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Studies of the Composition of Copper Sulfide Layers on Polyamide 6 Formed by the Use of Potassium Pentathionate

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A polyamide 6 film if treated it with the water solutions of potassium pentathionate, $K_2S_3(SO_3)_2$, sorbs sulfur in the form of pentathionate anion. The concentration of sulfur in polyamide 6 film increases when increase of the concentration of solution of $K_2S_3(SO_3)_2$ and duration of polymer sulfuration. Further interaction of the polyamide 6 films containing sorbed $S_3(SO_3)_2^{2-}$ ions with Cu(I) salt solution leads to the formation of copper sulfide layers on the polymer surface. The concentration of copper in polyamide 6 films increases, when the temperature and the concentration solution of $K_2S_3(SO_3)_2$ and the exposure time of the polymer in solution of $K_2S_3(SO_3)_2$ were increased. The molar ratio of Cu : S in copper sulfide layers varied from 1 : 1.52 to 1 : 4.78. Results of X-ray diffraction analysis confirmed the formation of Cu_xS layers of various phases. Comprising in itself mainly phases of hexagonal chalcosine, Cu_2S prevails in the composition of Cu_xS layers on polyamide 6 films surface. The sheet resistance of copper sulfide layers on PA 6 films varied from 4.30×10^3 to 7.05 kΩ/□.

Keywords: potassium pentathionate, polyamide, sulfuration, layers of copper sulfide.

INTRODUCTION

Polymers modified with thin layers of d-metal sulfides are ascribed to composites. They are needed in modern and advanced technologies. For example: the polymers modified with layers of copper sulfides, Cu_xS, are used in solar radiation absorbers [1], radiation filters [2], solar cells [3, 4] and solar radiation control coatings [5]. These modified polymers might be used as semiconductors [6, 7] or gas sensors functioning at temperatures tending to room temperature [8, 9] as well as photodiodes, photo resisters [10], micro converters in microelectronics [11].

Adsorption-diffusion method of obtaining thin electro conductive or semi-conductive layers of copper sulfides [12] on polyamide 6 (PA 6) was proposed recently. At the first stage, PA 6 is sulfurated [13] and at the second stage, polymer is treated with an aqueous solution of copper(I-II) salt [14]. Depending on the sulfur concentration in the PA 6 and the period of the treatment with the solution of the copper salt brown or even black stoichiometric CuS, Cu_2S and non-stoichiometric Cu_xS ($x = 1.12 \div 1.95$) layers were obtained.

Hydrophilic and semi-hydrophilic polymers are capable of absorbing ions of various electrolytes from aqueous solutions [15]. This fact enabled us to introduce the anions of polythionates, $S_n(SO_3)_2^{2-}$, i.e. compounds containing divalent sulfur atom chains [16] from aqueous solutions in polyamide 6. After treating such polythionates ions containing polymer films with Cu(I-II) salt water solutions Cu_xS layers of various electrical conductivity and composition can be obtained on their surface depending on experimental conditions [17].

This work was basically inspired by an increasing interest in new semiconductor as a material for an application in flexible and efficient gas sensors production. The research has been undertaken also for clarifying the kinetics of the diffusion of the sulfur into PA 6 surface and some structural and electrical properties of such films has been investigated also.

Our main task was to form the binary copper sulfide layers on PA 6 surface using the pentathionate, $S_3(SO_3)_2^{2-}$ and to investigate dependence of the Cu_xS layers composition on the condition of its formation.

EXPERIMENTAL

In searching for new sulfide composition we have chosen the potassium pentathionate, $K_2S_5O_6 \cdot 1.5\ H_2O$, as a source of sulfur(II) containing anionic particles for its inclusion into polymer. The salts of potassium pentathionate, $K_2S_5O_6 \cdot 1.5\ H_2O$, were prepared and chemically analyzed according to published procedures [18 – 20].

The layers of sulfides were deposited on PA 6 film (specification TY 6-05-1775-76, grade PK-4, Russia) tape of 70 μm thickness. This film is close to a nonporous material, because the pores of PA 6 are much less than 1.5 nm. The porosity was measured by BET method using a Quantasorb (USA) [21]. Prior to the experiments pieces of the PA 6 film of 15 mm × 70 mm in size were boiled in distilled water for two hours to remove the remainder of the monomer. After that they have been dried by filter paper and than in the desiccator over $CaCl_2$ for 24 h.

