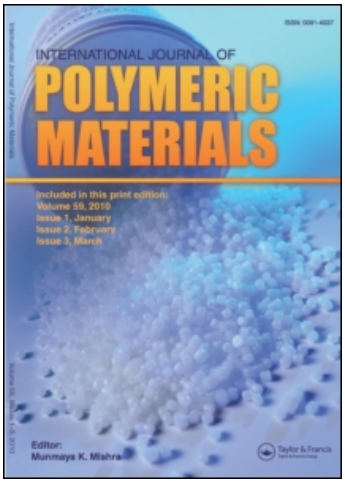

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Stabilization of Plasticized Polyvinyl Chloride by 3-Mercapto-1,2,4-Triazine-5-one Derivatives

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Mercaptotriazinone derivatives can be used for the stabilization of plasticized polyvinyl chloride.

KEY WORDS PVC, stabilization, plasticizers, mercapto-triazines.

INTRODUCTION

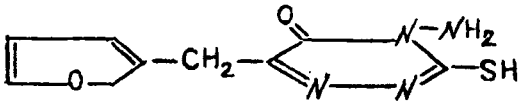
Traditionally, nitrogen-containing compounds accelerate thermooxidative degradation of polyvinyl chloride (PVC), and only some of them are capable of stabilizing PVC.[1] Of the latter compounds, the heterocyclic nitrogen-containing ones, in particular, benzimidazole, quinazoline-4, benzazole derivatives and so on are of practical interest.[2–4] The best results have been obtained with nitrogen-containing stabilizers-antioxidants in the stabilization of plasticized (usually by esters) PVC; the characteristic effect of "echo-stabilization" of PVC is responsible for the above phenomenon.[5] In this case, nitrogen-containing stabilizers, including those containing amine groups, suppress efficiently the free-radical oxidation of plasticizers. This results in PVC stabilization owing to another characteristic effect, namely the solvation stabilization of the polymer.[6]

EXPERIMENTAL PART AND DISCUSSION

In line with this concept, 3-mercapto-1,2,4-triazine-5-one derivatives, which also have the stabilizing effect on thermooxidative degradation of plasticized PVC, are of interest.

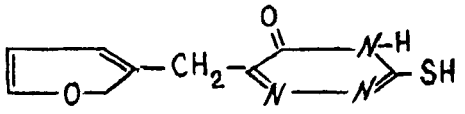
In this work, the stabilizing activity of the following compounds is studied by the chemiluminescence method:

3-mercapto-4-amino-6-furfuryl-1,2,4-triazine-5-one (I),



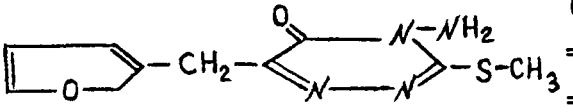
(mp 474 ± 1 K; MM* = 224; ν** = 1170, 1270, 3320 cm^{-1}; λ*** = 270 nm)

3-mercapto-6-furfuryl-1,2,4-triazine-5-one (II),



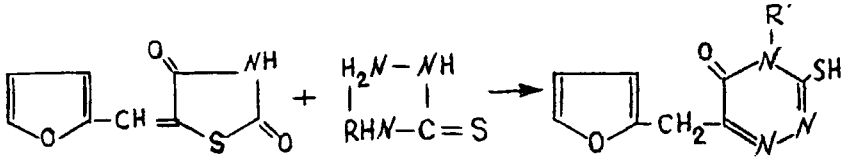
(mp 411 ± 1 K; MM* = 209; ν** = 3180, 1710, 1270 cm^{-1}; λ*** = 265 nm)

and 3-methylthio-4-amino-6-furfuryl-1,2,4-triazine-5-one (III)

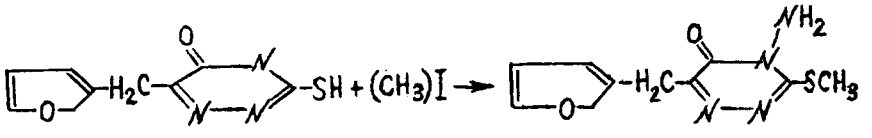


(mp 465 ± 1 K; MM* = 238; ν** = 3180, 1725, 1280 cm^{-1}; λ*** = 230 nm).

Compounds I and II (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 KOH at 365 ± 5 K for 3 h.[7] The reaction occurs according to the following scheme: (R′ = H or N—H_2)



Compound III was prepared by the reaction of 3-mercapto-4-amino-6-furfuryl-1,2,4-triazine-5-one (0.010 mol) with methyl iodide (0.011 mol) in a medium of anhydrous alcohol in the presence of sodium ethylate at 340 ± 5 K for 0.5 h[8]:



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%.

In the experiments, C-70 PVC [GOST (State Standard) 14322-69] and dialkylphthalate (TY-6-05-1611-78) were used.

The chemiluminescence (CL) in thermooxidative degradation of PVC was recorded with the instrument analogous to that described in References 9–11. An ampoule containing 50 mg of a sample under study was placed in the thermostatted

*The data are obtained with the MS-80 Kratos mass spectrometer.
**The IR spectra are obtained with the UR-20 Specord 75 IR.
***The spectra are obtained with the SF-26 spectrophotometer.

