THE DETECTION OF FORMALIN.

BY OTTO HEHNER.

(Read at the Meeting, March 4, 1896.)

SCHIFF'S reagent as a test for formaldehyde is far from satisfactory. Apart from the fact that it reacts with all aldehydes, and is, therefore, not applicable to fermented beverages or fluids, such as wine or vinegar, which contain naturally traces of acetaldehyde, or to food-substances which by fermentation might yield traces of acetaldehyde, it acts but very slowly when very small quantities of formaldehyde have to be looked for, such as would be present in milk when preserved with formalin in accordance with the instructions furnished by the vendors. If these instructions are complied with, about one part of formaldehyde only is present in about sixty thousand parts of milk. Schiff's reagent is quite capable of indicating such traces, but only after some hours, or when the distillate from the milk plus Schiff's reagent has stood over night. As pointed out by Richmond and Boseley in their recent paper (*ANALYST*, xx. 154), when an excess of sulphurous acid is used in the preparation of the reagent, no reaction is obtained with traces of formaldehyde, while "the red coloration appears on warming Schiff's reagent, on blowing air through it, or even on placing it in an uncorked bottle." I can fully confirm these statements, and can further add that Schiff's reagent may give a red coloration on standing for a short time even with pure distilled water in stoppered cylinders, or with a distillate from milk which is perfectly free from formalin. Thus, if to 25 c.c. of water only one or two drops of Schiff's reagent are added, a red colour appears already in half an hour,

the amount of oxygen contained in the water being sufficient to oxidize the sulphurous acid contained in the added reagent, even though the mixture has been placed in a stoppered cylinder filled to the neck. When a little more Schiff's reagent is added—say ten drops—the coloration does not appear. It follows that an analyst who is not aware of this circumstance—and so far attention has not been drawn to it—may in one of two samples of milk, both equally free from formalin, apparently find formalin in the one and not in the other, although he may have apparently operated under precisely the same conditions in both.

I find that the best way of operating is to add about five drops of the reagent to the distillate from 100 c.c. of milk (amounting to about 25 c.c.), place the mixture in a stoppered cylinder, to observe the colour next morning, and then to add a few drops of sulphurous acid solution. After a short time any colour which may be due to oxidation will have vanished, while that due to the presence of an aldehyde remains. There is certainly a difference in the tint produced by colour oxidation, which resembles that of rosaniline, and that of the aldehyde compound, which is violet; and with those small traces with which we have often to deal, only a comparison of the relative colours would allow of anything like a safe conclusion being drawn.

From the experience I have collected I am clearly of opinion that Schiff's test is a dangerous one, and should only be used as a confirmation.

I have made some experiments as to the rate at which formalin disappears from milk on keeping. To three portions of pure milk formaldehyde was added in the proportions of 1 of the aldehyde to 25,000, 1 to 50,000, and 1 to 100,000, the milk thus preserved being kept in stoppered bottles. After one week no formalin could be detected in the sample containing 1 part in 100,000; after two weeks none in the 1 in 50,000 sample; while after three weeks there was only the faintest trace discoverable in the 1 in 25,000 sample. These experiments were made in January, when the temperature was low, the Schiff's reagent being used with the precautions described.

The reaction which Messrs. Richmond and Boseley have described in the paper alluded to (*loc. cit.*) as having been first pointed out to them by myself, and which depends upon the blue colour produced when milk containing formaldehyde is mixed with sulphuric acid, is infinitely more characteristic than Schiff's reaction, especially when the test is applied in the form given it by Mr. Richmond, where the milk to be tested is allowed to float upon the surface of sulphuric acid, anhydrous, or nearly so, contained in a test-tube. I find that in this way one part of formaldehyde can be readily detected in 200,000 parts of milk. Acetaldehyde does not give this reaction, and as no distillation is required, the test is of the simplest possible nature as regards milk. I cannot bear out the statement of Messrs. Richmond and Boseley that it is possible to obtain a blue coloration with formaldehyde to which some peptone solution had been added. The peptones which I used, and which undoubtedly were rich in peptone, gave no blue coloration. Egg-albumen does give the reaction in the presence of formalin, but so feebly as to lead me to conclude that it is not the albumen itself, but some trace of impurity contained in it, which enters into the reaction. Casein precipitated from milk, re-dissolved in alkali, and again precipitated and dissolved, gives the colour most strongly. Milk-whey also gives it, but gelatin, as already pointed out by Richmond and Boseley, does not. I have tried

many other substances likely to be present in milk, but have found nothing so satisfactory as casein.

