Physical Chemistry under the supervision of doctor L. A. Chetkina.

As a first approximation the problem of protecting of white and coloured rubbers against thermooxidative destruction can be solved by using four-five phenolic stabilizers-derivatives of mono-, bis and trisphenols.

The development of production and application of phenolic stabilizers, as well as other products of industrial organic synthesis, depends considerably on two factors: availability of raw materials and level of technology. Our investigations allowed to develop simple methods of manufacturing of main phenolic stabilizers on the base of available and cheap phenol for rubber and latex goods, particularly new methods of production of mixture of α-methylbenzylphenols (Agidol 20), Adidol 2, Agidol 40 and some other products. Protection system developed by us for white rubbers including two phenolic stabilizers: bisphenol and mononuclear phenol is of practical interest.

Unfortunately despite of the efforts of many scientists, the problem of protection of white rubbers against ozone cracking is still unsolved. The search for nonstaining antiozonants is an important way of investigation in the field of stabilization of white and coloured rubbers in the next decade.