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Dodecathionic Acid as Precursor for Formation of Semiconducting and Conducting Layers on the Surface of Polyamide 6

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By a study of IR and UV absorption spectra it is shown that the dodecathionate anions, $S_{12}O_6^{2-}$, are sorbed-diffused into a polyamide 6 films if they are treated with the $4\cdot10^{-3}$ mol·dm^{-3} water solution of dodecathionic acid, $H_2S_{12}O_6$, at the temperatures of 10 °C – 40 °C. The values of sulfur concentration obtained in polyamide 6 (up to ~11 mmol·cm^{-3}) are significantly higher than those, obtained in the studies in which the sorption of pentathionate ions from the $K_2S_5O_6$ solution or from $2\cdot10^{-3}$ mol·dm^{-3} water solution of dodecathionic acid, $H_2S_{12}O_6$, by PA films has been studied. The concentration of sorbed dodecathionate ions increases with the increase of time of treatment, concentration and temperature of a $H_2S_{12}O_6$ solution. The copper sulfide, Cu_xS, layers are formed in the surface of polyamide 6 film if the sulfurized polymer is treated with a solution of Cu(II/I) salt at 80 °C temperature: the anionic particles $S_{12}O_6^{2-}$ containing sulfur atoms of low oxidation state react with the copper ions. The conditions of a polymer initial sulfurization determine the concentration of copper and the composition of sulfide layer: the concentration of copper in the polyamide 6 film increases with the increase of time and temperature of initial sulfurization, and varies from ~0.5 mmol·cm^{-3} to ~3.0 mmol·cm^{-3}; the stoichiometrical composition of Cu_xS layers on polyamide 6 formed according the data of chemical analysis varies from $Cu_{\sim0.3}S$ to $Cu_{\sim1.0}S$. The regularities determined enable formation by sorption-diffusion method of electrically conductive (~60 Ω/□ – ~1.0 Ω/□) copper sulfide layers using the solution of dodecathionic acid as a polyamide 6 sulfurization agent.

Keywords: dodecathionic acid, polyamide, sorption-diffusion, copper sulfide layers.

INTRODUCTION

The binary chalcogenide thin layers have a number of applications in various fields, including coatings, solar cells, photoconductors, IR detectors, semiconducting films, microelectronic devices and etc. [1]. Copper chalcogenide thin layers have a number of applications too: in various devices such as solar cells, super ionic conductors, photodetectors, photothermal conversion, electroconductive electrodes, etc. [2 – 4]. The layers of copper chalcogenides are produced by the various methods [5]. But their formation is more convenient by the use of sorption methods.

Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [6]. Over the last decade, a sorption method for the formation of thin copper sulfide, Cu_xS, layers on the surface of polyamide 6 (PA) based on the initial treatment of a polymer with the solutions containing anions of polythionates, $S_nO_6^{2-}$, has been under extensive investigation [7 – 14]. It was shown that during treatment the anions of lower polythionates – trithionate, tetrathionate and pentathionate, $S_3O_6^{2-} – S_5O_6^{2-}$, containing chains of divalent sulfur atoms of low oxidation state, $^{-}O_3S–S_x–SO_3^{-}$ [15 – 18], are sorbed by a polymer. Thin layers of copper sulfide are formed on a PA surface if a polymer sulfurized in such conditions later is treated with a solution of copper(II/I) salt [7 – 11, 13, 14]. The lower polythionates such as sodium trithionate, $Na_2S_3O_6\cdot H_2O$, sodium tetrathionate, $Na_2S_4O_6\cdot 2H_2O$, and potassium pentathionate, $K_2S_5O_6\cdot 3/2H_2O$, were used for PA sulfurization in previous studies looking for the formation of Cu_xS layers on PA surface [8, 9, 12, 13].

Few experiments using a solution of dodecathionic acid, $H_2S_{12}O_6$, for the PA sulfurization showed that significantly higher concentration of sorbed-diffused sulfur could be obtained in PA [7, 14] and the electrically conductive copper sulfide layers have been formed on PA surface.

The aim of this study was to obtain high quality layers of copper sulfide of various composition on the surface of PA film using as a precursor the 0.004 mol·dm^{-3} solution of dodecathionic acid, and to investigate their chemical composition and electrical properties.

