

THE INFLUENCE OF MILK PRESERVATIVES.

BY MR. A. W. STOKES.

(Read at Meeting, June 3rd, 1891.)

DURING about a year I have been interested in determining the acidity of milk as influenced by temperature and by the addition of preservatives. Between four and five hundred determinations of acidity have been made for that purpose under various conditions. Though there is much more remaining that might be done to complete the enquiry the results so far obtained may be of interest.

Milk as delivered to the London trade is always acid, this acidity on an average is equal to 0·2 per cent. of lactic acid. Such an amount of acidity usually develops in the milk within eight hours of its coming from the cow.

In England, according to the temperature, in from 30 to 40 hours after it has reached an acidity of 0·2 per cent., its acidity rises to 0·35 or 0·4 per cent., at which point it has acquired an acid taste, and is said to be sour.

Usually at an acidity of 0·6 to 0·7 per cent. it separates or coagulates.

If kept for a long period milk rarely develops a greater quantity of lactic acid than 2 per cent. In some milk, the acidity of which I determined (see ANALYST, xii., 226), the highest acidity found was 2·34 per cent. after 117 days of keeping. The reason of this is, that when this amount of acidity is reached the acid formed is destructive to the fungus forming it. Milk that has not yet developed an acidity of 0·3 per cent., but is near it, will coagulate on boiling; it is therefore customary in the trade to test the freshness of a milk, if it is suspected to be stale, by boiling it.

To find how long a milk, not sealed up, will keep fresh, without becoming at all sour to the taste, I took a large quantity of the same milk and divided it into 11 parts; one part was kept in its original state, another part was boiled, and to the others various preservatives were added. All these were placed in separate bottles, which were kept open; at intervals of about four hours their acidity was determined.

They were shaken each time that the acidity was determined.

The time was noted when each became sour.

Taking the moment when the unpreserved milk became sour as the starting point I find that the others kept fresh to the following extent longer:—

Samples containing one part per 1,000 of a mixture of equal parts of (dry) carbonates of soda and potash kept fresh five hours longer and became sour to the taste at an average acidity of 0.32 per cent. lactic acid.

Samples containing two parts per 1,000 of the above mixture kept fresh for twenty hours longer and tasted sour at an average acidity of 0.45 per cent.

Samples boiled kept fresh twenty hours longer than the ordinary milk and tasted sour at 0.32 per cent. acid.

Samples containing 10 per cent. of a saturated aqueous solution of salicylic acid kept fresh twenty hours longer, tasting sour at about 0.44 per cent. acid.

Samples containing one part per 1,000 of borax (crystal) kept fresh for seventeen hours longer, tasting sour at about 0.4 per cent. of acid.

Samples containing two parts per 1,000 of borax, kept fresh for twenty-five hours longer, tasting sour at about 0.42 per cent. of acid.

Samples containing one part per 1,000 of boracic acid kept fresh for twenty-four hours longer, tasting sour at about 0.44 per cent. of acid.

Samples containing two parts per 1,000 of boracic acid kept fresh for forty-two hours longer, tasting sour at about 0.46 per cent. of acid.

Samples containing one part per 1,000 of a mixture of equal parts of borax and boracic acid kept fresh for twenty hours longer, tasting sour at about 0.42 per cent of acid.

Samples containing two parts per 1,000 of above mixture kept fresh twenty-seven hours longer, tasting sour at about 0.49 per cent. of acid.

The average temperature was 65° F.

The usual proportion recommended by the vendors of preservatives (almost all of which are, in my experience, composed of borax or boracic acid, or mixtures of the two) is about one part to 1,000 of the milk.

Salicylic acid is too insoluble to make it possible to use much of it; personally, I have never found it in milk.

From these experiments I find that boracic acid is the best preservative. Whatever the preservative, the milk tastes sour when it reaches about the same acidity 0.4 per cent. to 0.49 per cent.

Though the addition of carbonates of soda and potash or borax reduces the original acidity of the milk, and should therefore apparently give it a longer range and time before it reaches the acidity at which it must turn sour, and while on the other hand boracic acid adds to the original acidity and so apparently lessens the range and time, yet the action is reversed and boracic acid is the best preservative.

How great the apparent difference is may be noted from an instance: a sample of milk had an acidity of 0.15 per cent.

On adding two parts per 1,000 of borax its acidity sank to 0.11 per cent.

While that to which two parts per 1,000 of boracic acid was added had an acidity of 0.23 per cent.

Boiling the milk seems as efficacious as the use of one part per 1,000 of any the preservatives.

Four years ago I endeavoured to find the limit at which borax could be detected by the turmeric reaction in milk.

I found that a drop of milk containing the thousandth of a grain of borax would give the reaction if treated thus:—On a porcelain slab place one drop of the milk with two drops of strong HCl and two drops of a saturated turmeric tincture. Dry this on the water bath, take it off directly it is dry. Cool. Add a drop of ammonia by means of a glass rod. A slatey-blue colour changing to green is produced. Even less than this will give the green tint, but not the blue. The turmeric tincture must be fresh, otherwise it is better to use the powdered turmeric.

Even half this quantity of boracic acid can thus be detected; in such case the HCl should be omitted from the test.

