CONDENSED HETEROAROMATIC SYSTEMS INCLUDING A THIOPHENE RING. XXXI.* CHELATES BASED ON BENZO[b]THIOPHENE AND STABILIZATION OF POLYCAPROAMIDE FIBERS

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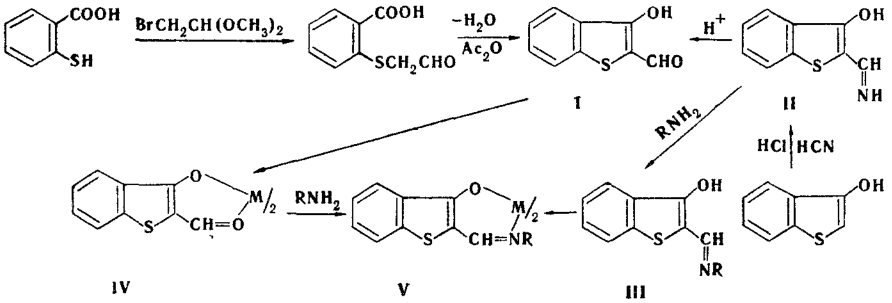
A number of complexes based on 3-hydroxy-2-benzo[b]formylthiophene and its Schiff bases were obtained and investigated as stabilizers for polycaproamide fibers. It was established that {N,N-bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediaminato}-copper(II) which makes it possible to simultaneously improve the thermal stability and photostability of polycaproamide fibers, is the most effective stabilizer of the investigated compounds.

The unusual (with respect to this scale) increase in the number of investigations of complexing and chelate compounds is associated with the progressive expansion of their areas of practical application; in only a decade (1960-1969) the potential industrial significance of only some chelate compounds is estimated to be several thousands of literature references [2]. Metal-containing chelate compounds are used to increase the thermal stability and photostability of diverse polymeric materials [3]. An undertaking of this sort also has important significance for polyamides, and this compelled us to investigate chelate compounds based on benzo[b]thiophene, which we obtained for the first time, as inhibitors of the thermal and photooxidative destruction of polyamides [4].

We have shown [5] that 3-hydroxy-2-benzo[b]formylthiophene (I), 3-hydroxy-2-iminomethylbenzo[b]thiophene (II), and the Schiff bases (III) formed by them react with metal salts to give chelates of the IV and V type. However, the details involved in the preparation of both ligands I-III themselves and chelates IV-V were not given in [5].

Compound I was obtained by the method of Rodionov and co-workers [6] from thiosalicylic acid. In addition, hydroxyaldehyde I was also synthesized by the Gattermann-Koch reaction from 3-hydroxybenzo[b]thiophene [7], which is, specifically, an industrial intermediate in the synthesis of thioindigo dyes (from example, see [8]). The overall scheme for the preparation of ligands I-III and chelates IV and V can be represented in the following form:



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[*] See [1] for communication XXX.

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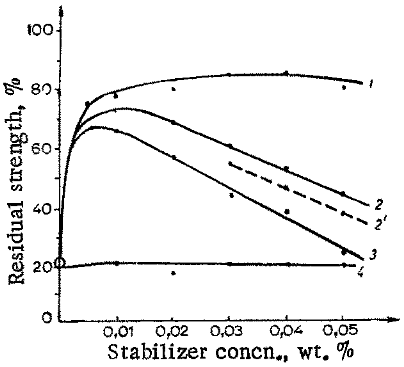

Fig. 1. Effect of stabilization of a capron fiber during destruction in air at 200°C for 2 h: 1) copper chelate Vb; 2) copper chelate Va; 2') copper chelate Va containing 0.01 wt.% copper acetate; 3) copper chelate IV; 4) without a stabilizer, zinc chelate Vc, and ligands I-III.

For simplicity, ligands II and III are considered to be in the hydroxy form, although we have found [5, 9] that, in contrast to hydroxy aldehyde I, they exist primarily in the oxo form in solution.