EXPERIMENTAL

A PA 6 film (specification TY 6-05-1775-76, grade PK-4, 70 μm thick) produced in Russia was used. Prior to the experiments, pieces of the film 15 mm × 70 mm in sizes had been boiled in distilled water for 2h to remove the remainder of the monomer. Then they were dried with filter paper and kept in a dessicator over $CaCl_2$ for 24 h.

PA films were sulfurized in a thermostatic vessel up to 6 h at a temperature of 10 °C – 40 °C using a continually stirred 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ prepared by the method given in [19]. At certain time intervals, the PA film samples were removed from $H_2S_{12}O_6$ solution, rinsed with distilled water, dried with filtration paper, left over $CaCl_2$ for 24 h and then used in further experiments and analysis.

Sulfur concentrations (C_s) in PA film samples were determined potentiometrically [20]. Firstly a sample of a sulfurized PA film was treated under heating with 10 ml – 15 ml of 10 mol·dm^3 KOH and diluted with the same

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amount of distilled water. Standard calomel and platinum electrodes were used for the potentiometric titration of the solution obtained in KOH with 0.05 N solution of iodine under stirring. For the potentiometric measurements, a pH-meter – pH-673 M millivoltmeter was used.

For the formation of Cu_xS thin layers the samples of sulfurized PA were treated with Cu(II/I) salt solution at 80 °C. Cu(II/I) salt solution was made from crystalline $CuSO_4 \cdot 5H_2O$ and a reducing agent hydroquinone [21]. Then the PA sample was rinsed with distilled water, dried over $CaCl_2$ and used in consequent experiments.

The concentration of copper in PA sample was determined using an atomic absorption spectrometer "Perkin-Elmer 503" [22]. Before the analysis, samples of PA with copper and sulfur containing thin layers have been mineralized. Samples were treated with concentrated HNO_3 to destroy PA. Heating with concentrated hydrochloric acid removed the excess of nitric acid. For the conditions described above, the sensitivity of AAS method is 1 $\mu g \cdot ml^{-1}$ copper for the 1 % absorption [22].

The UV, VIS (200 nm – 400 nm) and IR (400 cm^{-1} – 1300 cm^{-1}) spectra were obtained with the aid of Spectronic^R Genesys^{TM} and Perkin−Elmer GX spectrometers, system FT−IR.

The resistance to constant current of Cu_xS layers with different composition was measured on an E 7–8 numerical measuring device with special electrodes.

RESULTS AND DISCUSSION

The nature of sulfur-containing particles sorbed by a PA film was studied by means of IR and UV absorption spectra of the polymer films treated in a dodecathionic acid solution.

It was found (Figs. 1, 2) that the peaks of most intensive bands in the IR spectra of PA samples sulfurized in a $H_2S_{12}O_6$ solution, recorded by the compensation method (PA absorption eliminated) were in the intervals 408 cm^{-1}– 469 cm^{-1}, 497 cm^{-1}– 579 cm^{-1}, 610 cm^{-1}– 733 cm^{-1}, 835 cm^{-1}– 1102 cm^{-1}, 1127 cm^{-1}– 1293 cm^{-1}. According to the literature data [17, 18, 23, 24] the peaks in the first interval were assigned to the valence vibrations in the S–S bond ($\nu_{S–S}$), in the second interval – to the asymmetric deformation O–S–O vibrations, δ_{as}(O–S–O), in the third interval to the symmetric deformation O–S–O vibrations, δ_s(O–S–O), in the fourth interval – to the symmetric valence S–O vibrations, ν_s(S–O), and in the fifth interval – to the asymmetric valence S–O vibrations, ν_{as}(S–O). The similarity of the IR spectra of sulfurized PA samples and of the polythionates–selenopolythionates indicates that the sorption of dodecathionate ions by a PA occurs during the polymer treatment with the solutions of $H_2S_{12}O_6$.

The UV absorption spectra of PA samples sulfurized for different periods of time in the solutions of $H_2S_{12}O_6$ recorded by the compensation method (PA absorption eliminated) are shown in Figs. 3 and 4. Four absorption maxima are observed in these spectra: at ~225 nm as a weak shoulder, at ~250 nm as a clear peak, at ~290 nm as a broad peak and ~330 nm – 340 nm as a clear peak or shoulder. According to the data of the study of the UV absorption spectra of polythionates [18, 25 – 27], the absorption maxima of polythionate ions as shoulders and peaks are at ~215, ~250, ~290 and ~340 nm. Thus, the similarity of the UV spectra of sulfurized PA samples and of the polythionates indicates again that the sorption of dodecathionate ions by a PA occurs during the polymer treatment with the solutions of dodecathionic acid.

