

FORMATION OF ULTRAFINELY DIVIDED LEAD BY THE THERMOLYSIS  
OF ITS COMPLEX COMPOUNDS

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The method of preparation of finely divided metals from complex compounds developed by the authors [1] makes it possible to obtain lead in the form of an ultrafine powder with particles in a narrow size range (from 0.2 to 0.8  $\mu\text{m}$ ), whereas the possibilities of existing processes are limited to particle sizes of not less than 5  $\mu\text{m}$ , with a wider size range. Ultrafinely divided lead has potential for the manufacture of flexible composite materials employed for protection against radiation, and has also been found useful as an additive to lubricating materials [2].

A lead complex was obtained by mixing oleic acid alkylolamide with lead formate by the method described in [2]. In contrast to the alkylolamide spectrum (Fig. 1, curve 1), the IR spectrum of the resultant compound (curve 2) has, in the range of NH-group valence fluctuations, separate maxima with frequencies of 3320 and 3280  $\text{cm}^{-1}$  and a weak band at 3080  $\text{cm}^{-1}$ , which is also linked with NH-group fluctuations. Usually, this manifests itself when intermolecular bonds are present in amides, and NH groups split up or their orientation changes [3].

Thus, an undivided nitrogen electron pair probably reacts with a lead cation. Yet the C-N bond remains unbroken, as otherwise a C=O carbonyl absorption band would appear near 1700  $\text{cm}^{-1}$ . Also preserved is the double bond in the oleic acid residue with a transarrangement of the substitute, which absorbs at 3030  $\text{cm}^{-1}$  =CH- valence fluctuations and at 930  $\text{cm}^{-1}$  hydrogen deformation fluctuations in the -CH=CH- structure (i.e., at the same frequencies as in a molecule of the free acid). The Pb-O-C bond, too, remains unbroken. This bond is characterized by a band at 850  $\text{cm}^{-1}$ , which is thus, compared with the absorption spectrum of lead formate, displaced by 10  $\text{cm}^{-1}$  toward shorter wavelengths as a result of a change in the electron state of the metal.

An alkylolamide molecule is characterized by  $\begin{array}{c} \text{O} \\ \diagup \\ \text{---C} \\ \diagdown \\ \text{NH---} \end{array}$  group fluctuations, to which in the

spectrum there corresponds a 1080-1035  $\text{cm}^{-1}$  band doublet. In this group, owing to resonance, the bond between carbon, oxygen, and nitrogen has a binary character [4], and consequently, it is difficult to establish to the reaction between which atoms is each band in the doublet related. However, the fact that one of them (the low-frequency band) disappears during the

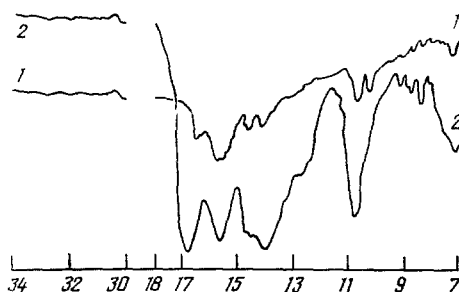


Fig. 1. IR spectra of alkylolamide (1) and aminocarboxylate complex of lead (2).

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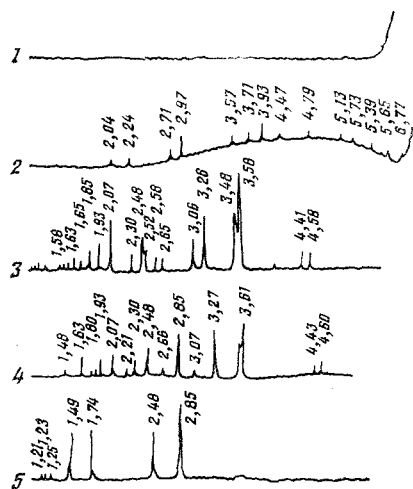


Fig. 2

Fig. 2. X-ray line intensity diagrams of starting complex with 20%  $Pb^{++}$  (1) and complexes heated at 150 (2), 190 (3), 210 (4), and 240°C (5).

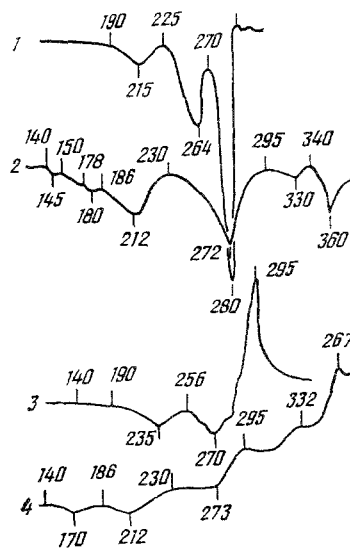


Fig. 3

Fig. 3. DTGA (1, 2) and DTA (3, 4) curves of lead formate (1, 3) and of complex containing 2%  $Pb^{++}$  (2, 4).

formation of the complex lead compound points to a redistribution of electron density in this group and hence to reaction between lead and nitrogen.

