

**THE PHYSICAL CHEMISTRY OF DEHYDRATED**

**MILK PRODUCTS.**

A Thesis submitted to the University of  
Glasgow for the Degree of Doctor of  
Philosophy in the Faculty of Science.

by

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**September, 1944.**

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ACKNOWLEDGMENT.

The author wishes to thank the Council of the Hannah Dairy Research Institute for the facilities they have accorded him in carrying out this work. He also thanks Dr N.C. Wright for his interest and encouragement and Dr J.A.B. Smith for his help and advice during the course of the work.

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## S Y N O P S I S

Experiments have been carried out to determine how the storage life of spray-dried full-cream milk powder might be extended. In powders of low moisture content the only important type of storage deterioration is fat oxidation, which leads to the development of objectionable tallowy flavours. The specific object of the present work was to devise means by which the onset of such tallowiness could be delayed as long as possible.

Details of the various analytical methods are given in Part I.

In Part II storage tests at 47°, 37°C and room temperature are described in which powders made on three different types of commercial spray-drier were used. The experiments showed that an increase in the temperature to which the milk was heated before drying had a marked effect on the keeping quality of the resulting powder, the storage life being increased two- to three-fold by this means alone. Various preheating temperatures from 160° to 200°F were studied. Clarification of the liquid milk had no effect and selection of the milk with the best bacteriological properties had a significant effect only when a low preheating temperature of 165°F was used. With a preheating temperature of 190°F selection of the milk did not significantly affect the keeping quality of

the powder.

The higher preheating temperatures imparted to the milk powder a slight cooked flavour, and although this was not objectionable, experiments were undertaken to find whether a powder of equally good keeping quality but without the cooked flavour could be made by adding antioxidants to the milk before drying. In preliminary work carried out jointly with members of the staff of the Low Temperature Research Station, Cambridge, ethyl gallate and ascorbic acid were found to be the most promising antioxidants of the many substances which were investigated. It was therefore decided that these two antioxidants should be tested on a commercial spray drier. In Part III the experiments undertaken with this object in view are described. It was found that in powder containing 0.07% of ethyl gallate tallowiness took about three times as long to develop as in the control powder, and that ethyl gallate was not itself destroyed during storage. With 0.110% ascorbic acid the storage life was 70% longer than that of the control, but the ascorbic acid decreased as the storage period increased.

In Part IV some preliminary experiments are detailed in which it is shown that under the packing conditions used in this work glass and lacquered tinfoil containers gave an increase in storage life of from 10 to 40% over that obtained by packing in plain tinfoil containers.

## INTRODUCTION.

The work described in the following pages forms part of a series of investigations devised to determine the feasibility of various methods of increasing the storage life of full-cream milk powder. When milk powder is stored two main types of deterioration may occur.

In one type the powder becomes increasingly insoluble and develops most objectionable stale, "cardboardy" or glue-like flavours and a brown discolouration (Findlay et al., 1944). The changes which occur involve the protein and probably also the lactose of the milk. They are closely related to the moisture content of the powder for, if the moisture content exceeds 4%, this type of deterioration renders the powder unpalatable in a few weeks in temperate climates and in a few days at 37°C. The higher the moisture content, the more rapidly the deterioration sets in. It can be avoided entirely by ensuring that the powder is manufactured and stored in such a way that the moisture content never exceeds 2.5%.

The other main type of deterioration presents a problem which is not so readily solved. In this type the fat of the powder becomes oxidised, with the result that tallowy flavours develop which sometimes render the product quite unpalatable even after only three months storage at moderate temperatures. The



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present work is concerned with the prevention of this type of deterioration.

The development of tallowiness is influenced by at least five factors: (1) the nature of the powder, (2) the oxygen content of the gas in which the powder is packed, (3) the storage temperature, (4) the balance of pro- and anti-oxidants present in the powder, and (5) the type of container. It will be useful at this stage to discuss briefly each of these five factors.

(1) The nature of the powder.

Milk powder may be made from either separated or full-cream milk and it may be dried by either the "roller" or "spray" process. Separated milk powder dried by either process contains only about 1% of fat. Consequently the development of tallowiness is not an important problem in this type of dried milk. In full-cream powder, however, there is usually about 27% of fat in which small portions of the unsaturated components such as oleic and linoleic acid can readily become oxidised to form foul-tasting tallowy compounds. Under similar conditions of storage roller-dried full-cream powder usually develops tallowiness more slowly than the spray-dried product. The latter is however far superior to the roller-dried product in its much greater solubility, in its relative freedom from "processed" flavours, and in the closer resemblance which exists between the reconstituted powder and fresh

liquid milk. The present work has therefore been confined to a study of methods by which the storage life of full-cream spray-dried powder may be extended so that a satisfactory keeping quality may be added to the other desirable properties possessed by this product.

(2) The oxygen content of the gas in which the powder is packed.

The exclusion of oxygen from the powder by packing it in nitrogen or by compressing the powder into blocks has already been extensively studied by Lea et al. (1943), Waite (1942), Thiel (1941), and Findlay et al. (1942). These authors have shown that when the oxygen content of the gas in contact with the powder is reduced to 2 or 3%, the storage life of the dried milk is extended several years, while by reducing it to less than 1% the powder can be stored indefinitely. Both inert gas-packing and blocking require, however, costly apparatus and expert labour to make them successful. In the present investigation attempts have therefore been directed towards establishing simpler methods by which the storage life could be extended, if not indefinitely, at least sufficiently long for all practical purposes, - the minimum storage life aimed at being 2 to 3 years in temperate climates and 1 to 1½ years in tropical climates.

(3) The storage temperature.

Except when oxygen is almost entirely removed from

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the gas associated with the powder, the storage temperature is of great importance in determining the length of successful storage. Data which have been collected in the present work on storage at different temperatures have shown that the rate at which tallowiness develops increases two- or three-fold for each increase in storage temperature of 10°C. Valuable information is thus available regarding the probable storage properties of dried milk destined to pass through, or to be stored in, the tropics.

(4) The balance of pro- and anti-oxidants in the milk.

Milk contains both pro- and anti-oxidants and the balance between these systems can be altered by raising the temperature at which the liquid milk is heated before it is dried. It is possible that the higher temperature destroys some of the pro-oxidants, but probably its main effect is to produce compounds containing sulphhydryl groups which act as antioxidants and so postpone the onset of tallowiness. The longer keeping quality of roller-dried milk, to which reference has already been made, is almost certainly due to this type of change, for in roller-drying the heating, though of short duration, is far more intense than in spray-drying. Other methods by which the pro- and anti-oxidant balance in the milk might be altered so as to retard oxidation include the selection of fresh milk of good bacteriological quality, clarification of the

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milk and the addition to the liquid milk of substances known to have antioxidant properties. In the present investigation a detailed study of the effect on the storage life of the dried product of various preheating temperatures, of milk selection, of clarification and of the addition of antioxidants to the liquid milk, has therefore been included.

(5) The type of container.

Lea (1944a) has shown that the keeping quality of a fat may vary with the type of container in which it is stored. Opportunity has therefore been taken in the present experiments to study the importance of this factor in milk powder storage.

## PART I.

### METHODS.

#### Moisture content.

Since the specific defect under investigation in the present experiments was tallowiness, it was essential to ensure at the outset of each experiment that the moisture content of the powders to be used was below 2.5%: otherwise the interpretation of the results would have been complicated by the simultaneous development of defects due to changes in the protein and lactose. The apparent moisture content of a milk powder varies slightly with the technique employed. The following method was found to give concordant results and was adopted throughout.

1 g. of powder was weighed into a flat aluminium dish, 6 cm. in diameter and 1.5 cm. in depth and provided with a tightly fitting lid. After the uncovered dish had been heated for 3 hours at 100°C, it was removed from the oven, covered, and allowed to cool for 30 minutes in a desiccator containing P<sub>2</sub>O<sub>5</sub>. It was then weighed and the results expressed as grams of moisture per 100 g. of the original powder.

#### Solubility.

If reconstituted milk powder is to resemble normal milk it is important that the powder should be readily soluble. It was necessary, therefore, to ensure that any alterations in the methods of manufacture which were made during the present work did not adversely affect the solubility of the powder.

The standard method used for determining solubility was the rapid method of Howat et al. (1939).

1 g. of powder was weighed into a 15 ml. centrifuge tube. About 2 ml. of water was added from a burette and the mixture stirred well with a glass rod which had been previously wetted. When all the powder had become thoroughly moistened, more water was added until a total of 9 ml. had been used. The tube was then stoppered and kept in a water bath for 5 min. at either 20 or 50°C. It was then shaken rapidly (4 to 6 double excursions per second) for one minute. When the solubility at 50°C was required the tube was shaken in an insulated container. It was then centrifuged for 20 minutes at 3000 r.p.m., the volume of sediment noted, and the fat and supernatant layer removed as completely as possible to another tube. The total solids content of the mixture in this tube was then estimated by the method of Golding (1934). The ratio of the dissolved solids to the solids initially present in the original gram of milk powder gave the solubility index as described by Howat et al.

It was found that for a very soluble powder the solubility index obtained in this way sometimes exceeded 100 by almost two units. It appeared possible that this might be due to the fact that in milk powder the lactose is almost entirely anhydrous, whereas when it is dissolved in water and dried at 100°C it is converted to the hydrated form. Thus in the determination of the solubility the 0.35 g. lactose contained in 1 g. powder would become hydrated and the total solids would be increased by 0.018 g. of water of crystallisation. To allow for this addition of water, it would be necessary to subtract 1.8 from the solubility index in calculating the percentage solubility.

To test this hypothesis the requisite correction

TABLE I.

The solubility of powders at 20°C estimated by the rapid method of Howat et al. (1939) and corrected for the hydration of lactose compared with values obtained by the method of Lampitt and Bushell (1931a).

<u>Spray-dried full-cream powder prepared on the following types of plant</u>	<u>Method</u>	
	<u>Howat et al.</u>	<u>Lampitt &amp; Bushell</u>
Gray-Jensen	92.0	92.5
Milka1	98.1	98.6
Kestner	92.0	90.7
Krause	99.0	99.5
Spray-dried separated milk	98.5	98.6

was applied in a series of determinations in which the rapid procedure of Howat et al. was compared with results obtained by the more elaborate and lengthy method of Lampitt and Bushill (1931a) in which the solubility is estimated from the actual weight of undissolved solids contained in the sediment after centrifuging the reconstituted powder. Typical results, which are recorded in Table 1, demonstrate that the values so obtained show excellent agreement.

#### Assessment of flavour.

The most sensitive of all tests so far available for detecting deterioration in dried milk is simply that of tasting the reconstituted product. For this test the powders were always reconstituted with eight times their weight of water at 25°C and labelled in a code unknown to the tasters. A reconstituted control powder known to be of good quality was included with the others as a standard. A panel of five workers, all with experience in assessing the flavour of milk powder, tasted the samples within two hours of their being prepared. Each member of the panel wrote his verdict on a form specially provided for the purpose. A number was then allotted to each sample for each taster according to the following scheme:- 0 = very good and palatable, 1 = fairly good, still quite palatable, 2 = slightly unpalatable due to the presence of slight but definite off-flavours, 3 =



definitely unpalatable due to more pronounced off-flavours, and 4 = extremely tallowy. The values recorded by the five tasters for each sample were averaged to give the off-flavour score by which the palatability of the powder was quantitatively assessed. These off-flavour scores were then plotted against the storage time to give curves such as those shown in Fig.2. When the curves so obtained pass off-flavour score 1, the trained tasting panel are beginning to detect the development of slight off-flavours. When score 2 is reached the off-flavour would be sufficiently obvious to be noticed by the average untrained consumer.

With tallowy powders there is a tendency for the objectionable taste to linger on the palate and to make the tasting of subsequent samples more difficult. As far as possible, therefore, the samples which obviously smelt tallowy were tasted last. Even when this was done it was found advisable to clear the palate with the control sample after a milk of doubtful quality had been tasted.

It was also essential to rinse the mouth with tepid water between each sample. Cold water should not be used since it reduces the sensitivity of the palate. For reliable results, it was found that not more than eight samples should be tasted at one time:

with greater numbers the tasters became fatigued and the value of the results was reduced.

This technique was used in the work on inert gas-packing by Lea et al. (1943) and was found to be most reliable. Weaver (1939) in work on milk flavour has also found that tasting tests are dependable even when four of his seven tasters were inexperienced in such work.

The absorption of oxygen by the powder.

