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"INVESTIGATION OF FUNDAMENTAL PROPERTIES OF LEAD COMPOUNDS
USED OR FORMED IN LEAD ACID STORAGE BATTERIES"

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ABSTRACT

This report is a discussion of the problems involved in our investigation of the pressure-temperature-color, conductivity and structure study being made of lead monoxide. Some discussion on the effect of calcination of lead monoxide in nitrogen is given.

INTRODUCTION

The previous report (Seventh Quarterly Report) indicates that several phases of the study would be reported in this the Eighth Quarterly Report. At that time it seemed to us that we were dealing with three separate and apparently distinct problems each of which was capable of practical completion in a short time. Additional data were obtained, however, which are causing us to completely reassess the body of data concerning lead monoxides. This report will therefore discuss these data and the progress of the investigation in a qualitative way and will attempt to outline the present problem.

It must be remembered of course that in approaching the problem of lead oxide properties we have a long manufacturing and experimental background in which no small area is occupied by a myriad of instances in which peculiar lead oxide products or results have been produced or obtained without any intention on our part to do so. In some instances apparently identical materials have refused to produce identical results in a customer's plant. Minor (apparently) changes in furnace design may sometimes produce major changes in the use properties of an oxide product. As a result the manufacturing of lead oxides has grown along empirical lines. Each new type of furnace gives a product that must be very carefully evaluated and tested before the manufacturer can be sure of what it is good for. Some furnaces or processes appear to be very sensitive to many influences while others are not.

Most of these diverse products are very similar chemically and have very similar impurities both as to kind and quantity. In any attempt to rationalize the differences one is almost forced to conclude that the differences are physical rather than chemical. Yet the study of the physical differences have not cleared up the picture and have only contributed more data to further confuse the issue. Products having nearly all the colors of the rainbow have been seen. Yellow products have been examined that yield "red" (tetragonal) x-ray diffraction patterns while other red and purple samples have yielded "yellow" (orthorhombic) patterns.

There are marked differences in the "red" and "yellow" diffraction patterns shown by various preparations. Yet when one attempts to relate these differences to the method of their preparation results are not conclusive. The intensities of the stronger lines of several oxide patterns may show considerable variation.

Samples of lead oxides assumed to contain both the red and yellow modifications may yield for example a reasonably good pattern of the yellow form and a few of the lines of the red pattern. In some instances this partial pattern of the red form will not consist of the stronger lines but only a few of the weaker ones.

Careful and precise specific gravity measurements of oxides of various colors and diffraction patterns do not resolve the puzzle although the data are helpful in setting up phase limits.

The study of these observations and the mass of data accompanying them is the real purpose of this investigation.

THE EXPERIMENTAL WORK

A Discussion of Its Present Status

1. Low Temperature Color Study

The completion of this phase of the study has been postponed until we are more certain of the oxide materials we will need to study. Since we have no local source of liquid nitrogen (closer than Kansas City) it is planned to complete this study in a continuous campaign when once started. The peculiar colors of the oxides obtained under high pressure have caused us to delay this phase.

2. Pressure-Temperature-Conductivity Study

The initial test cell set up for use at pressures up to 120,000 psi has given results in fair agreement with data obtained from some of the International Critical Table literature references. Under our conditions fabricated mica insulators are showing electrical leakage and mechanical weakness. Substitutes are being sought for the mica.

The physical changes taking place in the oxide samples under pressure at various temperatures have been most surprising and these data will, we believe, lead to a better understanding of the entire Pb/O system. In brief and qualitatively, here is the story.

Starting with a freshly calcined yellow litharge and applying 120,000 psi pressure for one hour at various temperatures the following products have been obtained:

Temperature	Color	Yellow X-Ray Diffraction Pattern
80°F (27°C)	Dull Red	" " " "
200°F (93°C)	Brown-Red	" " " "
400°F (204°C)	Blue-Red	" " " "
600°F (316°C)	Yellow-Red	" " " "

Although the 400°F product gave a yellow diffraction pattern it had a specific gravity of 9.39 which indicates that the sample is mostly the red form (sp. gr. 9.32) instead of the yellow (sp. gr. 9.67). It does not seem reasonable that the addition of pressure to a dense form would produce a less dense modification, yet this has apparently occurred. A fairly plausible explanation is that during the application of the pressure the grains move with respect to each other and shearing and "smearing" of the yellow lattice results. After full pressure is attained diffusion permits the re-establishment of the yellow lattice. This diffusion is naturally more rapid as the temperature increases and in agreement with this explanation the sp. gr. of the 600°F sample is higher at 9.59.

A sample of red PbO produced by steaming, ball milling and low temperature annealing was converted to a yellow product which gave a yellow diffraction pattern by pressures in the order of 200,000 psi at room temperature.

