

THE ANALYSIS OF LITHOPONE.*

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THE chief estimations required for the technical valuation of lithopone comprise the determination of the zinc sulphide, zinc oxide, and barium sulphate. Several other zinc compounds have been shown to be present, in varying amounts, in the mixture, such as the carbonate, normal sulphate, and basic sulphate. Coffignier (*Bull. Soc. Chim.*, 1902, **27**, 829, 943) has also drawn attention to the occurrence of soluble salts of zinc and of the hydroxy-sulphide $\text{Zn} \begin{smallmatrix} \text{OH} \\ \text{SH} \end{smallmatrix}$ in cases where the product has been imperfectly calcined; but such constituents are to be regarded as abnormal, and should not be present in lithopones that have been properly prepared and washed. In addition, lithopone sometimes contains a small proportion of barium carbonate, and traces of impurities, including ferric oxide, alumina, lime, and magnesia. Whilst the determination of these secondary products is seldom required, their presence is of importance in selecting a method of analysis. This is especially the case in regard to the influence of the iron and calcium on the estimation of the zinc, and also in regard to the possible presence of zinc compounds, other than the sulphide and oxide, as any soluble salts of zinc are, of course, of no value as a pigment. The presence of barium carbonate can be readily determined by a separate estimation if required.

The numerous methods that have been proposed for the analysis of lithopone consist in the determination of the total zinc, the total sulphide, and the barium sulphate. By calculating the total sulphide to zinc sulphide, and subtracting its equivalent in zinc from the total zinc found, the proportion of zinc other than

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sulphide is calculated and generally expressed as oxide. As a check on this last factor, the zinc oxide and carbonate can be extracted either with dilute acetic acid or with a mixture of sodium acetate and acetic acid, and estimated separately.

These determinations have involved simply a combination of ordinary methods of analysis, of which the following may serve as examples:

P. Drawe (*Zeitsch. angew. Chem.*, 1902, **15**, 174, 229, 297) estimates the total zinc by precipitation as carbonate and the zinc present as sulphide by treating the sample with 1 per cent. acetic acid, to remove the oxide and carbonate, and precipitating the remaining zinc again as carbonate. Kochs and Seyfert (*Zeitsch. angew. Chem.*, 1902, **15**, 802) precipitate the total zinc as sulphide, and estimate the oxide and carbonate by solution in 5 per cent. acetic acid and precipitation as sulphide. Amsel (*Zeitsch. angew. Chem.*, 1902, **15**, 174) also extracts the oxide with 5 per cent. acetic acid, and estimates both it and the total zinc volumetrically by titration with calcium ferrocyanide. For the estimation of the sulphide-sulphur as an indirect means of determining the content of zinc sulphide, J. F. Sacher (*Farbenzeitung*, 1910, **15**, 1810) recommends treatment with metallic tin and hydrochloric acid, passing the evolved sulphuretted hydrogen into an ammoniacal solution of hydrogen peroxide, and precipitating the ammonium sulphate formed with barium chloride, whilst H. Wolff (*Farbenzeitung*, 1910, **15**, 1859) estimates the sulphuretted hydrogen volumetrically by absorbing it in iodine solution, and titrating back the excess of the latter with thiosulphate. J. S. Remington and C. Smith (*Caoutchouc and Gutta-Percha*, 1909, **6**, 3259) estimate the sulphide-sulphur by oxidation with bromine and precipitation as sulphate, and the total zinc as carbonate, or, if salts of iron, calcium, or barium (soluble in hydrochloric acid) are present, as sulphide.

The alternative to these many proposals that we recommend is to estimate the total zinc volumetrically and the zinc sulphide indirectly by oxidising the sulphide-sulphur to sulphate. The gravimetric estimation of the zinc as carbonate is inaccurate in presence of calcium and iron, both of which are usually present, and precipitation as sulphide is a tedious determination. A direct estimation of the sulphide-sulphur is especially desirable, as the value of the pigment is chiefly dependent on the proportion of zinc sulphide present, and of the various methods available oxidation followed by precipitation is simpler and easier to carry out than the determination of the sulphuretted hydrogen evolved on decomposition.

