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Characterization of lead oxides by X-ray photoelectron spectroscopy and thermal analysis methods

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X-ray photoelectron spectroscopy (XPS) and thermal analysis were used to study a series of lead oxides. X-ray photoelectron spectra suggest that some minium (Pb_3O_4) samples contain carbonate groups and an excess of oxygen in superficial layers. These samples, if used in paints' production cause their premature thickening. The combined results provide compositional evidence for the mechanisms occurring at surfaces of underoxidized minium and leading to the formation of hydroxyl and subsequently carbonate species.

1. Introduction

Minium (Pb_3O_4) [1] is one of the most common red pigments which is still of great importance in the paint industry despite its toxicity and some other unfavourable properties, because it has still not been surpassed in its anticorrosive properties. It was formerly prepared by combustion of white lead in the air; at present it is usually prepared by oxidation of metallic lead in air at elevated temperatures.

When mixed with paint organic components, some minium samples cause premature thickening of paints. This is a serious disadvantage which impairs the paint. The reasons for such behaviour are not completely clear yet. The results of our previous studies [2, 3] have indicated that these effects are related to the content of water (about 1%) and minor oxygen overstoichiometry in the surface layers of minium.

These papers [2, 3] have demonstrated the important effect of a generally low water content (about 1%) and low oxygen overstoichiometry on the properties of minium pigment and premature thickening of minium based paints. In view of these results we have found it especially interesting to study a series of lead oxides including minium by a combination of surface selective X-ray photoelectron spectroscopy and thermal analysis methods.

2. Experimental

2.1. Samples

Most of the minium samples used in the present study were industrial samples declared as anticorrosive pigments (produced by Spolana Velvary).

The PbO_2 and PbO (litharge) oxides were analytical grade laboratory chemicals (Avondale Laboratories, Oxon, UK).

The PbO (yellow) was a laboratory chemical of analytical grade (Zaklady chemiczne, Chemifarm, Chorzov-Batory, Poland).

2.2. Methods

Thermoanalytical measurements were carried out on a Netzsch STA 409 analyser connected by a capillary coupling system (Netzsch 403/4) to a Balzers QMG 420 mass spectrometer used for analyses of gases evolved during sample heating, evolved gas analysis (EGA). Corundum crucibles (size 0.28 ml) and corundum powder as standard sample were employed for thermogravimetric (TG) measurements. The experiments were carried out in argon under a dynamic atmosphere (Ar of 99.997% purity) at a flow rate 75 $cm^3 min^{-1}$ and heating rate 10 $°C min^{-1}$ in the range 0–700 °C; the thermocouples were Pt–PtRh, type S. The sensitivity of differential thermal analysis (DTA) was 35 $\mu V mW^{-1}$. Temperature and power calibration was carried out using ICTA standards. The sample weights ranged between 170 and 180 mg. Results of the measurements were evaluated using Netzsch software with an on-line HP-310 computer.

The photoelectron spectra were recorded in a VG ESCA 3 Mk II electron spectrometer. The background pressure was in the low 10^{-6} Pa range. The XPS measurements were performed using Al $K\alpha$ (1486.6 eV) source at a power of 220 W. The spectrometer was operated in the fixed analyser transmission mode with a pass energy of 20 eV giving resolution of

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1.1 eV on Au ($4f_{7/2}$) line. The Fermi level of the spectrometer served as an energy reference. The spectra were calibrated using C (1 s) – binding energy of adventititous carbon at 285.0 eV.

The specimens were prepared by dusting the lead oxide powders onto gold substrate or by spreading them on double-sided adhesive tape (3M) attached to the specimen probe.

Spectra of Pb (4f), O (1s) and C (1s) electrons were recorded. Curve fitting of high resolution spectra was accomplished using the lines of Gaussian–Lorentzian shape and the damped non-linear least square procedure [4]. Core level binding energies were determined with an accuracy of ± 0.2 eV.

Peak area computation was performed after the non-linear background [5] was removed. Quantification of oxygen/lead ratio was accomplished by correcting the photo-electron peak areas for their cross section [6] and accounting for the dependence of inelastic electron mean free path on kinetic energy [7].

