

Studies of the Composition of Copper Sulfide Layers on Polyamide

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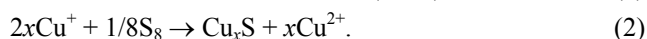
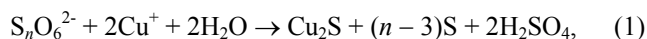
The Cu_xS layers on polyamide obtained by sorption-diffusion method using highly sulfured polythionic acids ($\text{H}_2\text{S}_n\text{O}_6$, $n = 21 \div 33$) are studied. These layers are formed when sorbed into polyamide ions of higher polythionates and sulfur react with a solution of copper(I-II) salt. By potentiometric study it is determined that a value x in electrically conductive or semiconductive copper sulfide layers varies in the interval $1 < x < 2$. That was confirmed by X-ray diffraction studies of the layers obtained. It is determined that the Cu_xS layers obtained are of three phases, comprising in itself *yarrowite*, $\text{Cu}_{1.12-1.18}\text{S}$, *anilite*, $\text{Cu}_{1.7-1.8}\text{S}$, and *djurleite*, $\text{Cu}_{1.91-1.95}\text{S}$. The ratio between the concentrations of phases depend on the period of polyamide sulfuration in a solution of polythionic acid and on the period of sulfured polymer treatment with a copper(I-II) salt solution. *Djurleite* prevails in the composition of Cu_xS film if PA is sulfured shortly (few min) in a solution of $\text{H}_2\text{S}_n\text{O}_6$. When the period of sulfuration is prolonged the peaks of *djurleite* slightly decreases and the peaks of *anilite* increases, and on further prolongation – the phases of *anilite* and *yarrowite* become dominating. When the polyamide sulfured under the same conditions is shortly (few min) treated in a solution of copper(I-II) salt the *yarrowite*, *talnakhite*, $\text{Cu}_{1.06}$, and *anilite* phases are detected, but if treatment in a Cu(I-II) salt solution is prolonged – formation of sulfide phase containing more copper – *anilite* is observed. Thus, in the course of sulfured polyamide treatment with a solution of Cu(I-II) salt, the phase composition of Cu_xS film changes in the direction of increasing values of x .

Keywords: high polythionic acids, polyamide, layer of copper sulfide.

INTRODUCTION

Electrically conductive and semiconductive composites are widely used in various fields of modern technology. Polyamide (PA) with layers of copper sulfides belong to this group of composites too [1]. Use of these composites is determined by their electrical properties and the last vary significantly even when the chemical composition is changed slightly [2]. Its electrical resistance increases more than 6 times when a value of x in Cu_xS is increased from 1 to 2.

Copper sulfide layers on PA are formed by sorption-diffusion method via heterogeneous chemical reactions [3]:



Molecules of the elemental sulfur in the PA forms [3, 4] during the decomposition of higher polythionic acids:



In the first stage of the process ions of higher polythionates diffuse into the PA when keeping it in the solution of higher polythionic acid, $\text{H}_2\text{S}_n\text{O}_6$ ($n = 9 \div 45$) [3, 4]. In the second stage PA sulfured is treated with the solution of copper(II) sulfate containing as a reducing agent hydroquinone [1, 3].

In the work [3] we found that the physical properties of the PA films with deposited layers of Cu_xS , for instance, their electrical conductivity is determined by the sorbed sulfur concentration in PA and by conditions of sulfured PA treatment with a solution of copper(I-II) salt. Cu_xS is a semiconductor of p type, having hole conductivity. The charges of the Cu^{2+} ions are holes. The hole transfer the

charge. Therefore the more are holes the better is conductance. The most conductive is the sulfide layer the composition of which is closer to CuS [6].

We have established [3] that at a lower sorbed sulfur concentration in PA, thin copper sulfide layers of a low electrical conductance are formed. When the sulfur concentration is sufficient and the period of interaction with copper salt is rather short more conductive layers are obtained, because their composition (according to the data of chemical analysis) differs significantly from that of Cu_2S . After keeping such sulfured films in a solution of copper salt for a longer time, the copper ions diffusing into sulfide change not only the thickness but the stoichiometric composition as well [3]. Simultaneously, they fill the vacancies in the copper lattice and increase the x value. At that time the composition of layers approaches to that of Cu_2S , and conductivity decreases. Thus having measured resistance one can determine the surface layer composition.