For the volumetric estimation of the zinc we have employed a method devised by A. Voigt (*Zeitsch. angew. Chem.*, 1889, **2**, 307) for the analysis of zinc ores and products which is sufficiently accurate for the estimation, and which has the advantage that the results are not affected by the presence of iron or calcium. For the oxidation of the sulphide-sulphur either bromine or nitric acid may be used; we have found the former preferable, and carry out the estimation on the same lines as proposed by Remington and Smith (*loc. cit.*). Whilst, therefore, there is no claim to originality in the methods employed, we have found the combination adopted more rapid and adaptable than previous proposals, and sufficiently accurate for technical purposes.

The method of analysis is as follows: 5 grms. of the finely-ground sample are treated with concentrated hydrochloric acid and a little potassium chlorate, the

whole evaporated to a small bulk on the water-bath, taken up with boiling water, and the residual barium sulphate filtered off and thoroughly washed. The filtrate is collected in a 250 c.c. graduated flask, made up to the mark, and aliquot portions taken for the estimation of the total zinc by Voigt's method. The potassium ferrocyanide solution is made up by dissolving 46 grms. of the crystallised salt in a litre of water, and is standardised by a solution of zinc chloride containing 12.4476 grms. of pure zinc oxide per litre; 1 c.c. of this solution is equivalent to 0.01 gm. of zinc. For the estimation, 50 c.c. of the above filtrate are taken, 10 c.c. of a solution of tartaric acid (200 grms. per litre) and 10 c.c. of a solution of ferric chloride (60 grms. per litre) added, the whole diluted to about 200 c.c., made just alkaline with ammonia, and titrated; the completion of the reaction is determined by adding a drop of the solution to dilute acetic acid (1 : 3) on a pitted porcelain plate until a permanent blue colour is produced. After a preliminary estimation a sharp end-reaction is easily secured, and it is not affected by the presence of an excess of ammonia. In a series of tests made, in which the quantity of ammonia added was increased up to twice the amount necessary for neutralisation, the maximum difference in the titrations did not exceed 0.15 c.c.

For the estimation of the sulphide-sulphur, 0.5 gm. of the sample is oxidised with bromine, after the addition of water, hydrochloric acid added, the residual barium sulphate filtered off, and the sulphuric acid in the filtrate precipitated by barium chloride. By calculating the sulphur thus found to zinc sulphide, and subtracting its equivalent of zinc from the total zinc estimated volumetrically, the content of zinc, other than sulphide, is obtained by difference, as stated above.

The following results were obtained by this method with three different samples of lithopone; the zinc, other than that present as sulphide, is calculated as oxide :

	I.	II.	III.
BaSO ₄	64.36	67.59	72.80
ZnS	30.98	27.82	24.14
ZnO	0.55	1.82	0.88
CaO, Fe ₂ O ₃ , BaCO ₃ , Moisture, etc.	4.11	2.77	2.18
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

As a check upon the volumetric estimation of the zinc, that in Sample No. 1 was also estimated by precipitation as sulphide, the result obtained being 21.44 per cent. zinc, as against 21.20 per cent. by titration. The indirect determination of the zinc oxide was also checked by treating 2 grms. of each sample with 5 per cent. acetic acid at the ordinary temperature for one hour, with occasional agitation, the dissolved zinc filtered off, precipitated as sulphide, and finally estimated as oxide in the usual manner. The results obtained were as follows :

	I.	II.	III.
ZnO (calculated)	0.55	1.82	0.88
ZnO (estimated by precipitation) ...	0.75	1.70	0.90

These data confirm the reliability of the indirect method of estimation, and also show that the zinc, other than sulphide, in the samples analysed is practically all present as oxide.

DISCUSSION.

