velopment of heat on moistening dry coal, support this theory. The heat development by the moistening of dry coal may contribute appreciably to the spontaneous heating of some coals in storage.

APPLICATION OF THE DIMETHYL SULFATE TEST FOR DETERMINING SMALL AMOUNTS OF PETROLEUM OR ASPHALT PRODUCTS IN TARS¹

By CHARLES S. REEVE AND RICHARD H. LEWIS

INTRODUCTORY

The recent production of mixtures of tar with various asphalt and petroleum products for use in the road and paving industry has necessitated a satisfactory method for determining the proportions of each type of material present in such mixtures. The authors have based their research on the well-known dimethyl sulfate test proposed by Valenta² and later investigated and reported upon by Graefe³ and Harrison and Perkin.⁴ A. Sommer⁵ modified the test in order to render it applicable for the estimation of asphalt in tar-asphalt mixtures, and Chapin⁶ now uses it in a modified form for the detection of adulterants in coal tar creosote sheep dips. A brief review of the literature upon the test to date will, therefore, prove of value, before submitting our data.

THE DIMETHYL SULFATE TEST

Valenta's purpose in originating the test was to determine the amount of tar oils present as an adulterant in paraffin and rosin oils, and he claimed as a result of his investigations that while aromatic hydrocarbons are freely miscible with dimethyl sulfate, the open-chain hydrocarbons are entirely insoluble in that reagent. It was, therefore, only necessary to thoroughly agitate a measured volume of the sample under examination with a measured volume of dimethyl sulfate, and the increased volume of the latter would indicate the amount of aromatic hydrocarbons which had gone into solution. This is in general, but not absolutely, correct, and the real facts regarding the test as brought out by later investigations are briefly summed up by Chapin as follows:⁷

"1. Aromatic hydrocarbons and derivatives thereof are completely soluble in dimethyl sulfate, being miscible in all proportions.

"2. Open-chain hydrocarbons show varying degrees of solubility in dimethyl sulfate, ranging from zero to a considerable percentage, light oils as a rule being the more soluble.

"3. Treatment of a mixture of aromatic and open-chain hydrocarbons with dimethyl sulfate results in the formation of two layers; the upper contains most of the open-chain hydrocarbons plus a varying but usually small amount of aromatic hydrocarbons retained in solution; the lower layer contains practically all of the dimethyl sulfate, holding in solution most of the aromatic hydrocarbons plus a varying

but usually small amount of the open-chain hydrocarbons.

"The test, therefore, is no absolutely quantitative one, as indeed is to be expected from the laws of solubility. Results obtained thereby may, however, under favorable circumstances, closely approach quantitative values, and so may prove very useful for practical work."

In order to make the test applicable to solid and semi-solid bitumens which could not be directly treated with the reagent, A. Sommer⁵ proposed distilling the sample to coke.

"Four cc. of the distillate obtained are then put in a ten cc. graduated cylinder with ground glass stopper and six cc. of dimethyl sulfate are added and shaken thoroughly for one minute. If the distillate is not entirely soluble, separation takes place within a few minutes and a separating mark can be accurately read. The percentage of solubility is calculated from this reading."

His results show that not only the open-chain hydrocarbons but also the distillates from native bitumens—largely polymethylenes—are insoluble in dimethyl sulfate. A mixture of 20 per cent. tar and 80 per cent. asphalt yields a distillate which is 15 per cent. soluble in the reagent, while a mixture of 80 per cent. tar and 20 per cent. asphalt yields a distillate which is 60 per cent. soluble. These are the extreme proportions reported upon by him. The authors, upon attempting to detect 10 per cent. of asphalt in several tar asphalt mixtures, failed to get any indication of its presence by this method, and since some current specifications provide for smaller proportions than 10 per cent., the necessity for a more delicate modification of the method gave rise to the following research.

