

refractive index of each fraction at 18° C. determined, and also the percentage of carbon bisulphide in them. The percentage of carbon bisulphide varied from as low as 0.1 to 3.05 per cent. The following table was the result of examining the sample which contained 3.05 per cent. of carbon bisulphide:—

TABLE III.

Distillate in fractions of 10 c.c. each.	Temperature of distillation.	Refractive index at 18°.	Percentage of carbon bisulphide.
	° C.		
10 c.c.	74	1.4791	—
20 "	75	1.4773	—
30 "	76.3	1.4716	—
40 "	77.3	1.4667	4.0
50 "	77.8	1.4637	3.0
60 "	78	1.4625	1.9
70 "	78	1.4617	1.33
80 "	78	1.4618	0.75
90 "	78	1.4619	0.35

In the residue in the flask 0.10 per cent. of carbon bisulphide still remained. This sample was also tested in Abel's flash-point apparatus to see if this amount of carbon bisulphide, viz., 3.05 per cent., could be detected, but with negative result.

In conclusion, I have to thank Prof. W. H. Perkin, F.R.S., for a sample of triethylphosphine, and Mr. J. F. Dunworth for his valuable assistance in carrying out the numerous determinations.

## DISCUSSION.

The CHAIRMAN said the author had apparently come across two new reactions of carbon tetrachloride which might prove to be of considerable theoretical interest. It was interesting to note that the highest amounts of bisulphide stated in the paper did not render the tetrachloride inflammable and he asked whether the author had determined at what percentage of bisulphide such a mixture would become dangerous, as far as fire risks were concerned.

Mr. H. L. TERRY inquired whether any commercial significance could be attached to the examination.

Mr. W. H. COLEMAN asked whether the author had tried the method of estimation of carbon bisulphide by converting it into ammonium thiocyanate by digesting with ammonium sulphide.

Mr. R. E. CROWTHER asked if the presence of carbon bisulphide in the tetrachloride interfered with its use in the estimation of oils and fats by Wijs' method.

Mr. L. G. RADCLIFFE said, in reply to Dr. Knecht's question, he had not been able to settle that point sufficiently to be able to make a definite statement. Chemically pure carbon tetrachloride was very costly, and it was not wise to use it over again for a flash-point test. He had used one sample containing as high as 6 per cent. of carbon bisulphide, and this did not flash. Beyond the 6 per cent. he could not say. In reply to Mr. Terry, he thought that it would undoubtedly be of considerable interest to users of carbon tetrachloride. He had not tried the method mentioned by Mr. Coleman.

## THE PARTIAL MERCERISATION OF COTTON CLOTH.

BY J. H. LESTER, M.Sc.

In a case recently submitted to me for examination, some cotton cloth was found to show under the microscope very marked differences in appearance in different parts of the same fibre. In many places the fibre was straight, full, and round, as is characteristic of mercerised cotton, whereas in other places it was spiral, flattened, and showing the wide central canal of normal raw cotton. It obviously became of interest to inquire as to the cause of this difference, and it was at once noticed that the well mercerised fibres were also much more deeply dyed than those which

were unmercerised; indeed, many of the unmercerised fibres were barely tinted with dye, though the cloth as a whole was of a deep purple colour. A simple further examination sufficed to show in what parts of the cloth or yarn the unmercerised and undyed parts of fibres existed. On dissecting the cloth and examining the yarns, it was seen that there were light patches in each of the hollows or bends produced by the surface contact of the warp and weft threads. It will follow from the above that the undisturbed dyed cloth showed a level and deep shade of dye, but that when the yarns were disturbed, either by tearing or otherwise, the minute light patches became visible. Examination under a very low power magnifying glass showed the effect most clearly. It was, of course, only to be expected that those parts of the cloth or fibre which were most completely mercerised should absorb the dye most completely, but I was greatly surprised to find such apparently enormous differences within such very short distances. In some instances the microscope showed three or four alternate lengths, well dyed and barely tinted, in the same ultimate fibre.