The PRESIDENT said that the specimens of lithopone that passed through his hands were usually ground in oil. Those who were experienced in work of this kind would know that it was never possible to extract the oil completely; some oxidised oil always remained unextracted, and this caused difficulty in the estimation of the sulphide sulphur by oxidation with bromine in an acid solution. His practice was first of all to add some caustic soda to the extracted lithopone, and then pour in the liquid bromine and acidify. Under those conditions no globules of sulphur or sulphur bromide escaped oxidation. With regard to the estimation of the zinc, he could understand that, in laboratories where such estimations were made very frequently, it would be worth while to use a volumetric process; but, when it was only necessary to make such estimations occasionally, a gravimetric process was, perhaps, equally expeditious. He should like to ask whether the authors had tried precipitating the zinc in a solution containing a minute trace of free mineral acid. Under those conditions the zinc was completely precipitated, and in a granular form. Of course, during the precipitation more acid was set free, and one must be careful to neutralise all but the very faintest trace. In the analyses given by the authors the proportions of what might be called impurities were larger than he had been accustomed to find.

Mr. T. MACARA asked whether the authors had tried the phosphate method of estimating zinc in the case of such a compound as lithopone. He thought that this method, which was proposed by the late Dr. Clark for the estimation of zinc in alloys, etc., would probably work well in such a case as this.

Dr. H. P. STEVENS asked whether the lime shown as CaO in the authors' analyses referred to caustic lime. Lithopone was used in rubber mixings, in which the presence of caustic lime was very undesirable.

The PRESIDENT added that a certain amount of soluble SO_3 was always present, and it was his practice to determine this, calculating it as calcium sulphate; and perhaps if that were done in these cases, some, at any rate, of the lime would appear as calcium sulphate. In many cases the quantities of CaO and of soluble SO_3 found were just equivalent to one another, showing that all the lime was present as calcium sulphate.

Mr. J. H. B. JENKINS asked whether the oxide of iron referred to in the analyses amounted to anything appreciable. One of the advantages of lithopone paint was its dead whiteness, and one would not expect this if any sensible quantity of iron were present. The majority of the samples of lithopone that he had examined contained more barium sulphate relatively to the sulphide of zinc than was shown in the authors' analyses. He believed that in the trade the proportions were supposed to be about 3 parts of barium sulphate to 1 part of zinc sulphide.

Dr. DYER incidentally observed—although, of course, the remark did not apply to genuine "lithopone"—that mixed pigments containing barium sulphate in the form of barytes sometimes contained considerable quantities of calcium fluoride, owing to admixture of fluor spar with the heavy spar from which the barytes was ground. He mentioned this because he had seen no published reference to it, and

it was at first puzzling to find a considerable quantity of calcium present in a form other than the familiar carbonate or sulphate.

Dr. KEANE, in reply, agreed that the method of estimating zinc as phosphate was an excellent one, but they wished to employ a volumetric rather than a gravimetric method, in order that the process might be as useful as possible for works purposes. He also agreed with the President as to the advantages of precipitating the zinc in the presence of a trace of mineral acid. Up to the present they had not had occasion to deal with small quantities of organic matter, such as would be derived from oil, but, in another connection, he had found that organic matter could be effectively got rid of by electrolysing the solution in presence of dilute nitric acid. In that way, even in the case of animal products containing a good deal of organic matter, a crystal-clear solution could be obtained containing no trace of organic matter. With regard to the lime, this undoubtedly was not present as such, but probably to some extent as sulphate, and as sulphide and carbonate. Of course, by estimating the soluble constituents one could always, if it were desired to do so, calculate the lime to calcium sulphate, as suggested by the President. The quantity of iron present was small, usually no more than a trace. The moisture was occasionally rather high, sometimes as much as 1 per cent. Of the samples analysed, the first was made in Germany, the other two being English products ; there are, of course, considerable variations in the relative proportions of barium sulphate and zinc sulphide in lithopones.