EXPERIMENTAL

A consideration of the conditions involved in Sommer's method of operation led us to the obvious conclusion that when 10 parts of a hard oil asphalt is fluxed with 90 parts of a fluid coal tar, the total distillate obtained by destructively distilling such a mixture to coke would contain but a very small percentage of anything but aromatic hydrocarbons. Since it is known, and will be again demonstrated, that such distillates are slightly soluble in dimethyl sulfate, such a small percentage in a 4 cc. sample might not be recognized. It was, therefore, thought probable that the procedure suggested by Chapin, *i. e.*, to work on separate fractions of high boiling point, might lead to our finding a fraction in which the proportion of other hydrocarbons to aromatic hydrocarbons would be sufficiently large to permit of the former being easily detected. In order to determine just which fractions might prove of most value, several varieties of products which are being used in tar-asphalt mixtures were first distilled and their higher boiling fractions tested by means of dimethyl sulfate in the method prescribed by Sommer. The distillation was made in an 8-ounce glass retort with the top of the thermometer bulb on a level with the bottom juncture of stem and body of the retort. A 100 cc.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² *Chem. Ztg.*, **30**, 266-7 (1906).

³ *Chemische Revue ueber die Fett- und Harz-Industrie*, **14**, 112-5 (1907).

⁴ *Analyst*, **33**, 2-11 (1908).

⁵ *THIS JOURNAL*, **2**, No. 5 (1910).

⁶ U. S. Dept. Agric., *Circular* **167**.

⁷ *Ibid.*, **167**, 2.

¹ *Loc. cit.*

sample was taken and Table I shows the results obtained. It will be understood that volume percentages are referred to throughout this paper unless otherwise noted.

TABLE I—DIMETHYL SULFATE TESTS ON DISTILLATES

Number of sample	Name of material	270-315° C.		315-350° C.		350-375° C.	
		Percentage distillate by volume	Percentage insoluble in (CH ₃) ₂ SO ₄	Percentage distillate by volume	Percentage insoluble in (CH ₃) ₂ SO ₄	Percentage distillate by volume	Percentage insoluble in (CH ₃) ₂ SO ₄
1	Oil asphalt Penetration 3.6 mm.	2.2	no test	11.8	80.0	28.8	90.0
2	Oil asphalt Penetration 17.0 mm.	3.7	no test	15.5	85.0	28.0	90.0
3	Oil asphalt Penetration 15.2 mm.	3.2	no test	16.8	87.5	17.2	90.0
4	California oil asphalt Penetration 7.3 mm.	13.0	85.0	32.5	82.5	7.0	75.0
5	Fluxed Bermudez asphalt Penetration 12.2 mm.	4.0	no test	12.0	85.0	17.1	85.0
6	Residual petroleum Specific viscosity Engler 50° C.—65.1	0.6	no test	6.8	90.0	25.2	90.0

It will be noted that in every case, except No. 4, the dimethyl sulfate insoluble tends to be greater in the higher fractions. The 270-315° C. fractions are too small for making the dimethyl tests with one exception, which in a measure indicates that it would be impossible to detect their presence in such fractions from mixtures containing small amounts of petroleum or asphaltic compounds.

These materials were then mixed with a crude coke-oven tar whose characteristics were as follows:

TABLE II—TESTS ON CRUDE COKE OVEN TAR

General character.....	Thin fluid
Specific gravity.....	1.173
Soluble in CS ₂	95.23%
Insoluble in CS ₂ (free carbon).....	4.71%
Ash.....	0.06%

DISTILLATION

Fractions	Percentage by volume	Percentage by weight	Character of distillates	Insoluble in (CH ₃) ₂ SO ₄
Water	0.6	0.5	Cloudy	
Up to 110° C.	1.6	1.3	Clear	None
110-170° C.	0.8	0.6	Clear	None
170-270° C.	17.5	15.5	1/2 solid	None
270-315° C.	9.4	8.2	1/3 solid	None
315-350° C.	11.0	9.7	Solid	None
350-375° C.	9.7	8.4	Solid	None
Pitch (over 375° C.)	49.4	55.8	Hard, brittle, glossy	
	100.0	100.0		

The mixtures were made, unless otherwise stated, by adding the given percentage by weight of petroleum or asphaltic product to the weighed amount of tar. The materials when necessary were rendered fluid by heating before mixing and in no case was there any separation of oil apparent. Distillations were then made in the manner above referred to, and fractions were taken at 270° C., 315° C., 350° C., and 375° C. Four cc. of the distillate from each fraction were treated with 6 cc. of dimethyl sulfate in a 10 cc. cylinder graduated to 0.2 cc. The resulting supernatant layer of insoluble oil was read and calculated to its percentage of the volume of sample taken. The results are shown in the following tables.