PA 6 films were sulfurized in a thermostatic vessel using continually stirred solutions of $K_2S_3(SO_3)_2$ up to 4 h. At certain time intervals of exposure in the solution of $K_2S_3(SO_3)_2$ the samples were removed, rinsed with distilled water, dried with filtration paper, left over $CaCl_2$ for 24 h and then used in further experiments and analysis.

The solution of copper(I) salt was produced from the solution of 0.4 mol·dm^{-3} $CuSO_4$ with addition of 0.36 mol·dm^{-3} reducing agent hydroxylamine sulfate by method presented in work [22]. Independently of temperature the

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all ions of divalent copper transit to ions of univalent copper in this mixture. After having kept in $K_2S_3(SO_3)_2$ solution, the PA 6 sample was 20 min treated at the temperature of 35 °C with a Cu(I) solution, then rinsed with distilled water, dried over $CaCl_2$ and used in further experiments.

The sulfur concentrations in PA 6 film samples were determined potentiometrically [23]. Firstly the sample of a sulfured PA 6 film was treated under heating with 10 ml – 15 ml of 10 mol·dm^{-3} KOH and diluted with the same 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.

The amount of copper in a PA 6 sample was determined spectroscopically by the atomic absorption – spectrometer "Perkin – Elmer 503" (USA) [24]. The PA 6 films were dissolved in 2 cm^3 of concentrated HNO_3, diluted up to 10 cm^3 with distilled water and boiled for 30 min (to make the PA 6 destruction irreversible and to oxidize sulfur compounds). Then the solution was diluted to a required volume and analyzed.

The sheet resistance at a direct current of Cu_xS layers of different composition was measured using an E7-8 numerical measuring instrument with special electrodes.

The phase composition of copper sulfide layer has been analyzed by means of X-ray diffraction using diffractometer DRON-6 (Russia) using CuK_α (λ = 0.154178 nm) radiation, 30 kV voltage and 20 mA current. The scanning range was $2\theta = 30° – 70°$. The scanning speed was 1° min^{-1}. X-ray diffractograms of PA 6 samples with Cu_xS layers were treated using the Search Match, Xfit, ConvX and Excel programs to eliminate the peaks of PA 6.

ANALYSIS AND RESULTS

PA 6 films were modified by formation on its surface layers of copper sulfide. First stage of this process is interaction of the PA 6 film with the solution of potassium pentathionate, $K_2S_3(SO_3)_2$. In the second stage the sulfurized polymer samples were treated with the aqueous solution of copper(I) salt.

The dependence of the sorption of $S_3(SO_3)_2^{2-}$ ions by polymer on the temperature and the concentration of the $K_2S_3(SO_3)_2$ solution were investigated. Preliminary experiments had shown that the sorption the anions of $S_3(SO_3)_2^{2-}$ from the solutions of lower concentration was too slow and insufficient. In our previous study was determined [25] that anions of $S_3(SO_3)_2^{2-}$ in solutions of pentathionate at higher temperature (40 °C – 50 °C) decomposed during the first half-hour of the experiment. Solution becomes mat, yellowish colour because of the fallen into the sediment particles of colloidal sulfur. Besides for this reason sulfur concentration in polymer treated with solution of $K_2S_3(SO_3)_2$ is reached up to 3.27 mg·cm^{-3} [25]. So the process of polymer sulfuration at temperatures higher as 30 °C further was not investigated.

Also in the study [26] it was noticed, that addition of acids makes the structure of PA 6 film amorphous and anions of electrolyte can be easy introduced between molecules of polymer. Therefore, the PA 6 film samples were affected with acidified (0.1 mol·dm^{-3} HCl, pH ~ 1.5) 0.025 mol·dm^{-3} – 0.1 mol·dm^{-3} solutions of $K_2S_3(SO_3)_2$ at 20 °C and 30 °C temperatures. Such interval of temperature was chosen because of the stability of $K_2S_3(SO_3)_2$ solution.

