

Birmingham Section.

Meeting held at Birmingham University, on Thursday,
December 9th, 1909.

MR. H. L. HEATHCOTE IN THE CHAIR.

A MODIFICATION OF ARMSTRONG'S METHOD OF TESTING TURPENTINE.

BY R. S. MORRELL, M.A., PH.D.

The literature on the examination of turpentine is very extensive and it is unnecessary to give more than two references to the most recent comprehensive contributions on the subject.

Richardson and Bowen (this J., 1908, 27, 613) have expressed their preference for the following method of estimating the amount of petroleum in adulterated pharmaceutical turpentine:—Fractional distillation of the turpentine combined with the determination of the refractive index of the distillation fractions for each 5° C. They are able to detect adulteration of American turpentine with American petroleum to 1.6 per cent. error.

J. Marcusson (Chem. Zeitung, 33) has recommended a modification of Burton's method [Amer. Chem. Jour. 12, 102] for the estimation of petroleum. The turpentine is oxidised by concentrated nitric acid and the quantity of petroleum present is determined by the weight of the unattacked spirit and by the weight of the nitro compounds separated from the products of oxidation of the turpentine. The analytical error of the method is stated to be 25 per cent.

From several years experience in the examination of American turpentine I rely chiefly on the behaviour of the oil on fractional distillation. Using a Young's 12 bulb dephlegmator, a good American turpentine gives about 90 per cent. distilling over between 155° and 165° C. The variation in the behaviour of high class American turpentine on fractional distillation is very small from year to year.

Any alteration in the colour and smell of the turpentine is accompanied by a change in the quantity and quality of the fractions.

I have found that a modification of Armstrong's polymerisation method [this J., 1882, 478] gave very satisfactory results and was accurate to within 2 per cent. The original method of Armstrong has been severely criticised. There was always an error arising from the difficulty in separating the unattacked petroleum from the liquid containing the polymerised turpentine. I found that the method could be modified to give satisfactory results if the two liquids obtained at each stage of the treatment with sulphuric acid were not separated, but the whole bulk was steam distilled. The polymerisation products of the turpentine remained in the distilling flask, whilst the hydrocarbons uncombined with the sulphuric acid passed over in the steam quantitatively. The difficulty of separating the two liquids disappeared by using this modification. I have tested the method by using turpentine adulterated with several varieties of petroleum and Borneo spirit.

It was impossible to separate the petroleum A from turpentine by the original Armstrong's method because the sulphuric acid and turpentine petroleum formed one liquid without any surface of separation. The solubility of petroleum A in cold sulphuric acid (4:1) was 0.35 per cent.; of petroleum B 16 per cent.; and of the Borneo spirit 3 per cent.

The accuracy of the polymerisation method is now brought to within 2 per cent., which is very satisfactory in view of the many stages of the process. I consider that the advantages of the modification lie in the simplicity of manipulation. The steam distillations require very little attention, a number can be performed at the same time, and no expensive apparatus is necessary. The time taken is really short, not more than a day and a half, and when once started, the experiment, so to speak, goes by itself.

I have found it advisable to treat the turpentine three times with sulphuric acid. The third treatment consists in warming the unattacked oil for two hours at 60° C. with concentrated sulphuric acid.

DISCUSSION.

Mr. H. L. HEATHCOTE said Richardson and Bowen had pointed out in 1908 that there was always a loss by the sulphuric acid method owing to some hydrocarbons remaining dissolved with the liquid. Dr. Morrell, by shortening the process, had actually given them a better one.

Mr. G. H. HOWSE asked for information as to the composition of the residue 1.5. Was it resin? Did Dr. Morrell know of Steifel's method for the separation of turpentine and petroleum spirit. He (Mr. Howse) understood that it depended for its success on the fact that pure turpentine was soluble in aniline oil whilst petroleum spirit was not. That test should be valuable, since it could be done in a few minutes.

