be represented as directly proportional to the area integrated and inversely proportional to the time or to some power of the time. Protective power may be represented as the inverse of this. Hence, $P = C t^n / A = K t^n / Q$, where K is a proportionality constant, t the time up to the maximum current, Q coulombs passed through the circuit up to the time t , and n an arbitrarily chosen constant. Relative values have been obtained by calling K unity and by assigning to the exponent n the values (D) 1 and (E) 2. This method may be used only in case of the one-coat tests. The quantitative results of the above methods are, for the sake of brevity, summarized below in a qualitative manner. The capital letters refer to the preceding methods, and the figures to the paint mixtures as follows: (1) zinc oxide, (2) zinc-lead chromate, (3) American vermilion, (4) red lead, (5) white lead, (6) iron oxide, (7) barytes, (8) silica, (9) carbon black, (10) graphite. The higher the position of a number in any column, the greater the excluding power, and as a rule, the less the depolarizing power of the paint film.

Two-coat tests.		One-coat tests.			
A, B.	C.	A.	B.	D.	E.
1	—	1	1	2	2
2	—	2	2	1	1
10	10	9	9	10	9
9	9	10	10	9	10
4	4	3	3	3	5
3	3	4	8	4	4
5	5	8	4	8	3
7	7	6	6	6	6
8	8	5	7	5	8
6	6	7	5	7	7

WORK NOT REPORTED.

Although the method uses current values, a large number of electromotive forces were measured, taken after the current readings and after breaking the circuit. Data relative to the change in resistance of the film were thus obtained. Direct measurement of resistance is greatly disturbed by the condenser-like action of the paint films. All this will probably be considered more fully later.

An attempt was also made to determine the cause for certain inexplicable deviations among the average values of the current readings that sometimes occurred during the course of a test. An examination of Plots I and II shows a few widely displaced points, especially on the third curve for red lead. All conditions were guarded as carefully as possible: the electrolyte was kept at constant level, thus preventing change in conductance due to change in concentration. Temperature changes were watched. The resistance of the electrolyte between bare iron cathodes and anodes was only 18.6 ohms, which formed a part of the resistance of the total circuit of about 119 ohms. This being the case and, further, the temperature changes in the tanks being small, no corrections were made in the current readings. These corrections would have accounted for but a few per cent. of the wide deviations referred to above. Except for a few days when the temperature varied $18 \pm 4^\circ$, it varied only $19 \pm 2^\circ$. The change in solubility of

oxygen was thus very small, and could not account for the deviations anyway, as they were frequently in the wrong direction.

CONCLUSION.

The work done thus far indicates that the method is sound in principle, reasonably practicable, and reliable, in that under the same conditions of testing, results can be duplicated. It determines definitely, and under artificial conditions made as nearly natural as possible, the excluding power of any paint film against water and air. As regards the testing of paints for use on iron and steel, the method should develop into one of especial value, as the nature of the corrosion through the painted surfaces (according to the electrolytic theory of corrosion) is entirely analogous to the mechanism of the reactions in the paint cell.

It has further been shown that, at least under the conditions maintained in the test—and it is probably true to varying degrees under conditions of actual service—films prepared from certain of the pigments experimented with possess a marked depolarizing action. This may be in part the saturation of unsaturated bonds in the linnoxyn by addition of nascent hydrogen, as it has been shown that linnoxyn will depolarize hydrogen under the conditions maintained; and it may be due in part to depolarizing properties possessed by the pigments themselves; but it appears that the rate of depolarization is determined largely by the character of the whole film—that is, pigment and vehicle combined. Increasing the porosity or the thinness of a film makes it possible for the depolarizing action to appear, but it apparently does not necessarily cause it to appear. The exact nature of the depolarizing action, and its true relation to the thickness of the film will be investigated more fully in the future.

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A SHORT METHOD FOR THE DETERMINATION OF SOLUBLE ARSENIC IN COMMERCIAL LEAD ARSENATES.

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As the result of a request for an immediate report on the amount of soluble free arsenic oxid in a sample of commercial lead arsenate, the writers began a series of experiments to develop a method of analysis which would give satisfactory results without incurring the tedious shaking of two liter bottles, eight times daily for ten days as in the procedure outlined in the standard A. O. A. C. method for this determination.

Since it was desired mainly to reduce the time,

the method which naturally suggested itself was one of determining the amount of continuous stirring at room temperature, that would be equivalent to the eighty shakings at intervals during ten days. Accordingly the samples were placed in a thermostat at 20° C. and stirred continuously by means of a hot air engine.

In order that the results might be directly comparable with the results obtained by the A. O. A. C. method it was necessary to use two liter bottles or less than two gram samples of lead arsenate. The thermostat available would not conveniently carry bottles with a capacity of more than 500 cc. and it did not seem advisable to use less than two gram samples.