Particularly sensitive to a change in the surroundings of a nitrogen atom is amide band I, which for alkylolamide is located at  $1660\text{ cm}^{-1}$ . Electrophilic attack by the lead cation on nitrogen brings about a rise in its frequency by  $15\text{ cm}^{-1}$ . Apart from this, changes in the surroundings of the carbonyl group shift amide band II toward lower frequencies: Its frequencies for alkylolamide and the complex are  $1575$  and  $1560\text{ cm}^{-1}$ , respectively. At the same time, the relative intensities of the amide bands undergo changes. Many investigators have noted changes in the intensities and positions of both amide bands when metal ions attached themselves to a peptide bond [5]. The observed changes can therefore be linked with the formation of a mixed ligand complex compound in which the divalent lead ion acts as a complex-forming agent.

Since in the ranges investigated the spectrum absorbs also a number of other bonds, it is difficult to arrive at a unique interpretation of the complex being formed. However, bearing in mind that an alkylolamide molecule contains two functional groups, CONH and OH, which are capable of participating in the complex-formation reaction and the fact that in the spectrum of the complex, as in the spectrum of the salt, there is evidence of absorption of an ionized carboxyl group (symmetrical fluctuations with a frequency of  $1390\text{--}1400\text{ cm}^{-1}$ ), it is reasonable to assume that the formate ion enters the outer coordination sphere and to represent the complex compound with the formula  $Pb[Z]^{+2} \cdot 2[HCCO]^{-}$ , where Z is alkylolamide.

During heating, the lead aminocarboxylate complex experiences a number of changes, which are registered by the high-temperature x-ray diffraction and complex thermal analysis methods. X-ray phase analysis was performed in a DRON-3 diffractometer over the angle range  $2\theta = 9\text{--}100^\circ$  at a goniometer displacement rate of  $1\text{ deg/min}$ . Use was made of  $Co\ K_\alpha$  radiation monochromatized with an Fe filter. The thermal transformations were recorded in an MOM derivatograph at a heating rate of  $2.5\text{ deg C/min}$  in the range  $20\text{--}400^\circ\text{C}$  in air.

The starting synthesized complex lead compound had, in contrast to the starting crystalline lead formate, an x-ray amorphous structure (Fig. 2, curve 1), and was a viscous paste-like substance of a yellowish brown color. Heating for 1 h at  $150^\circ\text{C}$  altered the x-ray line intensity diagram of the substance. In the range  $2\theta = 17\text{--}40^\circ$  it increased the diffuse scattering background and led to the appearance of very low-intensity scattering reflections of new crystal structures. The changes were apparently due to polymerization processes taking place in the starting complex and the subsequent thermal decomposition of new intermediate compounds.

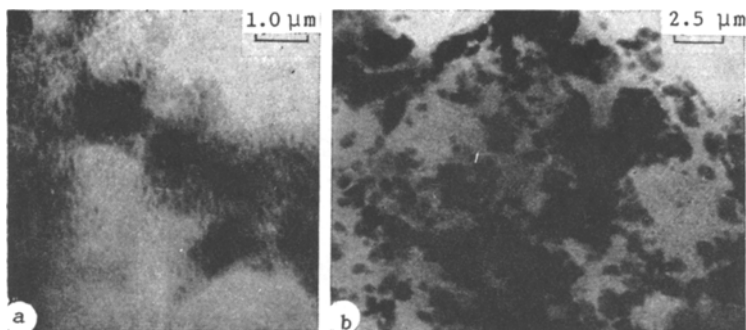


Fig. 4. Microstructures of lead particles obtained from complexes with 2 (a) and 20%  $Pb^{++}$  (b).

When the temperature was raised to 190°C, the system became mainly crystalline (Fig. 2, curve 3), and constituted a mixture of various compounds, of which only lead carbonate could be positively identified. With further rise in temperature, the intensities of reflections corresponding to different phases became redistributed and generally decreased, which was indicative of the complexity of the structural transformation processes. When 210°C was reached, reflections of metallic lead crystals appeared in the system and grew in intensity. After 1 h at 240°C the system contained only metallic lead, other crystalline phases having fully decomposed (Fig. 2, curve 5). Thus, the thermal decomposition process consisted of a series of successive stages linked with structural transformations.

The mechanism of the thermal decomposition was studied and the temperatures of formation of intermediate products were recorded using a Paulik, Paulik, and Eardey derivatograph, with the temperature being raised at a constant rate of 5 deg C/min ( $Al_2O_3$  reference standard, sample weight 500 g).

Metallic phase formed in the range 190-240°C. Here an endothermic effect with a minimum at 212°C was recorded (Fig. 3, curve 3), accompanied by a sharp weight loss from 8 to 22%. This was preceded by a less clearly defined endothermic effect in the range 140-180°C with a weight loss of up to 8%, which was probably due to a change in the structure of the complex and destruction of the outer coordination sphere, with the formation of volatile products. Evidence in support of this hypothesis was provided by a calculated specimen weight loss (7.2%), corresponding to the removal of one  $HCOO$  mole.