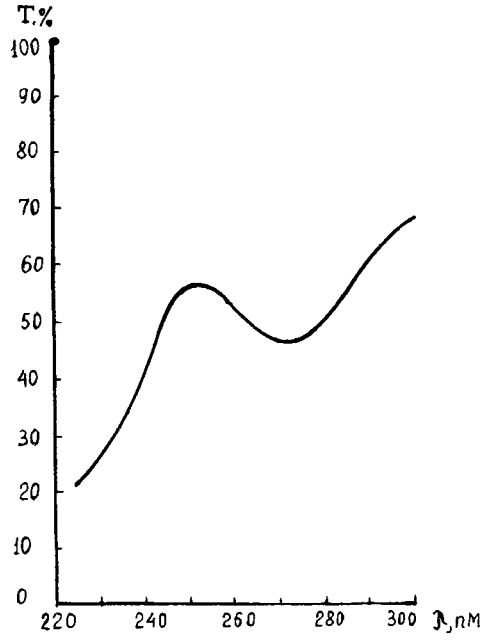


FIGURE 1 UF-spectrum of 3-mercapto-4-amino-6-furfuril-1,2,4-triazine-5 one in heptane (T = 293 K, $[C] = 1.3 \times 10^{-6}$ mole/l).

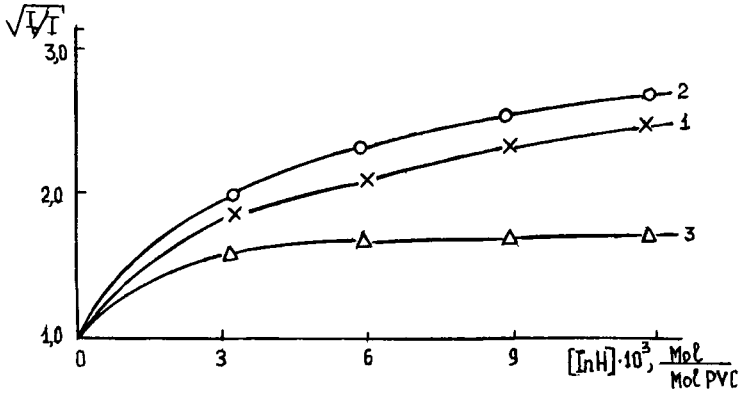


FIGURE 2 The relative intensity change of chemiluminescence during the thermooxidative (O_2) degradation of plasticized PVC in the presence of derivatives of 3-mercapto-1,2,4-triazine-5-one: 1—(I), 2—(II), 3—(III) 443 K, [Dioctylphtalate] = 30 mmol/mol PVC) on inhibitor concentration.

furnace of the CL-apparatus. When the dependence of the CL intensity on reaction temperature was measured, the temperature of the furnace and the rate of its heating (2 degree/min) were maintained in the automatic regime by an electronic block. Destruction of the samples was carried out in the flow of dried oxygen, which was fed directly to the sample surface at a rate of 2.5 l/h.

The experimental data show that 3-mercapto-1,2,4-triazine-5-one derivatives (example I) are weak UV-stabilizers (Figure 1), but have the marked inhibiting effect

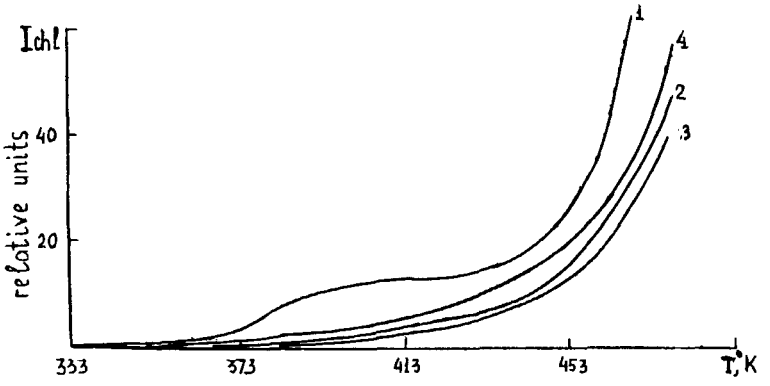


FIGURE 3 Temperature dependence of chemiluminescence intensity during thermooxidative (O_2) degradation of plasticized PVC (1) in the presence of derivatives of 3-mercapto-1,2,4-triazine-5-one (2–4): 2—(I); 3—(II); 4—(III), [Dioctylphtalate] = 30 mmol/mol PVC, [I], [II], [III] = 3 mmol/mol PVC.

on the thermooxidative degradation of plasticized PVC (Figure 2). As this takes place, the stabilization-oxidation functions reveal themselves in a wide range of temperatures (from 375 to 485 K and over) (Figure 3).

The effectiveness of the inhibiting action of 3-mercapto-1,2,4-triazine-5-one derivatives in the thermooxidative degradation of plasticized PVC (at least in the range 330–475 K) decreases in the following order: II > I > III. It is obvious that the structure of the substituents in the 3 and 4 positions of triazine heterocycle influences the efficiency of these compounds as stabilizers-antioxidants. The presence of the methylthio group in the 3 position of the heterocycle (compound III) decreases markedly the effect of the triazine derivatives on the process considered (compare the stabilizing action of the I and III compounds). For mercaptotriazinones containing the NH group in the 4 position, the better results are obtained compared to those for the corresponding derivatives containing the more basic NH_2 group.

Thus, the 3-mercapto-1,2,4-triazine-5-one derivatives are stabilizers-antioxidants of plasticized PVC.

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