A few preliminary determinations demonstrated that more than eighteen hours of continuous stirring did not appreciably increase the amount of arsenic oxide in solution. Also these results showed that no obvious direct relation existed between the A. O. A. C. results, and those obtained by continually stirring two gram samples in the thermostat with 500 cc. of water. The solubility of the lead arsenate itself entered in and caused the difference between results obtained by the two methods. The difference in the volumes of water used in the two methods amounted to 1500 cc. This quantity of water dissolves a considerable amount of lead arsenate.

This consideration involved a side problem. It has been pointed out by others, that arsenate of lead may mean the triplumbic arsenate $Pb_3(AsO_4)_2$ or plumbic hydrogen arsenate $PbHAsO_4$. Most commercial samples may consist of a mixture of these two, the amount of each depending upon the method and the conditions under which the precipitation was made. It is evident, also, that in some cases the by-products formed in the process of manufacture have not been washed out. In some samples the odor of acetic acid, which is formed when lead arsenate is made from lead acetate and di-sodium arsenate, would indicate that this step in the manufacture had probably gone no farther than the filter press.

Based on the theoretical percentage of As_2O_3 in lead arsenates consisting of mixtures of $Pb_3(AsO_4)_2$ and $PbHAsO_4$, and also upon the analysis of a number of samples from some of the leading manufacturers, it is evident that most commercial grades carry from 25 per cent. to 33 per cent. of As_2O_3 in the moisture-free product. As the solubility of these lead arsenates is low the variation within these limits is slight and a solubility factor may be determined which introduces no appreciable error within this range.

Lead arsenate is generally put on the market in air-tight containers in order to keep it in a moist condition until ready for use. After it has once been dried it is much more difficult to keep in suspension. This fact suggested the relative rate of solubilities of the dry arsenate and the commercial form which usually contains about 40 per cent. to 60 per cent. moisture. Investigation showed that the moist sample reached its maximum solubility in about 18 hours,

while the dry sample required several days. Because of this difference in the rate of solubility it is better to determine the water and then weigh out an amount of the moist sample equivalent to two grams of dry lead arsenate. All the following determinations were made on moist samples. To overcome the inconvenience of washing the moist sample from a weighing tube or watch glass, a small piece of oiled-paper may be balanced on the pan. The sample is weighed on this paper and the paper then transferred to the jar. It is necessary to stir the sample well into suspension with a glass rod before placing the jar in the thermostat.

Several experiments were made to determine the time required to bring the lead arsenate and water into equilibrium. It was found that with the temperature at 20° C. the maximum time was for all practical purposes not more than 18 hours. Satisfactory results were had where stirring had been continued only twelve hours. This makes it easily possible to complete the determination the second day. By the A. O. A. C. method the report is delayed until the eleventh day.

When 500 cc. jars are used as in these experiments, a 200 cc. portion of the solution is a satisfactory amount for analysis. Most lead arsenate solutions do not subside rapidly. In order to obtain a solution free from solid lead arsenate it is usually necessary to pour the contents of the jar on a filter and take the sample for analysis from the filtrate. In a few samples of commercial lead arsenate, small amounts of arsenious oxide were found. The exact amount may readily be determined by simply adding to this 200 cc. portion, the starch and bi-carbonate and titrating with a standard iodine solution.

The addition of bi-carbonate, starch and iodine solution does not interfere with the subsequent determination of arsenic oxide. In the reduction the bicarbonate is neutralized, the starch is converted into sugar and in the acid solution the iodine becomes a reducing agent. Since arsenious oxide is not always present, it is desirable to test for it qualitatively in a part of the solution remaining after the two samples of 200 cc. each have been taken.

The reduction of the arsenic oxide to arsenious oxide in the 200 cc. sample is readily accomplished by the modified method of Mohr. In this laboratory, 5 cc. of sulphuric acid and one gram of potassium iodide are added to the sample in a 400 cc. beaker and the solution boiled until the volume is reduced to 40 or 50 cc. The solution is then cooled and diluted to about 150 cc. In most cases the iodine will not all have been removed and the solution will retain a yellow color. This excess of iodine is removed by the addition of twentieth normal sodium thiosulphate solution added carefully from a burette.

If the flask or beaker is of colorless glass and set on a white plate carefully screened from reflected

colors, it is not necessary to add starch to determine the end point. The addition of the starch here is undesirable as will be noted later, and under these conditions the disappearance of the yellow due to the presence of iodine gives a satisfactory end point.