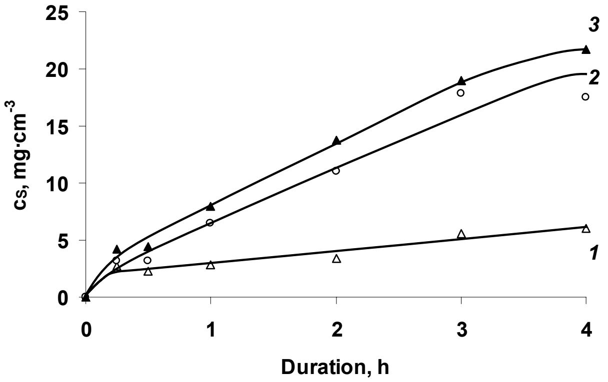

Fig. 1. Dependence of sulfur concentration (c_S) in PA 6 with time after treatment with the acidified (HCl c = 0.1 mol·dm^{-3}) at temperatures 20 °C solution of $K_2S_3(SO_3)_2$ at different concentration, mol·dm^{-3}: 1 – 0.025, 2 – 0.05, 3 – 0.1

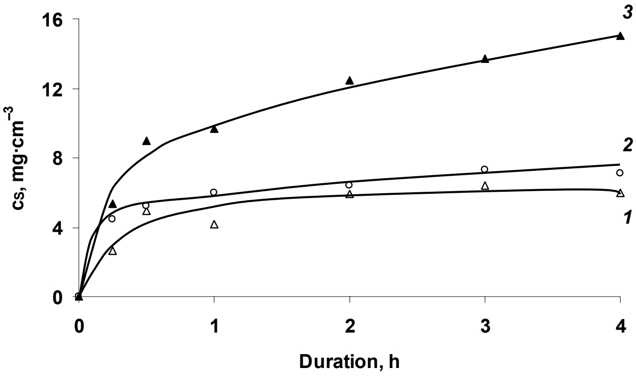

Fig. 2. Dependence of sulfur concentration (c_S) in PA 6 with time after treatment with the acidified (HCl c = 0.1 mol·dm^{-3}) at temperatures 30 °C solution of $K_2S_3(SO_3)_2$ at different concentration, mol·dm^{-3}: 1 – 0.025, 2 – 0.05, 3 – 0.1

To study the influence of concentration of $K_2S_3(SO_3)_2$ solution on a quantity of sulfur sorbed by polymer, solutions 0.025 mol·dm^{-3} – 0.1 mol·dm^{-3} concentration were selected. In this way it was established, that with an increase the concentration of solution, sorption the ions of $S_3(SO_3)_2^{2-}$ by polymer increased.

The kinetic data of sulfur concentration show, that the sulfur concentration in PA 6 samples treated with solution of $K_2S_3(SO_3)_2$ at 20 °C temperature increases faster and higher sulfur concentration were reached in polymer as one in solution at 30 °C temperature (Fig. 1 and Fig. 2). For example, sulfur concentration reached in PA 6 samples after treatment with 0.1 mol·cm^{-3} solution of potassium pentathionate 2 h and 3 h at different temperatures are 12.46 mg·cm^{-3}and 13.72 mg·cm^{-3} (30 °C) as 13.74 mg·cm^{-3} and 18.94 mg·cm^{-3} (20 °C). It has been explained by a lower stability anions of $S_3(SO_3)_2^{2-}$ in solutions at higher temperature. Then anions of $S_3(SO_3)_2^{2-}$ faster decomposed (equation (1)). When PA 6 films were sulfurized with 0.025 mol·dm^{-3} concentration solutions at both temperatures, the minimal sulfur concentration was found in polymer samples. It has been explained by insufficient concentration anions of $S_3(SO_3)_2^{2-}$ in solutions. The maximum concentrations of sulfur in PA 6 were reached after three and four hour treatment of polymer with solution of potassium pentathionate at temperatures of 20 °C. For example, if the concentration of $K_2S_3(SO_3)_2$ solution was raised from 0.05 mol·dm^{-3} up to 0.1 mol·dm^{-3}, the maximal sulfur concentration in PA 6 increased four times [19]:

$$S_3(SO_3)_2^{2-} \rightarrow 3S + SO_2 + SO_4^{2-}\,. \qquad (1)$$

The anions of pentathionate, $^{-}O_3S{-}S{-}S{-}S{-}SO_3^{-}$, possessed the divalent sulfur in their composition [16]. Therefore we expected, that copper sulfide layers on PA 6 sample previously sulfured with solution of potassium pentathionate and than treated with solution of Cu(I) salt will be formed.

Our investigations confirmed this presumption. PA 6 films after the sulfuration were colorless. The same polymer samples after treating it with solution of Cu(I) salt become light or dark brown reflecting "metallic" color. So, from the dielectric it becomes electro-conductive.