The investigation of the inhibiting activity of 3-hydroxy-2-iminomethylbenzo[b]thiophene (II) and its chelate compounds (V, R = H, M = Cu, Ni, and Zn) in the liquid-phase oxidation of hydrocarbons [10] showed that bis(3-hydroxy-2-iminomethylbenzo[b]thiophenato)Cu(II) (V, R = H, M = Cu) has the greatest effectiveness as an antioxidant. This chelate in principle can be considered to be a polyfunctional inhibitor, one molecule of which participates in termination of several oxidation chains. We decided to investigate a number of chelates and ligands based on benzo[b]thiophene as thermal stabilizers and photostabilizers of polycaproamide — benzoformylthiophene (I), 2-iminomethylbenzo[b]thiophene (II), N,N'-bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediamine [III, R = $(CH_2)_2$—], bis(3-hydroxy-2-benzo[b]formylthiophenato)copper(II) (IV, M = Cu), {N,N'-bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediaminato}copper(II) [Vb, R = —$(CH_2)_2$—, M = Cu], and {N,N'-bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediaminato}-zinc(II) [Vc, R = —$(CH_2)_2$—, M = Zn].

The results of the investigation showed that during thermal oxidation of polycaproamide fibers the investigated compounds display different stabilizing effects depending on both the nature and concentration of the additivies. The character of the change in the residual strength of the fibers stabilized by various compounds as a function of the concentration of the stabilizers added is presented in Fig. 1. A fiber stabilized by the copper chelate (Vb) has better indexes, inasmuch as the most residual strength after thermal oxidation is retained by the fiber containing this complex. At the same time, zinc chelate Vc and ligands I-III do not display appreciable stabilizing effects under similar conditions, and the strength of the fibers with them as additives remains at the level of the strength of the unstabilized fiber. Copper chelates IV and Va occupy an intermediate position with respect to their stabilizing effect between copper chelate Vb and zinc chelate Vc.

In addition, the stabilizing effect of copper chelates IV and Va decreases markedly when their concentration in the polymer is increased. This is apparently associated with partial decomposition of chelates IV and Va during the preparation of the polymer and liberation of a copper sol in a concentration that causes initiation of thermal oxidative destruction of the polymer. To confirm this assumption, copper acetate was additionaly added in 0.01 wt.% amounts (based on the weight of the monomer) to a melt consisting of the polycaproamide containing copper chelate Va (curve 2). It was found that copper acetate, which decomposes under the conditions of preparation of the polymer, increases the concentration of the copper sol and also facilitates initiation of the destruction of the polycaproamide fiber (Fig. 1, curve 2'). The catalytic action of the copper sol in the synthesis of polycaproamide was first pointed out in [11].

Copper chelate Vb probably does not decompose under the conditions of the preparation of polycaproamide to give a copper sol in a concentration sufficient for initiation of destruction and acts as an active inhibitor of thermal oxidative destruction. An increase in its concentration in the fiber from 0.01 to 0.05 wt.% leads to a small increase in the thermal stability (see Fig. 1, curve 1); samples with 0.03 wt.% copper chelate (Vb) were therefore used in the subsequent investigations of the effect of the additive on the properties of the polymer and the fiber.

Tests of the thermal oxidation, under identical conditions, of stabilized and unstabilized fibers showed that they differ markedly with respect to the relative viscosities of their solutions (Fig. 2). After thermal oxidation for 3 h, the relative viscosity of the solution of the unstabilized fiber decreased by 35% (from 2.48 to 1.60). In conformity with the decrease in the relative viscosity, the physicomechanical indexes of the fiber also