In this work the kinetics of sorption-diffusion of sulfur from the solution of dodecathionic acid into PA film was investigated (Figs. 5, 6). It was found that the concentration of sulfur in the samples (C_s, $mmol \cdot cm^{-3}$) during exposure in the solution of $H_2S_{12}O_6$ at 10, 20, 30 or 40 °C increases continuously with a time. Sulfur concentrations in the range ~1 $mmol \cdot cm^{-3}$– 11 $mmol \cdot cm^{-3}$ might be obtained by varying the temperature and concentration of the solution of $H_2S_{12}O_6$. The results of the kinetics presented show that a higher sulfur concentration was obtained at a higher temperature.

It is obvious that the values of sulfur concentration obtained in PA are significantly higher than those obtained in the studies in which the sorption of pentathionate ions from the $K_2S_5O_6$ solution of significantly higher concentration – by PA films has been studied [9, 12]. Thus, the results obtained provided conditions for the formation of copper sulfide, Cu_xS, layers on the surface of PA.

In order to form copper sulfide layers on the surface of sulfurized PA films, they were treated for 10 min with the Cu(II/I) salt solution at 80 °C. It was found that the concentration of copper in the sulfide layer increased with the time of PA sulfurization in the $H_2S_{12}O_6$ solution at all temperatures studied, and a different concentration of copper in the surface of PA at each temperature is reached (Figs. 7, 8).

The concentration of copper in the layer increases with an increase in the sulfur concentration reached at the temperatures of sulfuration 10 °C – 40 °C. That is completely understandable since with a higher concentration of sulfur sorbed-diffused into the PA a larger amount of copper ions may be involved in an reaction with the sulfur species. The molar Cu/S ratio in the copper sulfide layers on the PA surface was calculated from amounts measured in the PA films. It was found that the Cu/S ratio (Table 1) does not depend much on the time of initial PA sulfurization but in most cases decreases with the increase in temperature of the $H_2S_{12}O_6$ solution from 20 °C to 40 °C. By changing the conditions of sulfurization, it was possible to obtain copper sulfide layers on the surface matrix layer of PA of stoichiometrical composition varying from ~$Cu_{0.3}S$ to ~$Cu_{1.0}S$. When the time of treatment in the Cu(II/I) solution was 10 min after the initial sulfurization in $H_2S_{12}O_6$ solution at 20 °C during 0.5 h – 2.0 h, according to the chemical analysis, the stoichiometrical composition of the copper sulfide layers obtained was close to CuS; after the initial sulfurization at other temperatures during 1.0 h – 5.0 h – the stoichiometrical composition was closer to $Cu_{0.5}S$. The decrease of the molar ratio Cu/S with the increase in the temperature of the sulfurization solution may be explained by the fact that the concentration of sorbed-diffused into PA sulfur grows with increase of sulfurization temperature from 10 °C to 40 °C to significantly higher extent (from ~1 $mmol \cdot cm^{-3}$ to ~11 $mmol \cdot cm^{-3}$) compared with the extent of copper concentration increase (from ~0.5 $mmol \cdot cm^{-3}$ to ~3.0 $mmol \cdot cm^{-3}$) with the grow of $H_2S_{12}O_6$ solution temperature. It appears that the reaction product – copper sulfide hinders the further diffusion of copper ions into the polymer. From the data it was concluded, that the changing the conditions of PA sulfurization leads to the formation different composition of copper sulfide layers.