Copper sulfide layers on PA 6 are formed via heterogeneous chemical reactions [12]:

$$S_3(SO_3)_2^{2-} + 2Cu^+ + 2H_2O \rightarrow Cu_2S + 2S + 2H_2SO_4\,; \qquad (2)$$

$$2xCu^+ + 1/8S_8 \rightarrow Cu_xS + xCu^{2+}\,. \qquad (3)$$

Analysis of copper sulfide layers formed on PA 6 films showed, that the concentration of copper increases, when the concentration solutions of $K_2S_3(SO_3)_2$ and duration of sulfuration were increased (Fig. 3, 4). The main influence of copper concentration in copper sulfide layers on PA 6 film has the concentration solutions of $K_2S_3(SO_3)_2$. For example, in the samples of those processed in the solutions of 0.025 mol·dm^{-3} concentration at 30 °C, copper concentration after the first hour of working – 53.0 mg·cm^{-2} and after 4 h of working are 54.43 mg·cm^{-2} (Fig. 4, curves 1). With an increase in the concentration of the solution 4 times, at a temperature 30 °C, this difference is equal to respectively 96.27 mg·cm^{-2} and 280.4 mg·cm^{-2} (Fig. 4., curves 3). The copper concentrations in the solution of 0.1 mol·dm^{-3} close to duration increase 5.2 times.

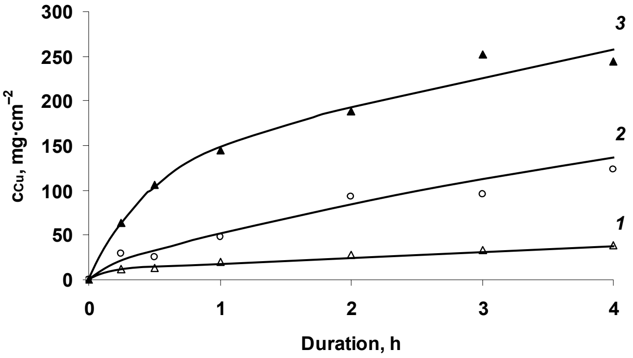

Fig. 3. Dependence of copper concentration (c_{Cu}) in PA 6 with time after treatment with the acidified (HCl $c = 0.1$ mol·dm^{-3}) solution of $K_2S_3(SO_3)_2$ at temperatures 20 °C at different concentration, mol·dm^{-3}: 1 – 0.025, 2 – 0.05, 3 – 0.1

The concentration of copper in copper sulfide layers formed on PA 6 films by used the solution of $K_2S_3(SO_3)_2$ at 30 °C temperature is higher as ones at 20 °C temperature. Meanwhile the sulfur concentration in the samples those processed is contrary lower at 30 °C temperature as ones at 20 °C temperature. For example, the concentration of copper in copper sulfide layers formed on PA 6 films sulfurized 4 h with the solutions of $K_2S_3(SO_3)_2$ at 20 °C and 30 °C temperatures are 244.3 mg·cm^{-2} and 280.4 mg·cm^{-2} (Fig. 3, curves 3 and Fig. 4, curve 3). The sulfur concentration in same polymer samples accordingly are 21.20 mg·cm^{-2} and 14.82 mg·cm^{-3} (Fig. 1, curves 3 and Fig. 2, curve 3).

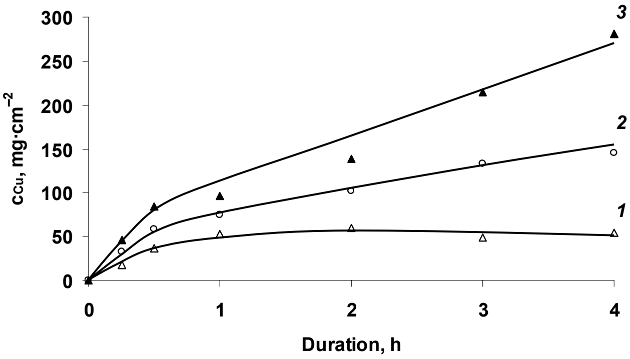

Fig. 4. Dependence of copper concentration (c_{Cu}) in PA 6 with time after treatment with the acidified (HCl $c = 0.1$ mol·dm^{-3}) solution of $K_2S_3(SO_3)_2$ at temperatures 30 °C at different concentration, mol·dm^{-3}: 1 – 0.025, 2 – 0.05, 3 – 0.1

This variation of copper and sulfur concentrations in PA 6 films samples can be explained by mentioned above equation 2 and 3, when only divalent and elemental sulfur take part to formation of copper sulfide layers. The parts of sulfur(VI) are washed out from polymer. The parts of (VI) sulfur form are more in polymer samples sulfurized at 20 °C as ones sulfurizes at 30 ° temperature.

