Synthesis of Bismuth (III) Stearates

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(Received July 11, 2002; in revised form October 1, 2002)

Abstract

The synthesis of bismuth (III) oxohydroxostearate through the interaction of stearic acid with bismuth-containing perchlorate or nitrate solutions is investigated by means of X-ray phase analysis, thermogravimetry, electron microscopy, IR spectroscopy and chemical analysis. The conditions for the formation of bismuth stearate of $Bi_6O_4(OH)_4R_6$ composition (where R is stearate anion) are determined. Reasonability of obtaining highly pure bismuth stearate from metal bismuth is demonstrated; the latter is preliminarily oxidized with oxygen of the air, the resulting Bi_2O_3 is dissolved in nitric acid (1 : 1); bismuth is purified from extrinsic metals by its precipitation in the form of oxohydroxostearate, which is formed on adding bismuth nitrate solution to sodium stearate solution at the temperature of (80 ± 10) °C, with molar ratio of the latter to bismuth 1.0–1.1, and the concentration of free nitric acid in solution 0.1 mol/l. The possibility to synthesize a solid solution of bismuth oxohydroxostearate and stearic acid of the $Bi_6O_4(OH)_4R_6 \cdot n$HR composition is demonstrated. A method for the synthesis of the neutral stearate of Bi_3R composition by means of alloying bismuth with stearic acid at the stoichiometric ratio at the temperature of (90 ± 10) °C is proposed.

INTRODUCTION

At present, bismuth carboxylates are used in the synthesis of bismuth-containing oxide materials: superconductors, piezoelectrics, catalysts, *etc*., as well as in the synthesis of bismuth-containing medicines [1–3]. Because of this, the development of simple and reliable methods for the synthesis of these compounds of high purity is urgent.

The compounds of bismuth (III) are usually synthesized using the Vi1 grade metal (containing not less than 97.7 % Bi) by dissolving it in the nitric acid of 9 mol/l concentration, followed by hydrolytic purification of bismuth from impurity metals at pH 1.5–2.0 [4]. Disadvantages of this method are the evolution of toxic nitrogen oxides at the stage of preparing bismuth nitrate solution, and low extent of its purification from the most abundant impurity metals, such as lead, iron, and silver. It was demonstrated [5] that preliminary oxidation of the metal as a result of adding bismuth oxide at (20 ± 5) °C into the melt at the temperature of (350 ± 50) °C under mixing, followed by temperature rise to (600 ± 50) °C, allows one to decrease the consumption of nitric acid by a factor of two at the stage of preparing bismuth nitrate solutions, and to eliminate the evolution of nitrogen oxides into the gas phase. The dissolution of metal bismuth in chloric acid is accompanied with explosion [6], but preliminary oxidation of the metal allows obtaining perchlorate solutions with bismuth concentration 1000–1400 g/l [5], which can be used, similarly to the nitrate solutions, for the synthesis of high-purity bismuth compounds.

The synthesis of bismuth carboxylates is usually performed from its compounds of the reagent purity grade, for example by the interaction of bismuth oxide with the corresponding monocarboxylic acid, substitution of ace-

tate ions in bismuth acetate with other carboxylate groups, precipitation from bismuth nitrate solutions in the presence of glycerol under addition of a solution of carboxylate of an alkaline metal [1]. It follows from literature data that one of the most promising classes of compounds, from the viewpoint of obtaining nanosized particles during thermal decomposition, is metal carboxylates of the fatty organic acids. The possibility to synthesize bismuth stearate by adding an aqueous-glycerol solution of sodium stearate to the aqueous-glycerol solution of bismuth nitrate under mixing and heating with water bath. The authors point that the product is a neutral salt of the $Bi(C_{17}H_{35}COO)_3$ composition with an admixture of hydroxostearate of the $Bi(OH)_2(C_{17}H_{35}COO)$ composition [7]. It has also been proposed to use stearic acid as an extracting agent for bismuth determination in the objects of complicated composition [8]. In doing this, microamounts of bismuth are extracted with a melt of stearic acid in paraffin in the form of BiR_3; the logarithm of bismuth extraction constant is −0.87. Thus, at the stage of bismuth precipitation in the form of stearate, its purification from the main impurity metals is possible, which allows one to obtain bismuth stearate directly from technological nitrate solutions of the production of bismuth-containing compounds.