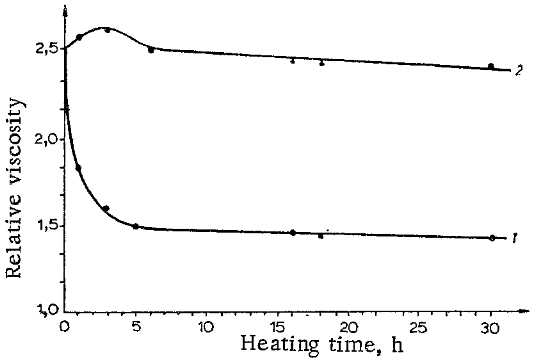

Fig. 2

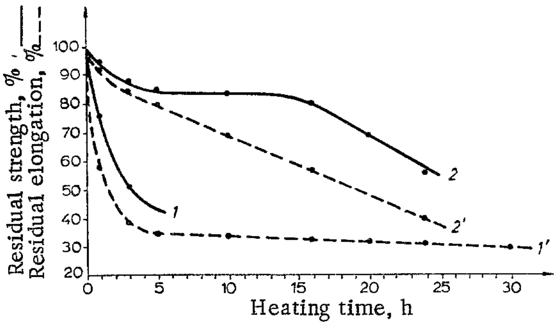

Fig. 3

Fig. 2. Change in the relative viscosity of 1% solutions (in 96% H_2SO_4) of capron fibers as a function of the oxidation time in air at 150°C: 1) without stabilizer; 2) with 0.03 wt.% of copper chelate Vb.

Fig. 3. Change in the strength and elongation of capron fibers after heating in air at 150°C. 1 and 1') without a stabilizer; 2 and 2') with 0.03 wt.% of copper chelate Vb.

decreased: the residual strength and elongation decreased (Fig. 3, curves 1 and 1'). At the same time, in the case of the stabilized fiber the residual strengths and elongation (Fig. 3, curves 2 and 2') change to a much lesser extent during the thermal oxidation period.

The chemical transformations that occur in the fiber during thermal oxidation can be judged to a certain extent from the change in the percentage of carbonyl and terminal amino groups and also from the accumulation of hydroperpoxides. Analysis showed that the stabilized fiber did not contain measurable amounts of hydroperoxides: only traces of them are detected. In addition, from comparative analysis of the stabilized and unstabilized fibers it is seen that chemical transformations leading to a slight decrease in the percentage of terminal amino groups occur in the stabilized fiber under the influence of air oxygen at 150°. At the same time, the percentage of carbonyl groups decreases sharply. However, in the case of the unstabilized fiber the buildup of carbonyl groups proceeds extremely intensively (see Table 1).

The above observations make it possible to assume that one of the possible reasons for inhibition of thermal oxidative destruction processes in polycaproamide and fibers prepared from it, stabilized by copper chelate Vb, is the ability to react with the active free radicals that carry on the oxidation chain. As a result of this, there is no appreciable accumulation of decomposition products containing aldehyde (carbonyl) groups.

Of no small importance is the fact that the introduction into the polycaproamide fiber of copper chelate Vb does not impart any color to it and at the same time leads to an increase in the photostability of the fiber. This is attested to by the data presented in Fig. 4 on the change in the strength of a fiber subjected to accelerated photodestruction during illumination with a xenon lamp for 150 h. Consequently, copper chelate Vb not only increases the thermal stability of polycaproamide fibers but also considerably improves their photostability.

EXPERIMENTAL METHOD

3-Hydroxy-2-iminomethylbenzo[b]thiophene (II). A total of 100 ml (2.56 mole) of dry HCN was added rapidly with cooling (ice—water mixture) to a solution of 76 g (0.05 mole) of 3-hydroxybenzo[b]thiophene [obtained by decarboxylation of 3-hydroxy-2-benzo[b]thiophenecarboxylic acid at 80-100°; bp 85-90° (0.1 mm), mp 71-72°] in 400 ml of absolute ether, and dry HCl was bubbled through the mixture for 3-4 h. After 12 h, the dark precipitate was removed by filtration and treated with a mixture of ice and dilute HCl. The 3-hydroxy-2-iminomethylbenzo[b]thiophene hydrochloride (II) was removed by filtration, and 25% ammonium hydroxide was added. After 1.5-2 h, the precipitate was removed by filtration, washed thoroughly with water, and air dried. Hydroxy aldimine II was obtained in 99% yield. Water