Though unpreserved milk usually turns sour to the taste when its acidity reaches 0.3 per cent. there are yet exceptions. I found three samples which, when they reached me they were quite fresh to the taste, though having an acidity of 0.5 per cent. In forty-seven hours later they were of an acidity of 0.54 per cent. At this stage I took parts of each and boiled them without their coagulating at all. Only at the 71st hour, when their acidity was 0.65 per cent., did they become at all sour to the taste. Such exceptions show that milk does not always decompose at the same rate as is asserted in some quarters.

To Mr. W. N. Yarrow I am greatly indebted for care and attention in carrying out much of this tedious enquiry.

The acidity in the above cases was determined by means of decinormal soda solution, using phenol-phthalein as an indicator.

Being asked some time ago to devise some method simpler than the burette for rapidly determining the acidity of milk for use in the milk trade, I had made some compressed pellets containing carbonate of soda and phenol-phthalein. By modern automatic machinery it is possible to weigh out successive quantities of as little as two tenths of a grain with great accuracy. So that, compressed into little pellets of $\frac{1}{8}$ inch diameter and weighing only one grain each, we have accurate quantities of the alkali and the indicator. Into a narrow tube milk is poured up to a 10 c.c. mark, a pellet is dropped into this milk and crushed by a glass rod. If a permanent pink colour is not produced other pellets are dropped in until the pink colour is permanent. The number of pellets used gives in tenths of a per cent. of lactic acid, the acidity of the milk. The accuracy of the method within the range of acidity in milk and within the limits of one-tenth of a per cent. have been vouched for by several analysts.

The principle of these pellets, that is, the use of accurate quantities of dry compressed reagents, may be useful in other branches of science—hence I may be excused for mentioning the subject.

DISCUSSION.

MR. CASSAL said that the use of boric acid and of other antiseptic agents for the preservation of food was a subject which required immediate and full discussion by

public analysts. Inasmuch as refrigeration when properly applied was a legitimate method of preserving milk, it would be interesting to know how long decomposition could be retarded by it under normal conditions. He did not gather that Mr. Stokes had made any experiments in this direction. He had reason to believe that refrigeration was found to be amply sufficient for all practical purposes, when it was deemed necessary to adopt precautions against premature decomposition. With regard to the tumeric test, evaporation on porcelain had already been mentioned at the Society as a useful modification of the application of this test. He understood that Mr. Stokes approved of this modification for the detection of minute quantities of boric acid. With regard to the acidity pellets, he (Mr. Cassal) was bound to say that he regarded with strong disfavour the introduction of all devices, which were calculated to make untrained persons of various degrees of ignorance imagine that they could act as their own analysts or consulting chemists. It was highly undesirable to put these "tests" into the hands of dairymen and others. They were edge tools likely to wound unskilled hands; while, from a professional point of view, it was objectionable also. As it was, the public, in their ignorance, were far too ready to believe that the whole of the work of analytical chemists consisted in the application of "tests" of this kind. He submitted that, in any case, such a step should only be taken after consultation, and with the general approval of the profession.

DR. VIETH said he supposed Mr. Stokes had made his experiments during the winter months, and he was quite sure that if they were repeated during the summer or autumn the results would be very different. The temperature of the room in which they were made was not the only factor to be taken into account. There was no doubt milk went sour much more quickly in summer and autumn, October and November being the most troublesome months. Farmers attributed this to the decaying leaves, and this was perhaps not far from the truth. He was rather surprised to see that the milk kept for about 170 days had contained 2.3 per cent. of lactic acid; his own experience was, that as soon as 1 to 1.5 per cent. was reached, fermentation practically ceased, or at any rate proceeded with extreme slowness. With reference to the retarding action of boracic acid on lactic fermentation, other experimenters had not got such good results as Mr. Stokes. His impression was that Mr. Stokes had made his experiments at a time most favourable for showing the best action of the preservative. As far as the milk trade of London was concerned, he most emphatically repeated what he had said on former occasions, viz., that in his opinion there was no reason whatever for using any preservative. Dr. Vieth added, that in cheese making it was a necessity that the milk should have a certain degree of acidity. During the last four years a number of tests had been introduced for determining the acidity of milk, and he thought that Mr. Stokes' was the most simple, handy and reliable that could be placed in the hands of the practical cheese maker.

The PRESIDENT said, that if allowance was made for the content of inert matter in borax, its activity was as near as possible the same as that of boric acid; this was shown by Mr. Stokes' experiments. As to hydrofluoric acid, his experience was that it kept milk samples perfectly for a great length of time.

In reply, Mr. Stokes said that the mass of milks referred to were analysed from January to May last. In reference to Mr. Cassal's objection to his supplying the milk trade with an apparatus that could be readily and cheaply used for stopping the sale of stale milk, he really thought such an apparatus would be an advantage to all parties. Acidity must be determined at the moment the milk is suspected. It would be impossible to send such samples to professional analysts, since, in the majority of cases, the milk would have so far changed in its passage to the analyst as to make an acidity determina-

tion then of very little value. He thanked Dr. Vieth for his generous testimony to the accuracy and simplicity of the pellet method referred to. If it only prevented, to some extent, stale samples being sent for analysis, it would save much trouble and not a few ambiguous results. Mr. Stokes certainly objected to milk being "preserved" by any other means than refrigeration or scalding.