When the concentrations of copper and sulfur in PA 6 films modified by copper sulfide layers has been determined, the values of molar ratio Cu : S were calculated. The values of molar ratio Cu : S in copper sulfide layers on PA 6 samples were dependent on the sulfuration condition and varied in range of 1 : 1.52 – 1 : 4.78. The molar ratio of Cu : S in layers of copper sulfide on the polymer decreases when the concentration and the temperature solution of $K_2S_3(SO_3)_2$ and the duration of sulfuration PA 6 films were increased.

Measurement of the sheet resistance of the copper sulfide layers on polymer surface showed, that its value depends on the conditions of sulfuration and copper concentration in copper sulfide layer. It varied from $4.30 \cdot 10^3$ to 7.05 kΩ/□ (Table 1). The sheet resistance decreases with an increase the concentration and temperature solution of $K_2S_3(SO_3)_2$. For example, the sheet resistance of copper sulfide layers on polymer, sulfured 2 h and more hours in solutions $K_2S_3(SO_3)_2$ of 0.05 and 0.1 mol·dm^{-3} concentrations decreases by thousands of times and only slightly depends on the temperature of solutions.

Table 1. The sheet resistance (kΩ/□) of Cu_xS layers formed in PA 6 matrices, depending on the duration of film exposure in solution of $K_2S_3(SO_3)_2$ at different temperatures (*T*, °C)

Solution of $K_2S_3(SO_3)_2$		Duration of treating the PA films in $K_2S_3(SO_3)_2$ solution, h				
c, mol·dm^{-3}	*T*, °C	0.5	1.0	2.0	3.0	4.0
0.025	20	$2.77\cdot10^3$	$2.60\cdot10^3$	$3.50\cdot10^3$	$2.94\cdot10^3$	$1.39\cdot10^3$
0.025	30	$2.94\cdot10^3$	$2.91\cdot10^3$	$1.99\cdot10^3$	$1.35\cdot10^3$	$1.58\cdot10^3$
0.050	20	$4.02\cdot10^3$	$3.39\cdot10^3$	159.0	7.05	13.63
0.050	30	$4.30\cdot10^3$	$3.51\cdot10^3$	178.2	24.9	16.87
0.100	20	$1.11\cdot10^3$	$1.33\cdot10^3$	$2.44\cdot10^3$	38.6	255.17
0.100	30	$3.16\cdot10^3$	$2.56\cdot10^3$	160.0	28.92	7.79

The direct dependence of electrical resistance on copper concentration is found not in the all cases. For example, after the sulfuration of the samples of PA 6 film in solution of 0.05 mol·dm^{-3} concentration at a temperature 20 °C for 3 h, and then processed by the solution of salt Cu(I), are found 6.733 mg·cm^{-3} copper (Fig. 3, curves 3), and in the polymer sulfured in solution of 0.1 mol·dm^{-3} concentration at a temperature 30 °C, in the same period, copper concentration composes 14.978 mg·cm^{-3} (Fig. 4, curves 3). The sheet resistance of these layers is equall respectively 7.05 kΩ/□ and 28.92 kΩ/□.

This is explained by the fact that the layers are formed, composition of which is very diverse and electrical conductivity of which greatly depends on chemical composition. For example, sheet resistance Cu_xS, with the decrease of x from 2 to 1 decreases by millions of times [27].

The variation molar ratio of Cu:S in PA 6 films from 1 : 1.52 to 1 : 4.78 was confirmed, that the composition of copper sulfide layers is varying in a wide range.

Structural studies of the Cu_xS layers deposited by the adsorption-diffusion method are limited by the polycrystallinity of the layers obtained, as well as by the existence of Cu_xS phases of various composition and structure, and by the crystallinity of the PA 6 film itself. The intensity of the peaks at $\theta < 13°$ exceeds the intensity of copper sulfide peaks several times. Therefore the area of $2\theta \geq 30.0°$ was investigated in more detail.

Analysis of the X-ray diffraction patterns, when PA 6 films initially treated with a solution of $K_2S_3(SO_3)_2$ (c = 0.1 mol·dm^{-3}, 20 °C in 0.1 mol·dm^{-3} HCl different time) and then with a Cu(I) salt solution 20 min, showed that the hexagonal chalcosine Cu_2S (PDF 72–1071) peak $2\theta = 38.4°$ prevailed in the composition of the copper sulfide film (Fig. 5, curves 3, 4), peak $2\theta = 38.2°$ (Fig. 5, curves 1, 2) were detected too.