TABLE 1. Results of the Analysis of Polycaproamide Fibers for the Percentages of Carbonyl and Terminal Amino Groups

Fiber type	Percentage, mole/g $\cdot 10^{-5}$	Heating time at 150°C, h									
		0	1	2	5	10	14	18	20	30	35
Stabilized by the addition of 0.03 wt. % of copper chelate Vb	Terminal amino groups	4,00	3,67	3,20	2,90	2,33	2,10	2,00	1,94	—	—
	Carbonyl groups	0	1,20	3,00	3,30	4,70	—	—	8,50	7,90	7,80
Without a stabilizer	Terminal amino groups	4,40	3,18	2,50	2,10	1,50	1,45	1,28	—	—	—
	Carbonyl groups	5,60	11,5	15,6	17,2	29,0	—	—	29,4	32,2	—

was added to a solution of 10 g of crude hydroxy aldimine II in 300 ml of acetone up to a total volume of 1 liter, the solution was filtered, the filtrate was vacuum evaporated, and the residue was removed by filtration and air dried to give 8.6 g (86%) of hydroxy aldimine II; after repeated similar treatment it had mp 160° (dec.). Found: C 61.1; H 3.9; N 7.9; S 18.4%; M* 171. C_9H_7NOS. Calculated: C 61.0; H 4.0; N 7.9; S 18.1%; M 177.

3-Hydroxy-2-benzo[b]formylthiophene (I). A) A mixture of 17.7 g (0.1 mole) of crude hydroxy aldimine II and 150 ml of 1 N NaOH was refluxed for 30 min, after which it was cooled, and the solution was filtered. Acetic acid (20% solution) was added to the filtrate until precipitation was complete, and the mixture was worked up to give 11.9 g (67%) of hydroxy aldehyde I with mp 109-110° (from alcohol) (mp 107° [6]).

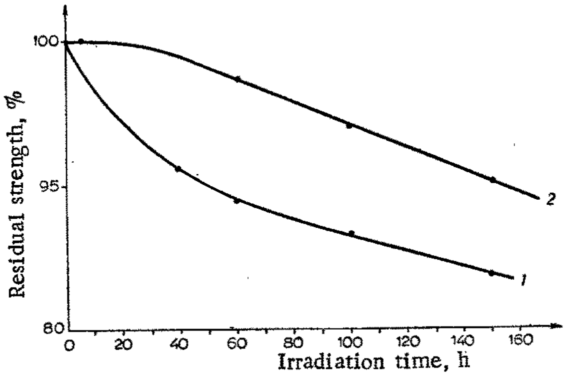

Fig. 4. Change in the strength of a capron fiber as a function of photochemical aging time in a Xenotest: 1) without a stabilizer; 2) with added 0.03 wt.% of copper chelate Vb.

B) Hydroxy aldehyde I was also obtained by the method in [6]. The melting points and UV spectra of hydroxy aldehydes I synthesized by methods A and B were identical. No melting-point depression was observed for a mixture of the two products.

N,N'-Bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediamine [III, R = $-(CH_2)_2-$]. This compound, with mp 216° [dimethylformamide (DMFA)], was obtained in 68% yield by a method similar to that in [5].

Bis(3-hydroxy-2-benzo[b]formylthiophenato)copper(II) (IV, M = Cu). A solution of 44 g (0.22 mole) of copper acetate in water was added to a solution of 70 g (0.39 mole) of 3-hydroxy-2-benzo[b]formylthiophene (I) in 750 ml of acetone, and the mixture was refluxed with stirring for 2 h. It was then cooled, and the resulting precipitate was removed by filtration, washed throughly with water and acetone, and vacuum dried over $CaCl_2$ to give 75 g (92%) of chelate IV. The product began to decompose at 330-332° (from DMFA). Found: C 51.8; H 2.3; Cu 15.6; S 15.2%. $C_{18}H_{10}CuO_4S_2$. Calculated: C 51.7; H 2.4; Cu 15.2; S 15.3%.