As it was mentioned above, the electrical properties of Cu_xS layers greatly depends on the layers composition. Therefore electrical measurements enable to get preliminary information about the composition of the layer obtained. More precise composition can be determined by X-ray diffraction studies.

The aim of present work was to study phase composition of Cu_xS layers in PA formed using highly sulfured $\text{H}_2\text{S}_n\text{O}_6$ on the basis of potentiometric measurements and X-ray diffraction analysis.

EXPERIMENTAL

The layers of copper sulfide were deposited on a PA PK-4 film of 70 μm thickness. The samples 15×70 mm in size were used and before sulfuration they were boiled in distilled water for 2 h to remove the remainder of the

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monomer. Then they were dried using filter paper and then over CaCl_2 for 24 h [4].

The PA samples thus prepared were exposed to the solution of polythionic acid [4].

The samples of sulfured PA were treated with a copper(I-II) salt solution consisting of $0.4 \text{ mol}\cdot\text{l}^{-1}$ CuSO_4 and $0.1 \text{ mol}\cdot\text{l}^{-1}$ hydroquinone (reducing agent). A Cu(I-II) salt solution was made from crystalline $\text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}$ and a hydroquinone as described in [3, 5].

Later on, the samples with Cu_xS layer formed were rinsed with distilled water, dried over CaCl_2 and used for further study.

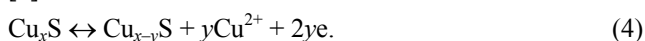
The amount of sulfur in a PA sample was determined by the amount of iodine used for a complete oxidation of polythionates diffused into PA [3, 4]. The amount of copper in the sulfide film after fusing in the concentrated nitric acid was determined by an atomic Perkin-Elmer absorptionmeter ($\lambda = 325 \text{ nm}$).

The electrode potential of PA film with Cu_xS layers (E) in acidic cupric sulfate solution was measured by an universal ЭВ-74 ionometer.

The phase composition of the copper sulfide layer was investigated by means of X-ray diffraction using a DRON-6 diffractometer (radiation $\text{Cu K}\alpha$). X-ray diffractograms of PA samples with layers of Cu_xS were treated using programs Sarch Match, Xfit, ConvX, Dplot95, and Photo Styler to eliminate the maxima of PA.

RESULTS AND ANALYSIS

Approximate composition of copper sulfide layers was estimated according to their electrode potentials. It is known [7] that the composition of copper sulfides can be estimated according to their electrode potentials in acidic CuSO_4 solution when the reversible reaction takes place [8]:



The values of potentials are practically independent on the composition of electrolyte. In this work the potential of electrode was measured in a $\text{Cu}_x\text{S}/\text{aqCuSO}_4 + \text{H}_2\text{SO}_4/\text{Cu}$ electrocell.

When x in copper sulfides increases, the potential of electrode (copper electrode being used for comparison) decreases from 290 mV for coveline (CuS) to 0 mV for chalcocine (Cu_2S) [7]. The values of copper sulfide electrode potentials in a $\text{Cu}_x\text{S}/\text{aqCuSO}_4 + \text{H}_2\text{SO}_4/\text{Cu}$ electrocell at different stoichiometry of Cu_xS are presented in the Table 1.

The data of later study [9] showed that such values of potentials not always correspond the copper sulfide phases indicated in the Table 1. This inadequacy in the work [9] was explained by two reasons. First reason is connected with the different experimental conditions of copper sulfide phase preparation. In the study [7] different phases were received by anodic oxidation of Cu_xS and the measurements were performed when a value of x was decreasing. Another reason is that having oxidized composition of Cu_xS layers, x value is decreased rather in the surface than in the volume of the sample; therefore a value of a surface electrode potential does not correspond to the average value of x . Both, results of the studies [9]

and [3] showed that the composition of Cu_xS layer changed rather significantly during 30 and even more days after the interaction of sulfured PA with a solution of copper salt.