The thickening test, determination of moisture and PbO_2 content of minium samples were carried out by standard procedures (Czechoslovak norm CSN 67 1476 [8]).

It should be noted that the samples were also studied by atomic absorption spectroscopy, powder X-ray diffraction technique, secondary ion mass spectrometry and infrared spectroscopy. Their surface areas were measured by low temperature adsorption of nitrogen and morphology of the minium particles was examined by transmission electron microscope.

3. Results and discussion

A series of industrial and laboratory samples were tested by the thickening test and characterized by the methods given above. Minor differences in the results of these methods were observed between samples causing premature thickening of paints and good quality samples. The content of trace elements (Cu, Fe, Mn, Zn) was nearly the same in both kinds of minium. The surface area of both types of samples was also nearly identical. Both powder X-ray diffraction patterns and infrared spectra of these varieties were practically identical. The differences were also not observed on electron micrographs. The results of these measurements are discussed in detail in our previous papers [2, 3].

3.1. Characterization of the lead oxide samples by the XPS method

The obtained core level binding energies of Pb (4f) and O (1s) electrons were consistent with the published data [9–11]. The calculated ratios of oxygen to lead atomic concentrations $c(O)/c(Pb)$ were higher than the nominal stoichiometric composition. The excess of

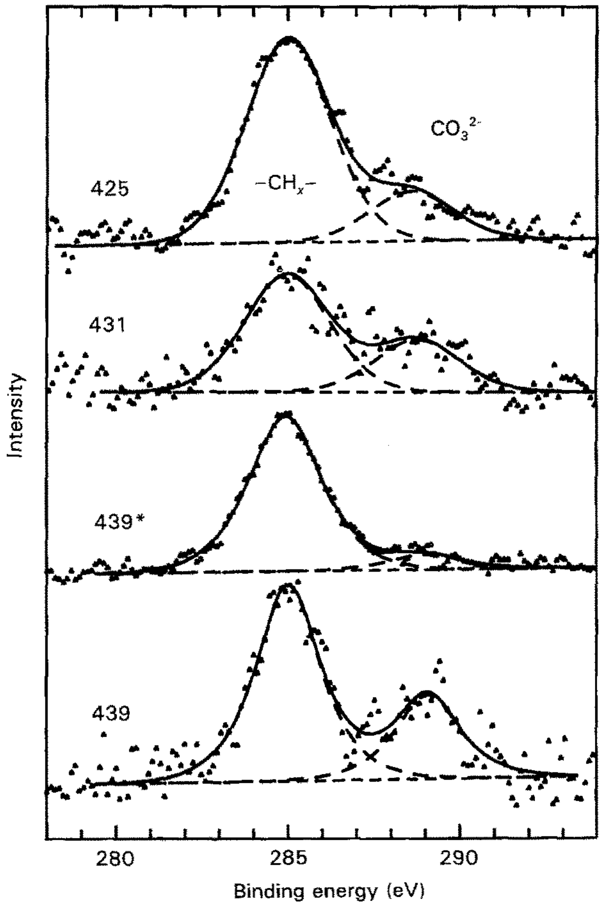

Figure 1 Typical C (1s) core level spectra of several Pb_3O_4 samples (spectrum 439* was obtained after heating sample 439 to 250 °C for 1 h.).