It was stated in the X-ray diffraction studies into hydrolysis of bismuth-containing perchlorate [9] and nitrate [10] solutions that at high bismuth concentration it exists in those solutions in the form of hexanuclear complexes of the $Bi_6O_4(OH)_4^{6+}$ composition. The hydrolysis of the indicated solutions is accompanied by the formation of solid products of the $[Bi_6O_4(OH)_4](NO_3)_6 \cdot nH_2O$ composition, where n is either 4 or 1 [10–12], as well as $Bi_6O_4(OH)_4(ClO_4)_6 \cdot 7H_2O$ [13]. The possibility of bismuth extraction with di-2-ehtylhexylphosphoric acid from chloric solutions is demonstrated, depending on pH and bismuth concentration in the organic phase, either in the form of acidic solvated $BiR_3 \cdot 2HR$ complex, neutral salt of dialkylphosphate BiR_3, and oxohydroxodialkylphosphate $Bi_6O_4(OH)_4(C_{16}H_{34}O_2POO)_6$ [14]. The possibility of the formation of oxohydroxocompounds of bismuth with polynuclear cation and organic ligand can be used for efficient separation of bismuth from impurity metals, sharp decrease in the consumption of organic acid for the synthesis of bismuth-containing oxide materials, broadening of the range of chemical precursors for obtaining the particles of metal or bismuth oxide with different morphology.

The goal of the present work is to make an attempt to synthesize bismuth (III) stearate in the form of oxohydroxocompound with the participation of polynuclear cation taking into account the above-mentioned data. Below we present the results of investigation of the composition of products formed in the interaction of stearic acid with bismuth-containing perchlorate and nitrate solutions, and purification of bismuth from impurity metals by means of its precipitation in the form of oxohydroxostearate.

EXPERIMENTAL

The initial bismuth-containing solutions were prepared by dissolving the oxide of "os.ch." (especially pure) 13–3 grade for single crystals, TU (technical specifications) 6-09-02-298–90, in perchloric acid (concentration: 8.7 mol/l) or in nitric acid (6.0 mol/l). The synthesis of bismuth (III) oxohydroxostearate started from the initial solution of bismuth perchlorate (1000 g/l Bi) which was preliminarily diluted with distilled water till the concentration of 315 g/l and added to sodium stearate solution at the temperature of 80 °C and pH 1.0. The volume of bismuth perchlorate solution was 0.3 l; after having added sodium stearate solution, total volume of the solution was corrected by adding distilled water till 0.7 l. The sodium stearate solution was obtained by dissolving the salt in distilled water or by neutralizing stearic acid with sodium hydroxide solution. The synthesis was performed in Teflon vessels equipped with mixers. The mixture was stirred for 1 h. After precipitation for 1 h, the precipitate was filtered under vacuum, washed on the filter with distilled water, and dried in the air.

The interaction of bismuth oxide with the stearic acid melt taken in the stoichiometric ratio was conducted by heating the mixture at

the temperature of (90 ± 10) °C for 6 h. The X-ray phase analysis (XPA) of the synthesis products was performed with DRON-3 instrument using CuK_α radiation at the counter rotation rate of 0.5 deg/min and I = 1000. The curves of differential thermal analysis (DTA) and mass changes (TG) of the samples under investigation were recorded with the derivatograph of MOM Co. (Hungary) at the heating rate of 10 °C/min. The IR absorption spectra (IRS) were recorded with Specord 75 IR spectrophotometer in the region 400–4000 cm^{-1}. The samples were prepared as tablets with the calcined KBr. Electron microscopic images were taken using the JEM-2000FXII transmitting electron microscope at the accelerating voltage of 200 kV. Metal concentrations (Bi, Pb, Ag, Fe, Cu, Zn) in the liquid and solid phases was performed by means of atomic absorption using Saturn 2M spectrophotometer. The synthesis products were preliminarily treated with the nitric acid solution (1 : 1).