Mr. F. H. ATCOCK said he supposed that Dr. Morrell did not approve of the polarimetric optical method. It was recognised that American turpentine rotated the ray of polarized light to the right; and the French variety to the left. Would it be possible to mix the two, and get a neutral optically active product? This aspect of the case came out forcibly years ago when terobine of the British pharmacopœia received considerable sanction as a remedy for bronchitis and other ailments. The polarimetric test was adopted by the pharmacopœia as a means of confirming polymerisation and the product could therefore be either genuine or a judicious mixture of the French variety with the American. They got practically an inactive rotating liquid, consequently the thing got into much disrepute. At that time during the process of polymerising turpentine he found, in the method, that much sulphur dioxide was generated; and did not know how to get rid of that and asked how Dr. Morrell succeeded? He did not quite see what the author meant by the residue referred to in his table, because in the process of distillation turpentine always left a residue unless it was rectified over alkaline substances such as soda or potash. Many years ago a Liverpool pharmacist suggested a simple method for testing

	By modification of Armstrong's Method.	Per cent. Residue.		By Armstrong's Method.	Per cent. Residue	
American turpentine.		1.5	{ Mean of results from examination of } samples from 200,000 galls.		2.5—3 per cent.	
American turpentine +1 per cent petroleum [A.]		2.0				0. Impossible to separate the two layers.
" +2½ "		3.5				
" +5 "		4.8				
" +10 "		9.7				
" +20 "		19.0				
" +2½ "		[B.] 4.4				
" +5 "		5.9				
" +16 "		17.9				
" +2½ "	Borneo spirit	2.9				
" +5 "	"	6.2				
" +10 "	"	11.8				
" +20 "	"	19.4				
Petroleum A. had a sp. gravity of 0.768 and flash-point 77° F.						11.2
B. " " " 0.803 " " 94°						
Borneo spirit " " " 0.809 " " 74—75°						

turpentine and terpeno bodies. He prepared a solution of equal volumes of the sample of turpentine with absolute alcohol, and from a burette dropped into the mixture distilled water, when after a certain amount had been added, separation ensued which varied with different varieties of volatile oils of this class. Dr. Morrell would be rendering a very great service if he could suggest how to overcome such difficulties as adulteration of turpentine. He hoped he would be pardoned if he asked the question "What is turpentine?" because it seemed to him to be so very indefinite and variable in composition, especially when one considered that it was a product of the *pinaceæ*, of which natural order there were several scores of varieties.

Mr. J. C. MANN enquired how the result of 100.5 in the first column was obtained. He had not personally come across a coal tar naphtha with the flash point given, and with such a low specific gravity. Should it not be 0.880? The low specific gravity pointed to it being a petroleum product. He had tried the use of carbon tetrachloride for raising the flash point and density of turpentine substitutes to those of American turpentine. The presence of this body was however quite noticeable owing to the slight green halo imparted to the test flame when the flash point was being taken. It was a quite conclusive test for even small percentages of carbon tetrachloride in a mixture of this kind.

Dr. MORRELL, in reply, said the residue of 1.5, obtained by the pulverisation process, consisted of hydrocarbon. It was not a resin body at all. With regard to the method of estimating turpentine by the use of aniline oil, he had seen an abstract of it but had not tried the process. His present paper was nearly two years old, and he believed that method was published later. As to Mr. Alcock's reference to the optical method he wished to say that it was a determination of the refractory, and not the rotary power. Upon that, he agreed, one could not rely. It was true that the use of sulphur dioxide had been abandoned, but it did no harm; and did not, in the least degree, interfere with the results. With regard to the enquiry as to what turpentine was, American turpentine generally had a distillation of about 90 per cent. between 150 and 160, with the hydrocarbon and light bodies mixed together. It was easy to distinguish between the varieties of turpentine by methods which were not chemical. Most of them differed in their fractional distillation—the Indian turpentine particularly. In reply to Mr. Mann, the result, less than 5, was merely the result of the experiment. Beyond that he could not say anything. Possibly he had placed the result a little too favourably. He believed coal tar naphtha was a blended substance. One might determine flash point by the carbon tetrachloride method, and the green light, which was a delicate test of its presence.