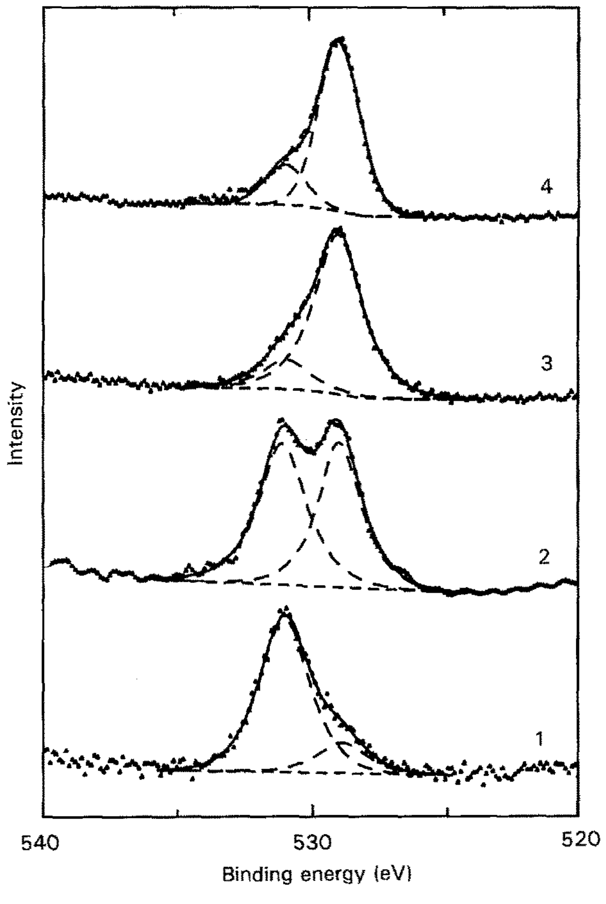

Figure 2 O (1s) core level spectra of as-received lead oxide samples: 1, PbO (yellow); 2, PbO (litharge); 3, Pb_3O_4; 4, PbO_2.

oxygen was noticeable especially with samples causing premature thickening of red lead paint. Additional interesting information was obtained from the more detailed analysis of O (1s) and C (1s) photoelectron lines.

Fig. 1 shows C (1s) spectra of several red lead samples. As can be seen from the spectra two chemically non-equivalent forms of carbon are present on sample surfaces. The line with binding energy 285 eV can be attributed to carbon atoms in hydrocarbon molecules (denoted $-CH_x-$) which are the usual contaminants of most surfaces while the line located at 289 eV belongs to carbonate species. The concentration ratio $c(-CH_x-)/c(CO_3^{2-})$ was found to depend on the history of the sample and could be changed by sample heating as shown in Fig. 1.

The O (1s) spectra of Pb_3O_4 and related lead oxides are shown in Fig. 2. Two different forms of oxygen can be resolved in these spectra. The peak located at 529 eV corresponds to lattice oxygen (O^1), while the peak at 531 eV can be assigned to surface OH groups and/or strongly adsorbed water (O^S). In addition, the electron emission from oxygen contained in carbonate groups contributes to the higher binding energy peak.

Our results indicated that the concentration ratio of the two different oxygen species also depends on the history of the sample. Therefore, we have performed XPS measurements with samples prepared by depositing them from water suspensions of lead oxides. After drying at room temperature the samples were heated in a vacuum in the preparation chamber of the spectrometer to 250 °C for 1 h and then transferred to the measuring chamber without exposure to ambient atmosphere. The resulting XPS spectra are displayed in Fig. 3. It follows from inspection of the O (1s) spectra in Figs 2 and 3 that the yellow form of PbO has highest affinity to water from the samples studied. Adsorbed water can be removed from the surface by heating to higher temperatures (Figs 4 and 5).

