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The composition and analysis of zinc-lead pigment

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Department:

A THESIS,

"THE COMPOSITION AND ANALYSIS OF

ZINC-LEAD PIGMENT."

FOR

THE DEGREE OF METALLURGICAL ENGINEER.

BY,

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Zinc-lead pigment has generally been spoken of by the trade and by chemists as if it were a mixture of zinc oxide and lead sulphate. It can, however, be proved by a few simple experiments that there is a chemical combination between the component parts of this pigment.

It has been generally conceded that the lead exists as a basic sulphate, (PbO. PbSO4.) the supposition being that all the lead oxide is combined with the sulphate. However, the decided pink tinge that some pigment shows is undoubtedly due to the presence of lead oxide (PbO) in an uncombined state.

Zinc is present as oxide and sulphate. There are also probably zinc and lead sulphites. It has been suggested that there may be carbonates in this pigment, but this is not probable as the high temperature of the furnace, the complete combustion of the fuel to CO2 and the large excess of SO2 gas in the bagroom would tend to prevent their formation. There is also a chemical combination betwwen the zinc oxide and the lead oxide which is probably a zinc plumbate.

Some light can be thrown on the subject by the following experiments:-

#1. Mix 50 grams zinc oxide, 20 grams lead sulphate and five grams lead oxide,this being about the proportions in which they occur in the pigment. Chemically pure salts should be used , the mixture should be thoroughly ground together and a portion taken for a test. Mix this test with turpentine and spread on a plate of glass. It will have a decided red color due to the presence of lead oxide.

Place the rest of the mixture in a crucible or scorifier and heat to redness in a muffle. When cool mix some of this pigment with turpentine and place beside the first test. The color after heating will be decidedly whiter than before. While the heated product may not be perfectly white it shows that most of the lead oxide has undergone a change and the conclusion is that there has been a combination between the lead oxide and the lead sulphate forming basic sulphate.

However, experiment #2 shows that this will not account for all the change that evidently takes place.

#2. Mix 5 grams of lead oxide and 95 grams of lead sulphate and heat as in experiment #1, testing with turpentine on a plate of glass before and after heating. It will be found that although the pigment is whiter after heating than before, the change is not as marked as in experiment #1, and that there are streaks of yellow

lead oxide through it, showing that all the lead oxide will not combine with the lead sulphate under these conditions.

#3. Mix 5 grams of lead oxide with 95 grams of zinc oxide and treat in the same manner as in the other tests. It will be found that the mixture is decidedly whiter after heating, the amount of yellow streaks remaining being much less than in experiment #2. This proves conclusively that there is a combination between the lead oxide and the zinc oxide.

As chemically pure reagents were used in these experiments there could have been no interfering compounds. The facts as stated are therefore conclusive and that a chemical reaction does take place is evident.

In making these experiments care must be taken that the temperature is not above redness and that the tests do not remain in the furnace too long. Unless these precautions are taken no results will be obtained.

Sulphur dioxide exists in the pigment as a gas and probably also as lead sulphite and zinc sulphite. In the manufacture of zinc lead pigment sulphur dioxide is to be avoided. Paints containing sulphur dioxide harden in the cans and become worthless. The limit that a pigment should contain is 0.05%.

Zinc sulphate is another constituent that is detrimental. If much zinc sulphate is present the paint will wash off. Only 1% zinc sulphate is allowable in pigment.

The methods of assaying pigments described here were developed in the laboratory of the Ozark Smelting & Mining Company, Coffeyvills, Kansas, and while they are not extremely accurate, they served the purpose very well. Results generally figure out within one half of one percent. of a total of one hundred. If the analysis figures out within this limit it is reported, no deductions or additions being made to make an even hundred.

Total Zinc:-

Weigh one gram of pigment into a #3 beaker and add a little water and stir to make an emulsion. Add 15c.c. of hydrochloric acid and stir until all the pigment is dissolved. This generally takes only a few minutes although heat is sometimes necessary. Dilute to 200c.c. with hot water and titrate with a standard solution of potassium ferrocyanide using uranium acetate as an indicator.

Zinc as sulphate:-

Weigh ten grams of pigment into a #3 beaker and add 200c.c. of hot water. Boil for five minutes, filter and wash with hot water. The filtrate will contain some zinc oxide and must be filtered again through a clean filter. Wash the filter with hot water. To the filtrate add 15 c.c. of hydrochloric acid and 10c.c. of a standard solution of zinc, one c.c. of which should contain one percent. zinc. Titrate with a standard solution of potas-

sium ferrocyanide, subtract the zinc added and divide by ten.

Suppose the strength of the ferrocyanide solution was one and that it took 12.2c.c. of it to precipitate the zinc, we then have:-

12.2 - 10 = 2.2. 2.2 ÷ 10 = 0.22% zinc as sulphate.