After the excess of iodine is removed the clear solution is made slightly alkaline. A sodium hydroxid solution is more convenient and rapid for this purpose than sodium carbonate and gives satisfactory results. The solution is again made acid with a few drops of dilute sulphuric acid and stirred well to make certain that all alkali is neutralized; the solution is made alkaline again with sodium bicarbonate and is ready for titration. A considerable excess of bicarbonate, as is sometimes recommended, has not been found necessary in these experiments. The solution is titrated with a standard iodine solution according to the equation given for the oxidation of free arsenious oxid in the original solution. Various comments have been made on the use of starch as an indicator in this reaction and many methods proposed for eliminating its objectionable features. A number of these methods were tried in these experiments. The digestion of the starch in dilute hydrochloric acid for twenty-four hours and subsequent drying at 100° C. for three hours is not entirely without merit, but was not found necessary when a good starch was procured and well boiled. The addition of three drops of a ten per cent. solution of potassium iodide increases the delicacy of the end point when only a part of a cubic centimeter of iodine solution is used. When a larger amount is used the potassium iodide in the iodine solution itself serves the purpose and makes further addition unnecessary.

In a few samples the lead was removed as sulphate before beginning the analysis for arsenic; but, with the amount of lead present in these samples, its presence was not found objectionable. The number of cases in which this was investigated, however, and the small amounts of lead present in all the samples preclude any generalization as to how far this statement will hold true.

The results thus obtained include all arsenic oxid in solution and are lower than those obtained by the A. O. A. C. method. This is because the solubility of lead arsenate is left out of consideration and the volumes of water are unequal. In order to fix the relation between the results obtained by the two methods it was necessary first to determine the solubility of lead arsenate. Accordingly, a number of samples were prepared in the laboratory and a number of commercial samples were selected and washed as free as possible from by-products with distilled water. The solubility of the lead arsenate in these samples was determined by stirring at 20° in the thermostat and also by the A. O. A. C. method. It was found that the amount of soluble arsenic determined by the A. O. A. C. method was exactly four times as much as that found by the short method, the amounts being directly proportional to the volumes of water used in the different methods. The average of the results obtained by the A. O. A. C.

method calculated to percentage was 0.605 per cent. while the average of the results obtained by the short method was 0.151 per cent. These results include the blank for the end point in the titration. The results obtained by both methods agree very closely. In order to obtain the amount of soluble arsenic not in the form of lead arsenate the above percentage should be subtracted from the total amount of soluble arsenic.

Manufacturers supplied us with 17 samples of lead arsenate which carried various amounts of soluble arsenic oxid. These samples were analyzed for soluble arsenic by the short method outlined above and also by the A. O. A. C. method. The results of these determinations are given in Table I. In this table, column 2 gives the results obtained by the short method; column 3 shows the results obtained by the A. O. A. C. method. No corrections are made in these columns for the solubility of lead arsenate. These results give the total percentage of soluble As_2O_5 . These samples contained no soluble arsenious

TABLE I.

Lab. no. of sample.	Per cent. of soluble arsenic by short method.	Per cent. soluble arsenic by A. O. A. C. method.	Per cent. soluble arsenic. Short method	Per cent. soluble arsenic.
			corrected for solubility of lead arsenate.	corrected for solubility of lead arsenate.
1	0.26	0.70	0.11	0.10
2	0.37	0.81	0.22	0.21
3	0.37	0.85	0.22	0.25
4	0.44	0.83	0.29	0.23
5	0.40	0.85	0.25	0.25
6	0.40	0.91	0.25	0.31
7	0.41	0.92	0.26	0.32
8	0.44	0.92	0.29	0.32
9	0.46	0.96	0.31	0.36
10	0.66	1.12	0.35	0.52
11	0.77	1.26	0.62	0.66
12	0.96	1.50	0.81	0.90
13	1.22	1.79	1.07	1.19
14	1.42	1.98	1.27	1.38
15	1.99	2.50	1.84	1.90
16	2.61	3.03	2.46	2.43
17	3.24	3.78	3.09	3.18

oxid. Column 4 shows the results obtained by the short method after subtracting the factor 0.151 per cent. for the solubility of the arsenate of lead. Column 5 shows the results by the A. O. A. C. method after making the correction of 0.605 per cent. The results given in columns 4 and 5 are practically identical.

Referring still to the table it is at once obvious that by correcting for the solubility of lead arsenate that the results determined by either method may be quickly changed to terms of the other. The corrected results obtained by the short method give only the soluble arsenic oxid uncombined with lead oxid. On this account it more truly tells the nature and quality of any commercial lead arsenate.

The A. O. A. C. method gives results uniformly 0.605 per cent. higher than the corrected results given by the shorter method. Stated otherwise, when 0.605 per cent. is added to the results obtained by this method the results become the same as those obtained by the A. O. A. C. method and with the expense of much less time. The result of this method

as given in column 4 gives the soluble arsenic oxid not combined with lead oxid.