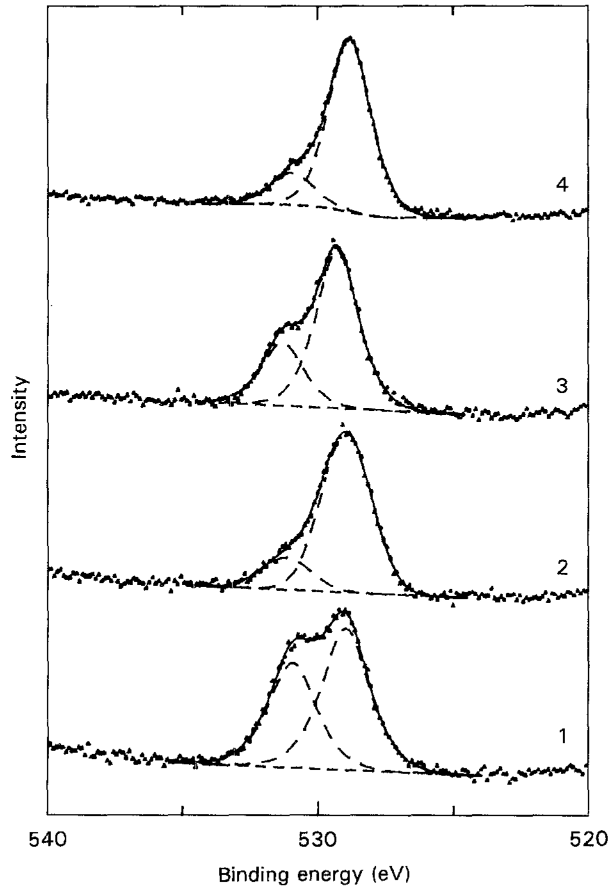

Figure 3 O (1s) core level spectra of lead oxide samples prepared from water suspension after heating to 250 °C for 1 h: 1, PbO (yellow); 2, PbO (litharge); 3, Pb_3O_4; 4, PbO_2.

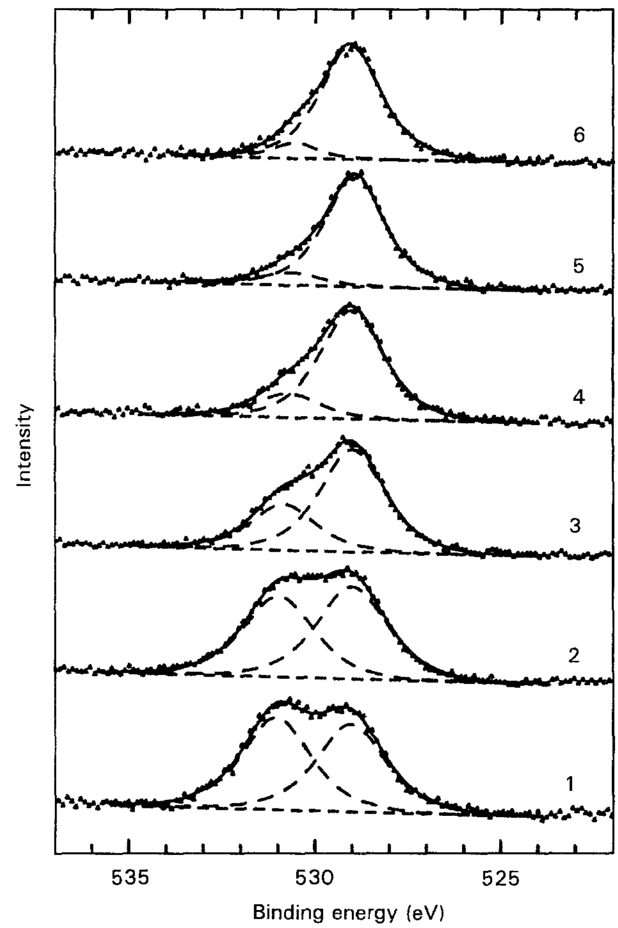

Figure 4 O (1s) spectra of Pb_3O_4 sample prepared from water suspension: 1, measured at 25 °C; the spectra 2–6 correspond to samples heated to 100, 200, 300, 400 and 500 °C respectively.

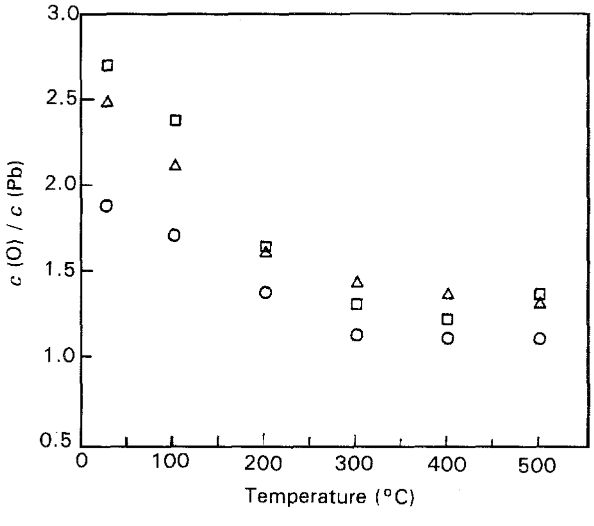

Figure 5 The temperature dependence of the oxygen/lead surface concentration ratio calculated from ESCA data for PbO and Pb_3O_4. ○, Pb_3O_4; □, PbO (y); △, PbO (r).

