NOTE ON THE DETERMINATION OF PETROLEUM IN TURPENTINE.

By J. H. COSTE, F.I.C.

(Read at the Meeting, March 3, 1909.)

THE author, in a paper published in this journal (1908, **33**, 219) on the examination of turpentine and turpentine substitutes, stated that "For the direct determination and separation of petroleum spirit in turpentine" he was "of opinion that the process of polymerisation and sulphonation proposed by Armstrong (*Journ. Soc. Chem. Ind.*, 1882, **1**, 480) is in every way preferable to the various drastic and even pyrotechnic processes suggested by later workers."

In the ANALYST for November, 1908 (p. 433), appeared an abstract of a paper in the *Oil and Colour Trades' Journal* (August 15, 1908, 503-506), by A. K. Turner, in which it is stated that "The results thus (by Armstrong's method) obtained are invariably very low—at times as low as 20 per cent. below truth." The writer then adduces experiments with mixtures of kerosene (!) and turpentine, in which the amount of unpolymerised steam distillate is certainly considerably less than the amount of kerosene present in the mixture. Apart from the fact that the experimental details differ materially from those described by Armstrong, the distinction made by that author between petroleum *oil* and petroleum *spirit* has been neglected. Armstrong, after stating that an exact distinction is difficult, adopts for the purposes of his paper the term "petroleum spirit" for the portion of petroleum distilling in steam at the ordinary pressure, and "petroleum oil" for the portion which is not so distillable. Kerosene, an unusual adulterant, and one which is easily detectable by fractional distillation, is a mixture of substances, only some of which can be distilled in steam. A sample examined in this laboratory flashing above 100° F. (Abel test) $D_{15.5}^{15.5}$ C. 0.7980, n_D^{20} 1.4434, and distilling from 150° C. to above 250° C., was distilled with steam. In one and a half hours 58.5 per cent. by volume had distilled, and only traces were then coming over. The distillate had the following properties: $D_{15.5}^{15.5}$ C. 0.7803, n_D^{20} 1.4332, and when treated with sulphuric acid in the manner described by Armstrong, lost only 5.2 per cent. of its volume—*i.e.*, was reduced to 55.5 c.c. The apparently considerable loss observed by Turner (*loc. cit.*) was due to the fact that the portion not volatile in steam was not measured by him; a preliminary steam distillation would have separated his mixture into petroleum oil, with traces of resinous matter and petroleum spirit, and turpentine. It is the petroleum spirit alone that the polymerisation method is intended to detect and estimate. The above experiment shows that this can be done with some accuracy, or at least that the diluted acids recommended by Armstrong have but little action on American petroleum. Armstrong states that shale oil is so much attacked by sulphuric acid that the method is not applicable. Turner evidently realises the cause of his low results, but is apparently not aware of Armstrong's distinction between petroleum oil and spirit.

The process adopted by Turner of shaking with concentrated sulphuric acid and measuring the separated top layer, which he calls petroleum, is more violent than Armstrong's. It may, as he states, yield results which approximate to the amount of petroleum added—in fact, it appears to do so—but these results are only due to a happy compensation of errors.

A pure turpentine treated by this process gave no distinct top layer, but was converted into a dark viscous homogeneous mass.

To some of the same turpentine a petroleum spirit having a refractive index at 20° of 1.4475 was added in the proportion of 20 c.c. in 100 c.c. of mixture. One hundred c.c. treated as described by Mr. Turner gave 23 c.c. of a colourless top layer having a refractive index 1.4763, and an odour of cymene. This was reduced by subsequent treatment to 19.5 c.c., the refractive index being lowered to 1.4736.

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Treatment with Nordhausen acid reduced the refractive index to 1.4642, which is still much higher than that of the petroleum added.

In another experiment a mixture was taken containing 80 per cent. by volume of turpentine ($n_D^{20} 1.4708$, $D_{15.5}^{15.5} \text{ C. } 0.8703$) and 20 per cent. of petroleum spirit* ($n_D^{20} 1.4421$, $D_{15.5}^{15.5} \text{ C. } 0.8000$). This finally yielded 18 per cent. by volume of a liquor having an odour like that of cymene and $n_D^{20} 1.4798$, $D_{15.5}^{15.5} \text{ C. } 0.8775$.