When the treating time in $K_2S_3(SO_3)_2$ solution is lower than 4 h, the peaks of other phases of copper sulfide also appear: orthorhombic coveline CuS (PDF 78–2122) peak $2\theta = 49.52°$ and 67.14° (Fig. 5, curve 1), orthorhombic aniline $Cu_{1.75}S$ (PDF 72–617) peak $2\theta = 40.7°$ (Fig. 5, curve 2), and rhombohedralic geerite, $Cu_{1.6}S$ (PDF 33–491) peak $2\theta = 33.45°$ (Fig. 5, curve 3).

This feature can be explained by the fact that the sulfide film formed was not sufficiently compact. As a result, no sufficient amount of copper ions reacted with the pentathionate ions, and sulfur accumulated on the surface of the polymer with the formation of a sulfide phase containing more copper according to the peaks in the X-ray diffraction patterns. Consequently, in the course of sulfured PA 6 films treatment, the phase composition of Cu_xS layer changed in the direction of increasing values of x.

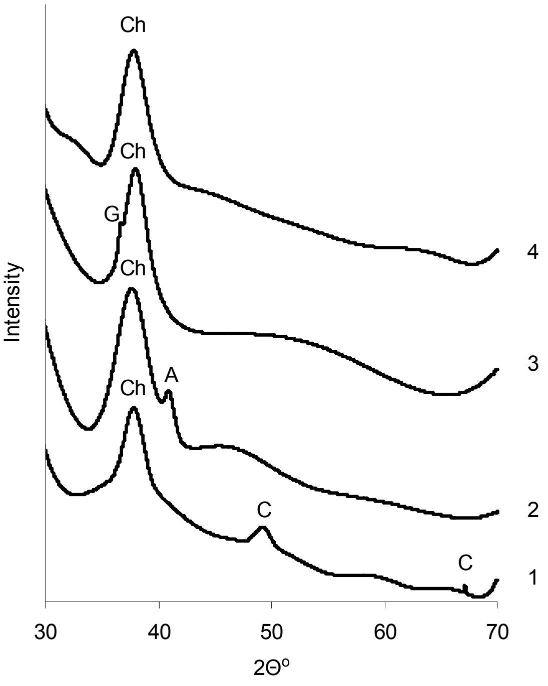

Fig. 5. X-ray diffraction patterns of the layers of Cu_xS on PKA (peaks of geerite – G, anilite – A, chalcosine – Ch, coveline – C). PA 6 initially treated with a solution of $K_2S_3(SO_3)_2$ (c = 0.1 mol·dm^{-3}, 20 °C in 0.1 mol·dm^{-3} HCl) different time (τ_s) and then with a Cu(I) salt solution 20 min τ_s, h: 1 – 0.5; 2 – 2; 3 – 3; 4 – 4

Summarizing the data of our investigation, we can affirme, that the copper sulfide layers on the semi-hydrophobic polymer polyamide 6 enables to obtain by adsorption-diffusion method as sulfuration agent used the potassium pentathionate.

CONCLUSIONS

1. The concentration of sulfur sorbed by a polymer increases with increasing the concentration of the potassium pentathionate solution and the duration of polymer treatment, it decreases with increasing the temperature of the potassium pentathionate solution.
2. The concentration of copper and the molar ratio of Cu:S in copper sulfide layers on PA 6 films increases with increasing of the duration treatment polymer samples with the solution of $K_2S_3(SO_3)_2$.
3. The sheet resistance of copper sulfide layers depends on the concentration of copper and the composition of copper sulfide layers. It decreases with an increase in copper concentration in the Cu_xS layer and varies from 4.30×10^3 to 7.05 kΩ/□.
4. Results of X-ray diffraction analysis confirmed the formation of copper sulfide layers of various phases. Comprising in itself mainly phases of hexagonal chalcosine Cu_2S prevails in the composition of Cu_xS film on PA surface sulfured in 0.1 $mol\cdot dm^{-3}$ solution of $K_2S_3(SO_3)_2$ at temperature 20 °C. When the treating time in potassium pentathionate is lower than 4 h, the peaks of other phases of copper sulfide also appear: orthorhombic coveline CuS, orthorhombic aniline $Cu_{1.75}S$, and rhombohedralic geerite, $Cu_{1.6}S$.

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