Tasting tests, however reliable they appear to be, are necessarily subjective. It is therefore important to have some objective test by which the general conclusions from the tasting results may be confirmed. As regards tallowness one such test will obviously be the rate at which the powder absorbs oxygen from the gas with which it is in contact, since this will furnish a direct measure of the degree of oxidation.

In the present experiments a given weight of powder was stored in gas-tight cans of known volume, and at intervals during the storage period a sample of gas was withdrawn (by the method already described by Waite (1941a)) and analysed in the usual way in a Haldane apparatus. By this means the percentage of oxygen in the atmosphere of the can was readily determined. In order to record the results in units which might be readily compared with the results of other workers who have used different types of milk

powder and different powder-can ratios, it was essential to calculate, from the percentage of oxygen in the gas, the weight of oxygen which had been absorbed per 100 g. powder. To do this the weight of powder in the can, the volume of the can and the barometric pressure and temperature on the day when the powders were packed all require to be known. The actual technique adopted in the present work, whenever gas analyses were undertaken, was to pack 90 g. of the powder in a cylindrical 6 oz. Danish Cream can. This was found to have a volume of 186 ml. when the sealing machine, by which the can was closed, was carefully adjusted to the normal setting. The volume was found to be the same whether the can was made of lacquered or plain tin plate. The method of calculation may be illustrated from the following typical experiment. The temperature when the cans were packed in the open packing-room was 12°C and the barometric pressure was 759 mm. The weight of oxygen absorbed by this powder at any given time during storage was arrived at as follows:- The density of milk powder solids is 1.31 (Lea et al. 1943).

The volume of 90 g. powder is therefore 68.7 ml.

The original volume of the air in the can containing 90 g. powder would therefore be  $186 - 68.7 = 117.3$  ml.

At N.T.P. this would be  $117.3 \times \frac{273}{285} \times \frac{759}{760} = 112.3$  ml.

The original volume of nitrogen in the can would therefore be  $\frac{79.1}{100} \times 117.3 = 92.8$  ml. under atmospheric conditions

or 88.8 ml. at N.T.P.

Suppose that on a given day during storage it was found by gas analysis that the nitrogen content of the gas was n%. Since the amount of nitrogen would remain unchanged during storage, the total volume of gas in the can on that day must have been  $\frac{8880}{n}$  ml.

The oxygen absorbed by 90 g. powder must therefore have been  $(112.3 - \frac{8880}{n})$  ml. at N.T.P.

But 22.4 ml. O<sub>2</sub> = 32 mg.

The weight of oxygen absorbed by 100 g. powder would therefore be  $\frac{32 \times 100}{22.4 \times 90} (112.3 - \frac{8880}{n})$  mg. = 1.588  $(112.3 - \frac{8880}{n})$  mg.

The amount of oxygen absorbed at any time could therefore be calculated by substituting the value found by gas analysis for n.

By substituting 100 for n, the total amount of oxygen available for absorption under the packing conditions used in this particular sample was therefore 37.3 mg.

The values recorded in the various tables and diagrams for oxygen absorption were all obtained in this way.

### Peroxide value.

Another objective method by which the conclusions obtained from flavour tests can be confirmed is to estimate the peroxide value of the fat contained in the milk powder. As the fat oxidises, peroxides are formed at the double bonds of a small proportion of the unsaturated fatty acid constituents, and under suitable conditions the peroxide can be determined by its property of liberating iodine from potassium iodide or of oxidising ferrous to ferric iron. Qualitative methods for detecting peroxides iodometrically have been described by Heffter (1904) and Powick (1923) and quantitative methods by Yoder (1926) and Delore (1929). A most thorough study of the subject has been made by Lea (1938) who has introduced a method for determining peroxide values in which the fat is extracted with peroxide-free ether, treated with potassium iodide, and the liberated iodine titrated with standard thiosulphate. The extraction of the fat from spray-dried milk powder presents some difficulty but for all samples complete extraction is possible if the moisture content of the powder has been raised to about 12%, (Lampitt and Bushill, 1931b). This can be done by exposing small weighed amounts of powder to an atmosphere of 100% relative humidity overnight. To avoid this complication and to obtain a more rapid method Smith (1939) suggested the extraction of the fat from the powder by a mixture of acetic acid and

chloroform. Almost complete extraction of the fat is obtained by this method, but the peroxide value is always lower than that obtained by Lea's method and it is unlikely that the first small traces of peroxide are detected. This lack of sensitivity is probably due to the fact that the acetic acid and chloroform extract other substances besides fat, which are capable of absorbing small amounts of the iodine liberated by the peroxide from potassium iodide. Moreover, all iodometric methods suffer from two disadvantages: first, they seldom detect peroxide before tallowiness is detected by taste, and second, the end-point tends to be unsatisfactory with the very dilute thiosulphate required (0.005 N or 0.002 N).

During the course of the present work a method of estimating the peroxide value of the fat in milk powder was published by Chapman and McFarlane (1943). It depends on the oxidation of ferrous to ferric iron in the presence of ammonium thiocyanate, the intensity of the resulting colour of ferric thiocyanate giving a measure of the peroxide originally present. This method was modified slightly and adopted in the later experiments of the present investigation. The details are as follows:-

2 g. lots of milk powder were weighed into small petri dishes and exposed in the dark to an atmosphere of 100% relative humidity for 24 hours or 48 hours. The powder was then transferred to 100 ml. volumetric flasks and refluxed for 20 minutes with 50 ml. acetone which had previously been redistilled twice

TABLE II.

The calibration of the Spekker Absorptiometer for the  
determination of peroxide values.

<u>Weight of ferric iron</u> <u>(<math>\mu</math>g./ml. solution)</u>	<u>Absorptiometer</u> <u>Reading</u>
0.00	0.010
0.09	0.026
0.50	0.096
0.70	0.146
0.93	0.186
1.16	0.218
1.60	0.302
2.30	0.436
3.70	0.620
4.90	0.790

over calcium chloride. The flasks were cooled and the contents made up to 100 ml. with redistilled acetone. They were well mixed and filtered through a Whatman No.42 paper. While this part of the process was proceeding, a reagent was made up by dissolving 1.0 g. ammonium thiocyanate in 7.5 ml. water in a 250 ml. flask and adding 100 ml. acetone. This was followed by 0.25 g. ferrous sulphate and acetone up to the 250 ml. mark. The mixture was well shaken and then allowed to stand for a few hours with occasional shaking after which it was filtered. 10 ml. of the reagent and 2 ml. of the acetone filtrate from the powder were mixed and warmed in a water bath for 1 minute at 70°C followed by 10 minutes at 50°C. The acetone mixture was then cooled and the concentration of ferric thiocyanate determined in a Spekker Absorptiometer which had been previously calibrated by using known concentrations of ferric chloride in acetone instead of the milk powder filtrate. A calibration curve was drawn from the figures in Table II which were obtained by using the Spekker Colour Filter No.6.

The peroxide value in milliequivalents per Kg. of powder was calculated as follows:-

Suppose the absorptiometer reading for a given sample showed the presence of  $n$   $\mu$ g. of ferric iron per ml. To obtain this reading 2 ml. of filtrate or one-fiftieth of the acetone extract from 2 g. powder had been made up to 12 ml. with 10 ml. of reagent. The amount of ferric iron equivalent to one kilogram of powder was therefore  $\frac{12n \times 1000}{2}$  g. ferric iron/Kg. powder.

Converted to milliequivalents this becomes

$$\frac{12n \times 50}{55.84 \times 2}$$

or 5.38 n milliequivalents of ferric iron or of peroxide.

In their original method Chapman and McFarlane did not however raise the moisture content of the milk powder before refluxing it with acetone. The advisability of raising the moisture content at any



rate with spray-dried powders, was demonstrated in preliminary work during the present study by determining the peroxide values for two samples of powder with and without previously raising the moisture content. The values before treatment were 1.1 and 2.2 milliequivalents per Kg. of powder whereas after treatment they were 3.4 and 9.6. The differences were undoubtedly due to the much more thorough fat extraction which occurred when the moisture content was raised to about 10%. Without such treatment very low peroxide values would clearly not be detected.

A brief comment should be made regarding the exact method used in raising the moisture contents of the powders. For results of the highest accuracy the powder should be kept, not at room temperature and in moist air, but at about 0°C in an atmosphere of moist nitrogen. Thus for one sample of powder a peroxide value of 9.6 was obtained by exposing the powder to moist nitrogen at 2°C, as compared with 12.0 by exposing it for the same time to moist air at room temperature. The latter method had obviously caused some additional oxidation during treatment. Exposure of a powder to moist nitrogen is not, however, feasible as a routine for large numbers of samples. In the present work uniform treatment in air at room temperature had, therefore, to be adopted as the only practicable alternative. This fact should not seriously invalidate the results, since the peroxide

values obtained with any given group of powders exposed to similar conditions will furnish comparable values, i.e. will indicate the relative extents of deterioration. Moreover it should in any event be noted that during fat oxidation peroxides are not merely being formed, but are also being continuously decomposed: thus by whatever method they are determined the results cannot be regarded as absolute.

Chapman and McFarlane state in the description of their method that the water content of the acetone in which the colour develops is of great importance. They recommend the use of acetone containing 4% of water but they do not give details as to the magnitude of the change which results from altering the water content. Since it is not always easy to be certain of the water content of the acetone within very narrow limits, an experiment was carried out in which the thiocyanate reagent was made up with acetone containing six different proportions of water and this reagent was then used to determine the peroxide value of a powder in which oxidation was just commencing and of a second powder in which deterioration was far advanced. From the results shown in Fig.1, it is obvious that with water contents ranging between 3 and 6%, the colour intensity is constant. It is true that absolute acetone gives a more intense colour than 97 to 94% acetone, and that the intensity quickly diminishes as the water content increases. Absolute acetone is, however, clearly

**Figure 1.**

**The influence of the water content of the reagent acetone on the apparent peroxide value expressed as milliequivalents per kilogram of powder (p.16 ).**

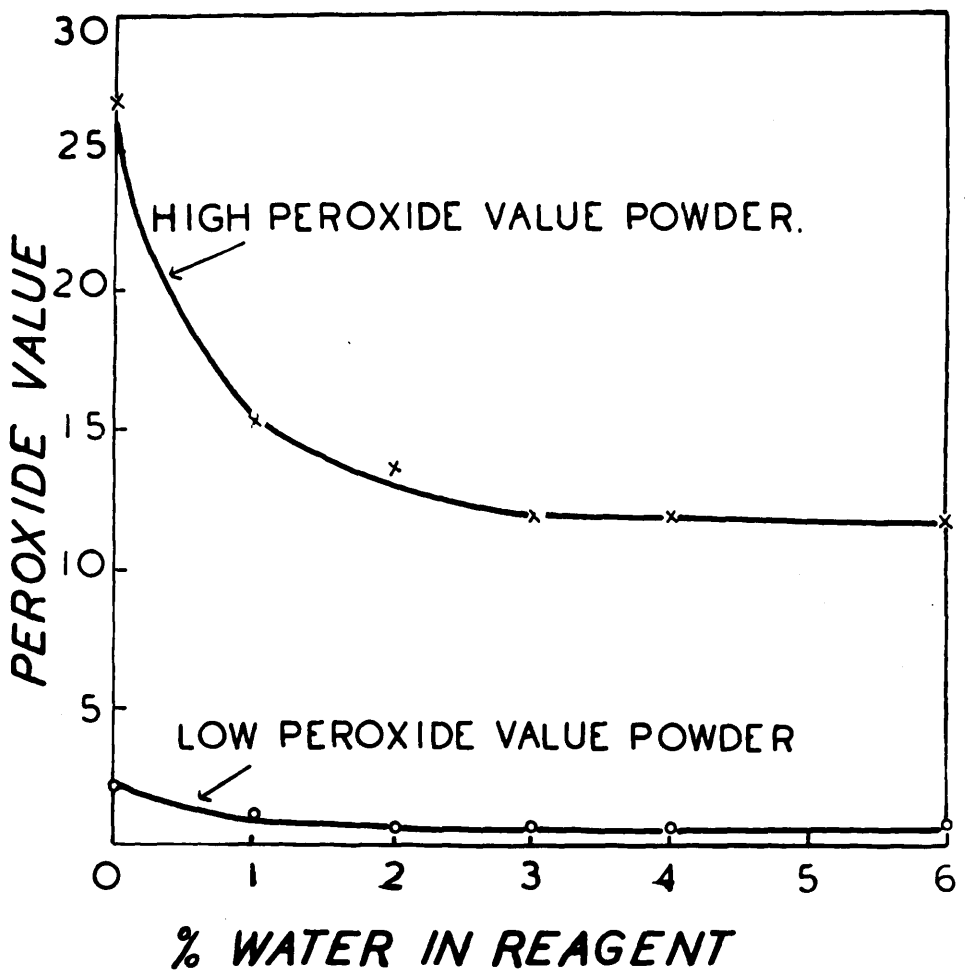


FIG. I

not suitable for routine work of this type, since it rapidly absorbs small amounts of moisture on exposure to air. Reliable results are more readily obtained by having 3 to 6% moisture present.