The method outlined in this paper gives a rapid and accurate procedure for determining soluble arsenic oxid in commercial lead arsenate. It is pointed out that the solubility of lead arsenate affects the total amount of soluble arsenic oxid and a correction is worked out which gives the amount of soluble arsenic oxid not combined with lead oxid.

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VALUATION OF FLUORSPAR.

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In the commercial analysis of fluorspar the determinations usually required are calcium fluoride, silica and calcium carbonate; in some particular cases lead, iron, zinc and sulfur. We have received several calls for percentage of barium sulfate but the most careful qualitative tests have failed to show the presence of this mineral, as will be shown later, in either what is known as Rosiclare or Fairview fluorspar.

There is no practical method for the separation of fluorine from silica and of determining fluorine direct in its ore, which answers the commercial requirements of a mine laboratory. The usual practice followed by most chemists is to determine the total calcium oxide and to calculate from this the amount of calcium fluoride, after deducting the amount equal to the calcium carbonate present, this latter being determined from a separate sample in the usual way by absorbing the liberated carbonic acid in soda-lime tubes. This method would be correct if all the calcium present were combined with either carbonic acid or fluorine and all the carbonic acid present combined with calcium. The first assumption is probably correct as all our experiments go to prove this, but the latter we know is wrong, for lead carbonate, zinc carbonate and iron carbonate are frequently present, especially in the gravel fluorspar. Consequently, the calculated amount for calcium carbonate will be too high and the calcium fluoride in consequence will be too low.

In view of the above error, I have found it better to dissolve all carbonates from the sample by acetic acid, leaving the calcium fluoride and silica as a residue on the filter ready for the determination of both silica and calcium fluoride. It must be remembered that calcium fluoride is slightly soluble in acetic acid. I have reduced this solubility to a factor which I use in my calculations. Generally the amount of calcium carbonate present is greatly in excess of the other carbonates, so that frequently it will be sufficiently accurate for commercial purposes to report the amount soluble in acetic acid after deducting the amount of calcium fluoride soluble in this acid as calcium carbonate. It is to be remembered that at this point there is opportunity for another small error

which, however, is limited, varying with the amount of base metals present; should they be present in considerable quantities the residue must be weighed, after drying at 110° C., to avoid an error caused by their oxidation. Ordinarily, however, this oxidation is so small that it need not be taken into account. In the separation of carbonates and ignition of residue, the loss will also include small amounts of water, volatile and organic matter. The residue left insoluble in acetic acid contains all the silica originally present in the ore. The silica is now determined by volatilizing the same as silicon fluoride. The presence of sulfides of iron, zinc and lead must be considered, and for this reason I have found it best to oxidize the sulfides in the residue by heating with mercuric oxide before evaporating with hydrofluoric acid. In this operation lead sulfide is entirely oxidized to lead sulfate, but the ferruginous zinc sulfide is but slightly acted upon and remains unaffected by hydrofluoric acid, in so far as final results are concerned, as shown by analysis of synthetical samples of known percentages.

In regard to the determination of calcium fluoride, I avoid decomposing the sample and eliminate the calcium fluoride by treating the residue obtained from the silica determination with hydrofluoric acid to transform the iron oxide into iron fluoride and extracting the same together with the lead and zinc by solution of ammonium acetate containing ammonium citrate. The method as used at present follows:

Weigh into a small Erlenmeyer flask one gram of the finely powdered sample, add 10 cc. of ten per cent. acetic acid, cover with a short-stemmed glass funnel and heat on a water bath for one hour, agitating from time to time. Filter through a 7 cm. ashless filter, wash with warm water four times and burn off the filter paper in a weighed platinum crucible at a temperature as low as possible. The loss in weight minus 0.0015 gram (the amount of calcium fluoride soluble in acetic acid under the conditions named) is calcium carbonate.

Add to the residue in the platinum crucible about one gram of yellow mercuric oxide in the form of an emulsion in water; break up any hard lumps that may have formed; evaporate to dryness and heat to a dull red heat; cool and weigh. Add about 2 cc. of hydrofluoric acid and evaporate to dryness, repeating this operation twice, using 1 cc. of hydrofluoric acid in each of the last two operations. Add a few drops of hydrofluoric acid and some macerated filter paper, as recommended by Dittrich, then a few drops of ammonium hydroxide to precipitate the iron and evaporate to dryness. Heat to a dull red heat, cool and weigh; the loss in weight is reported as silica. Now add 2 cc. of hydrofluoric acid and a few drops of nitric acid, cover the crucible with its lid and place on a moderately warm water bath thirty minutes; remove the lid and evaporate to dryness. If the contents of the crucible are not now perfectly white, evaporate again with hydrofluoric acid, add a few drops of hydrofluoric acid and 10 cc. of the solution of ammonium acetate (this ammonium acetate is