RESULTS AND DISCUSSION

Bismuth does not form complexes with perchlorate ions in the solutions of chloric acid. Depending on concentration, bismuth is present in these solutions either as Bi^{3+} aqua ions or as a polynuclear complex $Bi_6O_4(OH)_4^{6+}$; the hydrolysis resulting in the formation of oxohydroxoperchlorate proceeds at pH > 2. Taking these facts into account, we investigated precipitation of bismuth stearates from these solutions at the molar ratio of stearic acid to bismuth equal to 3 and 1. For the case of pH of solution equal to 1.0, the residual bismuth concentration in solution is 0.28 g/l (bismuth precipitation extent: 99.8 %); for pH 2.0 established by adding sodium hydroxide, the residual concentration does not exceed 0.001 g/l.

The data of XPA, IRS, thermal and chemical analysis are the evidence that the product of bismuth precipitation from perchloric solutions upon adding sodium stearate solution to them (or in the case of reverse order of pouring solutions together) at the temperature of (80 ± 10) °C, sodium stearate to bismuth ratio equal to 1, and pH 1 is bismuth oxohydroxostearate $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$; in the case of molar ratio equal to 3, it is a solid solution of bismuth oxohydroxostearate with stearic acid of the $i_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot n$HR composition. According to the data of chemical analysis, the concentration of perchlorate ions in the precipitation products does not exceed 0.01 %, while molar ratio of stearate ions and bismuth is 1.01 in the first case and 2.96 in the second case.

The X-ray investigation of structural characteristics of bismuth stearates demonstrated (Fig. 1) that characteristic diffraction maxima related to free stearic acid (curve *1*) and sodium stearate (curve *2*) are absent from these products. The two compounds have both common structural characteristics and substantial differences. For instance, reflections which can be identified as Bragg reflections from basal planes with (001) indices are present in the X-ray diffraction patterns of these compounds in the region of small angles. Such a pattern of X-ray diffraction is typical for all metal carboxylates investigated earlier; it determines layered ordering of metal ions (in the case under consideration, bismuth cations) and carboxylate anions. The interlayer spacing d_{001} for $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ and the solid solution of bismuth oxohydroxostearate with stearic acid, calculated from the experimental X-ray diffraction patterns, are close to each other and give approximately 51 Å. However, in spite of the observed similarity of the layered positions of ions in crystal structures of bismuth-containing species $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ and $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot n$HR, a substantial difference has been revealed in their structures. First, layered reflections of the $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ compound (see Fig. 1, curve *3*) are broadened substantially in comparison with those for $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot n$HR (see Fig. 1, curve *4*). Second, a broad amorphous halo is observed in the X-ray diffraction patterns of $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ in the region of large angles, while for $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot n$HR the X-ray reflections clearly recorded in this angle region determine reflections from the planes with (*hkl*) indices *h*, *k*, 0. In our opinion, this difference in the X-ray diffraction patterns of the compounds under consideration is an unambiguous evidence that long aliphatic chains are disordered in the