All apparatus used in the determination of the peroxide value was boiled with nitric acid and thoroughly rinsed before use. If this was not done, erratic results were obtained.

#### Copper content.

For many years it has been well known that copper is an active pro-oxidant in milk. As early as 1905 Golding and Feilmann observed that when milk was passed over copper-plated coolers it very rapidly acquired a tallowy flavour. In 1923 Supplee studied the effect of copper contamination in dried milk and found that it greatly accelerated the onset of tallowiness. With pure lard Rai (1917) found copper to be 16 times more active as a pro-oxidant than iron or zinc. It was therefore clearly essential to estimate copper in the samples of milk powder used in the present experiments in order to ensure that any observed differences in tallowiness between different samples of powder were not due to differences in copper content.

For determining copper the method of Sylvester and Lampitt (1935) was used. It was modified slightly in that the copper diethyldithiocarbamate was exhaustively extracted with carbon tetrachloride and

TABLE III.

The calibration of the Spekker Absorptiometer for  
the determination of copper.

<u>Mg. copper</u> <u>per 100 ml.</u>	<u>Absorptiometer</u> <u>Reading</u>
0.000	0.008
0.005	0.073
0.010	0.130
0.020	0.260
0.025	0.330
0.030	0.398

the final colour estimation was made in a Spekker Absorptiometer and not visually in Nessler tubes as in the original method. Diphenylthiocarbazone reagent was made up as described by Sylvester and Lampitt.

The absorptiometer had first to be calibrated. Into each of six 100 ml. flasks 2.5 g. ammonium sulphate, 15 ml. water, 3 ml. 5N ammonia and 5 ml. of 0.1% diethyldithiocarbamate were introduced. Sufficient copper sulphate solution was added to five flasks so that after the volumes were made up to the 100 ml. mark a range of 0.01 to 0.06 mg. copper per 100 ml. of solution would be obtained. To one of the flasks no copper was added. 50 ml. were transferred from each flask to a separating funnel and extracted five times with 2 ml. carbon tetrachloride, the carbon tetrachloride extracts being removed to a 10 ml. cylinder. After all the five extracts had been combined the carbon tetrachloride was made up to 10 ml. and filtered into a Spekker Absorptiometer cell. The reading was made with the Spekker No.7 colour filter. The calibration curve was drawn from the figures recorded in Table III.

The details of the method for estimating the copper in milk powder were as follows:-

20 g. of powder were accurately weighed into a silica basin and ashed by heating gently with a glass-tipped bunsen burner. The residue was cooled, 3 ml. concentrated  $H_2SO_4$  added and the basin heated till no more fumes were evolved. The basin was then kept in a muffle furnace at  $400^\circ C$  for 4 hours. The resulting ash was dissolved in 20 ml. 6N HCl and washed into a 250 ml. volumetric flask. It was neutralised with 5 N ammonia, acidified with 1 ml. 6N HCl and finally made up to the mark. Glass-distilled water was used throughout. An aliquot, the size of which depended on the amount of copper present was pipetted into a separating funnel and shaken vigorously with three 5 ml. portions of the diphenylthiocarbazone-chloroform reagent, each portion being washed with the same 10 ml. of water contained in a second funnel. The extracts were combined, the chloroform distilled and the residue boiled with 2 ml. 60% perchloric acid and 2 ml. concentrated  $H_2SO_4$  until it was

colourless. When it was cool, 10 ml. water were added and the solution neutralised with 5N ammonia. The neutral solution was then transferred to a 100 ml. flask, 3 ml. 5N ammonia and 5 ml. diethyldithiocarbamate reagent added and the volume made up to the mark with water. A suitable aliquot was then transferred to a separating funnel and the copper estimated exactly as described for the calibration of the absorptiometer.

Preliminary tests showed that once the details of the technique were mastered the method was very reliable. Thus, in one test, an analysis of a copper sulphate solution containing 0.020 mg. copper was carried through by the same technique as that used for the milk powders. The amount found to be present was 0.0199 mg. In another typical test, a milk powder was used which had been found by analysis to contain 1.40 parts of copper per million. To 20 g. of this powder in a silica basin sufficient copper sulphate solution was added to raise the copper content to 2.40 p.p.m. Copper was then estimated and found to be 2.28 p.p.m., a recovery equivalent to 88% of the added copper. From these and similar tests it is clear that copper can be estimated by the above method in concentrations as low as 1.0 p.p.m. with an error not exceeding 10-12%.

According to Sylvester and Lampitt (1935) the average copper content of uncontaminated cows' milk is 0.12 p.p.m. Since in drying, milk is concentrated about eight times, the assumption can be made that a copper content of less than 1.0 p.p.m. of dried milk indicates that no copper contamination has occurred during the drying process.



### Sulphydryl content.

When milk is heated to a sufficiently high temperature, sulphydryl groups are formed and a "cooked" flavour develops. (Josephson and Doan, 1939, Gould and Sommer, 1939). It appeared possible that the sulphydryl groups might act as antioxidants and prolong the storage life of the resulting milk product. It was therefore considered essential in the present experiments to obtain some estimate of the relative sulphydryl content of the various dried milk samples which were undergoing storage tests. For this purpose, a method very similar to that described by Josephson and Doan (1939) was used.

1 g. of powder was weighed into a test-tube, 5 ml. water added and the mixture thoroughly shaken for one minute. 5 g. "analar"  $(\text{NH}_4)_2\text{SO}_4$  were added and the mixture shaken again. It was then cooled in ice-water for a few minutes and again shaken with a few drops of 0.88 ammonia. When 5 drops of freshly made 5% sodium nitroprusside solution were added, a pink colour developed if sulphydryl groups were present. The intensity of the pink colour varied with the concentration of sulphydryl groups. If none were present, a dull brown colour resulted. Unless ice-water was used the colour was exceedingly transitory. In ice-water it remained relatively unchanged for 10 minutes or so and an estimate of its intensity could be made in a Lovibond Tintometer.

While the present work was in progress Townley and Gould (1943) published the results of experiments in which they made a very thorough investigation of the formation of sulphydryl groups in milk and for which they devised a new method of estimation. In this method the milk was aerated and the volatile sulphur

collected in zinc acetate and estimated colorimetrically. Townley and Gould found, however, that the amount of volatile sulphur removed from a sample of heated milk varied greatly with the length of the aeration period and other conditions. In the absence of a simpler and more reliable quantitative test, suitable for routine work, that used in the present study may, however, be regarded as providing a reasonably accurate indication of the relative sulphhydryl contents of the various milk powders under investigation.

#### Storage technique.

The methods of packing and storing the powders varied somewhat in each experiment. Details are therefore given separately in the succeeding pages.

## PART II.

### THE INFLUENCE OF THE PREHEATING TEMPERATURE, SELECTION AND CLARIFICATION OF THE LIQUID MILK AND IMPROVEMENTS IN THE CLEANLINESS OF THE PLANT, ON THE STORAGE LIFE OF FULL-CREAM MILK POWDER SPRAY-DRIED BY THREE DIFFERENT PROCESSES.

#### Introduction.

In experiments carried out in 1926 by Holm et al. three observations were made. (1) Butterfat prepared from milk which was 12 hours old was less susceptible to oxidation than fat from milk which was 24 hours old. (2) The removal of separator slime from milk by centrifugal force appeared to improve the keeping quality of dried milk. (3) Preheating the liquid milk at 181°F for 30 minutes before drying appeared to result in a powder of better keeping quality than when preheating temperatures of 145, 163 and 200°F were used. Unfortunately Holm and his colleagues published few details of their work: it is therefore difficult to assess the magnitude of the effects which they obtained.

More recently Jack and Henderson (1942) found that a roller-dried powder made from milk preheated at 175°F for 15 minutes kept for two years as compared with a control made from milk preheated at 142°F for 30 minutes which only kept for 5 months. The same authors observed that a spray-dried powder made from milk preheated to 220°F for 10 seconds kept for two years while the control deteriorated badly in 3 months.

Hollender and Tracy (1942) reported that preheating to

170°F for 30 minutes before drying resulted in a roller-dried powder of much better keeping quality than when 150° or 190°F was used. Although little detail was published in these papers it appeared clear that the preheating temperature could exert a marked influence on the storage life of the resulting powder. Confirmation of this finding, as applied to milk-fat generally, is available in the work of Kende (1932) who observed that the oxidative flavours which developed in some milks (particularly during low temperature storage) could be prevented by heating the milk at 185°F for 5 minutes. Dahle et al. (1941), Scheib et al. (1942), and Trout (1942) also found that the keeping quality of cream was much improved by preheating it to a temperature between 170° and 190°F. The cooked flavour produced in the cream by the higher temperatures was not considered to be objectionable.

No work has, however, been published in sufficient detail to enable a decision to be made as to the exact temperature of preheating which gives the greatest improvement in keeping quality, nor is information available as to whether clarification, cleaner milk supplies or increased attention to plant cleanliness can also bring about an increase in the storage life of the product. The following experiments were therefore designed\* to investigate these various points

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\*The general outline of the experiments was planned in conjunction with the Agricultural Research Council, the National Institute for Research in Dairying, Shinfield, Reading, and the Low Temperature Research Station, Cambridge.

TABLE IV.

The eight principal batches of dried milk made  
on the Kestner plant.

<u>Trial No.</u>	<u>Inclusive dates (1942)</u>	<u>Milk Supply</u>	<u>Collection daily</u>	<u>Clarifier</u>	<u>Pre-heating temperature</u>
1	July 27th-29th	Ordinary	Once	Not used	165°F
2	July 30th-Aug.1st	"	"	"	190°F
3	Aug.3rd-Aug.5th	"	"	used	190°F
4	Aug.6th-Aug.8th	"	"	"	165°F
6	Aug.13th-15th	selected	twice	not used	165°F
7	Aug.17th-18th	"	"	"	190°F
8	Aug.19th-20th	"	"	used	165°F
5	Aug.21st-22nd	"	"	"	190°F

in greater detail than had hitherto been attempted. Three types of spray-drying plant were available for the work. The experiments carried out at each plant and the results obtained on storage of the powder will be discussed in chronological order.

(a) A KESTNER SPRAY-DRYING PLANT.

Through the courtesy of the Directors of Messrs. Aplin and Barrett Ltd., the Kestner spray-drying plant installed at Frome, Somerset, was used for this experiment\*.

The general principle of the Kestner drying system has been fully described by Hunziker (1935), and by Scott (1932). Its special characteristic is the use of a centrifugal spray to convert the liquid milk into a fine mist in the drying chamber. Full details of the actual plant used in the present work will shortly be published by Mattick et al. (1944).

For the storage tests eight principal batches of powder were made from milk which had been treated as shown in Table IV.

It will be seen from this Table that three conditions were independently varied in the production of the powders for these tests: (a) the quality of the milk supply was either 'ordinary' or 'selected';

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\*The work at the factory was under the direction of Dr A.T.R. Mattick of the National Institute for Research in Dairying at Shinfield and of Mr E.L. Crossley of Messrs Aplin and Barrett Ltd.

(b) the milk was either clarified or unclarified, and  
(c) the milk was preheated to either 165°F or 190°F.

In preheating, the milk was held at the stated temperatures for 20 seconds and then for 3 to 5 minutes at a slightly lower temperature. As regards the quality of the milk supply 'ordinary' represented the type of milk received at the factory under normal conditions and a once daily system of collection; 'selected' represented milk of relatively low bacterial count collected twice daily, i.e. in the freshest possible state. On the completion of the eight trials samples of the powder in 1 lb. cans were sent to the Hannah Institute for storage tests.

#### Storage technique.

A number of the 1 lb. cans from each trial were opened and the contents well mixed. The powder was then packed in small brown glass bottles with screw-on caps and also in 12 oz. Danish Cream cans. Since storage at room temperature was expected to give results only after a very prolonged period, it was decided that 'accelerated' tests should be carried out. For this purpose samples were stored in incubators at 47 and 37°C as well as at room temperature. Several samples were nitrogen-packed in cans and stored at 0°C to act as controls. Owing to lack of storage room in the available 37 and 47°C incubators it was impossible at this stage of the work to store sufficient powder for the whole experiment in cans. It was therefore

TABLE V.

