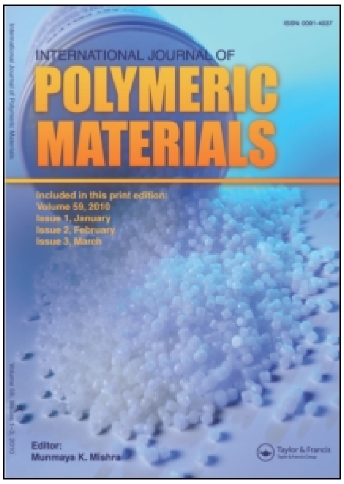

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Stabilization of Polyisoprene Rubber by 3-Mercapto-1,2,4-Triazine-5-One Derivatives

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In this work, attention focusses on mercaptotriazinone derivatives, which do not paint polymers and are effective stabilizers for thermooxidative degradation of carbon-chain polymers, in particular, of an isoprene rubber.

KEY WORDS Polyisoprene rubber, stabilization, thermooxidative degradation, mercaptotriazines.

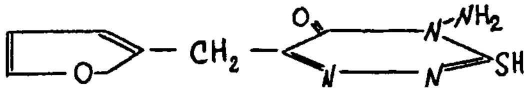
INTRODUCTION

A search for new effective unpainting low-toxic stabilizers for polymers is the important scientific and technical challenge. In terms of its investigation, proper attention should be given to 3-mercapto-1,2,4-triazine-5-one derivatives, which exhibit the stabilizing action in thermooxidative degradation of hydrocarbons, in particular, of the stereoregular polyisoprene rubber.

EXPERIMENTAL PART AND DISCUSSION

We used 1,4-*cis*-polyisoprene rubber (SIR) [GOST (State Standard) 415-53 $M_w = 8 \cdot 10^5$], which was obtained by stereospecific polymerization of isoprene in the presence of the ($tert$-$C_4H_9)_3Al$-$TiCl_4$ catalytic system with the component ratio (mol) of 1:1 and the following 3-mercapto-1,2,4-triazine-5-one derivatives, as polymer stabilizers: 3-mercapto-4-amino-6-furfuryl-1,2,4-triazine-5-one (1) [mp 474 ± 1 K; MM = 224 (the mass-spectrometry data); the IR spectrum (ν, cm^{-1}): 1170, 1270, 3320; the UV spectrum (λ, nm): 270], 3-mercapto-6-furfuryl-1,2,4-triazine-5-one (II) [mp 411 ± 1 K; MM = 209; ν, cm^{-1}: 3180, 1710, 1270; λ, nm: 265], and 3-methylthio-4-amino-6-furfuryl-1,2,4-triazine-5-one (III) [mp 465 ± 1 K; MM = 238; ν, cm^{-1}: *3180, 1725, 1280*; λ, nm: 230].

Compounds



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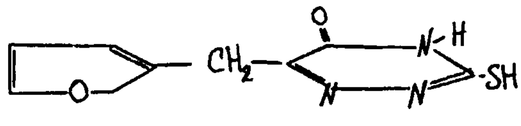
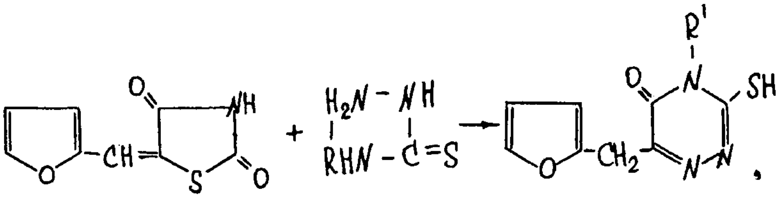
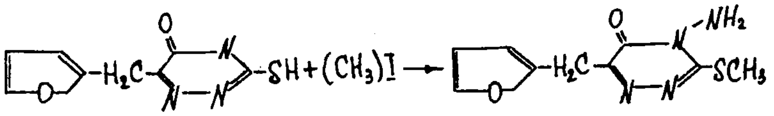


(the yields are equal to 85 ± 1 and 81 ± 1 wt%, respectively) were prepared by the reaction of 5-furfurylidenethiazolydine-2,4-dione (0.1 mol) with thiosemicarbazide (thiocarbohydrazide) (0.1 mol) in 100 ml of aqueous solution containing 0.5 mol of KOH at 365 ± 5 K for 3 h.[1] The reaction occurs according to the following scheme:



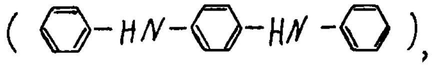
where R′ stands for H or NH_2.

Compound III was prepared by the reaction of 3-mercapto-4-amino-6-furfuryl-1,2,4-triazine-5-one (0.01 mol) with methyl iodide (0.01 mol) in a medium of anhydrous alcohol in the presence of sodium ethylate at 340 ± 5 K for 0.5 h[2]:



The product obtained was isolated at 273 K in water. This procedure was followed by filtration and lyophilic drying; the product yield was equal to 91 ± 1 wt%.

The effectiveness of 3-mercapto-1,2,4-triazine-5-one derivatives in SIR stabilization was compared with that of known antioxidants: N,N′-diphenyl-*p*-phenylenediamine (Diaphene Ph Ph)



octadecyl-(3′,5′-di-*tert*-butyl)-4-hydroxyphenyl propionale (Irganox 1076) (V), and 2,2′-methylenebis-(6-*tert*-butyl-4′-methylphenol) (Bisalkophene BP) (VI).