TABLE I Surface composition of minium samples

Premature paint thickening	$c(O^S + O^1)/c(Pb)$	$(c(O^S)/c(O^S + O^1)) \times 10^2$
None	1.5–1.6	7.1–9.6
Strong	1.6–1.8	16.6–28.1

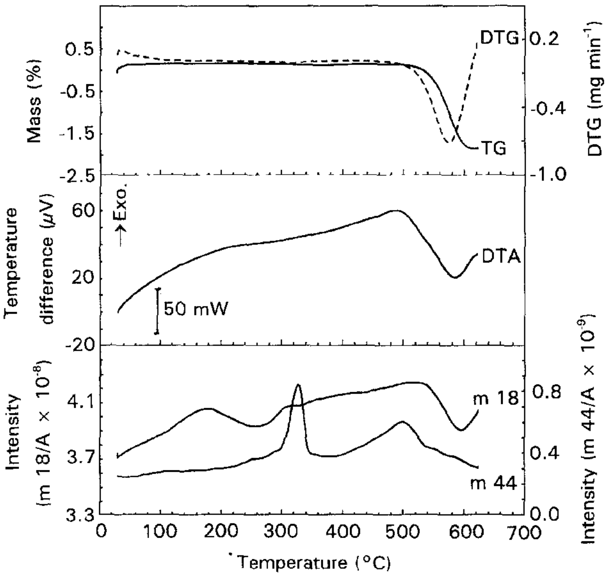

Figure 6 TG, DTG, DTA and EGA curves of the minium sample SO.

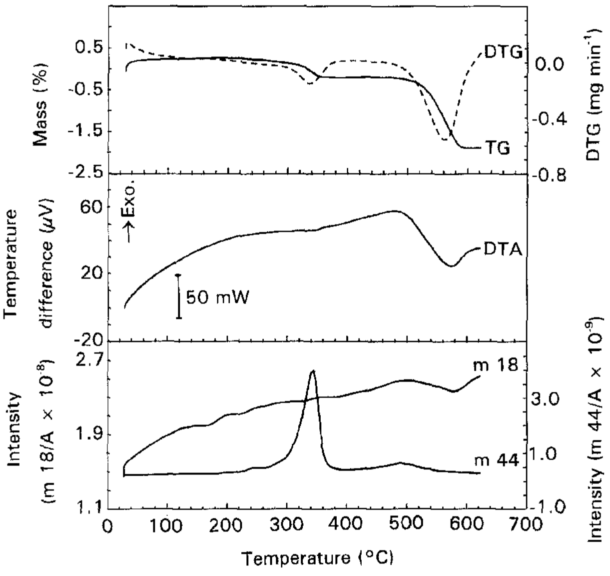

Figure 7 TG, DTG, DTA and EGA curves of the minium sample 441.

The comparison of the XPS results with behaviour of Pb_3O_4 samples in paints (Table I) shows that samples causing premature paint thickening contain more oxygen on their surfaces. These samples also exhibit increased surface concentration of carbonate groups which, in addition to OH groups, are responsible for the above-mentioned increased concentration of oxygen.

Our XPS results are consistent with the hypothesis that the samples with excess of surface oxygen originate from initially underoxidized minium. Due to the presence of increased concentration of lower oxidation states of Pb the surfaces of underoxidized minium are more susceptible to reactions with water molecules present in the ambient air. In this way OH groups are produced on the sample surface which subsequently may react with carbon dioxide thus forming carbonate groups.