The liquid separated shows a great tendency to form an emulsion during the washing with water, which is somewhat inconvenient. It is clearly not all petroleum, as is shown by its physical properties. Cymene ($n_D^{13.7} 1.4926$, $D_{15.5}^{15.5} \text{ C. } 0.8722$) and terpinene ($n_D 1.4845$, $D_{15.5}^{15.5} \text{ C. } 0.849$) are known to be formed by the action of sulphuric acid on turpentine. It appears highly probable that the liquor separated is principally one or other of these or a mixture.

Armstrong states that cymene is normally present with the most careful working in the final result of polymerisation by his method. It would appear that the use of a considerably greater volume of strong acid leads to the formation of much more cymene.†

When it is considered that the action of strong sulphuric acid on turpentine is very complex, including as it does isomerisation, polymerisation, sulphonation, and charring, with the evolution of some SO_2 , it is hardly to be expected that a product separating out by reason of its relatively low specific gravity and solubility should accurately represent the unattacked amount of an adulterant or addition. It is conceivable that if all the turpentine and its products were charred or sulphonated, the unaltered residue would represent the petroleum present in a mixture.

It should be stated that Armstrong's method yields, in the case of adulterated samples, liquids of low specific gravity which are evidently petroleum.

In conclusion, the author still maintains that Armstrong's method, based as it is on sound scientific principles, is capable of giving excellent results, if properly used—that is, if the petroleum *oil* be determined by distillation of the original sample in a current of steam, and petroleum spirit by polymerisation of either the distillate from this process or another portion of the original. He fully realises the ease with which a misapprehension as to Armstrong's original statements might arise on the part of a worker deprived of access to the actual paper, and obliged to rely on second-hand textbook statements, and is solely concerned to maintain the accuracy of his previous statement.

* Eighty-five per cent. of this was unattacked by sulphuric acid in the cold.

† It is admittedly remarkable that no cymene *separates* from pure turpentine when treated with sulphuric acid. The author suggests two possible reasons: (1) that in such a case it is sulphonated, whereas in the presence of petroleum it is dissolved in this substance and separated from intimate contact with the acid; (2) that its disappearance, and possibly the disappearance of petroleum in adulterated samples, is due to the formation of emulsions, or to its solution in the polymerides formed.

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The experimental work in connection with this subject has been carried out by Mr. R. Parsons, of this Department, to whom the author's thanks are due.

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DISCUSSION.

Mr. L. MYDDELTON NASH said that since Mr. Coste's previous paper he had made further experiments with the simple shaking test which he had then showed to be capable of detecting petroleum spirit in turpentine, and had found it possible to obtain fairly good *quantitative* results with it. A marked tube filled to the mark with the turpentine under examination was shaken, and the resulting froth compared with that produced by mixtures of known composition in standard tubes marked at the same height and with the same air space above the liquid. The amount of frothing was in direct proportion to the petroleum spirit present, turpentine giving no froth, but only large air bubbles, which broke immediately. A series of mixtures had been prepared for him which he had tested in this way with the following results :

Found.	Present.	Found.	Present.
25	25	50	50
10	10	10	10
50	50	5	10
5	5	20	20
10	15	25	15
20	10	10	10
10	10	35	25
75	80	35	25

The PRESIDENT asked whether other spirits, such as rosin spirit, would be shown by the test Mr. Nash had described, or would interfere with it.

Mr. NASH said that he had not tried the test with rosin spirit, as he felt certain it would be of no use, but only with petroleum spirit, not petroleum oil. He did not think that rosin spirit was now being used to adulterate turpentine. The petroleum spirit which he took for his tests was that which was being used in large quantities by manufacturers as a substitute for turpentine.

Mr. COSTE, in reply, said that it was remarkable that the shaking test mentioned by Mr. Nash should give results so near the truth. The direct treatment with strong sulphuric acid appeared to give results fairly near to the truth, although it was based on entirely incorrect premisses. It was, he believed, originally due to Herzfeld. For purposes of accurate determination he had found Armstrong's method to be a really good one. During recent years in London he had met with very little adulteration with petroleum, but he gathered that in the North of England this form of adulteration was still common.