Thermooxidative degradation of SIR was carried out in the presence of the stabilizers at 353 K in air. The samples in the form of 50 vm thick films supported on a fluoride plate were prepared from common solutions of SIR and antioxidants in methylene chloride; evaporation of the solvent and subsequent vacuum treatment of the samples at 10^{-3} torr were carried out. The kinetics of SIR thermal oxidation was followed by the accumulation of carbonyl and hydroxyl groups,[3] which were determined from IR spectra (by the band at 1720 cm^{-1} for the C=O groups and by the

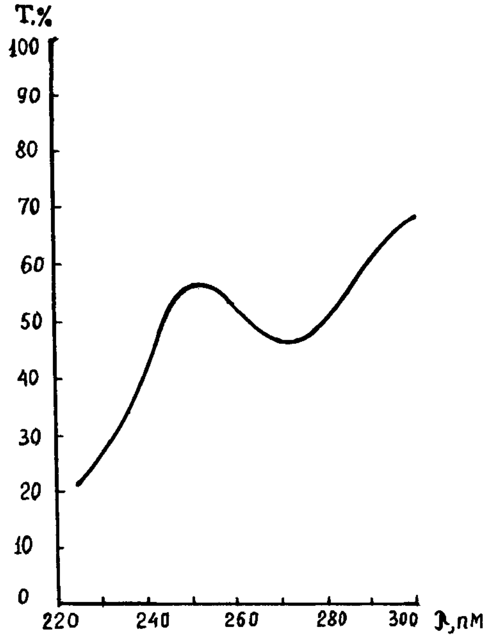


FIGURE 1 UF-spectrum of solution 3-mercapto-4-amino-6-furfuryl-1,2,4-triazine-5-one in heptane (T = 293 K, $[C] = 1 \cdot 10^{-6}$ mole/l).

band in the region 3200–3600 cm^{-1} for the OH groups). The antioxidants were compared in their effectiveness by the value of the induction period in SIR thermal oxidation.

The experimental data show that 3-mercapto-1,2,4-triazine-5-one derivatives (example 1) are weak UV-stabilizers (Figure 1), but have the marked inhibiting effect on the thermooxidative degradation of SIR (Figure 2). A higher effectiveness of compounds I and III, which contain the primary amine groups, compared to that of compound II appears to be caused by the preferred participation of the NH_2 group in destruction of hydroperoxides being formed in situ:

$$\text{InH} + \text{ROOH} \rightarrow \text{molecular products.}$$

However, the overall effectiveness of compounds I–III as stabilizers-antioxidants is substantially lower than that of IV (Diaphene Ph Ph), even if the amine group content is equimolecular (Figure 2). When compounds I–III are used in combination with phenolic antioxidants, V and VI, synergism (with respect to the value of the induction period, τ is observed in SIR thermooxidative degradation (Figure 2). This phenomenon allows us to reach a higher stabilization effect using synergistic triazine-phenol mixtures compared to that reached with individual Diaphene Ph Ph. The synergistic effect (with respect to the τ value) appears to reveal itself owing to the well-known reactions involving another antioxidant, which result in the regeneration of the triazine stabilizers-antioxidants:

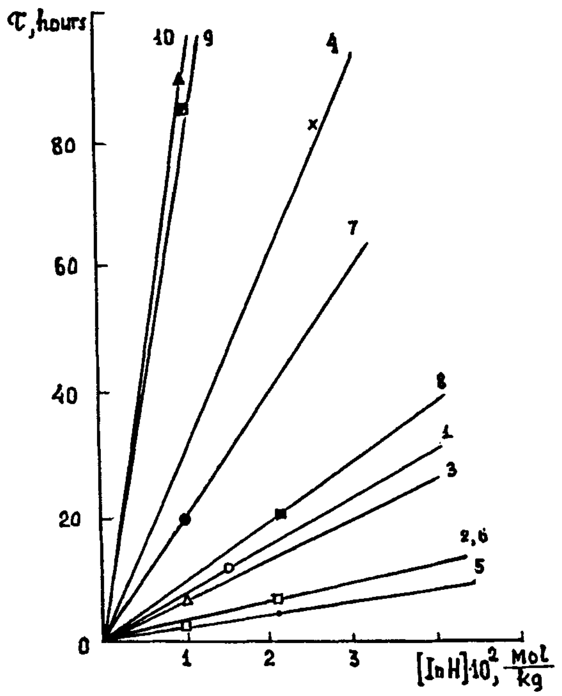


FIGURE 2 The dependence of induction period of *cis*-1,4-polyisoprene rubber on antioxidants content (353 K, antioxidants mixture 1:1 mole/mole). 1—3-mercapto-4-amine-6-furfuryl-1,2,4-triazine-5-one (I); 2—3-mercapto-6-furfuryl-1,2,4-triazine-5-one (II); 3—3-methylthio-4-amine-6-furfuryl-1,2,4-triazine-5-one (III); 4—N,N′-diphenyl-*n*-phenylenediamine (IV); 5—di-*tert*-buthyl-4-hydroxyphenylpropionate (V); 6—2,2-methylenebis-(6-*tert*-buthyl-4-methylphenole) (VI); 7—I + V; 8—II + V; 9—II + VI; 10—III + V.

$$R_2NH + ROO^{\cdot} \rightarrow R_2N^{\cdot} + ROOH$$

$$R_2N^{\cdot} + PhOH \rightarrow R_2NH + PhO^{\cdot}$$

In this case, a possibility of displaying the initiation function, which is usually realized by the reaction

$$In^{\cdot} + RH \rightarrow InH + R^{\cdot},$$

is excluded for the stabilizers-antioxidants.

Thus, synergistic mixtures based on the triazine and phenol derivatives are sufficiently effective systems for polyisoprene rubber stabilization. The substantial advantage of the above systems implies that contrary to the Diaphene Ph Ph, which is one of the most effective industrial stabilizers for a series of rubbers and plastics,[4-6] the stabilizers used in this work virtually do not paint polymeric materials and are low-toxic.

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