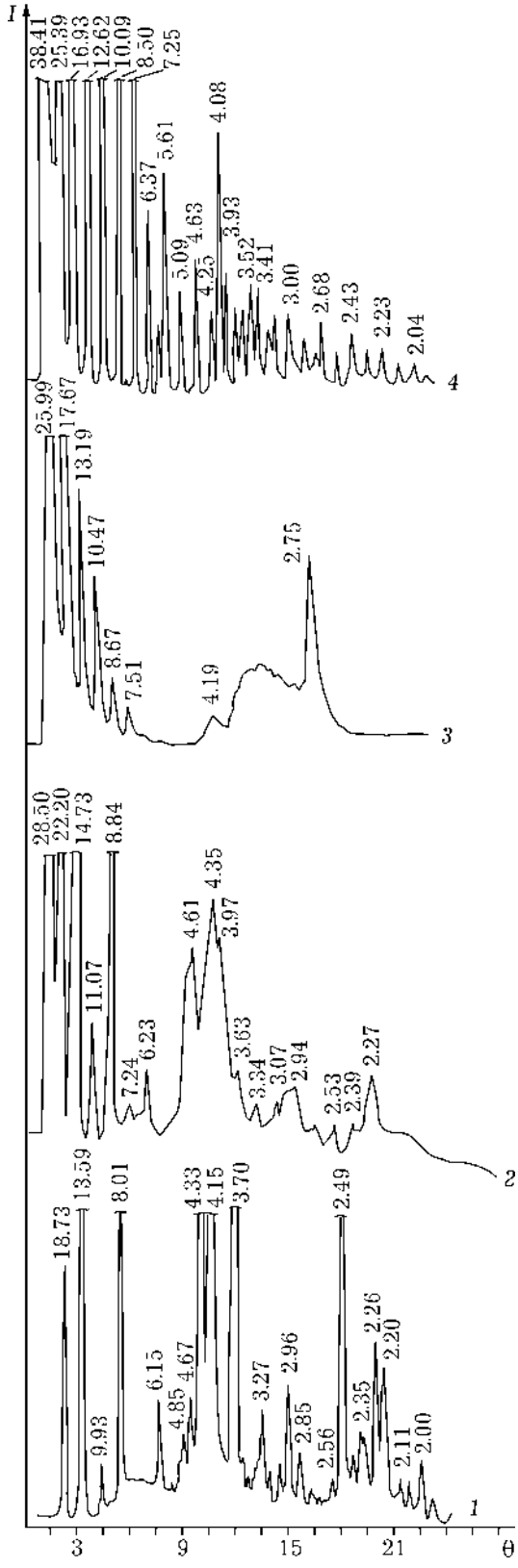

Fig. 1. X-ray diffraction patterns of stearic acid (*1*), sodium stearate (*2*), bismuth oxohydroxostearate (*3*) and its solid solution with stearic acid (*4*).

structure of $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$, unlike $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6 \cdot nHR$. Simultaneous presence of layered reflections and amorphous halo in the diffraction patterns characterizes the liquid crystal state of the substance, which is often observed in smectic crystals when passing from crystalline state to mesomorphous one [15]. Thus, the $Bi_6O_4(OH)_4(C_{17}H_{35}COO)_6$ compound exists initially in liquid crystal state.

According to the data of thermal analysis, the TG curve of bismuth oxohydroxostearate (Fig. 2, *a*) can be due to the destruction of stearate ions with two sharp exothermic effects on the DTA curve at 300 and 410 °C, which result in the formation of bismuth oxide. The endothermic effect on DTA curve at 150 °C is due to melting. The TG curve of the solid solution of bismuth oxohydroxostearate with stearic acid (see Fig. 2, *b*) exhibits two endothermic effects at 70 and 100 °C; the first one is likely to be due to melting of stearic acid, while the second one relates to the melting of bismuth oxohydroxostearate in the presence of stearic acid melt. Further temperature rise leads to the decomposition of bismuth oxohydroxostearate (sharp exothermic effects at 320, 380, 440 and 500 °C) with the formation of oxide.

Exposure of the samples for 5 h at 350 °C leads to the formation of bismuth oxide. However, in this case, due to incomplete oxidation, the oxide can contain fine metal bismuth as admixture. The DTA curve (see Fig. 2, *c*) exhibits endothermic effect at 271 °C, corresponding to metal bismuth melting; its oxidation takes place at the temperature above 500 °C. Endothermic effect at 729 °C is due to the polymorphous transformation of monoclinic a modification of Bi_2O_3 into high-temperature cubic face-centered δ modification; endothermic effect at 820 °C is due to melting of bismuth (III) oxide [16].

It follows from the comparison of the IR absorption spectrum of bismuth oxohydroxostearate with the spectrum of pure stearic acid (Fig. 3, curves *1* and *2*) that changes in the bands of the spectra are connected with the substitution of the hydrogen of hydroxyl group with the $Bi_6O_4(OH)_4^{6+}$ cation. Really, the spectrum of salt exhibits no bands related to the vibrati-