Table 1. The values of copper sulfide electrode potentials at the different stoichiometry of Cu_xS

Composition of Cu_xS	E , mV	Composition of Cu_xS	E , mV
$\text{Cu}_{2-1.95}\text{S}$	0 – 143	$\text{Cu}_{1.80}\text{S} + \text{Cu}_{1.68}\text{S}$	190
$\text{Cu}_2\text{S} + \text{Cu}_{1.95}\text{S}$	143	$\text{Cu}_{1.68-1.65}\text{S}$	190 – 202
$\text{Cu}_{1.95-1.91}\text{S}$	143 – 173	$\text{Cu}_{1.65}\text{S} + \text{Cu}_{1.40}\text{S}$	202
$\text{Cu}_{1.91}\text{S} + \text{Cu}_{1.86}\text{S}$	173	$\text{Cu}_{1.40-1.36}\text{S}$	202 – 268
$\text{Cu}_{1.86-1.80}\text{S}$	173 – 190	$\text{Cu}_{1.36}\text{S} + \text{CuS}$	268

In the present study, all the measured potential values were less than 290 mV and greater than 0 mV. Consequently, depositing sulfide layers by the method of sorption-diffusion, non-stoichiometric copper sulfide (Cu_xS) layers are obtained at x variability in the interval $1 < x < 2$.

When compared measured values of electrode potential and results of phase analysis (Cu_xS layers X-ray diffraction study) we have determined that the composition of copper sulfide deposited on a PA initially sulfured in the solution of $\text{H}_2\text{S}_n\text{O}_6$ depending on the sulfur concentration in PA and duration of sulfured PA treatment with a solution of copper(I-II) salt, contained three phases, x value of which changed in the regions: $1.12 \div 1.18$, $1.7 \div 1.8$ and $1.91 \div 1.95$. Therefore during following discussions of present study results the values of electrode potential (E , mV) according to the Cu_xS phases are considered as follow: $0 - 180 \text{ mV} - \text{Cu}_{1.91 \div 1.95}\text{S}$, $180 - 200 \text{ mV} - \text{Cu}_{1.7 \div 1.8}\text{S}$, $>200 \text{ mV} - \text{Cu}_{1.12 \div 1.18}\text{S}$.

PA treated different period of time with a solution of polythionic acid was affected with a solution of copper salt and then a potential of surface of a sample received was measured after 1 h, 1 day, 10, 30 and 60 days after the interaction with copper salt. Results received showed that the values of copper sulfide layer potential increase with increase of diffused into polymer sulfur concentration, c_s . The values of the last are increased when PA is treated with a solution of $\text{H}_2\text{S}_n\text{O}_6$ with higher value of n , when the temperature of $\text{H}_2\text{S}_n\text{O}_6$ solution is higher and the duration of PA treatment in a $\text{H}_2\text{S}_n\text{O}_6$ solution is longer [3, 4].

In the study [10] it was shown that under these conditions polymer structure [30] undergoes the most intensive amorphization resulting in more favourable conditions for the diffusion of sulfur compounds. Potentiometer readings show a decrease in the molar relation $\text{Cu}:\text{S}$, i. e., with an increase of c_s in the polymer sulfide layer, the composition of Cu_xS changes in the direction of x decrease.

The results of our research show that copper ions only slightly diffuse into boiled PA. After 30 minutes in a Cu(I-II) salt solution the mass of not sulfured PA increases by 1 – 3 %. X-ray structural tests of PA show [10] that acid medium as well as PA interaction with $\text{S}_n\text{O}_6^{2-}$ ions drastically change the crystal structure of PA. Favorable conditions for fast and easy diffusion of copper ions into PA are formed. This is proved by $\text{Cu}:\text{S}$ mol ratios (Table 2) calculated after having kept a PA sample in

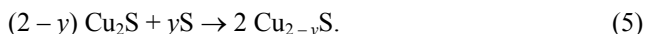
$H_2S_nO_6$ and Cu(I-II) salt solutions. The longer the PA is kept in $H_2S_nO_6$ solution the more PA structure changes and the greater number of $S_nO_6^{2-}$ ions is diffused and the more copper ions diffusion through the sulfide layer is obstructed.

Table 2. The molar ratio of Cu/S in the layer of copper sulfide. The duration of treating with a solution of Cu(I-II) salt – 15 min.

τ^* , min.	1	4	6	10	15	20	30	60
M_{Cu}/M_S	11.8	2.6	2.1	2.1	1.6	1.7	1.5	1.2

τ^* – the duration of treating with a solution of $H_2S_{21}O_6$.