It is interesting to note that the integral curve 2 (Fig. 3) has horizontal portions indicating the existence of compounds stable in certain temperature ranges, viz., 145-150, 173-178, and 180-186°C. This is further evidence that the starting lead complex experienced a series of transformations during heating. Subsequent thermolysis of the lead complex led to the boiling, evaporation, and decomposition of alkylolamide at 270-296°C, followed by vigorous oxidation and secondary reactions of condensation and polymerization of the decomposition products. These reactions were characterized by exothermic effects in the range 330-360°C.

Attention should be drawn to the fact that the fineness of such a lead powder depends on the  $Pb^{++}$  ion content of the complex during whose thermolysis it forms. It would appear that this fact is linked not so much with the structural characteristics of the complex as with the mechanism of formation and growth of metal nuclei in dilute and concentrated solutions. The less concentrated the complex in relation to  $Pb^{++}$  ions, the finer are the particles being formed.

Figure 4 shows electron micrographs of particles produced during the heat treatment of complexes of different lead concentrations. The solid phase obtained from a 2% complex consisted of discrete particles freely distributed in the dispersing medium. During the thermolysis of a 20% complex, the metal particles formed, because of their higher concentration, loose aggregates up to 2  $\mu m$  in size. The oval shape of the particles is indicative of their surface amorphization, and consequently their properties would be expected to differ markedly from those of the crystalline particles produced, e.g., by the thermolysis of lead formate [5].

Thus, by studying the structure of a lead complex and its thermal characteristics, it is possible to determine suitable conditions for the production of a lead powder of a given particle size.

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## CENTRIFUGAL PNEUMATIC DISINTEGRATION OF MELTS.

## II. PRODUCTION OF TIN-BASE POWDERS AND THEIR MAIN PROPERTIES

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Part I [1] contains a description of an injector for the combined centrifugal and pneumatic atomization (CPA) of liquid metals and an account of an investigation into the effect of some key process parameters on the technical and economic indicators of the process. In this article are presented the results of pilot-plant tests of this method in the production of PO1 tin and POSSu-30/2 (Sn-Pb-Sb) tin alloy powders and of a study of the particle size analyses and technological properties of these powders.

In the centrifugal hydraulic atomization (CHA) plant described in [2], use was made of a centrifugal pneumatic injector\* with a tangential supply of liquid metal and gas into the atomization chamber under the same pressure. Experiments were carried out with chemically pure nitrogen (MRTU 6-02-375-66), grade A argon (GOST 10157-79), and grade B helium (TU 51-940-80) - gases inert to the above molten metals but differing in density  $\rho$ , thermal conductivity  $\lambda$ , and kinematic viscosity  $\nu$ . Melt portions weighing up to 5 kg each were supplied at a temperature of  $\sim 573$  K under pressures of 0.8 and 1.2 MPa. Gas flow rates were measured with a GSB-400 meter, while metal flow rates were estimated from the process time and amount of powder obtained. The volumes of argon and nitrogen at a pressure of 1.2 MPa were 0.05-0.07 NTP  $m^3$ , and that of helium 0.015 NTP  $m^3$ , per 1 kg of powder, and were thus much smaller than those in the pneumatic ( $\sim 1$  NTP  $m^3/kg$  [3]) and pneumoacoustic ( $\sim 2.5$  NTP  $m^3/kg$  [4]) methods. Gas leaving the atomization chamber was purified from fine particles by passing it through a filtering unit with sintered metal elements.

Initially, Kh18N9T (Ti-stabilized 18% Cr - 9% Ni) stainless steel injectors, which have proved satisfactory in CHA, were used. However, because of severe erosion of the material by the gas-melt medium, their life was very short. Injectors made of grade MPG graphite were found to have a much longer useful life.

The main characteristics of the tin and tin alloy powders, averaged over three to five experiments, are given in Table 1. The fractional compositions of the powders were determined by the sedimentation method (GOST 22662-77) in an alcohol-glycerin solution, using a Sedigraph-5000 D automatic granulometer with mechanical mixing by means of a magnetic stirrer, and also by 5-min powder particle disaggregation with a UZDN-1 ultrasonic disperser. The calculating unit of the instrument supplies a differential size distribution curve, the mean  $d_m$  and modal  $d_{mod}$  particle sizes, and the rms deviation  $\sigma$ . The apparent densities  $\rho_a$  of the powders were determined by a standard method (GOST 19440-74). The oxygen content of  $<20\text{-}\mu\text{m}$ -fraction particles was determined from the weight change exhibited by a powder sample during melting together with colophony to a bead (GOST 9723-73) and also by neutron-activation analysis.

\*The design of the injector for pilot-plant tests was developed by engineer O. A. Ivanov.

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