TABLE III—TESTS ON DISTILLATES FROM 10% MIXTURE

No. of sample	Mixture	315-350° C. fraction		350-375° C. fraction	
		Percentage distillate	Percentage insoluble in (CH ₃) ₂ SO ₄	Percentage distillate	Percentage insoluble in (CH ₃) ₂ SO ₄
1	90% coke oven tar 10% oil asphalt No. 2	11.5	5.0	17.5	25.0
2	90% coke oven tar 10% fluxed Bermudez asphalt	12.0	5.0	13.2	12.5
3	90% coke oven tar 10% residual petroleum	11.6	10.0	13.0	22.5
4(a)	Refined tar preparation Free carbon = 19.36%	14.0	15.0	12.2	18.0
(a)	Said to contain 10% oil asphalt.				

In these 10 per cent. mixtures an excellent indication of the presence of oil asphalt is shown by the dimethyl sulfate test even in the 315-350° C. fraction, but there was no trace of open-chain compounds in the 270-315° C. fraction. No evidence of an oil product could be found in the total distillate obtained by distilling to coke by Sommer's method.

On account of the ease with which 10 per cent. could be detected by testing separate fractions, the test was not carried out with all the materials.

TABLE IV—TESTS ON DISTILLATES FROM 5% MIXTURES

No. of sample	Mixture	315-350° C. fraction		350-375° C. fraction	
		Percentage distillate	Percentage insoluble in (CH ₃) ₂ SO ₄	Percentage distillate	Percentage insoluble in (CH ₃) ₂ SO ₄
1	95% coke oven tar 5% oil asphalt No. 1	9.2	None	9.4	7.5
2	95% coke oven tar 5% oil asphalt No. 2	15.5	None	9.7	12.5
3	95% coke oven tar 5% oil asphalt No. 3	11.0	2.5	10.2	12.5
4	95% coke oven tar 5% Calif. oil asphalt	9.6	None	10.8	10.0
5	95% coke oven tar 5% fluxed Bermudez asphalt	11.0	None	10.8	8.0
6	95% coke oven tar 5% residual petroleum	8.5	7.5	12.5	12.5

In these 5 per cent. mixtures, the asphaltic base can still be detected in fairly large percentage in the last fraction (350-375° C.), but in only two cases (No. 3 and No. 6) out of six was there present a dimethyl sulfate insoluble in a lower fraction (315-350° C.).

TABLE V—TESTS ON DISTILLATES FROM 3% MIXTURES

No. of sample	Mixture	350-375° C. fraction	
		Percentage distillate	Percentage insoluble in (CH ₃) ₂ SO ₄
1	97% coke oven tar 3% oil asphalt No. 1	9.7	5.0
2	97% coke oven tar 3% oil asphalt No. 2	8.9	5.0
3	97% coke oven tar 3% oil asphalt No. 3	8.7	4.0
4	97% coke oven tar 3% Calif. oil asphalt	7.8	2.5
5	97% coke oven tar 3% fluxed Bermudez asphalt	8.1	1.25
6	97% coke oven tar 3% residual petroleum	10.4	10.0

In the 350-375° C. fraction of the distillations of the 3 per cent. mixture, the insoluble residue ranges

from 10 per cent. to 1.25 per cent. so that the detection of even three per cent. of asphalt is made possible by the method of fractionation which has been employed in this work. The 315°C. to 350°C. fraction did not give the slightest trace of insoluble products.