London Section.

Meeting held at Burlington House on Monday, March 7th, 1910.

DR. J. LEWKOWITSCH IN THE CHAIR.

SPONTANEOUS DECOMPOSITION OF BLASTING GELATINE.

BY J. B. HENDERSON, F.I.C., AND T. McCALL, F.I.C.

A most interesting, and so far as we know unprecedented case of spontaneous decomposition of blasting gelatine occurred in a Government magazine at Sellheim, Queensland, in December last.

On 19th May, 1909, a shipment of explosives arrived at Townsville, North Queensland, including one lot of

sixty cases of one inch blasting gelatine which had been manufactured on the 4th of February, 1909. The explosive was in good order on arrival, and was forwarded to the Sellheim Magazine, which is situated seventy-one miles from Townsville at an elevation of 835 feet above sea level. This magazine supplies the Charters Towers Goldfield. When examined again on the 9th of September, 1909, the explosive was apparently still in good order, the samples tested giving a heat test of twenty-one minutes.

On the 15th December an urgent telegram was received in Brisbane that the explosive was in a dangerous condition, decomposition having set in and exudation showing outside the wooden case in one instance. A reply was sent authorising the immediate destruction of all explosives in this state and the removal of the remainder from the magazine. One of us then left by the first steamer for Townsville (750 miles distant) to investigate matters. It was found that on the 15th of the month the magazine keeper noticed a "dark liquid like tar" exuding through the end of one case and dropping on to a lower case and then on to the floor of the magazine. The case was opened and "fumes of an acid nature poured out." The contents of one packet in the middle of the top row had swollen up and looked yellowish except where it came in contact with the rubber lining, where it turned black; he did not see any signs of the cartridge wrappers or of the cardboard package. This case of explosives with the exception of one piece of wood from the end, was destroyed by burning, no trouble being experienced, this and the whole of the remainder of the batch burning off quietly when destroyed, without any detonations.

The part of the end of the wooden case was brought to Brisbane and still shows the sticky mass adhering to the inside, through the dovetail joints, and down the outside. Remains of part of the rubber lining in a much decomposed state are stuck on to the wood by the explosive, most of the rubber being dissolved, the fibre still showing. Part of a cardboard box also shows, as a thin, soft material. The "nitrous" smell is still marked (7th January, 1910), and the explosive is strongly acid to litmus paper, and moistened explosive test paper held close to the mass soon shows the usual brown-purple stains. The decomposing explosive, after partly dissolving the rubber sheeting, was dark brown, not black.

After destroying the decomposing case, the magazine keeper at once started to examine the remaining 59 cases, and on the following day (16th) found the contents of one 5 pound package, the end one of a lower row, "starting to swell up like yeast," having burst the string and giving the "same sort of smell as before." (Explosives are stored in two rows of five cardboard packages, each package holding 5 pounds, the whole 50 pounds being enclosed in rubber sheeting in a wooden case.) He at once removed the case from the magazine and stored it in the open, protected carefully from the rain by sheet iron and bags, the weather being hot and severe thunderstorms coming up nearly every day. He did not replace the top package or nail down the lid.

On Mr. McCall's arrival four days later (20th December), he found the contents of the package containing the decomposing explosive had swollen up, filled the space above where the other package had been, and had overflowed down the sides of the box, occupying probably about three times its original bulk. The mass had a greenish yellow colour and there was no appearance of the cardboard box or paper wrappers, these having been more or less destroyed. Naturally no attempt was made to investigate this mass, as it is generally admitted that when an explosive of this class once starts to decompose it soon fires and detonates. The smell of the acid fumes from this package could be easily noticed three yards off to leeward.

Other plugs from this case, from those packages which looked all right, were not only normal in appearance, but one which was brought to Brisbane and tested stood the "heat test" for twenty minutes.

About three thousand plugs in the other 58 cases were examined and although no exudation of free nitro-glycerine