Upon such scanty information as the above, positive though I believe it to be as far as it goes, it would be unwise to found any comprehensive theory, but it appears quite warrantable to suggest that the mercerisation process may act first upon the surface fibres of cotton cloth; and where either the time, the temperature, or the strength of caustic solution are insufficient to effect complete mercerisation, the internal portions of the cloth where the fibres are brought into closest contact, will undergo mercerisation last.

## DISCUSSION.

The CHAIRMAN observed that the conclusion to be derived from the author's observations was that there had been an uneven absorption of tannic acid.

Mr. JULIUS HÜNNER said the difference mentioned would not be anything like so pronounced if the pattern had been dyed with a direct dyeing cotton colour, but being mordanted with tannic acid the basic dye would show up more strongly.

Mr. R. E. CROWTHER inquired whether the warps were heavily sized or whether any precaution had been taken to remove the starch. It appeared to him there were physical differences in the state of the cloth previous to mordanting.

Mr. J. H. LESTER believed that there was a physical difference from place to place in the fibres themselves, and the varying intensity of the dye would follow upon that. As to what the treatment might have been was a matter of surmise. There must have been a fair amount of scouring to have given the cloth the level appearance it had, and also to account for the difference between the light and dark places being practically the same in the warp and the weft.

## Newcastle Section.

Meeting held at Armstrong College on Thursday, 11th February, 1900.

MR. C. J. POTTER IN THE CHAIR.

## THE BASES CONTAINED IN THE TAR FROM OTTO-HILGENSTOCK COKE-OVENS.

BY FREDERICK GEORGE TROBRIDGE, B.Sc.

It was thought that as the conditions of distillation in retort coke-ovens were very different from those in gas retorts, and very different qualities of coal were used in the two cases, the bases in coke-oven tar might exhibit differences from those in gas tar. Accordingly, 100 gallons of tar from Messrs. Priestman's plant of Otto-Hilgenstock coke-ovens, Blaydon-on-Tyne, were washed with a 10 per cent. solution of sulphuric acid, the mixture being kept in a warm place to facilitate the separation of the acid from the tar. About 10 gallons of washings were

obtained of dark, brown-red colour, specific gravity 1.06, having a tarry smell, and still containing 6 per cent. of sulphuric acid. The liquid was first treated with steam in order to remove any volatile non-basic bodies. The residue was then made strongly alkaline by the addition of caustic soda and again treated with steam, 2000 grms. of basic oil being obtained. The bases which did not condense were passed over into dilute hydrochloric acid and were found to consist of ammonia with possibly traces of aliphatic amines.

The residue in the distilling vessel, from which the bases volatile in steam had been removed, contained a considerable amount of basic bodies non-volatile in steam, which separated as a thick tarry mass. On extraction with ether a part dissolved: the residue was a black, almost solid, basic substance, soluble in ethyl acetate; on long standing it set quite hard. The portion soluble in ether was a clear, dark yellow, almost solid base, easily and completely soluble in absolute alcohol, chloroform, benzene, and ethyl acetate, giving strongly fluorescent solutions. These bodies form hydrochlorides insoluble in ether but soluble in water to deep red solutions, which give microcrystalline precipitates with platinic chloride, mercuric chloride, stannous chloride, zinc chloride, and picric acid. On warming, however, the precipitates coagulate to oily masses.

The basic oil volatile in steam was distilled through a rod and disc still-head of 24 discs: the distillation was stopped when the temperature reached 170° C., 24 per cent. coming over below this temperature. Messrs. Brotherton and Co. of the Wear Fuel Works, Sunderland, inform me that about 70 per cent. of the bases from gas-tar distil below 140° C., whereas here we have only 24 per cent. below 170° C. The bases contained aniline, which was removed by means of the diazo-reaction, and the aniline-free base so obtained fractionally distilled 10 times.