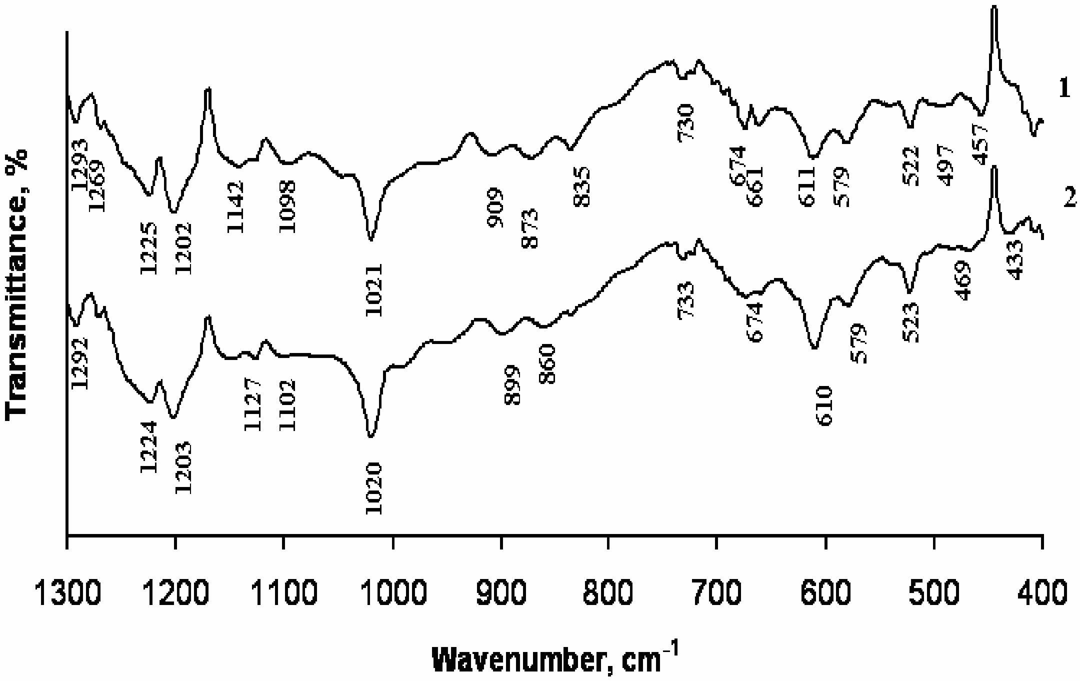

Fig. 1. IR absorption spectra of a PA films treated with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ at 10 °C different time. Sulfurization time, h: 1 – 2, 2 – 6

