

disintegration of liver tissue, the lecithin content of which is relatively high.

It must be remembered, further, that bacterial cells make up a considerable fraction of the dried feces. Nothing very definite is known of the fat content of the intestinal bacteria, but of certain bacteria from other sources it has been shown that the fat content is high. This is especially true of the tubercle bacillus,¹ but of the minute composition of such fats not much is given in the literature. In view, however, of the general nature of bacterial cells it is fair to assume the presence of lecithin-like bodies in their fat.

Since numerous investigations of recent years have shown the great importance of the lecithins in relation to problems of nutrition, metabolism, and immunity, we have undertaken a continuation of this work with the hope of defining more closely the nature of the phosphorus compounds in the feces fat.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,
CHICAGO, July, 1906.

DISCOLORATION OF FRUITS AND VEGETABLES PUT UP IN TIN.

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Received July 19, 1906.

A NUMBER of cases of discoloration of fruits and vegetables put up in tin have come to the attention of the writer. In most cases the discoloration was undoubtedly due to sulphides of the heavy metals, the discoloration in some cases being confined to the container, in others affecting the fruits and vegetables as well. The source of the hydrogen sulphide varied in different cases. Some micro-organisms are capable of evolving hydrogen sulphide through breaking down of proteid matter, but this would result only with goods which were not properly sterilized and is not so frequent as some other causes. Also such goods are unfit for consumption so that the discoloration is of minor importance. In other cases hydrogen sulphide resulted from the use of sulphites in connection with fruits, reaction having taken place between the sulphites and vegetable acids with the liberation of sulphurous acid, which, acting upon the tin of the container, had produced

¹ See among other authorities, De Schweinitz: This Journal, 25, 354 (1903).

hydrogen sulphide. Another source of hydrogen sulphide was the decomposition of proteid matter through the use of an exceptionally heavy process by the action of steam under pressure on the proteids. Where discoloration had taken place in the goods, the source of the heavy metals was the tin plate and solder of the container.

All fruits and vegetables, as has been shown by Leach,¹ have a greater or less solvent action upon the tin plate and solder of the container, taking up variable amounts of tin and lead, the extremely acid fruits, like rhubarb, being most active, though some of the vegetables, such as squash and pumpkin, take up very large amounts of tin.

Having pointed out the source of the heavy metals and the hydrogen sulphide, one can very readily understand how the discoloration of these goods would take place. A history of some cases in point will best illustrate the different forms of discoloration.

Recently, some badly discolored pears were sent in to the laboratory for examination. On opening the can a heavy brownish black deposit was discovered over the inside of the can, and wherever the pears came in contact with the can there was also the same deposit on the fruit, rendering it unsightly and unfit for the market. Previous experience by the director of the laboratory, Mr. E. W. Duckwall, at once suggested that sulphites had been used in the preparation of the fruit, and that the discoloration was probably due to their use. Determinations for sulphites were made and they were found to be present in very large quantity. The character of the discoloration, which almost assumed the form of a deposit, suggested to us that it was due to metallic sulphides, principally tin sulphide, resulting from the reaction between the sodium sulphite, vegetable acids and tin.

In order to ascertain whether this was the case or not, pieces of pear of good color were placed in two beakers with pieces of tin and solder in each. To one sodium sulphite was then added and the other simply left in water. The pear not treated with sodium sulphite kept its color perfectly on standing in contact with the tin and solder, but the pear in the beaker to which sulphites had been added soon began to darken, and in the course of two or three days the same brownish black appearance observed in the

¹ "Food Inspection and Analysis," p. 696.

discoloration of the pears in the case at hand had permeated nearly the whole pear tissue of the sample under treatment in the beaker. Some of the brownish deposit, also some of the discolored fruit from the can showing the discoloration, was treated with strong hydrochloric acid, which immediately destroyed the discoloration of the pear tissue and brought the deposit into solution. On diluting, filtering and precipitating with hydrogen sulphide, a small quantity of tin sulphide was obtained, which indicated that the discoloration was due to sulphide of tin and other metallic sulphides. This was further confirmed by treating the inside of the discolored can in which the pears had been put up with strong hydrochloric acid, and testing the fumes given off with lead acetate paper for hydrogen sulphide. A very positive reaction was obtained for sulphides, which was confirmed by other tests. In fact, the odor of hydrogen sulphide evolved from the decomposition of the sulphides seemed to be unmistakably present. This experimental data seemed to show conclusively to us that the discoloration was due to metallic sulphides resulting from the hydrogen sulphide which had been liberated by reaction between the sulphites and the tin, aided by the fruit acids present.

To further test this view pieces of tin foil were treated with sodium sulphite and also with sulphurous acid solution. The tin foil in the sulphurous acid solution quickly became discolored with a considerable brown deposit, which was shown to be tin sulphide, while that in the sulphite solution remained perfectly bright. This would indicate that there would not be much danger of discoloration from reaction between sulphites and tin in a neutral medium, but that where sulphurous acid would be liberated discoloration would be very sure to result.

Other pieces of tin foil were then treated in beakers with sodium sulphite solution to which various acids, such as acetic, lactic, tartaric, citric and others, had been added. In each case discoloration resulted, showing that the vegetable acids had liberated sulphurous acid, which in turn reacted with the tin to form tin sulphide, giving the discoloration. Most fruits contain appreciable amounts of such acids as citric and malic acid. In some cases, where fermentation has taken place to any extent, acetic or lactic acid is present, and fruits or vegetables containing any

of these organic acids, if treated with sulphites, are very sure to produce discoloration.