The fractions boiling above 125° C. were each treated with mercuric chloride, a solution of the bases in hydrochloric acid being added to a hot solution (generally about 10 per cent.) of mercuric chloride. For the fractions up to 155° C. two molecules of mercuric chloride were used to one molecule of base; for those boiling above that temperature sufficient was taken to allow for three molecules of mercuric chloride to one of base, the calculations being made on the assumption that the fractions boiling between 125° and 150° C. were picolines and those between 150° and 165° C. lutidines. The bases boiling above 165° C. have not yet been examined. The mercury compounds were recrystallised from water slightly acidified with hydrochloric acid till further recrystallisation made no improvement in the melting point; the bases were then recovered by removing the mercury with hydrogen sulphide. The boiling points have been determined with standard short-scale thermometers, and melting points either with these or with one that has been checked against them. Attention is directed to the double compounds that the hydrochlorides of these bases form with platinic chloride. Great discrepancies appear in the values recorded by the various authors for their melting points; e.g., Brühl states that pyridine platinichloride melts at 240° to 242° C.; Calm and Buchka (*Die Chemie des Pyridins*) quote a series of values, namely 216°–218° C., 223.5° to 225.5° C., and 228°–229° C.; while Garrett and Smythe (*Trans. Chem. Soc.*, 1902, Vol. 81) give 228°–229° C.

If pyridine platinichloride is prepared by adding a solution of platinic chloride to an acidified solution of the hydrochloride of the base in water and evaporating, crystals are obtained which melt at 241°–242° C., while if a solution of the chloride is added to a solution of pyridine hydrochloride in absolute alcohol and crystals obtained by the spontaneous evaporation of the liquid without heating, the compound formed melts at 228° C. Also the compound prepared from aqueous solution differs from that from alcoholic solution in colour and crystalline habit, but not in chemical composition. An exactly similar state of affairs was found with the other bases examined, with the possible exception of  $\gamma$ -picoline, the bodies prepared from alcoholic solution always being lighter in colour and having lower melting points than those from aqueous solutions that have been heated. In

the cases which have so far been examined, the bodies obtained in the two ways do not differ in crystallographic system, and, in some cases, at any rate, these compounds could be converted the one into the other by recrystallisation from the different solvents. It seems that this furnishes an example of dimorphism in which the two substances belong to the same crystallographic system. The pyridine aurichloride certainly exhibits the same phenomena but those of the other bases only gave very slight indications of anything similar.

The following bases have been isolated:—

Pyridine .....	B.p. 115.2° C. at 759.4 mm.
2.Methylpyridine ( $\alpha$ -picoline) .....	B.p. 128.8° C. at 749.7 mm.
4.Methylpyridine ( $\gamma$ -picoline) .....	Bp. 144.2° to 145° C. at 754.4 mm.
2.4.Dimethylpyridine ( $\alpha$ - $\gamma$ -lutidine) .	B.p. 158.2° C. at 753.4 mm.

*Pyridine*.—This base was obtained from the fraction boiling 110°–120° C. by removing the homologues of pyridine by heating with excess of a 5 per cent. solution of potassium permanganate. The platinum compound, prepared from an aqueous solution that had been heated, formed sparingly soluble red crystals of m.pt. 241°–242° C. without decomposition, and containing 34.33 per cent. of platinum. Obtained from absolute alcohol solution, the platinum compound gave sparingly soluble golden scales of m.pt. 228° C. without decomposition, and containing 34.38 per cent. of platinum ( $C_5H_5N$ )<sub>2</sub>H<sub>2</sub>PtCl<sub>6</sub> requires 34.33 per cent. of platinum.

The gold compound was prepared from alcoholic solution; it gave a mass of golden-yellow crystals sparingly soluble in cold, easily in hot alcohol, m.pt. 323° C. without decomposition, the fused mass however decomposing rapidly at 324° C. It contained 46.61 per cent. of gold. When prepared by the addition of gold chloride to an aqueous solution of pyridine hydrochloride, and heating for some time, fine lemon yellow crystals of distinctly lighter colour than those from alcoholic solution were obtained; these were sparingly soluble in cold, easily in hot water, and melted at 329° C. without decomposition. The fused substance decomposes at a slightly higher temperature. This compound contained 46.85 per cent. of gold ( $C_5H_5N.HCl.AuCl_3$  requires 46.85 per cent.).