The changes in the potentials with time show that the Cu_xS layer composition changes in the direction of x decrease. This change is particularly noticeable during the first 30 days, when the surface potentials grow on the average 10 – 20 mV. Measuring after 1, 2 and 3 months show that the potential had not changed (Fig. 1). In this case the changes in Cu_xS layer composition are caused by other factors than the changed structure of PA. Small potentials of Cu_xS layer surface 1 h after its formation show that the composition of the layers is in the proximity of $x = 1.91 \div 1.95$. These high values of x can be attributed to the agility of copper ions, slow stirring of Cu(I-II) salt solution as well as the swelling of PA in highly sulfured $H_2S_nO_6$ solutions and its more activated surface. However, in the course of time, due to the copper ions diffusion through the sulfide layer and interaction with the sulfur containing particles in the deeper layers of PA, the phase composition of the outer layer changes and the potential increases. A solid-phase reaction proceeds:



The stoichiometric composition of Cu_xS layers changes more significantly during the first 30 days (Fig. 1).

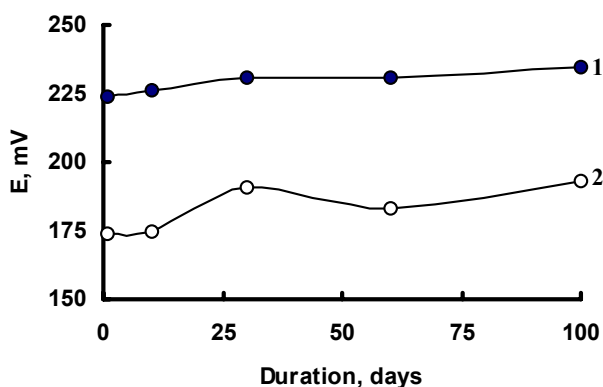


Fig. 1. The dependence of the electrode potential of Cu_xS layer formed on the surface of PA on time. PA was treated with a $H_2S_nO_6$ ($c=2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) solution at 50°C during 30 min. The number of sulfur atoms in $H_2S_nO_6$ molecule, n : 1 – 33; 2 – 23

The Cu_xS layer on PA potential depends on the length of keeping the PA in $H_2S_nO_6$ solution (Fig. 2). Up to 60 minutes in $H_2S_nO_6$ ($n = 33$) solution results in prevalence of copper sulfide of an average phase composition $Cu_{1.91-1.95}S$. An interval of 60 – 120 min

shows a marked increase in the potential and the layer phase composition approaches $Cu_{1.12-1.18}S$ and then remains almost stable. However, Cu:S molar ratio differs by only 0.03 after 60 – 120 min. Thus, the PA destruction is big enough and the sulfide layer is uniform and does not obstruct the movement of the diffusion flow. This results in a Cu_xS layer possessing fewer copper containing phases. Measurements of the potential after 30 days show that they had changed more for PA soaked in a $H_2S_nO_6$ solution for a shorter time (Fig. 2, curves 2, 4).

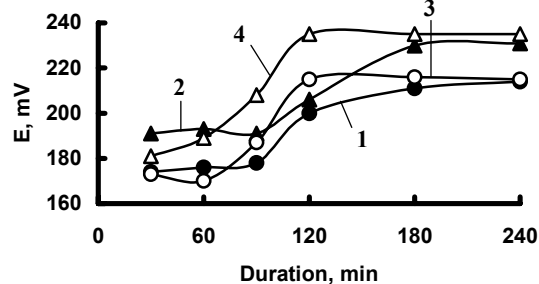


Fig. 2. The dependence of the electrode potential of Cu_xS layer formed on the surface of PA on duration of treating with a solution of $H_2S_nO_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) at 50°C . The number of sulfur atoms in $H_2S_nO_6$ molecule, n : 1, 2 – 21; 3, 4 – 33. The electrode potentials were measured after: 1, 3 – 1 h; 2, 4 – 30 days

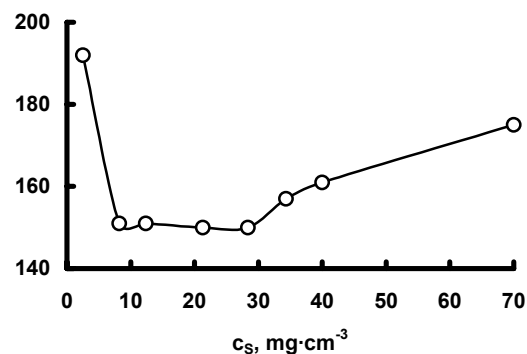


Fig. 3. The dependence of the electrode potential of Cu_xS layer formed on a surface of PA on sulfur concentration in the polymer. The PA samples were treated with a solution of $H_2S_{21}O_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) at 50°C . The duration of treating with a solution of Cu(I-II) salt – 15 min

The potentials of longer soaked PA changed insignificantly. This proves that diffusion processes are faster in PA with a more destructed crystalline structure due to a slighter blocking effect of the sulfide layer.