Soldering fluxes sometimes are somewhat acid, and if a little excess is used, permitting the acid to come in contact with the goods, if these are treated with sulphites, discoloration is very sure to be observed at points where the acid has come in contact with the fruit or vegetable. While it would seem that sulphites can be used without any danger of discoloration in neutral substances, there certainly is much danger of discoloration if they are used in products of a somewhat acid character put up in metal containers.

Discoloration from hydrogen sulphide evolved through the employment of a heavy process is illustrated by the following case: In order to secure the proper cooking of the large siftings of peas, which was not readily accomplished in the blancher, the packer had lengthened the process to fifty-five minutes at 240° , with the result that this pack of peas contained a very large percentage of cans containing discolored peas, while the smaller siftings of peas given a shorter process were free from the discoloration. An examination of the peas in the containers showed the cans to be very much discolored, the inside of the can being of a brownish-purple color, though there was nothing in the nature of a deposit. The discoloration of the peas was confined more particularly to those around the outer portion of the can and the discoloration did not extend into the peas to any great extent. Some of the more badly discolored peas were separated out and a determination of tin made, which was found to be present in considerable quantity. Also the discoloration, both of the peas and the can, was soluble in strong hydrochloric acid, which would be the case with tin sulphide. Reactions for hydrogen sulphide were obtained from the inside of the can quite readily, both with lead acetate paper and sodium nitroprussiate. This same discoloration of the can is noticeable wherever a heavy process is employed and had previously been found by the writer to react for sulphides, evidently being due to tin sulphide formed through hydrogen sulphide liberated during the processing. There is seldom discoloration of the contents, but in this case it seemed that sufficient hydrogen sulphide had been liberated, together with the tin and lead taken up by the contents of the can, to produce the discoloration. Experiments which have been made

show that when proteid substances are acted upon by steam under pressure ammonia and hydrogen sulphide are split off from the proteid molecule, with the formation of albumose and peptone. Dr. Long, in his recent work¹ in his discussion of proteid substances, gives special attention to the decomposition of proteid substances by steam under pressure, stating that if the temperature is high enough the reaction will extend even beyond the formation of ammonia and hydrogen sulphide, resulting in the complete destruction of the proteid molecule. This would explain the source of the hydrogen sulphide, and, taking into consideration the fact that tin and some lead would have been taken up by the peas, would explain the discoloration of the goods.

In order to assure ourselves that sufficient hydrogen sulphide would be produced under a very heavy process to cause the discoloration, two glass jars were filled with peas and to one 50 mg. of stannous chloride were added, and both were processed at 240° for an hour. The peas in the jar to which the tin chloride had been added showed a very marked brown discoloration, from which the other peas were entirely free, which would confirm our findings in this case.

In some cases, especially in corn, we have encountered a discoloration which was more local in character than in the case of the peas just described. In this case the discoloration was confined almost entirely to the vicinity of the seams and cap. As corn is a very stable product and does not change its position in the can it would appear that the discoloration in this case had come more particularly from the solder or from an excess of flux. It has been shown that where a poor grade of solder containing a large amount of lead is used, the action of the fruit or vegetable juice is greater, more metal being brought into solution. Also if an excess of soldering flux, especially if somewhat acid in character, should remain along the seam, it would result in more of the metal of the container being taken up by the contents of the can at those points, and then on liberation of hydrogen sulphide during the process discoloration would result at these points, while the contents of the can otherwise would be free from discoloration.

From the above, it can be stated that sulphites should not be used with goods of an acid character which are to be put up in tin.

¹ "Physiological Chemistry," p. 74.

Where a heavy process is necessary, care should be exercised to avoid the use of an excess of flux or the use of low-grade solder or tin plate which would tend to increase the amount of heavy metals taken up by the goods. Also the length of the process, in order to avoid evolution of hydrogen sulphide, should be as short as possible, consistent with complete sterilization of the goods.

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NOTES.

Note on the Insolubility of Ferric Hydroxide in Ammoniacal Solutions.—Some years ago difficulty was experienced in this laboratory from the very considerable solubility of ferric hydroxide in an excess of commercial ammonia. It was found, however, that if, after precipitation, the excess of ammonia was expelled by heating upon a steam-bath, the iron was precipitated quantitatively. No experiments were performed at the time to determine the nature of the substance which caused the difficulty, but since it was assumed that similar impurities were likely to be contained by any commercial ammonia, the precaution of precipitating iron with the smallest possible excess of ammonia and of expelling the greater part of this slight excess upon a steam-bath before filtration, has been rigorously followed since the time when the difficulty was first encountered.

The experiments described below were directed to determine, if possible, the extent of this solubility as well as its cause. Solutions of ferric chloride containing about 0.25 gram of iron were precipitated with redistilled laboratory ammonia. In different experiments both hot and cold solutions of the ferric salt were employed, and both a large and a small excess of ammonia. In every case filtration, without suction, was carried out immediately after precipitation. It was considered unnecessary to wash the precipitate. The filtrates were evaporated to small bulk and were then tested for the presence of ferric iron by adding hydrochloric acid (free from iron) and potassium sulphocyanate. Although in every case an extremely slight yellow color was produced, by comparison with standard tubes containing known quantities of iron it was determined that the amount of iron in the filtrate was never as much as one one-hundredth of a milligram.