To test wine or vinegar for formaldehyde, I add a drop of milk to the sample, and pour the mixture carefully on the surface of strong sulphuric acid contained in a test-tube. A blue ring appears at the zone of contact when formalin is present, while ordinary aldehyde gives no reaction.

The test is also well fitted for the detection of formaldehyde in butter, the aqueous liquor resulting when the butter is melted for analysis being used.

The following is another equally sensitive and characteristic test. If to the distillate from a sample of milk, etc., one drop of a dilute aqueous solution of phenol is added, and the mixture poured upon strong sulphuric acid contained in a test-tube, a bright crimson colour appears in the zone of contact. This colour is still readily seen with one part of formaldehyde in 200,000 of water. If there is more than one part in 100,000, there is seen above the red ring a white, milky zone, while in stronger solutions a copious white or slightly pink, curdy precipitate is obtained. This reaction has the advantage of the one above referred to, inasmuch as it is obtained with formaldehyde solutions of all strengths, while the blue colour with milk is not obtained with milk containing much formaldehyde. I have not ascertained the upper limit of sensitiveness of the reaction, but the blue colour is *only* obtained with traces.

Acetaldehyde also gives a coloration and a precipitate with phenol and sulphuric acid, but it is orange-yellow, not crimson.

Many other hydroxy-derivates of benzol, such as salicylic acid, resorcinol, and pyrogallol, give the red colour with formaldehyde. Hydroquinone does not give the red colour, only an orange-yellow one.

The reaction only succeeds when carried out as described above; the phenol must first be mixed with the solution to be tested and the mixture poured upon the sulphuric acid. Only a trace of phenol must be used. If the hydroxy-compound is first dissolved in the acid, and the formaldehyde solution then added, no colour is obtained.

Of course it is very well known that formaldehyde most readily causes the condensation of aromatic substances. Thus, the tannins readily condense in the presence of hydrochloric acid, forming insoluble compounds. Richmond refers to Kleeberg ("Annalen," 263, 283), who found that formaldehyde combines with phenols in the presence of hydrochloric acid, and Emil Nickel (*Zeit. f. anal. Chem.*, 1889, p. 249) states that the phenols are useful reagents for aldehydes, and *vice versa*, but as far as I am aware, the appearance of the red coloration with formaldehyde has not been previously noticed.

The precipitate obtained by sulphuric acid, formaldehyde, and phenol is so insoluble that it might well be utilized for the determination of the strength of dilute formalin solutions. When a trace of the precipitate is taken, a few drops of bromine water or iodine solution added, and then a little sodium hydrate solution, a strong violet-red coloration and a precipitate are obtained.

The silver reaction for aldehydes altogether fails with the faint traces of formalin which are readily recognisable with the milk-sulphuric and the phenol-sulphuric tests.

Moreover, all distillates from pure milk show a very faint browning with ammoniacal silver solution.

The diphenyl reaction referred to by Messrs. Richmond and Boseley is far less sensitive than the two reactions described in this paper.

DISCUSSION.

The PRESIDENT said that most of the tests hitherto employed for the detection of formaldehyde had been of such a character as to be applicable only to aldehydes as a class. The reaction shown by Mr. Hehner was, however, a very characteristic one, and likely to prove extremely useful. He had found that an aqueous solution of milk sugar gave a reaction with Schiff's reagent, and therefore distillation was necessary.