Potential values of a Cu_xS layer on PA kept in $H_2S_nO_6$ for a shorter time change in a different manner (Fig. 3). During the first 8 min there is a sudden drop in the potential followed by a stabilization phase for about 20 min. Then the value of the polymer Cu_xS layer starts to grow slowly. This shows that a Cu_xS layer is immediately formed on the polymer surface, its uniformity being higher if the PA structure is less destroyed. Further changes in the

potential are related to the changes in the phase composition due to slow copper ions diffusion through the sulfide layer as well as its reaction with the sulfur compounds in the deeper layers of the polymer.

While changing the interaction time of PA with a Cu(I-II) salt solution, the layer potential of Cu_xS layers changes as well (Fig. 4). It can be noted that a sulfide layer with the predominant phase $Cu_{1.12-1.18}S$ forms on the polymer surface during the first 5 minutes interaction with a Cu(I-II) salt solution. It has not yet "blocked" the movement of diffusion stream therefore it takes 5 min of interaction for the uniformity of the layer to start growing and x reaches $1.7 \div 1.8$. After 12 – 15 min of interaction with Cu(I-II) salt solution a sufficiently compact layer is formed, significantly slowing copper ions diffusion into the depth of the polymer and the phase $x = 1.91 \div 1.95$ becomes predominant.

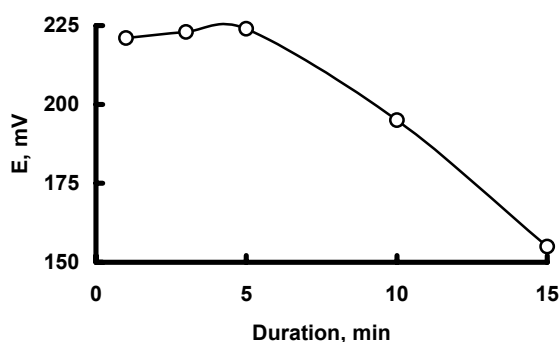


Fig. 4. The dependence of the electrode potential of Cu_xS layer formed on the surface of PA on duration of treating with a solution of Cu(I-II) salt at 78 °C. PA samples were treated with a solution of $H_2S_{21}O_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol dm}^{-3}$) at 50 °C. The concentration of sulfur – $70.0 \text{ mg} \cdot \text{cm}^{-3}$

An increase in the temperature of $H_2S_nO_6$ solution influences the composition of Cu_xS layers slightly more at the temperature range above 40 °C (Fig. 5), however it does not significantly depend on the number of sulfur atoms n in $H_2S_nO_6$ molecule.

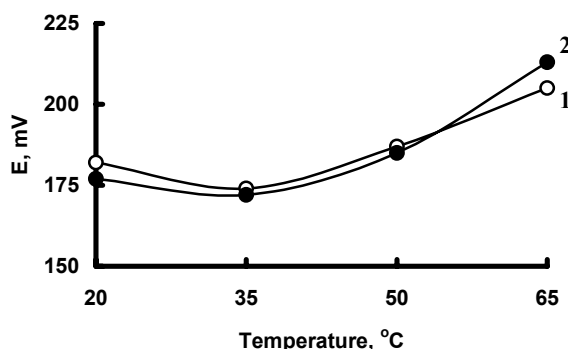


Fig. 5. The dependence of the electrode potential of Cu_xS layer formed on a surface of PA on the temperature of a $H_2S_nO_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$) solution. The number of sulfur atoms in $H_2S_nO_6$ molecule: 1 – 21; 2 – 27

Potentiometric tests of Cu_xS layer give reference knowledge about the phase composition of the layer formed on the polymer surface. The potential value highly

depends on the number of copper ions absorbed on PA and the degree of the polymer swelling resulting in a nonuniform sulfide layer. Therefore X-ray phase tests were applied to specify the data on the phase composition of the sulfide layer.

The phase composition of the deposited film was established by comparing its X-ray images with those of known minerals [11 – 13]. The chemical composition and crystal structure of the majority of Cu_xS minerals such as *chalkozine* – Cu_2S , *djurleite* – $Cu_{1.95}S$, *anilite* – $Cu_{1.75}S$, *yarrowite* – $Cu_{1.12}S$ and *covelite* – CuS were investigated [14]. The crystal structure of Cu_xS depends on the chemical composition and conditions of synthesis. The composition of Cu_xS deposited by chemical methods is little investigated.