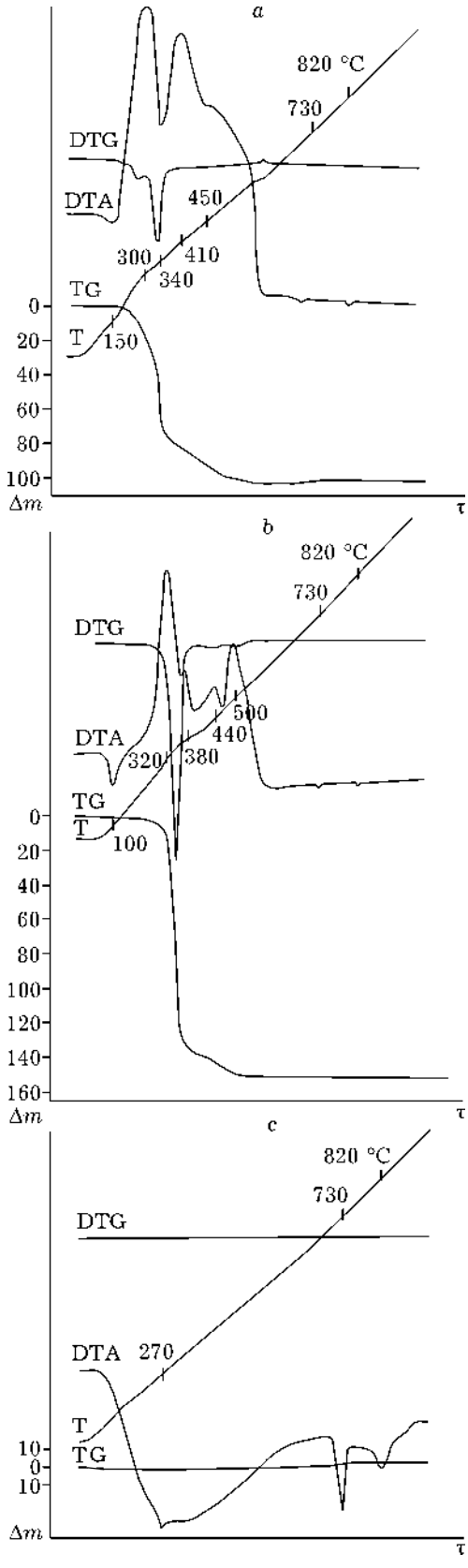

Fig. 2. Thermal analysis curves of the samples of bismuth oxohydroxostearate (*a*), its solid solution with stearic acid (*b*), and after calcinations for 4 h at 350 °C (*c*).

ons of carboxylic group: νOH – 3400–2500 cm^{-1}, δOH – 940 cm^{-1} and νC=O – 1710 cm^{-1}; instead, there are bands related to the vibrations of carboxylate ion: $\nu_{as}COO^-$ – 1525 $см^{-1}$ and 1540 cm^{-1}, $\nu_s COO^-$ + δCH_2 – 1415 cm^{-1} [17, 18]. The ratio of intensities of the maxima of stretching δCH_3 vibrations (in the region 1500–1450 cm^{-1}) is also changed. In addition, the intensity of the band with the maximum at 1300 cm^{-1} (combined vibrations δOH + νC–O of the acid dimer) decreases sharply. The presence of a series of bands in the region 1350–1150 cm^{-1}, assigned to the fan vibrations of CH_3 and characterizing the length of the hydrocarbon chain [17], is the evidence of transposition of these groups with respect to each other. Similarly to the case of sodium stearate, the band of torsion vibrations of methyl group (540 cm^{-1}) is shifted with respect to its position in the spectrum of the acid (550 cm^{-1}) [17]. Weak bands with the maxima at 560 and 620 cm^{-1}, as well as those in the region 1200–1050 cm^{-1}, are likely to belong to the vibrations of $Bi_6O_4(OH)_4^{6+}$ cation. The presence of OH groups in this compound is evidenced by the appearance of absorption band at 3560 cm^{-1}, which can be assigned to the stretching vibrations ν $(OH)^-$ [17, 19].

The IR absorption spectra of the solid solution of bismuth oxohydroxostearate and stearic acid differ substantially from that of bismuth oxohydroxostearate (see Fig. 3, curves *2* and *3*). For instance, along with the band $\nu_{as}COO^-$ 1565 cm^{-1}, the spectrum of the product contains the bands related to the vibrations of carboxylic group ν(OH) (3400–2500 cm^{-1}) and νC=O (1700 cm^{-1}). The shift of the maximum of the later in the spectrum of the product, in comparison with its position in the spectrum of pure stearic acid (1710 cm^{-1}), confirms the formation of a compound of bismuth oxohydroxostearate with the acid. This is also the reason of the shift of $\nu_{as}COO^-$ and ν(OH) bands of the complex $Bi_6O_4(OH)_4^{6+}$ ion (1525 → 1565 and 3565 → 3600 cm^{-1}, respectively). The difference of the spectrum of solid solution of bismuth oxohydroxostearate and stearic acid from the spectrum of bismuth oxohydroxostearate in the region below 1500 cm^{-1} is also due to the presence of stearic acid in the product. Washing with ethanol leads to the

