

The results presented below were obtained on solutions of definite strength prepared with 90 per cent. alcohol. Results obtained with commercial extracts are also submitted.

Extract.	Strength. Per cent.	Oil recovered. Per cent.
Lemon.....	5.0	5.0
“	1.0	1.0
Peppermint.....	1.0	1.0
“	3.0	3.0
“	5.0	5.0
Clove.....	1.0	1.0
“	10.0	10.2
Cassia.....	1.0	1.0
Wintergreen.....	1.0	1.1
“	2.0	2.0
“	5.0	5.1
Bitter almonds.....	1.0	1.0
“ “	3.0	2.5
Citral (pure, optically inactive).....	3.0	3.0
“	0.5	0.5

COMMERCIAL EXTRACTS.

Variety.	Oil by precipitation.	Oil by polarizator
Lemon.....	4.8	4.80
“	4.6	4.63
“	4.0	4.10
“	5.0	5.00
“	4.40	4.50
“	4.8	4.70
Peppermint.....	3.8
“	5.6
“	12.4
Cinnamon.....	3.0
Checkerberry.....	4.0
“	12.5
Rose.....	0.6

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A COMPARISON OF TWO TESTS OF RED LEAD.

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The tests generally used for the determination of the amount of free litharge, PbO, in red lead are the lead acetate test and the lead peroxide test. The latter is made in two ways, by the gravimetric and volumetric methods.

We will first consider the lead acetate test. This test depends upon the solubility of lead oxide in a solution of lead acetate. A weighed quantity of red lead is taken, and to it is added, in a beaker, a like quantity of lead acetate crystals dissolved in about 150 cc. of hot water. After

stirring, the solution is brought to a boil, and allowed to boil from ten to thirty minutes. It is then filtered through a tared filter, the residue washed thoroughly, dried, and weighed. The loss of weight between the amount of red lead taken and what remains is the weight of free litharge.

The lead peroxide test can be used in two ways, the gravimetric, which is a direct, and the volumetric, which is an indirect method. We will first consider the gravimetric method. This consists in treating the red lead with nitric acid in a warm solution. The peroxide formed is collected on a tared filter, washed thoroughly, dried and weighed. The amount found is then calculated to Pb_3O_4 . The loss between the original sample taken and the amount of Pb_3O_4 found is the weight of the free litharge.

The volumetric method consists of changing the red lead into lead peroxide, heating gently and adding a known quantity of $N/5$ oxalic acid solution, then boiling. This decomposes the peroxide of lead. While still hot, $N/5$ permanganate solution is added until the color remains for a few seconds. The volume of $N/5$ permanganate solution required is deducted from the amount of $N/5$ oxalic acid solution taken, the resulting volume of the $N/5$ oxalic acid solution is calculated to lead peroxide and from that of red lead, Pb_3O_4 .

So much for the tests themselves. Now red lead as it is made commercially, no matter by what process, is pig lead carried through the various stages of oxidation until we come to the point where oxidation practically ceases. The oxygen which is used for oxidation is taken from the air at the temperature at which the lead is worked in the furnaces. In some cases the first part of the oxidation is obtained from oxygen given up by chemical compounds in order to produce new chemical compounds. Therefore from the methods of producing red lead, we can readily see that it is impossible to obtain a pure compound, Pb_3O_4 . Red lead is therefore not a pure compound, but consists, outside of very slight quantities of impurities such as lead sulphate, silica, oxide of iron, etc., of various oxides of lead, namely protoxide, PbO ; sesquioxide, Pb_2O_3 ; and minimum, Pb_4O_6 . Now the sesquioxide, Pb_2O_3 , is insoluble in a solution of lead acetate, while on the other hand it is soluble in nitric acid. This is one of the fallacies of both tests, but sesquioxide of lead is not harmful in red lead in connection with its physical properties, and should therefore not be taken into consideration as an impurity.

On the other hand, litharge, or the protoxide of lead, if present in considerable quantity, is objectionable and especially deleterious to the physical properties of red lead. It is on account of this impurity that red lead is tested, as it is beneficial not only as a protection to the

buyers, but also to the manufacturer, who loses profit if a considerable quantity of protoxide of lead is present.

In order to compare more closely the tests of lead acetate, and lead peroxide, I prepared some red lead as pure as I could get it, by boiling with lead acetate solution and very dilute acetic acid, washed it thoroughly, put it through a No. 21 silk bolting-cloth and dried it. After it was thoroughly dry I made an analysis of it by lead sulphate method and obtained an average result of 99.95 per cent. pure red lead.

Part of this sample with the lead acetate test gave average results of 99.98 per cent. Other samples of this red lead were put through the peroxide tests, using different conditions in each case and gave the following results:

No. 1 sample.—10 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 99.16 per cent.

No. 2 sample.—30 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 94.64 per cent.

No. 3 sample.—50 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water = 89.02 per cent.

No. 4 sample.—50 cc. nitric acid, sp. gr. 1.42, 150 cc. of hot water and boiled = 77.66 per cent.

The above shows that lead peroxide is affected under certain conditions and that it is soluble in the stronger acid and also upon boiling. Therefore, this test is practically useless in the test for purity of red lead and should not be used. The volumetric method depends upon the formation of peroxide, but gave lower results in all the above cases.

Now red lead which is made from the protoxide of lead produced in the formation of nitrite of soda, will, after it comes through the various processes, contain a small quantity of sodium hydroxide and sodium nitrite. The peroxide test in this case, is even more useless than in the case of red lead made by the processes which carries on the oxidation from pig lead to red lead direct in the furnace. The nitrite of soda present acts upon the peroxide of lead and gives even greater solubility than if added after the peroxide is formed.

In the case of the lead acetate test upon such samples of red lead we first neutralize the caustic soda with very dilute acetic acid, and then proceed with the test. Of a quantity of tests made upon red lead containing caustic soda and less than 0.05 per cent of sodium nitrite, the lead acetate test gave results which varied very little, but in the case of the peroxide test the results were quite varied, some showing a difference of about 10 to 12 per cent.

It seems, therefore, that the peroxide test is much less reliable than that with lead acetate.