Dr. RIDEAL remarked that allusion had been made to a paper published by himself on the subject of formalin, but he thought that was hardly the right way to put it. It would be remembered that in the course of the previous year Mr. Bevan had promised a paper on the use of formalin for preserving milk samples, which he was unable to bring forward on the date for which it was announced. He (Dr. Rideal) happened to be present at the meeting on that date, and had ventured to make a few remarks regarding formalin and its detection, which the President suggested should be published, in the form of a note, in the ANALYST. Seeing that he had not attended the meeting with the intention of reading a paper, the appearance of the note in question was only due to the kindness of the meeting and the suggestion of the President; but, in the event of any question arising as to the use of Schiff's test in connection with formalin, it was rather unfortunate that this short note should have been placed after the papers of Mr. Bevan and Messrs. Richmond and Boseley, inasmuch as it was read at a previous meeting to that at which those papers were presented.

With regard to Mr. Richmond's modification of Schiff's test, it was necessary to remember that formaldehyde was the only volatile aldehyde which had to be looked for, and that the original method of applying Schiff's reagent to the distillate tested was not merely for the detection of the presence of an aldehyde, but for that of a volatile aldehyde. It seemed, therefore, to be preferable to adhere to the method suggested by himself, rather than to follow one which involved the application of the reagent to the original milk without distillation.

The colour-test mentioned by Mr. Hehner seemed to be especially useful, for the reason that it was manifested when the sulphuric acid was added to the milk in sorting samples by the machine.

Mr. WHITE observed that in the case of milk containing formalin, the clot formed on the addition of hydrochloric acid to the milk was much more difficult to dissolve than when no formalin had been added.

Mr. W. NORTHFIELD YARROW remarked that the clot referred to by Mr. White also took a yellowish tinge, if much formalin were present, while it remained whitish if there was none.

Mr. C. A. MITCHELL mentioned two tests which he had found useful for detecting

formaldehyde. One was the reduction of chromates by aldehydes, and the subsequent formation of a violet modification of the chromic salt. A mixture of 1 c.c. of nitric acid and an equal quantity of potassium chromate solution added to the distillate from the liquid under examination, produced, after a shorter or longer time, according to the quantity of the aldehyde present, a violet coloration. The other test was dependent upon the action of formaldehyde on Nessler's solution. A very small trace of formaldehyde was sufficient to produce a yellow colour, which gradually darkened and produced a precipitate at first resembling ferric oxide, but finally becoming dark gray. Ordinary aldehyde did not give this reaction.

Dr. RIDEAL remarked that the test of smell, which had not been mentioned either by Mr. Richmond or by Mr. Hehner, was very useful in detecting the presence of formalin. In milk, 1 part of formaldehyde in 25,000 could easily be recognised by its odour on warming the milk.

In the process of distillation, preliminary to the application of Schiff's test, the first portions of the distillate possessed a pronounced odour of formalin.

Mr. RICHMOND said that the fact of the non-occurrence of the blue reaction with sulphuric acid when formaldehyde was present in large quantity was mentioned in the paper by himself and Mr. Boseley (*ANALYST*, xx. 155), and the insolubility of the casein referred to by Mr. White had been noticed by Mr. Seyler.

The President had said that, under some conditions, milk sugar gave a reaction with Schiff's test, but he (Mr. Richmond) had never been able to observe such a reaction, and would like to hear under what conditions it was obtained.

Dr. Rideal had claimed priority with regard to the use of Schiff's test. As far as he (Mr. Richmond) and his colleague were concerned, they freely admitted the justice of Dr. Rideal's claim; in fact, so far from making any claim for its use, they were the first to point out its unreliability.

With regard to Dr. Rideal's remarks as to the modification of Schiff's test which they had suggested, he would like to point out that acetaldehyde was volatile as well as formaldehyde, and that its antiseptic properties (although inferior to those of formaldehyde), were sufficient to admit of its use as a milk preservative.

Mr. HEHNER said it seemed to him ridiculous to talk of priority at all in connection with Schiff's test. Long before formaldehyde came into use as a preservative, it was known that it gave a reaction with Schiff's reagent.

With regard to the test of smell, no doubt the nose was a very useful organ, but it required backing up by something more definite. Such a test was not, as a rule, accepted by chemists; in legal cases especially something in addition was required which was discernible to the eye.

The PRESIDENT said it was very difficult to define the conditions under which Schiff's test did or did not succeed, and therefore, although he had observed the coloration with milk sugar, he could not exactly lay down the conditions under which it would appear. It might be due to a small quantity of alkali.