Structural studies of the Cu_xS layers deposited by sorption-diffusion method are limited by polycrystallinity of layers obtained, as well as by the existence of Cu_xS phases with various compositions and structures, and by the crystallinity of the PA film itself. The intensities of its peaks at $\theta < 13^\circ$ exceeds intensity of copper sulfide peaks few times. Therefore the area of $2\theta \geq 26.0^\circ$ was investigated in more detail.

Presence in PA of non-reacted crystalline cyclo-octasulfur [3, 4] makes difficulties for the X-ray study too. Reason of the crystallization of diffused into PA sulfur is reduced solubility in PA, when the samples of PA are removed from the polythionic acid solution and washed with distilled water are cooled to the room temperature.

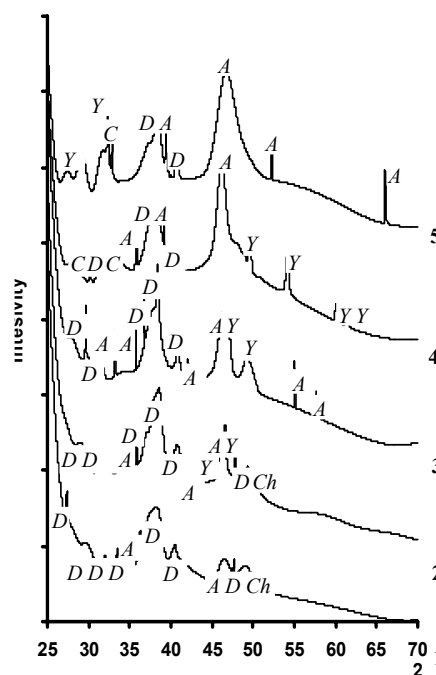


Fig. 6. X-ray diffraction patterns of the layers on PA (peaks of *djurleite* – D, *anilite* – A, *chalkocite* – Ch, *yarrowite* – Y, *covelite* – C). PA initially treated with a solution of $H_2S_{21}O_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, 50 °C) different time (τ_s , min) and then with a Cu(I-II) salt solution 15 min. The concentration of sulfur in polymer c_s , $\text{mg} \cdot \text{cm}^{-3}$: 1 – 2.5 ($\tau_s = 4$); 2 – 21.3 ($\tau_s = 10$); 3 – 28.4 ($\tau_s = 15$); 4 – 40.0 ($\tau_s = 30$); 5 – 70.0 ($\tau_s = 60$)

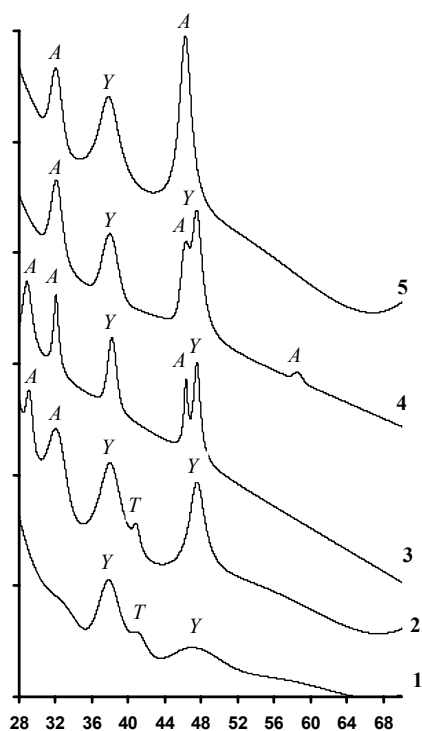


Fig. 7. X-ray diffraction patterns of the layers of Cu_xS on PA (peaks of *talnakhite* – T, *yarrowite* – Y, *anilite* – A). The sulfur concentration in PA is 70.0 mg cm^{-3} . The period of treatment (min) with a Cu(I-II) salt solution at 78°C is 1.0 (1), 3.0 (2), 5.0 (3), 10.0 (4), 20.0 (5)

Keeping PA samples with sorptive polythionates and sulfur for a different period in a copper salt solution at 351 K, Cu_xS layers of different composition were obtained. The X-ray diffraction patterns of the layers showed that peaks of various copper sulfide phases exist in the layer rather than only one (Fig. 6, 7).

