

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION
OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

FOREIGN COLORING-MATTER IN MILK.

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THE employment of artificial color by dishonest dealers to improve the appearance of milk has been practiced for many years, and while by no means as prevalent now as formerly, by reason of the stringent laws passed by various states regulating the sale of milk, the practice even to-day is by no means rare. Even in Massachusetts, which of all states is foremost in prosecuting the milk laws, artificially colored milks are occasionally found. Statistics of the Massachusetts State Board of Health show that out of 23,098 samples of milk collected throughout the state and analyzed during five years (from 1894 to 1898 inclusive), 151 samples or 0.6 per cent. were found to contain foreign coloring-matter. Of these samples, about 88 per cent. contained annatto, approximately 10 per cent. were found with an aniline orange, and about 2 per cent. with caramel.

Until comparatively recently, annatto was employed almost exclusively for this purpose. Caramel is least desirable of all the above colors from the point of view of the milk dealer, in that it is difficult to imitate with it the natural milk color by reason of the fact that the caramel color has too much of the brown and too little of the yellow in its composition. Annatto, on the other hand, when judiciously used and with the right dilution, gives a very rich, creamy appearance to the milk even when watered, which accounts for its popularity as a milk adulterant. Of late, however, the use of an orange aniline has been on the increase, and so far as a close imitation of the cream color is concerned, it is quite as efficient as annatto.

It is unfortunate for the milkman that artificial color of any kind is not analogous to the natural color of milk, which confines itself so largely to the cream. The artificial color, on the contrary, is dissipated through the whole body of the milk, so that when the cream has risen in a milk thus colored, the underlying layers, instead of showing the familiar bluish tint of skimmed milk, are still distinctly tinged below the layer of the fat, espe-

cially if any considerable quantity of the color has been used. This distinctive appearance is in itself often sufficient to direct the attention of the analyst to an artificially colored milk in the course of handling a large number of samples.

The addition of artificial color to milk is in most instances employed as a means of covering up evidences of watering, but this is not true in all cases. About 95 per cent. of the milks found colored in Massachusetts show, on analysis, the fraudulent addition of water. On the other hand, an orange aniline color was found by the writer in a milk containing over 17 per cent. of total solids, a conviction being secured on this case in court.

As to the nature of the orange aniline preparations employed for coloring milk, a few samples of these commercial "milk improvers" have fallen into the hands of the Department of Food and Drug Inspection of the Massachusetts Board of Health, and have proved, on examination, to be mixtures of two or more members of the diazo compounds of aniline. A mixture of what is known to the trade as "Orange G" and "Fast Yellow" gives a color which is practically identical with one of these preparations secured from a milk dealer and formerly used by him.

For purposes of prosecution or otherwise the generic name of "aniline orange" has been applied to this class of dyes in milk, and whatever particular mixture has been employed to make up the color, the tests which are given below have never failed to detect it when present in the milk.

The general scheme employed by the writer for the examination of milk samples suspected of being colored is as follows: About 150 cc. of the milk are curdled by the aid of heat and acetic acid, preferably in a porcelain casserole over a Bunsen flame. By the aid of a stirring rod, the curd can nearly always be gathered into one mass, which is much the easiest method of separation, the whey being simply poured off. If, however, the curd is too finely divided in the whey, the separation is effected by straining through a sieve or colander. All of the annatto or of the aniline orange present in the milk treated would be found in the curd, and part of the caramel. The curd, pressed free from adhering liquid, is picked apart, if necessary, and shaken with ether in a corked flask, in which it is allowed to soak for

several hours or until all the fat has been extracted and with it the annatto. If the milk is uncolored, or has been colored with annatto, on pouring off the ether the curd should be left perfectly white. If, on the other hand, aniline orange or caramel has been used, after pouring off the ether the curd will be colored more or less deeply depending on the amount of color employed. In other words, of the three colors annatto, caramel, and aniline orange, the annatto only is extracted by the ether. If caramel has been used, the curd will have a brown color at this stage; if aniline orange, the color of the curd will be a more or less bright orange.

The ether extract, containing the fat and the annatto, if present, is evaporated on the water-bath, the residue is made alkaline with sodium hydroxide and poured upon a small, *wet* filter, which will hold back the fat and, as the filtrate passes through, will allow the annatto, if present, to permeate the pores of the filter. On washing off the fat gently under the water tap, all the annatto of the milk used for the test will be found to have been concentrated on the filter, giving it an orange color, tolerably permanent and varying in depth with the amount of annatto present. The confirmatory test for annatto with stannous chloride may afterward be applied to the colored filter, producing the characteristic pink color.

The fat-free curd, if colored after the ether has been poured off, is examined further for caramel or aniline orange by placing a portion of the curd in a test-tube and shaking vigorously with concentrated hydrochloric acid. If the color is caramel, the acid solution of the colored curd will gradually turn a deep blue on shaking, as would also the white fat-free curd of an uncolored milk, the blue coloration being formed in a very few minutes, if the fat has been *thoroughly* extracted from the curd; indeed it seems to be absolutely essential for the prompt formation of the blue color in the acid solution that the curd be free from fat. Gentle heat will hasten the reaction. It should be noted that it is only when the blue coloration of the acid occurs in connection with a *colored* curd that caramel is to be suspected, and if much caramel be present the coloration of the acid solution will be a brownish blue. If the above treatment indicates caramel,

it would be well to confirm its presence by any of the usual tests on a fresh sample of the milk.¹

If the milk has been colored with aniline orange, the colored curd, on applying the strong hydrochloric acid in the test-tube, will *immediately* turn pink. In the case of the caramel, the color of the curd itself remains unchanged, the solution only turning blue and that gradually; on the contrary with the aniline orange the curd itself takes the pink color the moment the acid touches it. If a large amount of the aniline orange has been used in the milk, the curd will sometimes show the pink coloration when hydrochloric acid is applied directly to it, before treatment with ether, but the color reaction with the fat-free curd is very delicate and unmistakable.

SUMMARY OF SCHEME FOR COLOR ANALYSIS.

Curdle 150 cc. milk in casserole with heat and acetic acid. Gather curd in one mass. Pour off whey, or strain if curd is finely divided. Macerate curd with ether in corked flask. Pour off ether.

Ether Extract.

Evaporate off ether, treat residue with NaOH and pour on wetted filter. After the solution has passed through, wash off fat and dry filter, which if colored orange, indicates presence of annatto.

(Confirm by SnCl_2).

Extracted Curd.

(1) *If Colorless.*—Indicates presence of no foreign color other than in ether extract.

(2) *If Orange or Brownish.*—Indicates presence of aniline orange or caramel. Shake curd in test-tube with concentrated hydrochloric acid.

If solution *grad-* If orange curd
ually turns blue; *immediately* turns
indicative of car- pink; indicative
mel. of aniline orange.

(Confirm by test-
ing for caramel in
whey of original
milk.)

THE REPEATED USE OF THE DOUBLE CHLORIDE OF COPPER AND POTASSIUM FOR THE SOLUTION OF STEEL OR IRON IN ESTIMATING CARBON.²

By GEO. WM. SARGENT.

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IN the *Chemical News*, Vol. 79, p. 169, which appeared April 14 of last year, there is an article headed: "The Estimation of

¹ See Nineteenth Annual Report of the Mass. State Board of Health (1887), p. 183.

² Read at the March meeting of the Philadelphia Section of the American Chemical Society.