The solubility and moisture contents of the powders prepared on the Kestner plant.

<u>Trial</u> <u>No.</u>	<u>Sediment at</u>		<u>Solubility at</u>		<u>Moisture</u>	<u>Copper</u>
	<u>20°C</u>	<u>50°C</u>	<u>20°C</u>	<u>50°C</u>	<u>%</u>	<u>(p.p.m.)</u>
1	0.3	0.05	92	98	1.7	0.6
2	0.3	0.05	93	98	1.9	0.7
3	0.3	0.05	92	98	1.2	0.6
4	0.3	0.05	92	98	1.9	1.0
5	0.3	0.05	93	100	2.2	0.6
6	0.3	0.05	93	100	1.5	0.6
7	0.3	0.05	92	100	1.8	0.6
8	0.3	0.05	94	100	2.2	0.8



decided that it would be best to store a part of the powder in bottles and the remainder in cans, and to use the bottles first. When all the bottles had been used, they were cleaned, dried and re-filled from the cans.

It will be observed from Table IV that more than three weeks elapsed between Trial 1 and Trial 5, so that the powders were of different ages when they arrived at the Hannah Institute. The powders were therefore placed in the 47 and 37°C incubators at such intervals that they would all be of the same storage age when tasting tests began. For this purpose one day at room temperature was considered equivalent to 6 hours at 37°C or 3 hours at 47°C. Any error involved in making this assumption was negligible compared with the duration of the whole storage experiment.

At suitable intervals during the storage period samples were reconstituted and the flavour of the reconstituted milk assessed by the method described on p. 10.

### Results.

#### Moisture and solubility.

The moisture content and solubility of the various powders are recorded in Table V. None of the moisture contents exceeded 2.5%. so that there was no danger of the protein-lactose type of deterioration complicating the results. The solubilities were, within the limits of the experimental error of the method, all identical.

The high preheating temperature to which the milks were subjected in Trials 2, 3, 5 and 7 did not result in any reduction in the solubility of the powder.

#### Copper content.

The copper contents are also recorded in Table V. With the exception of powder No.4 the values obtained were uniformly low. It is obvious from these low values that there could not have been any measurable degree of copper contamination from the plant (cf.p.22). As will be noted later, the higher value for No.4 may have contributed towards the relatively short storage life which this powder possessed.

#### Sulphydryl content.

Tests for the presence of sulphydryl groups gave only a brown tinge with the low temperature milks (Nos.1, 4, 6 and 8), but a very marked pink colour was obtained with all the high temperature powders. Preheating of the liquid milk had therefore been sufficient to produce very definite amounts of sulphydryl compounds in these milk powders.

#### Initial flavours.

Examination of the fresh powders divided them into two easily distinguishable groups according to the preheating temperature. The powders of the low temperature group were very palatable and tasted fresh and uncooked, but had that characteristic flavour frequently found in spray-dried powder which suggests incipient tallowiness to the trained taster. Differences

TABLE VI.

The keeping quality of the powders made on the Kestner plant.

<u>Trial No.</u>	<u>Nature of the milk dried</u>	<u>Pre-heating temperature (°F)</u>	<u>Weeks to deteriorate to "off-flavour score of"</u>							
			<u>1.0</u>		<u>2.0</u>		<u>1.0</u>		<u>2.0</u>	
			<u>at 47°C.</u>		<u>at 37°C.</u>		<u>at 15°C.</u>			
1	Ordinary unclarified	165	3.6	5.7	7.7	11.9	42	61		
4	Ordinary clarified	165	2.1	3.9	6.4	10.0	38	54		
6	Selected unclarified	165	7.4	8.7	13.6	18.9	47	70		
8	Selected clarified	165	6.4	7.9	15.1	19.1	47	66		
2	Ordinary unclarified	190	10.7	12.3	23.3	26.1	>92	>92		
3	Ordinary clarified	190	11.4	13.7	30.0	31.3	>92	>92		
7	Selected unclarified	190	11.7	13.1	32.9	35.0	>92	>92		
5	Selected clarified	190	13.6	14.6	32.9	34.6	>92	>92		
Mean for ordinary milk preheated to 165°F		(a)	2.9	4.8	7.1	11.0	40	57		
Mean for selected milk preheated to 165°F		(b)	6.9	8.3	14.4	18.6	47	68		
Mean for ordinary milk preheated to 190°F		(c)	11.1	13.0	26.7	28.7	>92	>92		
Mean for selected milk preheated to 190°F		(d)	12.7	13.9	32.9	34.8	>92	>92		
Increase in storage life	) <u>Selecting the milk.</u>									
	) (1) When preheating to 165°F b/a		2.4	1.7	2.0	1.7	1.2	1.2		
	) (2) When preheating to 190°F d/c		1.1	1.1	1.2	1.2	-	-		
	) <u>Raising the preheating temperature from 165 to 190°F</u>									
(expressed as ratios) caused by	) (1) With ordinary milk c/a		3.8	2.7	3.8	2.6	>2.3	>1.6		
	) (2) With selected milk d/b		1.8	1.7	2.3	1.9	>2.0	>1.4		
	) <u>Selecting the milk and raising the preheating temperature d/a</u>		4.4	2.9	4.6	3.2	>2.3	>1.6		

between the individual powders of the low temperature group were slight. The powders from the high temperature milks all possessed a boiled milk or cooked flavour but were none the less very palatable.\* The verdict of the tasting panel was that the slight boiled taste was not in any way objectionable. It was of a type frequently associated with milk products. It was much less noticeable than in boiled or sterilised milk and was not so intense as in the average roller-dried powder. It possessed no element of staleness.

#### Deterioration during storage.

The average off-flavour scores recorded by the tasting panel are shown diagrammatically in Fig.2 in which the results have been plotted in pairs, the difference between the powders in each pair being that one of them was made from milk preheated to 165°F and the other from milk preheated to 190°F\*. The quantitative differences in the keeping qualities of the powders are best seen by reference to Table VI, in which the times required for each sample to reach off-flavour scores 1.0 and 2.0 are tabulated.

Storage at room temperature has not progressed sufficiently for off-flavours scores of 1.0 and 2.0 to be passed by the more stable powders; nevertheless the

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\* For key to numbers in Fig.2, see Table IV.

Figure 2.

The deterioration in flavour of the Kestner samples stored at 47°, 37°C and room temperature. Nos.1, 4, 6 and 8 were made from milk preheated to 166°F. Nos.2, 3, 5 and 7 were made from milk preheated to 190°F.

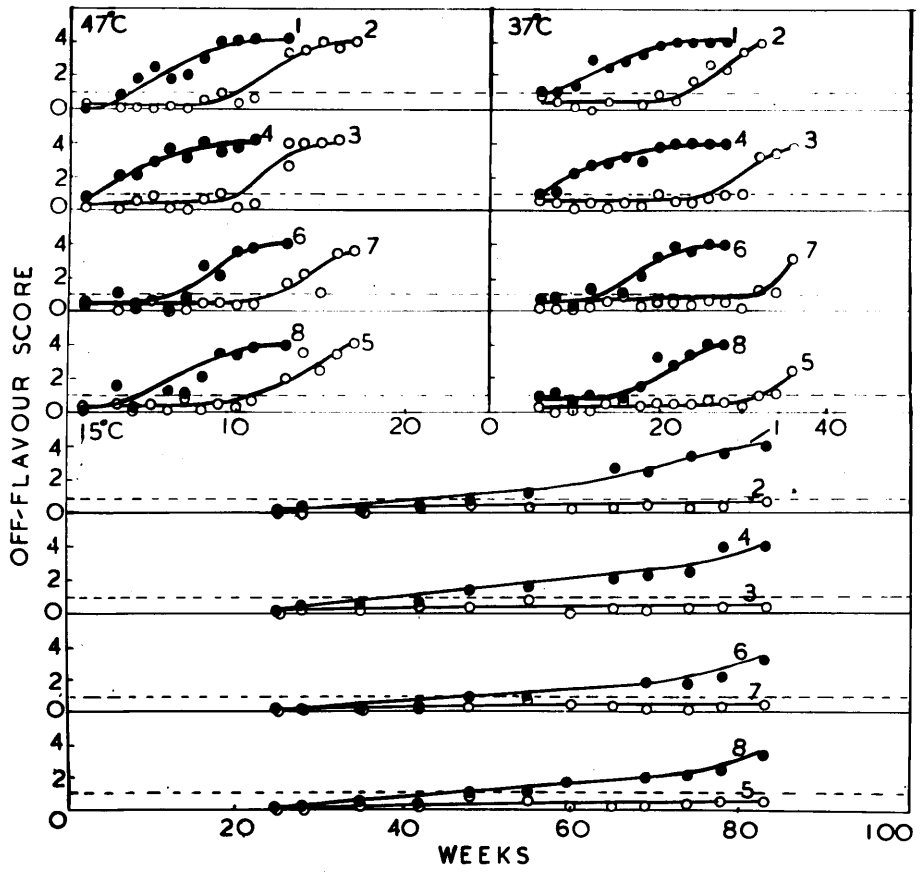


FIG. 2

issue is sufficiently clear-cut to enable reliable conclusions to be drawn from the available data.

### Peroxide values.

The method of Chapman and McFarlane (1943) was not published until this work was well advanced. It was only possible, therefore, to apply it to the powders stored at room temperature. Values were determined at intervals for all eight powders and are recorded diagrammatically in Fig.3\*

### Discussion.

The results shown in Fig.2 and Table VI are best discussed by dealing first with the factor which had least effect on the storage life of the milk powder, namely clarification. When this factor has been disposed of, the more important effects, due to the selection of the milk and to the raising of the preheating temperature, stand out more clearly.

### Clarification.

There are three main points to observe. First, clarification had no significant effect with selected milk whether the preheating temperature was 165° or 190°F. Second, with ordinary milk and a preheating temperature of 190°F, clarification had no effect on the storage life at 47°C, but at 37°C it appeared to result in a slight extension in storage life. Thus the number of weeks required to reach off-flavour scores of 1.0 and 2.0 was increased from 23.3 and 26.1 for powder No.2 to 30.0 and 31.3 for powder No.3. Storage has not yet continued

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\* For key to numbers in Fig.3, see Table IV.

Figure 3.

Peroxide formation, expressed as milli-equivalents per kilogram of powder, in the Kestner powders stored at room temperature. Nos. 1, 4, 6 and 8 were made from milk preheated to 165°F. Nos. 2, 3, 5 and 7 were made from milk preheated to 190°F.