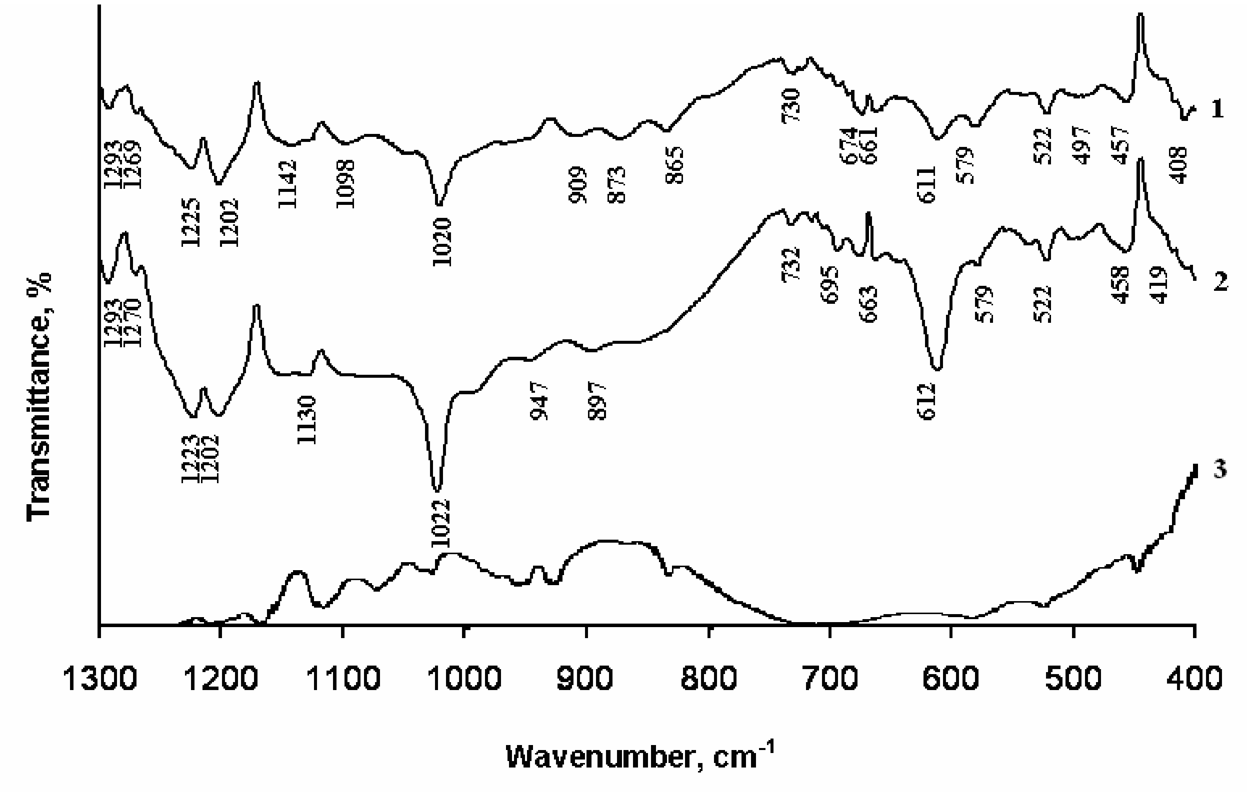

Fig. 2. IR absorption spectra of a PA films treated during 2 h with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ (1, 2) and of initial untreated PA (3). PA treatment with $H_2S_{12}O_6$ temperature, °C: 1 – 10, 2 – 20

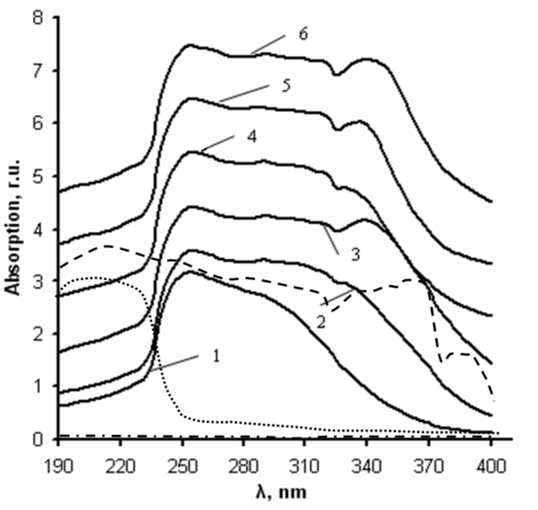

Fig. 3. UV absorption spectra of PA films (····· – without compensation, – · – · – using PA absorption compensation), PA films treated with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ at 20 °C different time and of the 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ – – – –. Sulfurization time, h: 1 – 0.25, 2 – 0.5, 3 – 1.5, 4 – 3.0, 5 – 4.0, 6 – 5.0

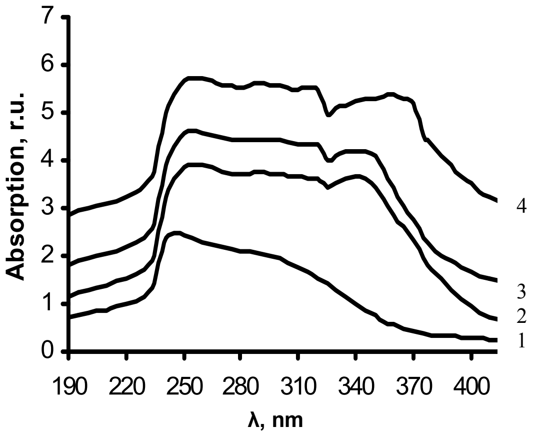

Fig. 4. UV absorption spectra of PA films treated 1.5 h with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ at different temperature. Sulfurization temperature, °C: 1 – 10, 2 – 20, 3 – 30, 4 – 40

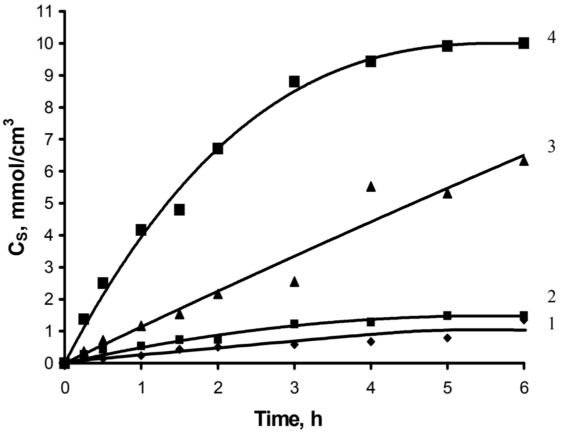

Fig. 5. Change of sulfur concentration in PA with time during its treatment with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ at different temperatures. The temperature (°C) of $H_2S_{12}O_6$ solution: 1 – 10, 2 – 20, 3 – 30, 4 – 40