3.2. Characterization of the lead oxide samples by thermoanalytical methods

The results of DTA, TG, and DTG measurements as well as results of analyses of the evolved gases of two minium samples of substantially different quality are presented in Figs 6 and 7. The results obtained with PbO (litharge) and PbO (yellow) are given in Fig. 8 and Fig. 9, respectively.

The most conspicuous effect observed during heating of minium samples is the endothermic effect at

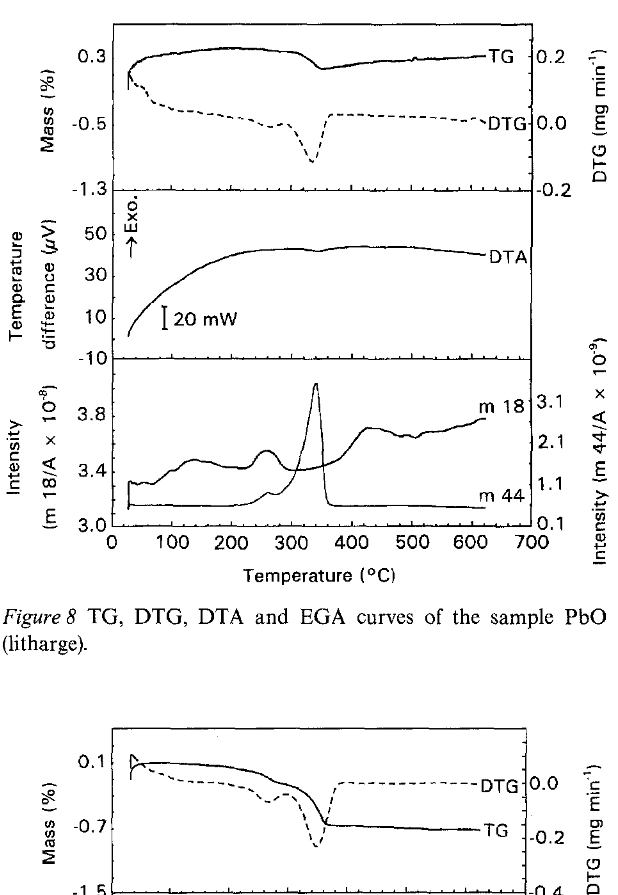

Figure 8 TG, DTG, DTA and EGA curves of the sample PbO (litharge).

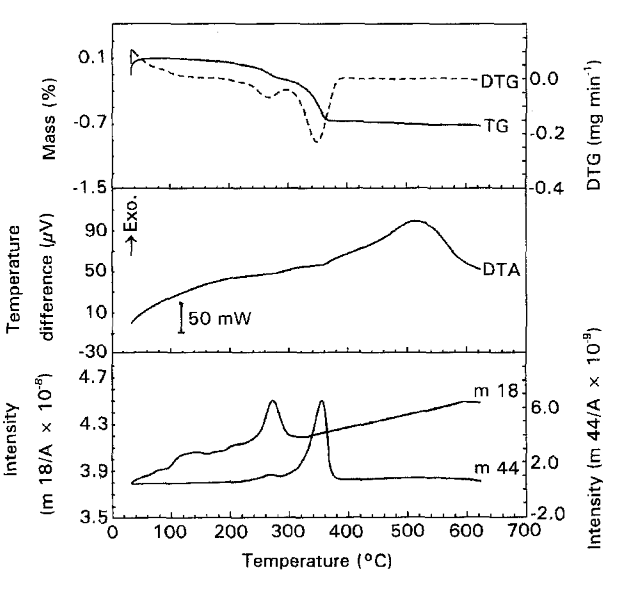

Figure 9 TG, DTG, DTA and EGA curves of the PbO (yellow) sample.