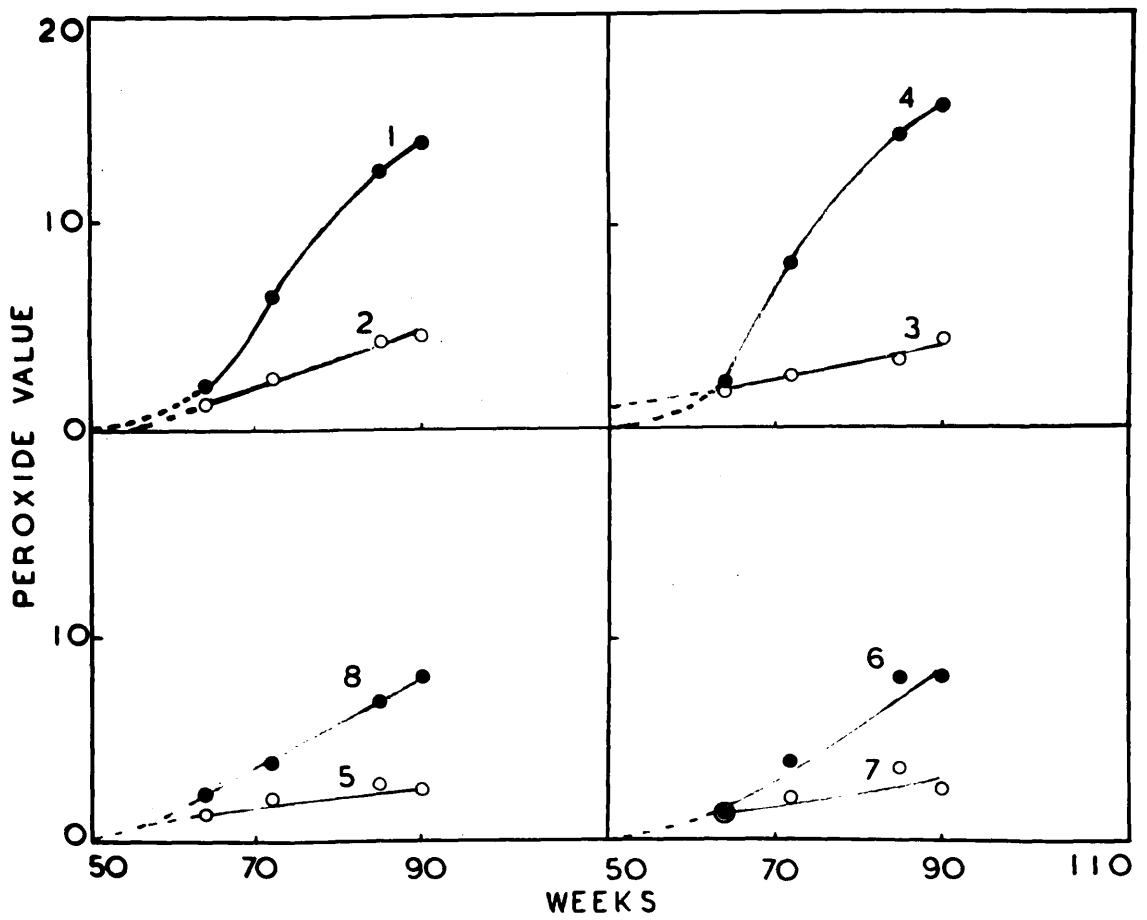


FIG. 3

long enough for this effect to be confirmed at room temperature. It is, however, in any event a very small increase and of doubtful significance. Third, with ordinary milk preheated to 165°F, clarification appeared to be deleterious, since it caused a decrease in the storage life of the powder at all three storage temperatures. It is very questionable, however, whether clarification per se was responsible for the shorter storage life of powder No.4. It has already been noted (Table V) that this particular powder had a higher copper content than the remainder. Moreover, when all the details of its manufacture were obtained it was found that some doubt existed as to whether the preheating temperature of 165°F had been consistently reached by all the liquid milk dried during this experimental period. These factors would almost certainly exert a far greater effect on keeping quality than clarification.

Except, therefore, for the slight difference with Nos.2 and 3 at 37°C, clarification appears to have had no beneficial effect on the powders. In considering the remaining two factors, milk selection and preheating temperature, clarification can clearly be neglected. The results for the paired powders, 1 and 4, 6 and 8, 2 and 3, and 7 and 5 have therefore been averaged, as shown in Table VI.

### Selection of the milk.

The effect of milk selection is shown as a ratio in the lower half of Table VI. With a preheating temperature of 165°F, the storage life at 47°C and 37°C was roughly doubled by using selected milk, though at room temperature the increase in storage life was only about 20%. With a preheating temperature of 190°F, the effect of milk selection on the storage life at 47° and 37°C was much less, the increase in keeping quality being only some 10 or 20% and of doubtful significance.

### The preheating temperature.

The greatest effects were obtained by raising the preheating temperature from 165° to 190°F. With ordinary milk there was a three- to four-fold increase at 47° and 37°, while at room temperature the "high temperature" powders have already kept for almost twice as long as the "low temperature" powders and are not yet deteriorating significantly. With selected milk a two-fold increase was observed at the two higher storage temperatures and there is every indication that this will ultimately be confirmed at room temperature.

When the combined effect of milk selection and the high preheating temperature are considered, it is found that practically a four-fold increase in storage life was obtained at 47 and 37°C.

### The temperature coefficient.

The rate of deterioration at 47°C has been

TABLE VII.

The temperature coefficients of the rate of deterioration of the Kestner powders for differences of 10°C in storage temperature.

<u>Range</u>	<u>Measured at off-flavour score of</u>	<u>Low temperature preheated samples</u>					<u>High temperature preheated samples</u>				
		<u>1</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>Average</u>	<u>2</u>	<u>3</u>	<u>5</u>	<u>7</u>	<u>Average</u>
47-37°C	1.0	2.1	3.0	1.8	2.4	2.3	2.2	2.6	2.4	2.8	2.5
	2.0	2.1	2.6	2.2	2.4	2.3	2.1	2.3	2.4	2.7	2.4
37-15°C*	1.0	2.2	2.2	1.8	1.7	1.9	-	-	-	-	-
	2.0	2.1	2.2	1.7	1.8	1.9	-	-	-	-	-

\*  $C_{10}$  for the temperature range of 37°C-15°C was calculated from the relationship:  $C_{10} = N - 2.2$  where N is the number of weeks required for an off-flavour score of 1.0 or 2.0 to be reached at 15°C divided by the number of weeks required at 37°C.

The average room temperature was taken as 15°C.

compared with that at 37°C and the latter with the rate of deterioration at room temperature and the temperature coefficients for 10°C obtained as shown in Table VII. Considering that these values have resulted from tasting tests, they are reasonably consistent. Average values of 2.3, 2.4 and 2.5 for the temperature coefficient between 47 and 37°C compares well with that of 2.2 observed by Lea et al. (1943) for the same 10° difference between 47° and 37°C in their experiments on inert gas-packing. Similarly, the value of 1.9 for a 10° difference between 37° and 15° compares well with that of 2.05 recorded by Lea et al. for the corresponding temperature range. By the use of the appropriate coefficient it should be possible to obtain a reliable indication of the keeping quality of this particular type of powder at any temperature between 15° and 47°C provided the keeping quality at any other temperature within the range is known.

(b) A KRAUSE SPRAY-DRYING PLANT.

In the experiment with the Kestner plant the most important factor influencing keeping quality was found to be the preheating temperature. It was therefore decided to carry out a further experiment on a different type of plant in which five different preheating temperatures could be tested. The two main objects of this second experiment were (1) to

find whether the preheating temperature was equally important on a different type of plant, and (b) to find what particular preheating temperature would give a powder with the longest storage life.

Through the courtesy of the Directors of Dried Milk Products Ltd. an experiment was carried out on a Krause plant at Northallerton, Yorkshire\*. The principle of the Krause plant has been described in detail by Hunziker (1935) and by Scott (1932). As in the Kestner plant, the milk is converted into a fine spray by centrifugal force, but the type of disc from which it is sprayed and the arrangement of inlets and outlets for the hot air differ from those used in the Kestner plant.

During the experiment the plant was run normally except that five different preheating temperatures were used. These were 160°, 170°, 180°, 190° and 200°F. For the four higher temperatures the liquid milk was passed through two heaters. The first heater warmed the milk to about 150°F, while the second raised the temperature to the desired degree. For the preheating temperature of 160°F only one heater was required. The milk was held at the various temperatures

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\*The work at the factory was under the direction of the Manager and Assistant Manager, Mr Wood and Mr Shutter, while extensive bacterial tests were carried out on milk sampled at various points throughout the plant and on the resulting powder by Dr C. Higginbottom of the Hannah Institute.

TABLE VIII.

Various chemical and physical data for  
the powders made on the Krause plant.

<u>Trial No.</u>	<u>Temperature of Preheating OF</u>	<u>% Moisture content</u>	<u>Copper content</u>	<u>Sulphydryl content Red units<sup>1</sup></u>	<u>Solubility % at</u>	
					20°C	50°C
1	160	1.3	1.4	0.5	99	99
2	170	1.2	3.5	0.6	100	100
3	180	0.9	3.6	0.8	100	99
4	190	1.6	1.1	1.0	100	99
5	200	1.1	1.5	1.1	99	99
	Average	1.2	-	-	-	-

<sup>1</sup> 0.5 yellow units were used throughout.

for about 20 seconds. Each preheating temperature continued in use for two consecutive days, the milk powder for the storage tests being collected on the second day. Any risk of contamination of powder from one trial with powder remaining in the filter bags from a previous trial was thus avoided. The samples for storage tests were packed in 21 lb. cans and sent to the Hannah Institute.

#### Storage technique.

At this stage of the work more storage accommodation was available. It was therefore decided to store the powder in sufficient 6 oz. Danish Cream cans of plain tinplate to make gas analyses possible at frequent intervals during the storage periods. It was hoped that by this means objective confirmation of the tasting tests would be obtained. 90 g. of powder were therefore packed in each can, the seams of the cans lacquered externally to ensure that they were gas-tight, and the cans stored at 47°, 37°C and room temperature. A number of nitrogen-packed cans were stored at 0°C as controls.

#### Results.

##### Moisture content.

The moisture contents of the powders are recorded in Table VIII. They were all below 2.0%, so that there was again no risk of the occurrence of the protein-lactose type of deterioration, which might otherwise have confused the results.



TABLE IX.

The storage life of the powders made on the Krause plant, packed in tinfoil cans and judged by flavour.

<u>Trial No.</u>	<u>Preheating temperature</u> °F	<u>Weeks to reach off-flavour score of:</u>					
		<u>1.0 2.0</u> <u>at 47°C</u>		<u>1.0 2.0</u> <u>at 37°C</u>		<u>1.0 2.0</u> <u>at room temperature</u>	
1	160	6.0	9.0	6.0	9.0	16.0	19.2
2	170	4.2	7.0	6.2	8.8	15.8	20.0
3	180	8.8	12.0	14.8	17.2	41.0	47.2
4	190	10.0	12.0	21.0	23.6	*	*
5	200	9.0	11.6	18.8	21.6	*	*

Relative storage life expressed as a multiple of the storage life of the shortest-lived powder.

1	160	1.4	1.3	1.0	1.0	1.0	1.0
2	170	1.0	1.0	1.0	1.0	1.0	1.0
3	180	2.1	1.7	2.4	1.9	2.6	2.5
4	190	2.4	1.7	3.4	2.7	*	*
5	200	2.1	1.7	3.1	2.5	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

### Solubility.

Increasing the preheating temperature from 160° to 200°F did not diminish the solubility of this extremely soluble powder (Table VIII).

### Sulphydryl content.

The effect of increasing the preheating temperature on the sulphydryl content can be seen from Table VIII, where the results are expressed in Lovibond red units. A brownish tint was obtained with Nos.1 and 2 and an increasingly vivid pink with Nos.3, 4 and 5.

### Copper content.

Copper was estimated in all the samples by the method already described. The results, which are recorded in Table VIII, show that Nos.1, 4 and 5 had low values ranging from 1.1 to 1.5 p.p.m., while in Nos. 2 and 3, the values were as high as 3.5 and 3.6 p.p.m. At one stage in this plant the liquid milk had to pass through a tank in which the copper surface was exposed and which obviously led to different degrees of contamination on different days. As shown in the following discussion, this variation in copper content had a significant effect on the results.

### Assessment of flavour.

The tasting results are shown in Fig.4, and the times necessary for off-flavour scores of 1.0 and 2.0 to be attained are collected in Table IX. The powders made from milk preheated to the three higher temperatures had a slight cooked flavour initially, but

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**Figure 4.**

**The deterioration of the Krause powders on storage in tinfoil cans at 47°, 37°C and room temperature, as measured by flavour and the rate at which oxygen was absorbed.**

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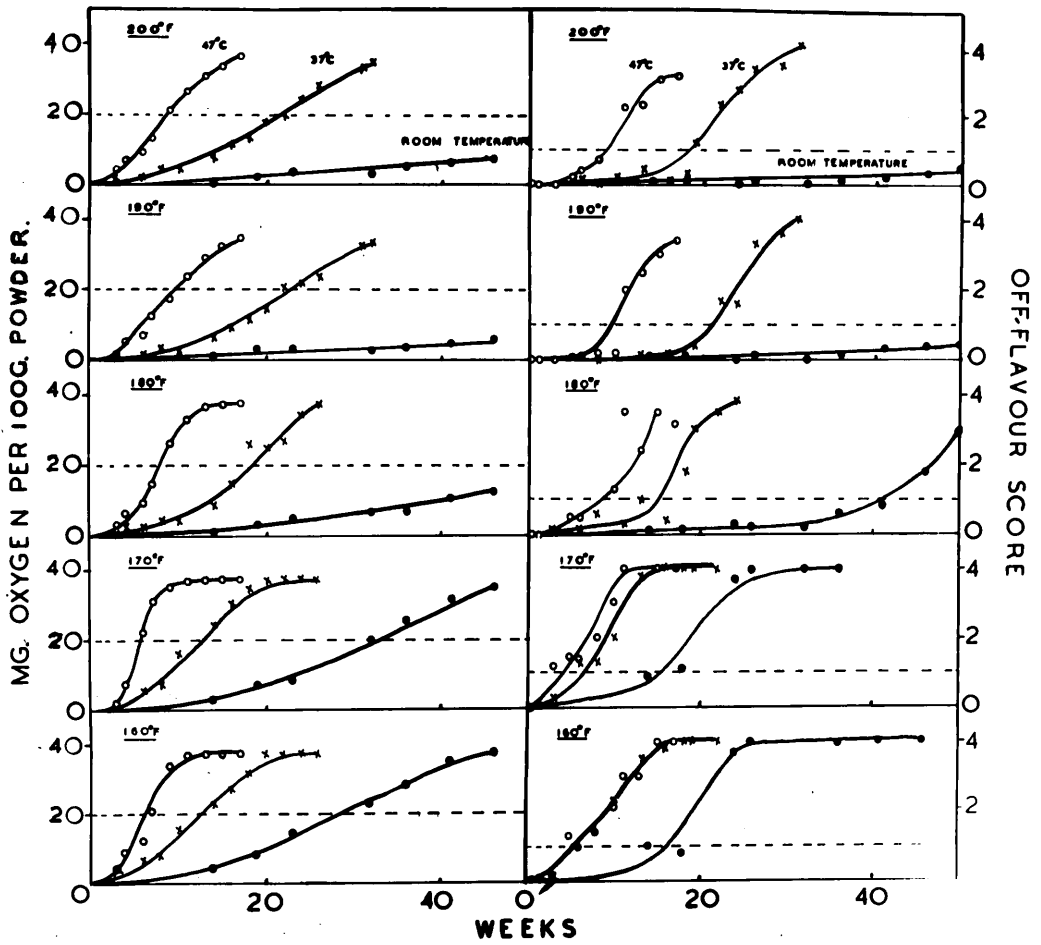


FIG.4

TABLE X.