Lead as sulphate and lead as oxide:-

The lead as sulphate and the lead as oxide are determined in the same portion of ore. Weigh one gram of pigment into a #2 beaker and add 50 c.c. of a 30% solution of acetic acid and boil for five minutes. Filter into a #3 beaker, allow to drain but do not wash as the lead sulphate will run through an ordinary filter when washed. The lead sulphate which runs through the filter will balance any lead oxide that is left in the filter by not washing.

When the assay has drained remove the filter from the funnel open it and wash the contents into the #2 beaker, placing the paper also in the beaker, and add 25 c.c. of ammonium acetate solution. (This solution is made by mixing one part of stronger ammonia with two parts of 30% acetic acid. It should be acid.)

Place both beakers on the stove and boil. Rub down the sides of the #2 beaker with a policeman and wash. Titrate with a standard solution of ammonium molybdate,

using a freshly prepared solution of tannic acid as an indicator.

The result obtained from this titration represents the lead as sulphate. To complete the assay add the filtrate from the #3 beaker and titrate again. The additional result represents the lead as oxide.

Suppose the strength of the ammonium molybdate solution is one percent, and that the first titration took 23.4 c.c. , and the second 3.6 c.c., we would then have:-

Lead as sulphate ---------- 23.4%

Lead as oxide ---------- 3.6%

Total lead ---------- 27.0%

Some objections have benn made to this method claiming that lead sulphate is soluble in acetic acid. It is slightly soluble but not enough so to materially affect the results. The following figures are taken from Comey's Dictionary of Solubilities:-

Not more soluble in dilute aceticacid than in water. (Bischof.)

Soluble in 22,816 parts of water at 10°. (Fresenius A. 59. 125.)

Soluble in 31,569 parts of water at 15°. (Rodwell, C. N. 11. 50.)

Soluble in 13,000 parts of water. (Kremers, Pogg. 85. 247.)

Sulphur dioxide:-

The assay of the pigment for sulphur dioxide, although a simple operation, is the most important assay made in the laboratory of a zinc oxide plant, and samples from the bagroom are often assayed in addition to the daily packout.

Sulphur dioxide is determined by titrating an acid solution with a standard solution of iodine, using a solution of wheat starch as an indicator. The solutions are prepared as follows:-

Weigh 0.397 grams of resublimed iodine into a #2 beaker and add one gram of potassium iodide and 5 c.c. of water. Stir until dissolved and dilute to one liter. One cubic centimeter of this solution corresponds to 0.0001 gram, or 0.01 % sulphur dioxide.

To prepare the starch solution take about one gram of wheat starch and grind in a mortar with 10 c.c. of water. Pour into a #2 beaker and add about 100 c.c. of hot water. This solution should be prepared each day.

Weigh one gram of pigment into a #2 beaker and add 100 c.c. of hot water and 5 c.c. of hydrochloric acid. To this add about 10 c.c. of starch solution and titrate with the standard iodine solution until the blue color of the assay is permanent. The number of c.c. will give the percent. of sulphur dioxide in hundredths. If the burette

read 6.4 c.c. then the amount of sulphur dioxide would be 0.064 %. Duplicate assays check within 0.01 of 1.0 %.

Water is determined by weighing ten grams of the pigment into a casserole and drying at 110° for one hour. It is then reweighed and the loss in weight divided by ten. If the second weighing was 9.995 grams, we would have :-

10.000 - 9.995 = 0.045. 0.045 ÷ 10 = 0.0045 grams or 0.45 %.

We now have all the data neccessary for calculating the composition of the pigment:-

Total zinc ---------- 48.97 %.

Zinc as sulphate ---------- 0.22 %.

Zinc as oxide -------48.97 - 0.22 = 48.75 %.

Lead as sulphate ---------- 23.40 %.

Lead as oxide ---------- 3.60 %.

Sulphur dioxide ---------- 0.064 %.

Water ---------- 0.45 %.

65(A.Wt.of zinc):161(Mol.Wt.of zinc sulphate) = 0.22 : X, X = 0.61 %.

65(A.Wt.of zinc):81(Mol.Wt.of zinc oxide) = 48.75 : X, X = 60.75 %.

207(A.Wt.of lead):303(Mol.Wt.of lead sulphate)= 23.4 : X, X = 34.25 %.

207(A.Wt.of lead):223(Mol.Wt.of lead oxide) = 3.6 : X, X = 3.87 %.

Composition of the pigment:-

Zinc oxide	60.75 %.
Zinc sulphate	0.61 %.
Lead oxide	3.87 %.
Lead sulphate	34.25 %.
Sulphur dioxide	0.064 %.
Water	0.45 %.
Total	99.994 %.

Joplin, Mo., 5-18-07.

Faculty of the Missouri School of Mines,

Rolla, Mo.,

Gentlemen:-

I hereby make application for the Degree of Metallurgical Engineer, and respectfully submit for your consideration the enclosed Thesis.

Yours truly,

Evans H. Buskett