The colors of the press products at various temperatures are most interesting. At 400°F the pellet is essentially an opaque blue red by reflected light but is a blood red by transmitted light and even fragments nearly 1 mm thick will transmit considerable light. The 200°F product is duller in color and transmits less light. The 600°F product is yellow opaque and fragments are apparently masses of yellow crystals of such size that the reflection of light from individual crystal faces can be seen with about a 15 power magnification. These yellow crystals are sensitive to touch becoming red in color when touched with a needle or tweezers. There are apparently thin crystalline red layers in which the red crystals are oriented in parallel positions. Whether or not these red crystals formed on cooling and the release of pressure is not known.

Although the body of the press product will have a given color the color may not be uniform at the surfaces. Yellow and green streaks and spots are frequently observed at the lower temperatures. It was at first thought that perhaps the litharge was reacting with the ends of the polished steel rams. These were then covered with a thin disc of sheet lead with no change in surface color.

The texture of the products produced at 200°F and 400°F are interesting in that they have almost waxy characteristics.

When the red press products are slowly ground in a small mortar the red changes to yellow (!) and further grinding gives a brown red product.

Tests made at various press times up to 10 hours show that beyond 1 hour very little change takes place. This might not be true at low temperatures.

The yellow x-ray diffraction patterns obtained on these press samples have several peculiar characteristics. Of about 30 lines that could be precisely measured 17 are in near perfect agreement with our best data on yellow PbO. The strongest line of Red PbO by our best data does not appear and the second strongest is displaced. Only about four lines appear to have a Red PbO component as their origin. The other lines are accounted for by displacements of the yellow pattern.

Displaced lines in these oxide patterns (in some instances a line appears to be split into two weaker lines close together) have concerned us for a long time but these samples produced under pressure are the first indication of how they could be consistently prepared for study. Patterns are being carefully measured and indexed to determine if possible the physical significance of this shift.

Any attempt at this time to interpret these data which are not complete amounts to speculation. One of the most reasonable appearing assumption would be that lead monoxide can exist at room temperature in a third form which is non-crystalline to x-rays, of a blue or blue-red color, and has a specific gravity of about the same order as the red tetragonal form. This form may be only an extremely fine particle size tetragonal red or it may be the residue from "smearing" either a red or yellow lattice without re-crystallization having occurred. If the non-crystalline form is the result

of smearing it is reasonable to expect that certain structure planes of the original oxide might persist longer than the rest and yield diffraction lines of their relict structure. These lines would not necessarily be the most intense lines of the original oxide, and some shift in their position would not be unreasonable.

This hypothetical non-crystalline blue-red form would have to be capable of coexisting with the yellow form at room temperature. The specific gravity data on the 400°F sample indicates about 20% yellow in a matrix of 80% essentially non-crystalline material. The addition of a blue or blue-red material to a yellow oxide would go a long way towards understanding the colors of PbO obtained by various processes; brown, yellow-green, olive green, green, with or without red.

Our data lead us to believe that this blue-red product is very reactive since samples exposed to the air for several days showed a sp. gr. of only 8.8 (with no change in appearance) which low value is probably due to the pickup of moisture or CO₂. Because of its waxy nature its apparent surface area is very small.

Further data to more exactly outline the pressure-temperature areas need to be acquired before conclusions can be drawn.

3. The Reaction of Lead Oxides With Nitrogen

The literature on lead oxides almost unanimously indicates that molten lead or hot lead oxides do not react with nitrogen gas. This may be true since our experimental furnacings have not been able to produce good evidence that such a reaction does exist. On the other hand this negative evidence does not entirely settle the problem in the light of certain experimental observations and discrepancies (that perhaps have other explanations).

Although it appears probable that no chemical reaction leading to a Daltonian compound does exist between lead oxides and nitrogen gas the possibility that nitrogen gas is or can be absorbed into the oxide lattice at calcination temperatures has not been excluded. In this respect it seems reasonable to postulate that the chemical reaction with oxygen at high temperatures may be initiated by the physical absorption of oxygen in the oxide lattice before any chemical combination occurs with the production of tetravalent lead ions. If this concept is true it is not unreasonable to expect some nitrogen absorption in the lattice, which absorption will be accompanied by the slight shift of at least some of the lines of the diffraction pattern. Since the nitrogen is assumed to be absorbed interstitially a slight increase in density is expected. On this basis a number of preparations have been furnaceed and the products analyzed. The results when analyzed do not resolve the problem in an unequivocal manner. They have, however, suggested other experiments that are in progress.

The x-ray diffraction patterns of oxides calcined in oxygen when compared with those calcined in nitrogen show some unexpected differences which with the data at hand cannot be explained on a reasonable basis. Some of this work is being repeated with the addition of one or more calcinations in helium.

One thing appears certain. The temperature of transition of red PbO to yellow PbO, or for the decomposition of red lead to yellow PbO, and the decomposition of lead dioxide to lead monoxide are much influenced by the gas in contact with them. Furthermore the data on specific gravity of the oxide preparations are not always in agreement with the major crystalline phase present as determined by x-ray diffraction. The data suggest the presence of a variable amount of non-crystalline transition material of apparently quite low density.

SUMMARY

The progress of the study is proceeding along several fronts, none of which have produced data suited to detailed reporting at this time.

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