The time required for 10 and 20 mg. oxygen to be absorbed by 100 g. of powder at 47°C, 37°C and room temperature.

<u>Trial No.</u>	<u>Preheating temperature</u> °F	<u>Weeks required to absorb</u>					
		<u>10mg. at 47°C</u>	<u>20mg. at 47°C</u>	<u>10mg. at 37°C</u>	<u>20mg. at 37°C</u>	<u>10mg. at room temperature</u>	<u>20mg. at room temperature</u>
1	160	4.8	6.8	8.4	13.2	20.8	28.8
2	170	4.4	5.6	8.0	12.4	22.8	32.8
3	180	5.6	7.6	14.4	18.0	40.4	*
4	190	6.0	9.6	17.2	23.2	*	*
5	200	5.6	8.4	16.0	22.0	*	*

Relative times for the absorption of oxygen taking the shortest time as 1.0

1	160	1.1	1.2	1.1	1.1	1.0	1.0
2	170	1.0	1.0	1.0	1.0	1.1	1.2
3	180	1.3	1.4	1.8	1.5	1.9	*
4	190	1.4	1.7	2.2	1.9	*	*
5	200	1.3	1.5	2.0	1.8	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

TABLE XI.

The peroxide values of powders stored in plain tinplate cans at room temperature.

<u>Trial No.</u>	<u>Preheating temperature</u> °F	<u>Milliequivalents of peroxide/kg. powder</u>	
		<u>After 36 weeks</u>	<u>After 51 weeks</u>
1	160	12.7	14.2
2	170	15.8	16.6
3	180	2.2	10.1
4	190	2.5	2.0
5	200	1.8	2.4

this was not in any way objectionable.

#### Gas analysis.

The rate at which oxygen was absorbed by the powders was determined for all three storage temperatures. The results are recorded in Fig.4. The times which elapsed before 10 and 20 mg. oxygen were absorbed by 100 g. powder are shown in Table X.

#### Peroxide values.

Peroxide values were determined on two occasions for all the powders during storage at room temperature. The results are recorded in Table XI.

#### Discussion.

##### The effect of the preheating temperature on storage life.

The results in Table IX show that at 47° and 37°C the three highest temperature powders (Nos.3, 4 and 5) kept for about twice or three times as long as the two lower temperature powders (Nos.1 and 2). Moreover at room temperature Nos. 3, 4 and 5 have already kept for more than twice as long as Nos.1 and 2, and Nos.4 and 5 are still very palatable. The advantage of high preheating temperatures is thus very clearly demonstrated.

On examining the results in Table IX in more detail, it will be found that powder No.2 kept for a shorter time than powder No.1 at 47°C and for about the same time at 37°C and room temperature in spite of the 10° rise in preheating temperature. This result, which at first sight appeared anomalous, was undoubtedly

due to the higher copper content of powder No.2 (3.5 p.p.m.) as compared with powder No.1 (1.4 p.p.m.). Such a high copper value in powder No.2 would markedly shorten the storage life of the powder and so nullify the effect of increasing the preheating temperature.

With powders 2 and 3, preheated to 170° and 180°F, the copper content was almost identical and the increase of 10°F in preheating temperature approximately doubled the storage life of the powder. This therefore provides a clear-cut example of the effect of an increase in the preheating temperature with two otherwise comparable powders.

It is impossible to assess the value of raising the temperature from 180° to 190°F (Nos. 3 and 4), since this increase was unfortunately accompanied by a decrease in copper content from 3.6 to 1.1 p.p.m. (Table VIII), - a decrease which would itself cause a marked extension in storage life. For powders preheated to 190° and 200° (Nos.4 and 5) the copper contents were, however, very similar, but no differences were shown in the storage life. It is therefore apparent that no advantage was gained in this particular plant by raising the preheating temperature beyond 190°. It would appear, therefore, that the critical temperature lies somewhere between 170 and 190°F.

The oxygen absorption results in Table X confirm in general the conclusions obtained for the tasting

results. Thus it will be observed that the rate of oxygen absorption (and therefore of deterioration) was greatest with Nos. 1 and 2 and least with Nos. 4 and 5, with No.3 falling within these two extremes. There was also little difference between Nos.1 and 2, a marked difference between Nos. 2 and 3, and little difference between Nos. 4 and 5.

It is not reasonable to expect the flavour and gas analysis results to confirm one another in every detail, for oxygen absorption will not necessarily run strictly parallel with the subsequent decomposition of the oxidised products to give foul-tasting compounds of smaller molecular weight. This may explain the fact that the oxygen absorption figures for Nos. 3, 4 and 5 did not differ so much from those of Nos.1 and 2 as did the off-flavour figures. This fact also emphasises the practical value of tasting tests in the study of food storage problems, since flavour and not oxygen absorption is the ultimate criterion by which the powder will be judged.

Reference to the peroxide values in Table XI also shows the advantage of the higher preheating temperatures. After 9 months at room temperature, the peroxide values of Nos. 1 and 2 had risen to 12.7 and 15.8 compared with values of about 2 for the remaining three powders. After another 4 months, the peroxide value of No.3 had risen to 10.1, while the corresponding values for the two highest temperature powders were



TABLE XII.

Temperature coefficients for the Krause samples (calculated from the flavour results).

<u>Trial No.</u>	<u>Preheating Temperature</u> °F	<u>Calculated for 10°C from the off-flavour score</u>			
		<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>
		<u>at 47°-37°C</u>		<u>at 37°-15°C</u>	
1	160	1.0	1.0	1.6	1.4
2	170	1.5	1.1	1.5	1.5
3	180	1.8	1.5	1.6	1.6
4	190	2.1	1.9	*	*
5	200	2.1	1.9	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

TABLE XIII.

Temperature coefficients for the Krause samples (calculated from the oxygen absorption data).

<u>Trial No.</u>	<u>Preheating temperature</u> °F	<u>Calculated for 10°C from oxygen absorbed.</u>			
		<u>10mg.</u>	<u>20mg.</u>	<u>10mg.</u>	<u>20mg.</u>
		<u>at 47°-37°C</u>		<u>at 37°-15°C</u>	
1	160	1.8	1.9	1.5	2.2
2	170	1.8	2.2	1.6	2.4
3	180	2.6	2.4	1.6	*
4	190	2.9	2.5	*	*
5	200	2.9	2.6	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

still only about 2. This rapid increase in No.3 was probably due to its high copper content.

The effect of increasing the preheating temperature from 160° or 170° to 180° or 190°F and the reliability and value of tasting tests has therefore been clearly shown in this experiment.

#### Temperature coefficients.

The temperature coefficients of the rate of deterioration, as measured by taste and oxygen absorption tests, are recorded in Tables XII and XIII. Between 37°C and room temperature, the coefficients varied between 1.4 and 1.6 for a difference of 10°C when calculated from the tasting results. The corresponding coefficients for the time required to absorb 10 mg. oxygen were very similar, ranging from 1.5 to 1.6, but for 20 mg. oxygen they increased to 2.2 and 2.4. Evidently as the temperature increases, the rate of absorption increases more rapidly than the rate of the development of off-flavours. Similarly for the 47° to 37° range of storage temperatures the coefficients calculated from the oxygen absorption results were higher than those from the tasting results. One very unexpected observation was made regarding the temperature coefficients for the 47° to 37° range. It was found from both the flavour and gas analysis results that the temperature coefficient of storage increased with the preheating temperature. As far as flavour is concerned the low temperature powders deteriorated

almost as rapidly at 37° as they did at 47°C, while the high temperature ones kept twice as long. No explanation for this observation can yet be advanced.

(c) A GRAY-JENSEN SPRAY-DRYING PLANT.

The object of this experiment was to determine whether raising the preheating temperature, clarification and greater attention to the details of processing would improve the keeping quality of milk powder made on a Gray-Jensen plant. This type of plant differs markedly from both the Kestner and the Krause plants. In the Gray-Jensen plant the milk is converted into a spray by forcing it through a fine orifice under high pressure. Moreover the hot air leaving the drying chamber is passed through the liquid milk thus effecting its partial pre-condensation. At the same time, any powder in the air leaving the drying chamber is washed out into the precondensed milk and thus passes back to the drying chamber. The preheating system and the type of condenser also differ markedly from those of the other two plants. Details of a typical Gray-Jensen drier are given by Hunziker (1935) and by Scott (1932).

Through the kindness of Mr W.B. Barbour, Managing Director of the Scottish Milk Powder Co. Ltd., a plant of this type was made available for experiment at Kirkcudbright\*. The preheating system in use at

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\*The experiment was under the direction of the Manager of the factory, Mr M. Neilson and of the present author.

TABLE XIV.

The pre-heating and holding temperatures for a typical day in the control period and for a typical day in the experimental period.

<u>Time</u>	<u>Preheating temperature OF</u>	<u>Temperature in holding tank OF</u>
<u>Control period</u>		
<u>A.M.</u>		
10.00	171	168
10.30	170	169
11.00	169	165
11.45	170	167
<u>P.M.</u>		
12.15	172	170
2.15	179	178
5.00	179	178
7.00	173	178
8.30	171	176
9.00	180	178
Mean	<u>173.4°F</u>	<u>172.8°F</u>
<u>Experimental period</u>		
<u>A.M.</u>		
10.00	179	176
10.30	180	180
11.00	180	175
11.30	182	180
<u>P.M.</u>		
12.30	180	179
2.00	180	179
4.00*	180	179
Mean	<u>180°F</u>	<u>178.4°F</u>

\* Shorter period of running; only morning's milk was used.

the plant did not allow a free choice of preheating temperature, nor was it possible to limit the heating of the milk to only a few seconds. The temperature of the milk had to be raised by pumping it continuously from a holding tank through a heater and back to the holding tank until its temperature was about 170°F. It was then held at or near that temperature for perhaps three-quarters of an hour until it could be passed to the condenser and thence to the drier. The holding tank contained about 1,000 gallons.

It was decided, in view of the difficulties involved in the control of the time and temperature of preheating, to limit the temperature changes to the maximum which could be effected under existing practical conditions, although it was realised that the differences between the control and experimental periods might be relatively small. It will be seen from the typical days' runs in Table XIV that the average preheating temperatures of the control and experimental periods varied by about 7°F and the holding temperatures by about 5°F.

The experiment, as finally planned, comprised two main periods, of which the details may be summarised as follows:-

Control period of 6 days.

- (1) The running of the plant was carried out according to the usual procedure at this factory.

TABLE XV.

The sampling times in the Gray-Jensen experiment.