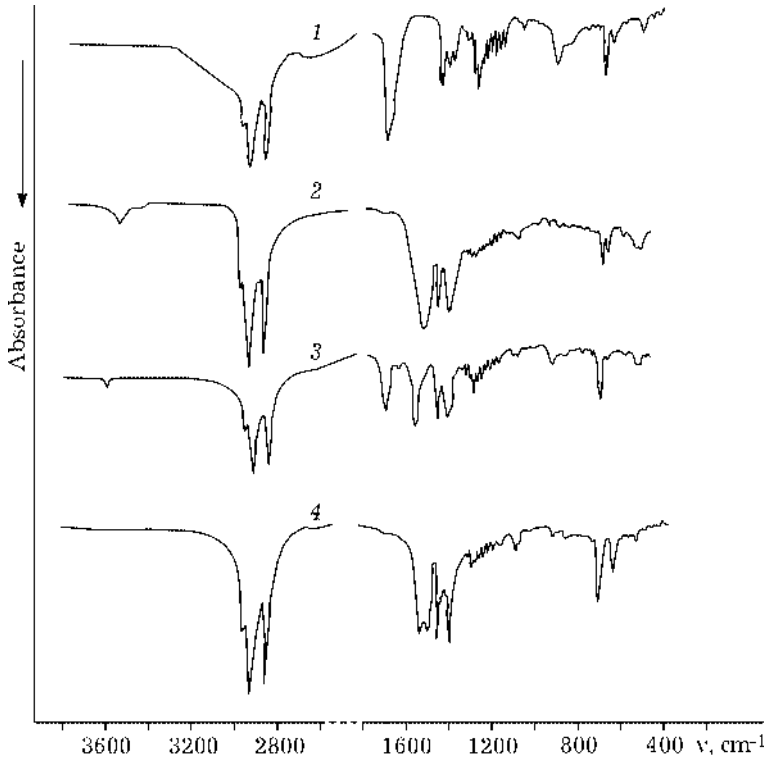

Fig. 3. IR spectra of stearic acid (*1*), bismuth oxohydroxostearate (*2*), its solid solution with stearic acid (*3*) and neutral bismuth stearate (*4*).

removal of stearic acid, after which the product is bismuth oxohydroxostearate.

For comparison, we performed the synthesis of the neutral salt of $Bi(C_{17}H_{35}COO)_3$ composition according to the procedure based on adding the aqueous-glycerol solution of sodium stearate to the aqueous-glycerol solution of bismuth nitrate [6]. However, the data of XPA and IRS are the evidence that the obtained product is mainly a solid solution of bismuth oxohydroxostearate with stearic acid. The indicated salt of the $Bi(C_{17}H_{35}COO)_3$ composition was synthesized by the interaction of fine crystalline bismuth oxide with the melt of stearic acid at the molar ratio of 3, at the temperature of 100 °C under mixing. Bismuth oxide, in the form of oriented splices of elongated prismatic (almost needle-like) crystals with the size of a single crystal ~ 5 μm, was obtained in this case by adding bismuth nitrate solution into the sodium hydroxide solution, with the free concentration of the latter in solution 1.0 mol/l at the temperature of 20 °C [20].

According to the X-ray data, the $Bi(C_{17}H_{35}COO)_3$ compound has characteristic diffraction maxima with d/n equal to 2.68, 3.56, 3.80, 3.85, 5.13, 5.75, 6.56, 7.63, 9.03, 11.33 and 14.43 Å. Similarly to the case of previously considered compounds of bismuth oxohydroxostearate and its solid solution with stearic acid, the diffraction patterns of $Bi(C_{17}H_{35}COO)_3$ contain Bragg reflections in the region of small angles; they characterize layered ordering of bismuth ions and stearate anions. However, unlike bismuth oxohydroxostearates, the interlayer spacing for the neutral salt was 46 Å. The DTA curve of the neutral salt exhibits an endothermic effect at the temperature of 100 °C, which differs from the temperatures of phase transformations for bismuth oxohydroxostearate and its solid solution with stearic acid. Temperature rise leads to the decomposition of bismuth stearate (exothermic effects at 350, 380, 430 and 500 °C) resulting in the formation of oxide.