The analysis of the X-ray images showed that the orthorhombic *djurleite* ($x = 1.95$) prevails in the composition of sulfide film for PA, sulfured shortly (during first 4 min.) (Fig. 6) in a solution of $\text{H}_2\text{S}_{21}\text{O}_6$ ($c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, at 323 K; the temperature of the Cu(I-II) salt solution – 351 K and the period of the treatment with a Cu(I-II) salt solution – 15 min) but the phases of orthorhombic *anilite* ($x = 1.75$) and *chalcocite* ($x = 2$) are detected too (Fig. 6, curve 1). When the period of treatment in the polythionic acid solution is prolonged until 10 min the changes of film composition occurs: the intensity of the peaks of orthorhombic *djurleite* slightly decreases and the intensity of the *anilite* peaks increases and already after the 15 min PA treatment in the solution of $\text{H}_2\text{S}_{21}\text{O}_6$ *anilite* phase predominates in the composition of sulfide film (Fig. 6, curve 3). After longer period of sulfuration *yarrowite* ($x = 1.12 - 1.18$) peaks appear (Fig. 6, curves 3 – 5) and when the period of treatment in a solution of $\text{H}_2\text{S}_{21}\text{O}_6$ prolonged further the phases of *anilite* and *yarrowite* become dominating.

X-ray images of PA sulfured under the same conditions ($\text{H}_2\text{S}_{21}\text{O}_6$, $c = 2.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, at 323 K, the sulfur concentration in PA $C_s = 70 \text{ mg} \cdot \text{cm}^{-3}$) but treated for different period of time in a solution of a Cu(I-II) salt at 351 K (Fig. 7) showed that after short treatment (up to

3 min) the peaks of *yarrowite* ($x = 1.12$), *talnakhite* ($x = 1.06$) and *anilite* ($x = 1.75$) are present (Fig. 7, curves 1 and 2). When the period of treatment in a Cu(I-II) salt solution is prolonged (5 min) the intensity of peaks of *yarrowite* and *anilite* phases increases and both these phases become the dominating ones (Fig. 7 curve 3) in the sulfide film. That can be explained by energetically preferable formation of *yarrowite* and that the sulfide film formed is still not sufficiently compact. On further prolongation of the period of treatment in a Cu(I-II) salt solution (10 min) the compact sulfide film forms and slows down the diffusion flux. As a result sufficient amount of copper ions not reacted with the polythionate ions and sulfur accumulates on the surface of the polymer and formation of sulfide phase containing more copper – *anilite* ($x = 1.75$) is observed according peaks in the X-ray images (Fig. 7, curve 5). Consequently, in the course of sulfured PA treatment, the phase composition of Cu_xS film changes in the direction of increasing values of x .

CONCLUSIONS

1. The copper sulfide, Cu_xS , layers on a surface of PA formed by the use of highly sulfured polythionic acids, $\text{H}_2\text{S}_n\text{O}_6$ ($n = 21 - 33$), were studied by potentiometric and X-ray diffraction methods.
2. It is shown that the Cu_xS layers on PA formed by the method of sorption-diffusion are non-stoichiometric and a value of x varies in the interval $1 < x < 2$.
3. By X-ray diffraction studies it is determined that the Cu_xS layers obtained are of various phases, comprising in itself mainly phases of *yarrowite* – $\text{Cu}_{1.12-1.18}\text{S}$, *anilite* – $\text{Cu}_{1.7-1.8}\text{S}$ and *djurleite* – $\text{Cu}_{1.91-1.95}\text{S}$. *Djurleite* prevails in the composition of Cu_xS film if PA is sulfured shortly (4 min) in a solution of $\text{H}_2\text{S}_{21}\text{O}_6$, but when a period of sulfuration is prolonged (10 min) the peaks of *djurleite* slightly decreases and the peaks of *anilite* increases. After longer period of sulfuration *yarrowite* peaks appear and on further prolongation – the phases of *anilite* and *yarrowite* become dominating.
4. The phase composition of Cu_xS films also depends on the sulfured under the same conditions PA further treatment in a solution of copper(I-II) salt time. After short treatment (3 min) peaks of *yarrowite*, *talnakhite* – $\text{Cu}_{1.06}\text{S}$, and *anilite* are present. If treatment is prolonged the formation of sulfide phase containing more copper – *anilite* is observed. Thus, in the course of sulfured PA treatment with a Cu(I-II) salt solution, the phase composition of Cu_xS film changes in the direction of increasing values of x .

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