Bis(3-hydroxy-2-iminomethylbenzo[b]thiophenato)copper(II) (Va, R = H, M = Cu). A solution of 5.7 g (0.029 mole) of copper acetate in 70 ml of water was added to a solution of 10 g (0.056 mole) of 3-hydroxy-2-iminomethylbenzo[b]thiophene (II) in 120 ml of ethanol, and the mixture was refluxed for a few minutes. It was then cooled, and the resulting precipitate was removed by filtration, washed with water and alcohol, and recrystallized from DMFA to give 9.8 g (83%) of chelate Va with mp 217-218°. Found: C 52.1; H 2.6; Cu 14.8; S 15.0%. $C_{18}H_{12}CuN_2O_2S_2$. Calculated: C 52.0; H 2.9; Cu 15.3; S 15.4%.

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*The molecular weight was determined cryoscopically in benzene solution.

{N,N'-Bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediaminato}copper(II) [Vb, R = $-(CH_2)_2-$, M = Cu]. A) An alcohol solution of 0.1 g (0.5 mmole) of copper acetate was added to a hot solution of 0.18 g (0.47 mmole) of ethylenediamine [III, R = $-(CH_2)_2-$] in 500 ml of ethanol, and the mixture was refluxed for a few minutes. It was then cooled, and the resulting light-green crystalline precipitate was removed by filtration, washed with alcohol, and dried to give 0.17 g (60%) of chelate Vb with mp > 280° (dec.). Analysis showed the presence of one water molecule. Found: C 52.3; H 3.7; Cu 13.6; S 13.9; H_2O 4.08%. $C_{20}H_{14}CuN_2O_2S_2 \cdot H_2O$. Calculated: C 52.2; H 3.5; Cu 13.8; S 13.9; H_2O 3.92%.

B) A total of 20 ml of DMFA was added to 1.35 g (3.2 mmole) of bis(3-hydroxy-2-iminomethylbenzo[b]thiophenato)Cu(II) (Va), the mixture was heated to the boiling point (a part of the chelate did not dissolve), and 0.22 g (3.7 mmole) of ethylenediamine was added (after which the chelate dissolved completely). The hot solution was filtered, the filtrate was evaporated until a precipitate began to form (6-7 ml), and the solution was allowed to stand at room temperature for 2 days. The precipitate was removed by filtration, washed thoroughly with acetone, and dried to give 0.38 g (27%) of chelate Vb with mp 280° (dec.). Found: C 54.3; H 3.1%. $C_{20}H_{14}CuN_2O_2S_2$. Calculated: C 54.4; H 3.2%.

{N,N'-Bis(3-hydroxy-2-benzo[b]thenylidene)ethylenediaminato}zinc(II) [Vc, R = $-(CH_2)_2-$, M = Zn]. This compound was obtained in 84% yield by a method similar to that used to prepare chelate Vb (method A) by mixing solutions of ligand III and zinc acetate in DMFA. The product decomposed above 400°. Found: C 51.9; H 3.5; S 12.6%. $C_{20}H_{14}N_2O_2S_2Zn$. Calculated: C 52.0; H 3.5; S 13.3%.

The additives investigated as stabilizers were added to the ε-caprolactam prior to polymerization. The fibers were formed with a laboratory testing unit at 266° and were stretched at 300 m/min and a stretching frequency of 4.63.

The effectiveness of the action of the stabilized additives was estimated from the change in the viscosity of 1% solutions of the fibers in 96% sulfuric acid and from the change in the physicomechanical indexes of the fibers after heating for a definite time at 150 and 200°.

The fibers were subjected to photochemical aging in a Xenotest apparatus (Original Hanau System type 150) for 150 h at 32° and a relative humidity of 55%.

The analytical and physicomechanical tests were accomplished by known methods [12, 13].

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