Bands corresponding to the vibrations of carboxyl group of the acid νC=O and ν,δOH (1710, 3400–2800, 940 cm^{-1}) and $Bi_6O_4(OH)_4^{6+}$ cation (560, 620, 3560 cm^{-1}) are almost completely absent from the IR absorption spectrum of the neutral salt (see Fig. 3, curve *4*). The spectrum contains only bands related to the vib-

rations of carboxylate ion: a doublet 1545, 1520 cm^{-1} ($\nu_{as}COO^-$) and 1410 cm^{-1} (ν_sCOO^- + δCH_2). In the region 1400–650 cm^{-1}, changes in the bands of stearic acid in the spectra of bismuth stearate and oxohydroxostearate are almost identical.

According to the data of electron microscopic investigation of the precipitation product, the crystals of bismuth oxohydroxostearate, solid solution of bismuth oxohydroxostearate with stearic acid, and the neutral salt are plate-like; as a rule, they do not exhibit strict facing. The thickness of the resulting crystals is 50–100 nm; linear size (length) of the plates is up to 1 μ.

The synthesis of bismuth-containing compounds is usually performed by means of hydrolytic processing of bismuth-containing nitrate solutions obtained by dissolving the metal of Vi1 grade in nitric acid [4]. The investigation into bismuth precipitation from nitrate solutions provides evidence that, similarly to the case of perchlorate solutions, the formation of bismuth oxohydroxostearate takes place. In order to obtain bismuth oxohydroxostearate of high purity, we investigated the possibility to synthesize it from technological solutions of the production of bismuth-containing compounds. In the investigation, we used the metal of the Vi1 grade containing, % mass: bismuth, 98.5; lead, 0.88; zinc, 6.4 10^{-4}; iron, 6.2 10^{-3}; antimony, 1.0 10^{-3}; copper, 9.5 10^{-3}; silver, 5.6 10^{-2}; arsenic, 1.3 10^{-4}; tellurium, 8.2 10^{-5}. The metal was preliminarily oxidized in a reactor made of stainless steel, equipped with a screw for mixing the melt; 20 % bismuth oxide was introduced into the reactor at 350 °C and mixed; temperature was subsequently increased up to 600 °C [14]. The obtained technical oxide was dissolved in nitric acid of the "ch." grade (pure) with the concentration of 6 mol/l; the bismuth-containing solution contained 420 g/l bismuth and 80 g/l of the free HNO_3. This composition of the solution corresponds to those usually used in the technology of bismuth compounds.

The bismuth (III) oxohydroxostearate was synthesized by adding the bismuth nitrate solution to sodium stearate solution obtained by neutralizing stearic acid with the sodium hydroxide solution at the molar ratio of stearic acid to bismuth equal to 1.05, temperature of 80 °C, and pH 1.0. The precipitate was once washed with the nitric solution with pH 1, twice washed with distilled water at the temperature of 60 °C, and dried at 100 °C. The resulting oxohydroxostearate contained, % mass: bismuth, 42.04; lead, 1 10^{-5}; zinc, 1 10^{-5}; iron, 8 10^{-6}; antimony, 4 10^{-6}; copper, 5 10^{-7}; silver, 5 10^{-7}; arsenic, < 1 10^{-5}; tellurium, < 1 10^{-5}.

CONCLUSION

Thus, the synthesis of high-purity bismuth (III) stearate can be performed by processing bismuth-containing nitrate solutions from the production of its compounds by means of the following operations: preliminary oxidation of the metal melt by the oxygen of the air to form oxide, which allows decreasing the consumption of nitric acid by a factor of two and decrease the evolution of toxic nitrogen oxides into the atmosphere at the stage of obtaining bismuth nitrate solutions; its hydrolytic purification by bismuth precipitation in the form of oxohydroxostearate on adding bismuth nitrate solution into sodium stearate solution under mixing with the molar ratio of stearate ions to bismuth equal to 1.0–1.1, temperature of 80 °C, and the concentration of free acid in the solution 0.1 mol/l.

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