TABLE II Bulk and surface composition of lead oxides

Sample	Premature paint thickening	Bulk composition, wt%		Value of x in PbO_x formula	A[a]	B[b]	C[c]
		Pb	PbO_2				
425	None	91.10	32.10	1.62	7.1	0.8	0
439	Strong	91.24	25.64	1.82	16.6	4.0	2.2
441	Very strong	88.25	23.80	–	–	5.2	4.5
SN	Strong	91.10	19.36	1.66	28.3	5.1	4.3
SO	None	90.42	29.10	1.64	8.5	0.7	0.9
PbO_2	Not measured	86.95	97.65	–	–	0.8	9.2
PbO (1)[d]	Not measured	92.91	0	–	48	4.5	8.0
PbO (y)[e]	Not measured	92.70	0	–	82	6.8	2.8

[a] $A = [c(O^S)/c(O^S + O^1)]$

[b] area of CO_2 peak on EGA graph (arbitrary units)

[c] area of H_2O peak on EGA graph (arbitrary units)

[d] PbO (litharge)

[e] PbO (yellow)

560–580 °C, accompanied by marked mass loss and release of oxygen. This effect corresponds to Pb_3O_4 decomposition leading to the formation of PbO. The minium samples differing in paint thickening do not exhibit significant differences both in the position of this peak on the temperature axis and related weight loss.

However, differences were observed on EGA curves in the temperature interval 250–350 °C. These are not related to oxygen evolution which takes place at higher temperatures but they are connected with CO_2 and H_2O release. Both types of PbO samples exhibit even more extensive CO_2 and H_2O evolution than minium samples, as is obvious from Figs 8 and 9. It should be noted that temperatures of CO_2 and H_2O evolution and peak shape are similar for both PbO and Pb_3O_4.

These processes are well distinguished in the yellow modification of PbO (see Fig. 9). It is obvious from Fig. 9 that there are two separated phenomena. The H_2O evolution ($m = 18$ curve) and evolution of a small amount of CO_2 ($m = 44$ curve) occur at 272.5 °C. Greater amounts of CO_2 (the $m = 44$ curve) are evolved in the further endothermic process. Qualitatively similar features are observed on EGA curves obtained with PbO and Pb_3O_4 samples in this temperature region.

The peaks on these curves are located at nearly the same temperatures but they differ in intensity. It is obvious from the fact that water is evolved at temperatures near 300 °C that it is not present in the form of physically adsorbed molecules but more likely as OH groups.

The surface and volume compositions of different minium samples together with the results of thermal analysis of these samples and their activity in premature paint thickening are summarized in Tables I and II. It is clear from these tables that the minium samples causing premature paint thickening are characterized by excess of oxygen in the surface layers, which is accompanied by lower PbO_2 content in the sample and by the presence of endothermic effects connected with release of CO_2 and H_2O.

The results of EGA measurements are thus in agreement with the results of surface chemistry investigations by XPS.

4. Conclusions

One can conclude from the above results that our Pb_3O_4 samples contain significant amounts of strongly-bound water and carbonate groups in their superficial layers. The amount of both these species is distinguishably higher in the minium samples with a lower degree of oxidation of lead, which also contain greater amounts of oxygen in the surface layers, i.e., a higher ratio $c(O^S + O^1)/c(Pb)$ as evidenced by the XPS method.

These observations may be tentatively explained in the following way. The lower oxidation degree of Pb_3O_4 sample results in a higher content of more basic Pb^{2+} ions in the minium structure resulting in higher affinity of such samples towards water and carbon dioxide. A similar course of CO_2 evolution from PbO and Pb_3O_4 samples observed on thermoanalytical curves supports this idea. Neither the higher total oxygen content ($O^S + O^1$) in surface layers of these samples is surprising. It is well known [12, 13] that some metal oxides exhibit an ability to bind water by substitution of O^{2-} ions by OH^- ions in their oxygen lattice substructure. The resulting charge deficit is compensated either by vacancies in place of cations or by the decrease of oxidation degree of cations for conservation of the overall electroneutrality of the crystal and its structure. The structure of such a defective crystal lattice is similar to the structure of a dehydrated crystal. Such a crystal should exhibit relative oxygen overstoichiometry and surface-bound oxygen as determined by XPS method as well. This explanation seems probable for the investigated minium samples where there is no evidence of the existence of a separate phase even in samples with the lowest oxidation degree. The defects generated in this way, especially in the surface layers could result in higher chemical reactivity of minium samples, including reactions causing the premature thickening of minium based paints.

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