The picrate was prepared by addition of picric acid to an alcoholic solution of the base. It forms canary-yellow needles, easily soluble in water or alcohol, of m.pt. 163° C. without decomposition.

The density of the base was 0.9893 at 14° C. and the refractive index (sodium light) 1.5124 at the same temperature. The specific refraction, calculated on the Lorentz and Lorenz formula = 0.3038, and the molecular refraction 24.0.

2. *Methylpyridine* ( $\alpha$ -picoline). From the fraction boiling at 125°–135° C. a considerable quantity of a mercuric-chloride compound was obtained crystallising in small plates or stout prisms, of m.pt. 151° C.

It contained 59.69 per cent. of mercury



requires 59.61 per cent.). The base was a colourless liquid, easily soluble in water, and having a strong pyridine-like odour. The platinum compound, prepared from alcoholic solution, forms sparingly soluble yellow scales, of m.pt. 178° C. with decomposition, and contained 32.71 per cent. of platinum. ( $C_6H_7N$ )<sub>2</sub>H<sub>2</sub>PtCl<sub>6</sub> requires 32.72 per cent. From a heated aqueous solution the platinichloride was deposited as easily soluble orange-red prisms, of m.pt. 194° C. with decomposition. This product contained 32.53 per cent. of platinum. The gold compound was obtained from alcoholic solution as a mass of bright-yellow very easily soluble crystals, of m.pt. 175° C. without decomposition, and containing 45.32 per cent. of gold ( $C_6H_7N.HCl.AuCl_3$  requires 45.33 per cent.). The aurichloride, prepared from a heated aqueous solution, appeared exactly the same in all respects. The picrate forms small, pale lemon-yellow needles, easily soluble in water or alcohol, of m.pt. 161° C. without decomposition.

The density of the base is 0.9530 at 14° C., the refractive index (sodium light), is 1.4906 at 14° C. The

specific refraction = 0.3070, and the  
molecular refraction = 28.55.

The base was oxidised by a 5 per cent. solution of potassium permanganate, to picolinic acid, which crystallised in fine tufts, of m.pt. 134° C.

4. *Methylpyridine* ( $\gamma$ -picoline). From the fraction boiling at 145°—150° C. a mercury-chloride compound was obtained in fine needles of m.pt. 121° C. which melt in hot water to a heavy oil. The base was a colourless liquid, soluble in water, with an odour similar to that of pyridine, but less pungent. The platinumchloride is very sparingly soluble in alcohol, crystallising in fine golden scales of the orthorhombic system. M.pt. 208° C. with decomposition. It contained 32.73 per cent. of platinum;  $(C_6H_7N)_2H_2PtCl_6$  requires 32.72 per cent. When prepared from aqueous solution the platinum compound formed red crystals of the orthorhombic

soluble in alcohol and fairly easily in water. A quantity obtained from a heated aqueous solution appeared exactly the same in all respects. The compound contained 43.98 per cent. of gold ( $C_7H_7N.HCl.AuCl_3$  requires 44.13 per cent.).

The picrate forms pale yellow crystals, easily soluble in water of alcohol, m.pt. 178° C. without decomposition.

The density of the base is 0.9378 at 14° C.; the index of refraction (sodium light)=1.5033 at 14° C.; the specific refraction=0.3154; and the molecular refraction =33.75. On oxidation with potassium permanganate, the base was converted into lutidinic acid, of m.pt. 235° C.

Below is a table comparing the values obtained for the melting points of the platinum and gold compounds of the above bases with those quoted by other workers.

#### Platinum Compounds.

Base.	Brühl.	Calm and Buchka.	Garrett and Smythe.	Author's Values.	
				From alcohol.	From water.
Pyridine ..	240°—242° C.	228°—220° C.	228°—220° C.	228° C.	241° C—242° C.
$\alpha$ -Picoline ..	195° C.	178° C.	194° C.	178° C.	194° C.
$\gamma$ -Picoline ..	231° C.	231° C.	—	208° C.	208° C.
$\alpha$ - $\gamma$ -Lutidine ..	230° C.	219°—220° C.	216° C.	209° C.	216° C.

