lead

2 Copies for Dr. Kehoe

ETHYL CORPORATION
RESEARCH LABORATORIES
1600 WEST EIGHT MILE ROAD
FERNDALE 20
DETROIT, MICHIGAN

February 1, 1951

Dr. Robert A. Kehoe
University of Cincinnati
College of Medicine
Eden Avenue
Cincinnati 19, Ohio

Dear Dr. Kehoe:

Inclosed herewith please find a letter from our Dr. Lamb in response to yours of January 18.

Sincerely yours,

Harold Soroos

Harold Soroos, Manager
Chemical Research Operations

HS:gm
cc: Mr. C. M. Gambrill
Dr. F. W. Lamb

2 copies for Mr. Rollefs

ETHYL CORPORATION

RESEARCH LABORATORIES

1600 WEST EIGHT MILE ROAD

FERNDALE 20

DETROIT, MICHIGAN

January 30, 1951

Dr. R. A. Kehoe
University of Cincinnati
College of Medicine
Eden Avenue
Cincinnati 19, Ohio

Dear Dr. Kehoe:

In connection with preparing standards for our X-ray diffraction examination of engine deposits we have made a study of the decomposition products of PbO_2, $PbCO_3$ and $PbO \cdot 2PbCO_3 \cdot H_2O$. It has been found that Pb_2O_3 and Pb_5O_8 are both produced as decomposition products of PbO_2, the sequence of decomposition products with increasing temperature being, Pb_5O_8, Pb_2O_3, Pb_3O_4, PbO (red tetragonal), and PbO (yellow orthorhombic). In the case of $PbCO_3$ the sequence on heating in open atmosphere is; $PbO \cdot PbCO_3$, $2PbO \cdot PbCO_3$, Pb_2O_3, Pb_3O_4, PbO (red tetragonal) and PbO (yellow orthorhombic). The first decomposition product of $PbO \cdot 2PbCO_3 \cdot H_2O$ is $PbO \cdot 2PbCO_3$, which is then followed by the same sequence of products as obtained from the decomposition of $PbCO_3$. We are enclosing a sample of Pb_2O_3 prepared by heating PbO_2 at 380°C. for 72 hours in an open atmosphere. This material is identified by our analytical number M-20930 and was found by chemical analysis to have 89.61% Pb compared with a theoretical value of 89.62. We are also enclosing a sample of Pb_5O_8 prepared by heating PbO_2 at 328°C. for 72 hours in an open atmosphere. This material identified as M-20835 analyzed 88.92% Pb compared with a theoretical value of 89.00. The X-ray diffraction patterns of these two compounds indicate them to be isomorphous compounds, however, there is no evidence of solid solution at intermediate compositions. At intermediate compositions the patterns (1/4 rpm patterns obtained on the new Norelco Spectrometer) show simply mixtures of the two components.

It is assumed that the reported pattern for Pb_2O_3 to which you refer in your letter of January 18, is that in ASTM Index Card II-1167 taken from the work of A. Baroni, Gazz. chim. ital. 68, 391 (1938). The d values for our preparation of Pb_2O_3 are similar to his. In your review of the literature you have no doubt found considerable conflicting data on these two compounds. We have been particularly interested in the work reported by Clark in J.A.C.S. 59, 2305 (1937) in which "Pb_2O_3" is prepared by a pressure bomb technique from NaOH, PbO_2 and H_2O. A crystal structure analysis of this material was reported by S. T. Gross in J.A.C.S. 63, 1168 (1941) in which he found it to be monoclinic and to belong to space group C_{2h}^2 or C_2^2 with a = 7.03, b = 5.62, c = 3.93 A. and $\beta = 82°$. Later, A. Byström repeated the preparation and reported a similar crystal structure analysis in Arkiv Kemi, Mineral Geol. 18A, No. 23, p. 1 (1944). We have been able to prepare a small amount of the same material but not in

sufficiently pure state to permit a chemical analysis which would be satisfactory for either confirming or refuting the Pb_2O_3 composition. The X-ray diffraction data for our material checked well with the d values calculated from a reciprocal lattice treatment of the above structure data, indicating that we were able to prepare the same product. The X-ray diffraction pattern, however, is entirely different from that obtained on the Pb_2O_3 prepared by decomposition of PbO_2. We hope to be able to prepare Clark's "Pb_2O_3" in sufficient quantity for a satisfactory chemical analysis so as to determine where it fits into the complicated lead oxide picture.

Following the above publication on "Pb_2O_3" Byström has reported on the Decomposition Products of PbO_2 and the Oxidation Products of PbO in Arkiv Kemi, Mineral Geol. 20A, 1 - (1945), a long and fairly complete abstract of which appears in C. A. 41, 4053g (1947). In this article X-ray diffraction data are given for $\alpha\ PbO_x$ and $\beta\ PbO_x$ in which x is approximately 1.66 and 1.50, respectively, or Pb_5O_8 and Pb_2O_3. The data given agree closely with the data we have obtained for these two compounds. Byström compares the data on these two compounds with those obtained by other authors, however, he fails to make reference to his former work on "Pb_2O_3" or to that of Clark's. Another reference which we have found of interest in connection with these compounds is that of T. Katz on Contribution to the Study of the Lead-Oxygen System which appeared in Anales de Chimie, (12), 5, 5-65 (1950).

We are continuing to do considerable work on these systems and plan to publish the data obtained on them in the near future. It is hoped that our studies may lead to an answer to the questions, when is a compound Pb_2O_3 and when is it not and why? In the meantime, we trust that the enclosed preparations will be of assistance to you in answering your present problem. If you have any comments or suggestions on this subject or if we can be of any further assistance to you on this or related problems we should be pleased to hear from you.

Sincerely yours,

Frances W. Lamb

Frances W. Lamb

FWL/dr
Enclosed: 2 Samples

cc: Dr. H. Soroos
Mr. C. M. Gambrill

January 18, 1951

Dr. Harold Soroos
Ethyl Corporation
1600 West Eight Mile Road
Ferndale 20, Detroit, Michigan

Dear Doctor Soroos:

We have been trying to obtain a small amount of reasonably pure lead sesquioxide (Pb_2O_3) for X-ray diffraction comparison with a material which we suspect is the sesquioxide and which gives a pattern in good agreement with the reported pattern of the sesquioxide. So far we have been unsuccessful and it occurred to us that you might have some of this compound or know where we might obtain it.

If you could give us some help on this, it would be greatly appreciated.

Cordially yours,

Robert A. Kehoe, M. D.

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