	<u>Code letter</u>	<u>Hours after drying began</u>	<u>Time before or after change-over from control to experimental period</u>
<u>Control Period</u>	( A	2	) 6 days before change-over, no clarifier.
	( B	7	
	( C	15	
	( S1	2	) 3 days before change-over, clarifier in use.
	( S2	7	
	( S3	15	
	( D	2	) 1 day before change-over, no clarifier.
	( E	7	
	( F	12	
<u>Experimental Period</u>	( G	2	) 1 day after change-over, clarifier in use.
	( H	7	
	( I	9	
	( J	2	) 6 days after change-over, clarifier in use.
	( K	7	
( L	9		

- (2) The milk was the usual September milk supply, consisting of mixed evening and morning milk, and was collected once daily.
- (3) No clarifier was used except on one day in the middle of the period.
- (4) The plant was cleaned daily with hypochlorite solution renewed every 5 days.
- (5) The milk was preheated for a few minutes at 170-180°F and was then held at 168-178°F for an average of about 45 minutes. Since the milk flowed continuously through the heater to and from the holding tank, the holding time and temperatures cannot be stated more precisely.

Experimental period of 6 days.

- (1) Only selected morning milk was dried.
- (2) The clarifier was used throughout.
- (3) The plant was cleaned daily with fresh hypochlorite.
- (4) Except for the last day of the period, the temperature was rigidly maintained at 180°F  $\pm 1^\circ$  in the preheater while the holding temperature was 176-180°F. On the last day of the period the holding temperature dropped (for unavoidable technical reasons) to 170°F, though the preheating temperature remained unchanged.

Table XIV shows the temperatures for one typical day in each period. The plant was thoroughly cleaned and overhauled on the day before each period began. Representative samples of powder which were taken on the days and at the times shown in Table XV were taken to the Hannah Institute in 21 lb. cans for storage experiments. It will be observed that A and B in the control period (Table XV) correspond to G and H in the experimental period and that D and E correspond to J and K. C and F differ from I and L

TABLE XVI.

The solubility and moisture and copper content of  
the Gray-Jensen samples.

<u>Sample</u>	<u>Solubility</u>		<u>Moisture</u>	<u>Copper content</u>
	<u>20°C</u>	<u>50°C</u>	<u>%</u>	<u>Parts per million.</u>
<u>Control Period</u>				
A	92	98	1.9	2.4
B	94	99	2.0	0.8
C	90	98	1.7	0.7
S1	91	96	1.9	1.4
S2	91	99	1.9	0.8
S3	91	97	2.4	0.6
D	93	97	1.9	1.1
E	91	96	2.0	0.8
F	89	93	1.5	0.8
Average	90	96	2.0	-
<u>Experimental Period</u>				
G	89	97	2.0	0.8
H	92	97	1.5	0.8
I	90	96	1.7	0.8
J	92	94	2.1	1.1
K	94	97	1.6	0.8
L	92	95	1.6	1.0
Average	91	96	1.8	



in that they were taken after 15 and 12 hours of drying instead of after 9 hours. This was caused by the fact that only morning milk was used in the experimental period, with the result that the drying period only lasted for nine hours compared with 12-15 hours in the control period. S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub> correspond respectively to A, B and C and also to D, E and F except that the clarifier was in use.

The storage technique was identical with that used for the Kestner samples (p. 28). At each test the flavour of 15 samples had to be assessed. Since this was too large a number for the palate at one time, all the 5-hour samples and a control were tasted first. At least one hour later the 2-hour and final samples from each of the five days were compared with the 5-hour samples.

### Results.

#### Moisture content and solubility.

The results in Table XVI show that all the moisture contents were below 2.5%. Tallowiness was therefore the only type of deterioration to be expected. The solubilities showed variations within the individual periods, but the average for the control period was practically identical with that for the experimental period.

#### Sulphydryl test.

No clearcut positive test was obtained with any of the powders, although the keeping quality of most

TABLE XVII.

The storage life of the Gray-Jensen powders.

<u>Samples</u>	<u>Weeks to deteriorate to off-flavour score of</u>					
	<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>
	<u>at 47°C</u>		<u>at 37°C</u>		<u>at 15°C</u>	
A	4	6	9	15	30	46
B	6	11	22	28	*	*
C	8	12	21	26	*	*
D	7	9	19	25	59	69
E	9	14	27	32	73	*
F	14	16	29	33	*	*
S1	6	7	14	19	45	59
S2	21	25	-	-	69	80
S3	13	15	22	34	77	*
G	9	13	22	27	*	*
H	10	14	24	34	*	*
I	13	17	31	38	*	*
J	10	13	26	30	74	*
K	10	13	25	34	76	*
L	12	14	32	41	*	*
Mean for A, D, S1	6	7	11	20	45	58
Mean for G and J	9	13	24	29	*	*
Mean for B, C, E, F, S3	10	13	24	30	*	*
Mean for H, I, K, L	11	14	28	38	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

TABLE XVIII.

Relative storage life of the Gray-Jensen powders.

	<u>Samples</u>	<u>47°C</u>		<u>37°C</u>		<u>15°C</u>	
		<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
<u>Control</u> <u>Period</u>	A	1.0	1.0	1.0	1.0	1.0	1.0
	B	1.5	1.8	2.5	1.9	*	*
	C	2.0	2.0	2.3	1.7	*	*
	D	1.7	1.5	2.1	1.6	1.9	1.5
	E	2.2	2.3	3.0	2.1	2.4	*
	F	3.5	2.7	3.2	2.2	*	*
	S1	1.5	1.1	1.5	1.3	1.5	1.3
	S2	5.2	4.1	-	-	2.3	1.7
	S3	3.2	2.5	2.4	2.3	2.5	*
	<u>Experimental</u> <u>Period</u>	G	2.2	2.1	2.4	1.8	*
H		2.5	2.3	2.6	2.3	*	*
I		3.2	2.9	3.4	2.5	*	*
J		2.5	2.2	3.0	2.0	2.5	*
K		2.5	2.2	2.7	2.3	2.5	*
L		3.0	2.3	3.5	2.7	*	*
Mean for A, D, S1		1.0	1.0	1.0	1.0	1.0	1.0
Mean for G and J	1.5	1.9	2.2	1.5	*	*	
Mean for B, C, E, F, S3	1.7	1.9	2.2	1.5	*	*	
Mean for H, I, K, L	1.8	2.0	2.5	1.9	*	*	

\*Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

TABLE XIX.

The peroxide values of the Gray-Jensen powders  
after 85 weeks at room temperature.

	<u>Sample</u>	<u>Milliequivalents</u> <u>peroxide per kg.</u> <u>powder.</u>
<u>Control</u> <u>Period</u>	( A	17.6
	( B	3.1
	( C	3.2
	( D	7.0
	( E	1.5
	( F	4.9
	( S1	8.2
	( S2	4.3
	( S3	3.9
<u>Experimental</u> <u>Period</u>	( G	2.4
	( H	2.3
	( I	2.3
	( J	3.6
	( K	1.7
	( L	1.7

Mean for A, D & S1 (Group I) 10.9

Mean for G and J (Group II) 2.9

Mean for B, C, E, F and S3  
(Group III) 3.3

Mean for H, I, K and L (Group IV) 2.0

of them was good. It seems possible that the exceptional method of preheating and holding affected the test, but it was not feasible to investigate this point in detail.

#### Assessment of flavour.

The tasting results are shown in Figs. 5 and 6. The times required for off-flavour scores of 1.0 and 2.0 to be reached are recorded in Table XVII, and the relative storage life of the powders in Table XVIII.

#### Peroxide values.

The peroxide values of the powders were estimated after 85 weeks at room temperature. The results are recorded in Table XIX.

#### Copper content.

Copper was estimated in all the samples by the method given in Part I. The results, given in Table XVI show that the only badly contaminated powders were samples A and S<sub>1</sub>.

### Discussion.

#### Keeping Quality.

In all, 15 samples of powder were available (Table XV). The more important conclusions of the experiment can best be summarised by dividing these 15 samples into the following four groups:-

Group I A, D and S<sub>1</sub>, the three samples taken in the control period 2 hours after drying began, and which were contaminated with copper.

Figure 5. Deterioration in flavour of the Gray-Jensen powders made during the control period when the clarifier was not in use. The figure shows the results of the sensory evaluation of the powders stored at different temperatures (47°C, 37°C, and room temperature) during the control period. The results indicate that the powders stored at 47°C showed the highest deterioration in flavour, followed by those stored at 37°C, and those stored at room temperature showed the least deterioration.

Figure 5.

The deterioration in flavour of the Gray-Jensen powders made during the control period when the clarifier was not in use. x = powders stored at 47°C, o = powders stored at 37°C and ● = powders stored at room temperature.

Figure 6.

The deterioration in flavour of the Gray-Jensen powders made during the experimental period (samples G to L) and also of those made during the control period on the day when a clarifier was inserted (samples S<sub>1</sub>, S<sub>2</sub> and S<sub>3</sub>). x = powders stored at 47°C, o = powders stored at 37°C and ● = powders stored at room temperature.