#### Gold Compounds.

Base.	Brühl.	Calm and Buchka.	Garrett and Smythe.	Author's Values.	
				From alcohol.	From water.
Pyridine ..	unchanged	at 285° C.	—	323° C.	320° C.
$\alpha$ -Picoline ..	167°—168° C.	167°—168° C.	—	175° C.	175° C.
$\gamma$ -Picoline ..	205° C.	205° C.	—	203° C.	205° C.
$\alpha$ - $\gamma$ -Lutidine ..	—	—	94°	77° C.	77° C.

system, of m.pt. 208° C., and containing 32.71 per cent. of platinum. The aurichloride, obtained from alcoholic solution, gave easily soluble bright-yellow needles, of m.pt. 203° C. without decomposition, and containing 45.22 per cent. of gold.

Prepared from a heated aqueous solution, the gold compound gave bright-yellow needles of m.pt. 205° C. without decomposition, and containing 45.46 per cent. of gold ( $C_6H_7NHCl.AuCl_3$  requires 45.33 per cent.). The picrate forms small crystals of pale lemon-yellow colour easily soluble in water or alcohol, of m.pt. 160° C. without decomposition. The density of the base is 0.9603 at 12.5° C. The index of refraction (sodium light) =1.5065 at 12.5° C., the specific refraction is 0.3097, and the molecular refraction=28.80. This is practically the same as the value for  $\alpha$ -picoline. On oxidation of the base with potassium permanganate, isonicotinic acid was obtained, m.pt. 312° C. in a sealed tube.

2.4. *Dimethylpyridine*. ( $\alpha$ - $\gamma$ -lutidine). From the fraction boiling at 155°—160° C. a mercury compound was obtained in the form of white, hair-like needles, of m.pt. 128.5° C., containing 58.49 per cent. of mercury.  $C_7H_9N.HCl.2HgCl_2$  requires 58.35 per cent.

The base was a colourless liquid, more soluble in cold water than in hot, and having a rather pleasant odour. The platinumchloride was obtained from alcoholic solution as minute prisms with pyramidal ends, and of the monoclinic system; they melted at 209° C. with decomposition, and contained 31.13 per cent. of platinum

( $C_7H_9N)_2H_2PtCl_6$  requires 31.25 per cent. The platinum compound separated from aqueous solution as orange-red crystals of the monoclinic system, containing 31.15 per cent. of platinum m.pt. 216° C. with decomposition. The gold compound, prepared from alcoholic solution, formed a yellow oil, which crystallised on standing. The crystals melted at 77° C. without decomposition, and are easily

The author has pleasure in acknowledging his indebtedness to Messrs. Priestmans, Ltd., for their kindness in providing the raw material required, and to Prof. P. Phillips Bedson, in whose laboratory the work was carried out. The investigation is being continued.

## Yorkshire Section.

Meeting held at Hull on Monday, January 18, 1909.

MR. F. W. BRANSON IN THE CHAIR.

### A RAPID METHOD FOR DETERMINING CARBON DIOXIDE IN THE ATMOSPHERE.

BY S. H. DAVIES AND B. G. McLELLAN.

A rapid method of determining the condition of the atmosphere in schools, factories, and other places where people congregate, is of great importance. To do this with any certainty it is necessary within a brief interval of time to test the proportion of carbon dioxide at several points in the room. Given the number of people in the room and the area, it is then easy to calculate the rate of exchange of air for the room as a whole and to observe if the exchange is uniform, or whether there are any stagnant areas.

It is generally felt that Government regulations merely defining the cubic feet of space allotted to each worker in a factory, or each child in a school, must be replaced by regulations demanding a minimum exchange of air per head, supplied at a reasonable temperature.

In the First Report of the Departmental Committee appointed by the Home Office to inquire into the venti-