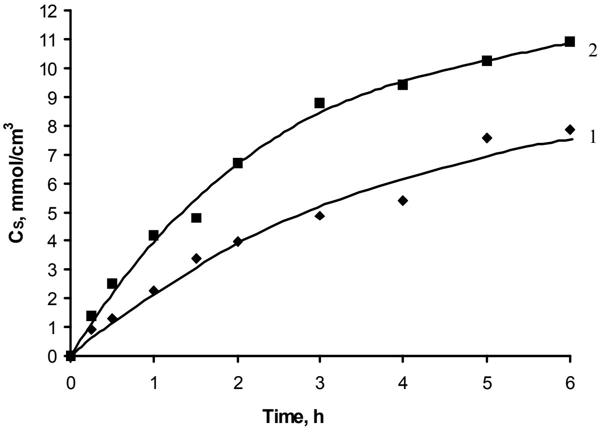

Fig. 6. Change of sulfur concentration in PA with time during its treatment with the solution of $H_2S_{12}O_6$ of different concentration at the temperature of 40 °C. Concentration, mol·dm^{-3}: 1 – 0.002, 2 – 0.004

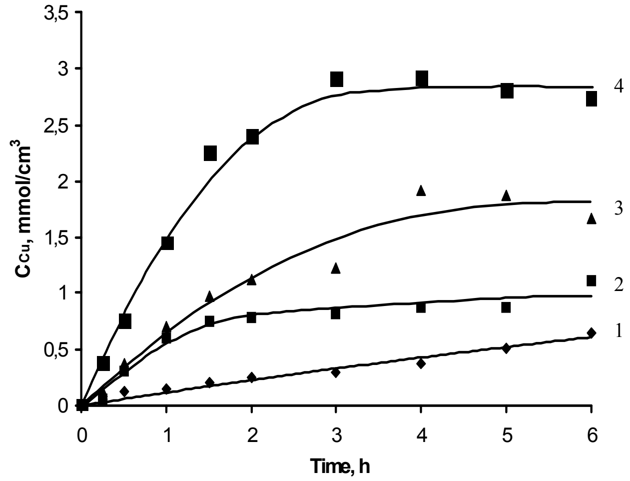

Fig. 7. Dependence of the concentration of copper in sulfide layer on PA film on sulfurization time when treating it with 0.004 mol·dm^{-3} solution of $H_2S_{12}O_6$ at different temperatures. The temperature (°C) of $H_2S_{12}O_6$ solution: 1 – 10, 2 – 20, 3 – 30, 4 – 40

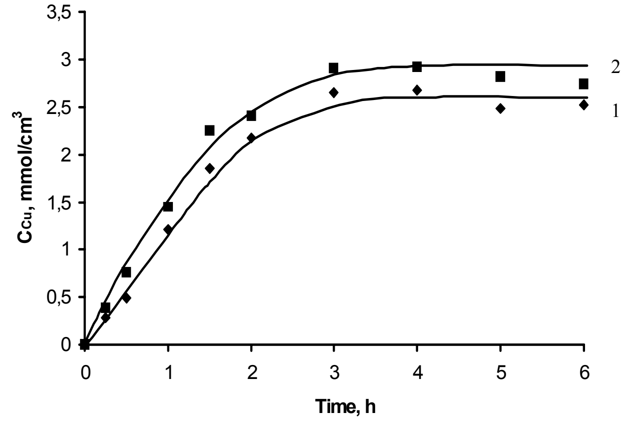

Fig. 8. Dependence of the concentration of copper in sulfide layer on PA film on sulfurization time when treating it with solution of $H_2S_{12}O_6$ of different concentration at the temperature of 40 °C. Concentration, mol·dm^{-3}: 1 – 0.002, 2 – 0.004

Table 1. The molar ratios Cu/S (S = 1) in the copper sulfide layers in the surface of PA first treated in $H_2S_{12}O_6$ solution and then – in Cu(II/I) salt solution