CONCLUSION

While the above results do not give any absolute idea of either the amount or exact nature of the material which has been fluxed with the tar, the authors feel that the improvement which they have made upon former methods may still prove of value, until a more exact method shall be forthcoming.

Specifications for tar-oil or tar-asphalt mixtures will be useless without some method of checking up the material submitted under them. We now think it possible, however, by specifying the grade and character of both the tar and petroleum or asphalt product to be used, and then obtaining data on similar laboratory mixtures, that we can determine with reasonable certainty whether our specifications are being fulfilled. In order to more closely determine the character of the material which has been fluxed with a tar, a volatilization test in conjunction with the dimethyl sulfate test will no doubt prove of great importance, and we feel that some accumulated data on these two tests will place us in a much safer position for specifying and identifying bituminous mixtures which present such difficulty to the chemist.

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THE DETERMINATION OF OXYGEN IN METALLIC TUNGSTEN POWDER AND SOME NOTES ON THE DETERMINATION OF OXYGEN IN STEEL

By CHARLES MORRIS JOHNSON

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It has been found a distinct advantage both in the manufacture and use of tungsten powders to know their oxygen content. In one of the laboratories

gen in steel; *i. e.*, the ignition of the substance in a stream of hydrogen, which method is credited to Ledebur.

The electrically heated furnace introduced by the author¹ in 1908 for the direct determination of carbon in iron, steel and alloys is utilized in the process which is described in detail in this paper.

Walker and Patrick,² in a paper read at the Eighth International Congress of Applied Chemistry, attack the accuracy of the Ledebur method on the ground that any oxides of manganese or silicon present in the steel would not be reduced. The author regards the Ledebur method as more practical than the proposed new one² above noted; even if the former process does not reveal the total oxygen present, it certainly shows enough of it to furnish a basis for judgment of the quality of the steel. If the steel is sufficiently dirty and poorly melted in actual open-hearth Bessemer or crucible practice to contain oxides of manganese and silicon, then it would surely contain enough oxide of iron to condemn it.

APPARATUS

The arrangement of apparatus is indicated in the drawing and the accompanying notes. The towers (or jars) are the author's design as are also J, I and C, and were first used as part of a combustion train.³ In this laboratory four furnaces are placed side by side. By the use of a Y tube at the outlet of jar F, one train from F to K can be made to serve two furnaces. Of course a separate set of A, B and C is necessary for each furnace. If, after making a large number of determinations, the blank begins to show a gradual increase, the contents of the various jars must be renewed.

METHOD

Blank.—Before introducing anything into the electric furnace, close all points marked "screw pinch cock." At B make a connection with a straight

APPARATUS

- A—Ignited asbestos and dry stick KOH.
- B—Glass wool plugs and P_2O_5 (anhydrous powder)
- C—Solution of KOH.
- D—A clamp to prevent the quartz tube from moving since it was found that results varied if the tube moved back and forth.
- E—Quartz tube.
- F—Ignited asbestos and P_2O_5 in alternate layers.
- G—Ignited asbestos and dry stick KOH in alternate layers.
- H—Asbestos and small lump (size of pea) CaCl_2 in alternate layers.
- I—50 cc. alkaline solution of pyrogallous acid.
- J—50 cc. KOH solution.
- K—Kipp generator (2 quart)

SOLUTIONS

- Potassium hydroxide: 1 gram KOH to 1 cc. water.
- Pyrogallous acid: 3 grams pyrogallous acid and 2 cc. water to 3 cc. KOH solution.
- Kipp Generator: Use stick zinc and dilute hydrochloric acid (1 : 1).

glass tube instead of the U tube shown. Insert

¹ J. Am. Chem. Soc., **30**, 773.

² Proc. 8th Intern. Cong. Appl. Chem., **21**, 139; also THIS JOURNAL, **4**, 799.

³ J. Am. Chem. Soc., **28**, 862.

under the author's direction, this determination is a matter of daily routine. The method involves the same principle used in the determination of oxy-