

Further uniformity of results might be expected if we could locate more precisely the point wherein the variation occurs. This feature of the case is receiving further study.

As bearing somewhat on the case, the following table is submitted. If any interpretation can be attempted from these results it would seem to be that the higher results are not always to be credited to the larger burner and the higher temperature. It is more likely that coals vary as to the ease or completeness with which they part with their last residuum of gas.

I am indebted to Mr. F. W. Whittum and Mr. J. M. Lindgren for the analytical results accompanying this paper.

TABLE III.

Table No.	Lab. No.	Kind of coal.	A. Standard method with kerosene, Sargent burner.	B. Standard method with kerosene, Fletcher burner.	B compared with A variation + or -.
1	117	Vermilion Co., Ill.	38.33	39.44	+1.11
2	128	Saline Co., Ill.	36.64	37.11	+0.47
3	214	Lignite, Mississippi.	44.29	44.35	+0.06
4	1762	Sangamon Co., Ill.	40.04	39.84	-0.20
5	1809	Williamson Co., Ill.	37.46	37.78	+0.32
6	1810	Franklin Co., Ill.	34.68	35.18	+0.50
7	1870	Christian Co., Ill.	39.31	39.65	+0.34
8	1878	Jackson Co., Ill.	34.53	34.22	-0.31
9	2902	Williamson Co., Ill.	33.77	34.16	+0.39
10	4083	Vermilion Co., Ill.	36.58	36.29	-0.29
11	4130	Franklin Co., Ill.	36.56	36.99	+0.43

In column A, the burner used is illustrated as No. 1000 in Sargent's catalogue. It has an internal diameter of 9 mm.

In column B, the Fletcher burner had an internal diameter of 11 mm.

UNIVERSITY OF ILLINOIS,
URBANA.

SOME NEW FEATURES IN THE ELECTROLYTIC DETERMINATION OF LEAD.

By JOHN G. FAIRCHILD.

Received Sept. 28, 1911.

It has been found that good deposits of lead peroxide, free from flakes and of close texture, can be obtained on a smooth platinum cylinder in two hours' time without rotation, and as much as 100-200 mg. in weight. This can be raised to 300 mg. but there is danger of flaking off. The secret of success is a low amperage to begin with and a hot solution, 50°-60° C.

For alloys high in lead two grams or more are weighed out and an aliquot taken to represent about 0.1 gram of metallic lead. The volume of electrolyte is 200 cc. in a 250 cc. beaker, and contains 30 cc. strong HNO₃. Heat to 50°-60° C., using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode should be burnished frequently and ignited previous to placing in the electrolyte. This ignition removes any greasy film adhering to the cylinder. Split cover glasses are used to prevent loss through

evaporation of the hot solution, which just completely immerses the edge of the anode cylinder. The current is started at 0.25 am. for one hour and a half when it is raised to 0.5 am. for half an hour longer to remove the last traces of lead, and the cover glasses are rinsed down. At the end of two hours deposition is complete, as shown by the newly immersed stem remaining bright. The beaker is lowered and removed, being replaced by one containing clean water for rinsing the cylinders, which are then disconnected, the anode being rinsed in a glass of alcohol, drawn through a flame to burn off what adheres while holding the cylinder in a vertical position. It is then held for a few seconds about a foot above the flame to dry thoroughly, and weighed. On adding ammonia to the electrolyte and passing H₂S, no more than a mere brownish color should show.

To prove the accuracy of this method, purified lead sulphate was taken as the standard. An amount equal to 0.7335 gram was put into a 500 cc. flask and dissolved in just enough hot am. acetate solution, 100 cc. being taken for analysis by means of a pipette standardized to the flask. After adding 30 cc. HNO₃ of 1.42 sp. gr., this aliquot was made up to 200 cc. The electrolyte is best kept hot throughout the run by means of a hot plate or burner. The results for lead sulphate and test lead were as follows:

PbSO ₄ .	PbO ₂ equiv.	PbO ₂ found.	Pb. Per cent. ¹
0.1467	0.1157	0.1156	99.92
0.1467	0.1157	0.1160	100.26
0.1467	0.1157	0.1155	99.83
0.1467	0.1157	0.1159	100.17
Test lead.			
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1143	98.72
0.1000	0.1157	0.1142	98.63
0.1000	0.1157	0.1147	99.14
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1146	99.04

Whenever a weight was low the lead was found to be not all deposited, due to faulty manipulation which is not likely to occur. If the electrodes short-circuit re-solution occurs with some lead flaking off.

Lead scrap and furnace dross can be treated thus: About 5 grams are dissolved in HNO₃ + H₂SO₄ in a Kjeldahl flask and evaporated till fumes appear. After cooling, the impure PbSO₄ is filtered off, the paper punctured and the precipitate rinsed back into the flask. It is then treated with just sufficient hot saturated am. acetate solution, which is warmed till solution is complete, then filtered into a 500 cc. flask, a proper portion being taken for electrolysis.

On comparison with pure lead it will be seen that material relatively low in lead will require only about half an hour at 0.5 am., a small percentage of lead being given a higher amperage. In this way can lead be readily separated from copper, manganese, silver, antimony, etc.? When a relatively large amount of copper is present, as in blister copper, only 20 cc. nitric acid may be present. The presence or absence of am. nitrate seemed to have no effect on the results.