Concentration of $H_2S_{12}O_6$ solution, mol·dm^{-3}	Temperature of $H_2S_{12}O_6$ solution, °C	Time of sulfurization, h								
		0.25	0.5	1.0	1.5	2.0	3.0	4.0	5.0	6.0
0.004	10	0.44:1	0.74:1	0.59:1	0.60:1	0.55:1	0.55:1	0.54:1	0.52:1	0.47:1
	20	0.42:1	0.71:1	0.97:1	0.92:1	0.93:1	0.78:1	0.75:1	0.70:1	0.63:1
	30	0.32:1	0.52:1	0.60:1	0.63:1	0.51:1	0.46:1	0.39:1	0.35:1	0.26:1
	40	0.28:1	0.30:1	0.35:1	0.36:1	0.36:1	0.33:1	0.32:1	0.30:1	0.27:1
0.002	40	0.31:1	0.37:1	0.54:1	0.57:1	0.55:1	0.52:1	0.47:1	0.36:1	0.32:1

Table 2. The sheet resistance (Ω/□) of Cu_xS layers on PA first treated in $H_2S_{12}O_6$ solution and then – in Cu(II/I) salt solution

$H_2S_{12}O_6$ solution		Time of sulfurization, h								
Concentration, mol·dm^{-3}	Temperature, °C	0.25	0.5	1.0	1.5	2.0	3,0	4,0	5,0	6,0
0.004	10	$3.5\cdot10^6$	$2.1\cdot10^6$	$1.1\cdot10^6$	$8.5\cdot10^3$	280	248	186	188	191
	20	59	15.6	10.2	7.6	7.5	6.9	6.7	4	1.2
	30	36	10	4.3	4	3.8	2.3	0.98	0.98	0.79
	40	20	3.93	1.35	0.75	0.78	1.68	1.9*	7.9*	5.6*
0.002	40	86	66	18	3.03	1.48	1.43	1.23	1.06	0.72

*Low quality Cu_xS layer – partly separated.

The data presented in the Table 2 show that the value of electrical resistance of the formed copper sulfide layer in all cases decreases with the increase in the temperature and concentration of PA sulfuration solution reaching even values of only one or few Ω/□.

The another tendency becomes clear while increasing the duration of PA sulfuration: the values of electrical resistance decrease with the increase in PA sulfuration time and especially for the samples sulfured at the temperatures of 20, 30 and 40 °C. When the $H_2S_{12}O_6$ solution of the temperature of 40 °C have been used for the PA sulfuration, the most electrically conductive Cu_xS layers were obtained.

From the data it was concluded, that changing of the conditions of PA sulfuration leads to the formation different composition of electrically conductive copper sulfide layers

CONCLUSIONS

1. The sorption of dodecathionate ions, $S_{12}O_6^{2-}$, from 0.004 mol·dm^{-3} water solution of dodecathionic acid, $H_2S_{12}O_6$, by polyamide 6 films has been studied by IR (400 cm^{-1} – 1300 cm^{-1}), UV (200 nm – 400 nm) absorption spectra and chemical methods.
2. The peaks in the IR spectra of the dodecathionate anions sorbed into a polyamide were found in the intervals 408 cm^{-1} – 469 cm^{-1}, 497 cm^{-1} – 579 cm^{-1}, 610 cm^{-1} – 733 cm^{-1}, 835 cm^{-1} – 1102 cm^{-1}, 1127 cm^{-1} – 1293 cm^{-1} and assigned to the ν_{S-S}, δ_{as}(O–S–O), δ_s(O–S–O), ν_s(S–O) and ν_{as}(S–O), respectively. Four absorption maxima were observed in the UV absorption spectra: at ~225 nm as a weak shoulder, at ~250 nm as a clear peak, at ~290 nm as a broad peak and ~330 nm – 340 nm as a clear peak or shoulder. The spectral data confirm that sulfur is sorbed by PA films in the form of dodecathionate ions.
3. The concentration of sulfur sorbed by a polymer increases with increasing the duration of polymer treatment in $H_2S_{12}O_6$ solution, the concentration and temperature of this solution. The layers of copper sulfide forms in the surface of polyamide 6 film when the sulfured in dodecathionic acid solution polymer later treated with copper(II/I) salt solution.
4. The concentration of copper in the sulfide layers increases with the increase of concentration of sulfur in polyamide. The chemical composition of copper sulfide layers depends on the conditions of the sulfurization process and varies between ~$Cu_{0.3}S$ and ~$Cu_{1.0}S$.
5. The regularities determined enable formation by sorption-diffusion method of electrically conductive (~59 Ω/□ – ~1.0 Ω/□) copper sulfide layers of desirable composition using the dodecathionic acid as a polyamide 6 sulfurization agent.

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