This method gives lower results than the chromate method; thus, by the latter 59.25 per cent. lead was

¹ Conversion factor 0.866.

found in a lead dross, by the electrolytic 58.85 per cent. On a copper matte high in lead, the figures gave 10.57 chromate, 10.32 electrolytic.

Material such as a copper matte can be dissolved in HNO_3 , the sulphur globule oxidized by adding KClO_3 crystals, then heated with H_2SO_4 till fumes come off.

The voltage of the hot solution is 2-2.5 volts. A straight platinum wire was first tried as cathode but metallic lead deposited on it. Also, with 1 ampere of current metallic lead deposits on the cathode. Even with a weak current in a cold solution there is danger of metallic lead separating. Results are best obtained with a low voltage and low current density.

In the early experiments, whenever lead sulphate was involved, this was changed to carbonate by digestion with ammonium carbonate, and the lead carbonate was dissolved in dilute nitric acid. These steps were soon found to be unnecessary, the simple solution of the lead sulphate in am. acetate greatly shortening the method.

U. S. GEOLOGICAL SURVEY,
WASHINGTON, D. C.

NAPHTHALENE IN ROAD TARS. I. THE EFFECT OF NAPHTHALENE UPON THE CONSISTENCY OF REFINED TARS.

By PREVOST HUBBARD AND C. N. DRAPER.

Received November 6, 1911.

Naphthalene, C_{10}H_8 , often occurs in coal tar in larger quantities than any other one hydrocarbon and for this reason it is natural to suppose that it exerts an appreciable influence upon the quality and applicability of coal tars used as road binders. In this country the use of tars in road treatment and construction has advanced rapidly during the past few years and upon the market to-day are to be found a number of tar preparations intended for such use. These preparations are as a rule made by distilling off the lighter and more volatile constituents from both crude coal tar and crude water-gas tar or mixtures of the two. The residual products, which vary in consistency according to the extent and method of distillation, are sold for road purposes. Many successes and many failures have resulted from the use of coal tar and water-gas tar road binders, and often no clew has been obtainable as to the reason for such diverse results. In view of this fact, a systematic study of the principal chemical constituents of road-tar preparations and their effect upon the quality of such preparations is now being made in the laboratories of the Office of Public Roads, United States Department of Agriculture.

In the present paper, which is the first of a series upon naphthalene, no attempt will be made to review the chemistry of this substance, since this discussion is reserved for a later publication which will cover the entire subject as presented in the individual papers. A few remarks concerning certain physical properties

of naphthalene may, however, not be amiss at this point.

Naphthalene, in the pure state, exists in white crystalline masses of thin rhomboidal scales melting at 79°C . and having a boiling point of 218°C . Its specific gravity at 15°C . is 1.1517. It has a very characteristic odor, commonly familiar in moth balls, and is extremely volatile, considering its high molecular weight, so much so that in the manufacture of coal gas it is only partially deposited in the condensers, while the remainder is carried into the purifiers and into the gas mains, where it deposits in the bends of pipes during cold weather and often causes them to become clogged. Naphthalene volatilizes far below its boiling point and, in crude tars, distills to a considerable extent with aqueous vapor and also with the light tar oils, which accounts for its occurrence in the first fractions. Even at ordinary temperatures, it volatilizes slowly and gives off a penetrating tarry odor. It is slightly soluble in hot water, but dissolves easily in alcohol, ether, fatty and essential oils, acetic acid, and especially in the phenols and lighter tar distillates. No entirely satisfactory method for the quantitative determination of naphthalene in tar has, as far as the authors are aware, been devised up to the present time, although methods have been put forth by various investigators for the determination of naphthalene in illuminating gas.

It is a rather generally accepted theory that, in the manufacture of coal gas, the formation of naphthalene is due to certain complex reactions which take place only at the high temperatures at which the retort is maintained in modern gas-house practice. According to Cooper,¹ "a few years ago—when lower temperatures were in vogue, and when lower makes per ton of coal carbonized were registered—naphthalene was an almost unknown quantity; but now that the stress of competition demands the highest possible output of gas, it seems also to bring in its train the formation of large quantities of naphthalene." It is certain, however, that other factors, such as the size, shape, and inclination of the retort with relation to the volume of the charge of coal, and the varying conditions to which the evolved gases are subjected before and during their passage from the retort, have a great deal to do with the quantity of naphthalene formed.

Tars used as road binders are for the most part soft pitches obtained by distilling from 15 to 30 per cent. of the lighter products from the crude material. The soft pitch contains a large proportion of the naphthalene which may have been present in the original tar, and it is the study of the effect of naphthalene upon this grade of material that is the subject of this paper. As consistency is one of the most important properties of a road tar, it was thought well first to investigate the effect of varying percentages of naphthalene upon a given tar.

From its very nature naphthalene itself can be considered as a binding material. For some time past it has been known, however, to serve as a flux

¹ Published by permission of Director. Office of Public Roads, U. S. Department of Agriculture.

¹ *J. Gas Light.*, 110, 498 (1910).