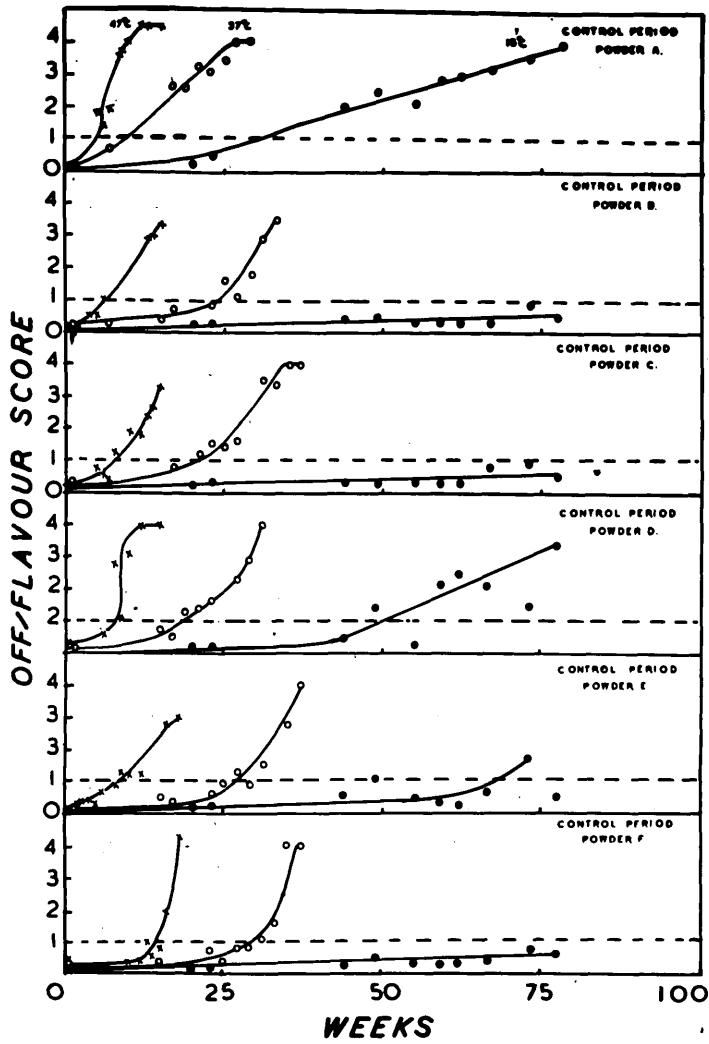


FIG. 5

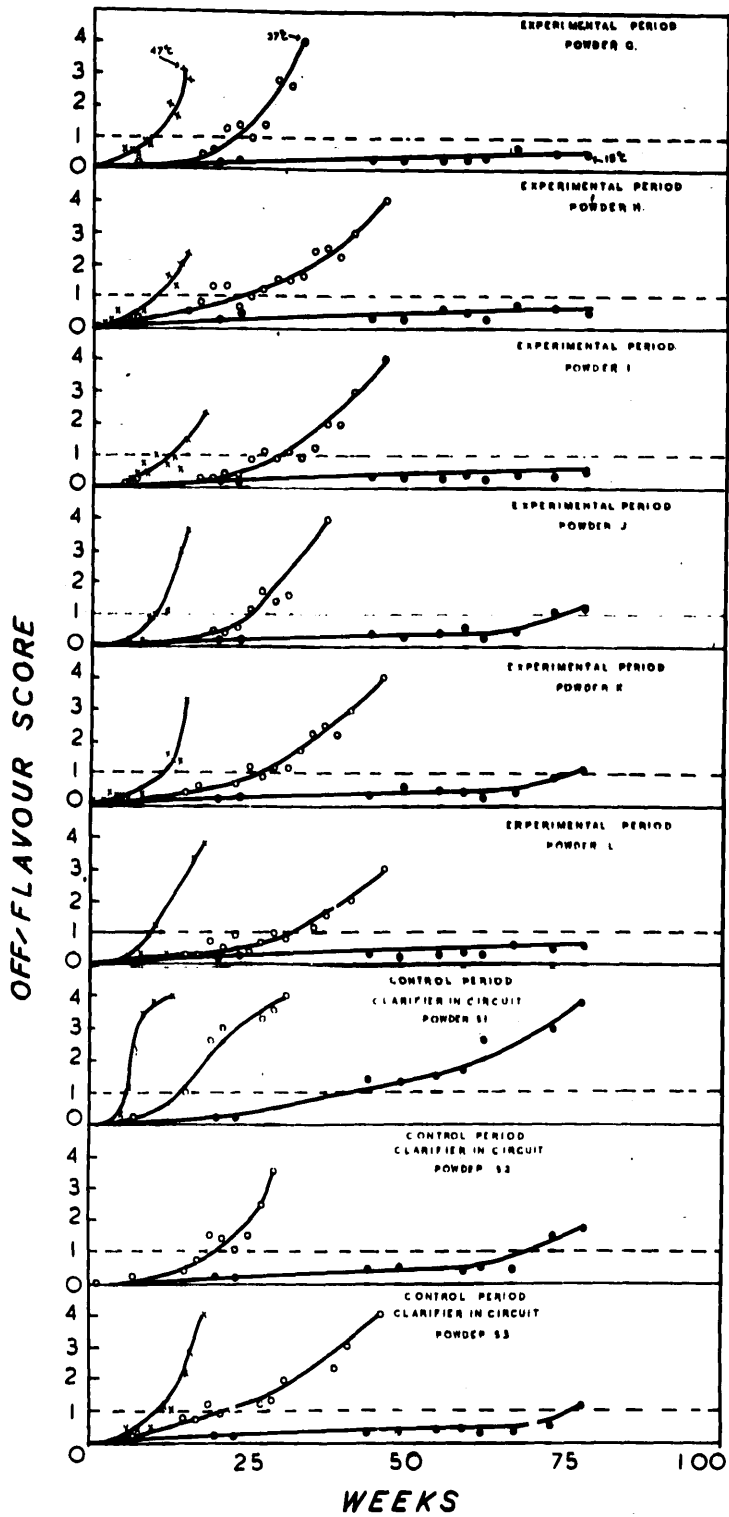


FIG. 6



Group II G and J, the two samples taken in the experimental period 2 hours after drying began.

Group III B, C, E, F and S<sub>3</sub>, the remaining samples taken in the control period.

Group IV H, I, K and L, the remaining samples taken in the experimental period.

Reference to Tables XVII and XVIII shows that the average storage life of the members of Groups II, III and IV was of the same general order except that Group IV was very slightly superior to the two other groups.

The powders in Group I, particularly sample A, possessed a much shorter storage life than any of the other powders. The high copper content of powder A would undoubtedly shorten its life and the same would apply to S<sub>1</sub>. Furthermore, these short-lived powders, A, D and S<sub>1</sub>, were all collected 2 hours after drying began.

Their short life, therefore, may also be due to insufficient attention being paid to the preheating of the liquid milk during the first hour or so of drying. Later in the day when the heating system may have become more stabilised and in the experimental period when the heating arrangements were under more strict control from the beginning of the day's drying, none of the samples showed this shorter storage life. This may be illustrated by samples H and J which had more and the same amount of copper respectively as sample D and yet had a much longer storage life.

From the fact that the powders in Groups II, III and IV were very similar in keeping quality, it would appear that with the Gray-Jensen plant - as normally

TABLE XX.

The temperature coefficients for the  
Gray-Jensen powders.

<u>Samples</u>	<u>Temperature coefficients (10°C)</u>			
	<u>37-47° range</u>		<u>Room temperature to</u>	
	<u>Off-flavour score of</u>		<u>37°C range</u>	
	<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>
A	2.2	2.5	1.7	1.6
B	3.3	2.5	*	*
C	2.6	2.2	*	*
D	2.7	2.8	1.7	1.6
E	3.0	1.8	1.6	*
F	2.0	2.1	*	*
S1	2.3	2.7	1.7	1.6
S2	-	-	*	*
S3	1.7	2.3	1.8	*
G	2.4	2.1	*	*
H	2.4	2.4	*	*
I	2.4	2.2	*	*
J	2.6	2.3	1.6	*
K	2.5	2.6	1.6	*
L	2.7	2.9	*	*
Average	2.5	2.4	1.7	1.6
Mean for A, D, S1	2.4	2.7	1.7	1.6
Mean for G and J	2.5	2.2	*	*
Mean for B, C, E, F, S3	2.5	2.2	*	*
Mean for H, I, K, L	2.5	2.5	*	*

\* Storage at room temperature has not yet proceeded sufficiently for these values to be obtained.

used in this particular factory - the storage life of the powders (which is usually very good) cannot be significantly improved by selecting the milk, by clarification or by paying additional attention to the cleaning of the plant. The fact that clarification per se had no significant effect on storage life is confirmed by the general similarity between S<sub>2</sub> and S<sub>3</sub> and B, C, E and F, - for all these powders were manufactured under comparable conditions except for the introduction of the clarifier during the manufacture of the "S" samples. These results confirm in general those obtained with the Kestner plant (p.32 ).

Moreover, as with the Kestner samples, milk selection also had no effect with samples in which the temperature of preheating was high. In this connexion it may be noted that with the Gray-Jensen plant the preheating was probably sufficiently drastic to cause the powders to resemble the 190°F samples made on the Kestner plant rather than the 165°F samples.

The peroxide values recorded in Table XIX for the individual samples and the average values for the four groups confirm the conclusions from the tasting tests.

#### Temperature coefficients.

The temperature coefficients between 47° and 37° recorded in Table XX varied considerably from sample to sample but for most of the powders the value lay

close to the average of 2.5 and 2.4 which is very slightly higher than that found for the Kestner powders (p. 34) and for the high temperature Krause powders over the same temperature range. Between  $37^{\circ}$  and  $15^{\circ}\text{C}$  the coefficient for  $10^{\circ}\text{C}$  lay between 1.6 and 1.8, which is intermediate between the corresponding values of 1.9 for the Kestner powders and 1.5 for the Krause powders (Tables VII and XII).

#### Conclusion and Summary to Part II.

1. A description has been given of experiments which were designed to improve the storage life of milk powder made on Kestner, Krause and Gray-Jensen plants.
2. Three main methods were employed. The preheating temperature was raised with the object of improving the antioxidant properties of the milk powder through an increase in the sulphhydryl content of the milk. The effects of clarification and of milk selection were also investigated, since it was felt possible that by these means any pro-oxidants resulting from the proliferation of micro-organisms in the milk might be reduced.
3. The preheating temperature was found to exert a greater effect on the keeping quality of a milk powder than any other factor. In the Kestner plant preheating at  $190^{\circ}\text{F}$  in place of  $165^{\circ}\text{F}$  for 20 seconds roughly doubled the storage life with selected milk and increased it three-fold with ordinary milk. With the Krause plant the storage life of the powders was

doubled by raising the preheating temperature from 170 to 180°F and more than doubled by raising it from 160° to 190°F. A further rise in temperature to 200°F, however, gave no further significant increase. It seems probable that the critical preheating temperature lies between 170 and 190°F.

4. With both the Kestner and Gray-Jensen plants clarification had no significant effect on the storage life of the powder.

5. With the Kestner plant, milk selection resulted in a doubling of the storage life when the preheating temperature was 165°F. With a preheating temperature of 190°F, however, milk selection had no significant effect.

6. The temperature coefficient for the rate of development of tallowiness has been calculated for a change in storage temperature from 37°C to 47°C and also for a 10°C difference in the temperature range between room temperature and 37°C. Except with the Krause powders made from milk preheated to 160° and 170°F, the average values for the range 47-37°C for each of the types of powder varied from 1.9 to 2.5. For the range between room temperature and 37°C the average values were about 1.9 for the Kestner powders, 1.5 for the Krause powders and 1.7 for the Gray-Jensen powders.

7. In all three plants the presence of excessive amounts of copper in some of the samples was detected.

The storage life of these samples was shortened, in some instances seriously, by the presence of this metal. The need for freedom from copper in both experimental and commercially-made powders is emphasised.

PART III.

ASCORBIC ACID AND ETHYL GALLATE AS ANTIOXIDANTS  
IN MILK POWDER.

Introduction.

The experiments so far described have shown that the keeping quality of full cream spray-dried milk can be greatly extended by increasing the preheating temperature of the liquid milk to 180° or 190°F. The higher preheating temperatures impart a slight cooked flavour to the resulting milk powder. To most unbiased tasters the cooked flavour is not objectionable, but however slight it may be, it admittedly tends to decrease the close resemblance that otherwise exists between the flavour of fresh milk and that of the best reconstituted powder.

It was thought possible that a milk powder of long keeping quality but having no undesirable cooked flavour might be secured by the addition of an antioxidant to the liquid milk before drying. Such a method of extending the storage life of a milk powder would be extremely simple to carry out under factory conditions. No specially skilled labour or unusual equipment would be required and the containers for the powder would not have to pass the exacting gas-tightness tests which are essential with powders packed in inert gas (Lea et al., 1943). The substance used

as an antioxidant in milk would of course have to conform to certain basic standards. It would have to be harmless to the human body, cheap, plentiful, tasteless and odourless.

For many years in many branches of food chemistry such substances have been sought. Recently Waite (1941b) used a small scale spray-drier to test the effect of a number of possible substances on the keeping quality of dried milk. He found hydroquinone to be effective when added to the liquid milk in an amount representing 0.12% of the dried powder. Hydroquinone, however, is toxic and at this concentration imparted a disagreeable metallic taste to the milk. Oat flour, which is believed to contain natural antioxidants, was found by Waite to afford only a very slight increase in keeping quality when present to the extent of 0.25% of the liquid milk. At higher concentrations it imparted a disagreeable 'oat' taste to the product.

In a cooperative investigation between workers at the Low Temperature Research Station, Cambridge, and the Hannah Institute, a number of possible substances were tested by incorporating them in liquid milk and drying the liquid milk in a laboratory spray-drier such as that described by Waite (1940). Among the substances tested in this way were ascorbic acid, reductic acid, and dehydroxy maleic acid, gallic acid and some of its esters, citric acid, potassium



metabisulphite, gelatin hydrolysate, sodium hypophosphite, cystine, tocopherol concentrates and synthetic chroman (6-hydroxy-2.2.5.7.8-pentamethyl chroman) and haematoxylin. The conclusion reached from these various investigations was that of all the substances tested, ascorbic acid and ethyl gallate were the two most promising antioxidants. Neither of them produced any flavour in the milk in effective concentrations and both markedly increased the resistance to the development of tallowiness of powders produced on a laboratory-scale spray-drier. (Findlay et al. 1944).

Gray and Stone (1939) had previously claimed that the addition of ascorbic acid or of gluco-ascorbic acid to milk before spray-drying improved the keeping quality of the powder, but their published data covered a storage period of only 7 weeks. More recently, Hollender and Tracy (1942) have investigated the efficiency of ascorbic acid as an antioxidant in milk powders prepared by the roller-drying (vacuum) process. They found it to be moderately effective. Lea (1944b) has studied a number of substances as possible antioxidants for edible fats. With dry butterfat he found that gallic acid was a very powerful antioxidant and showed that the activity of ethyl gallate, molecule for molecule, was equivalent to that of the acid, the activity decreasing with increasing molecular weight. He also showed that ethyl gallate

was odourless and tasteless in effective concentrations, and that it was therefore preferable to the acid itself and to its higher esters. This substance has been shown (Hilditch, 1944) to be non-toxic to the animal body.

Since the results with ascorbic acid and ethyl gallate seemed so promising in powders produced on a laboratory scale, it was decided to test them out on a commercial scale on a large factory drier.

Conditions in a commercial plant cannot be entirely duplicated in the laboratory. The method of pre-condensing the milk, the type of spray and the time-temperature treatment of the droplets of milk in a full-size drying chamber differ from those of a small laboratory drier. Moreover it had already been found from experience that powders made on a laboratory drier tended to have an unusually long storage life and that they did not develop the same off-flavours as commercially-made powders. These facts made it clearly essential to confirm the preliminary findings on a large scale drier..

#### Experimental.

The plant used for carrying out the commercial trials with ascorbic acid and ethyl gallate was the Gray-Jensen plant on which the powders were made for the experiments described in Part II (c) above. Owing to the high cost of ascorbic acid and to the fact that

ethyl gallate cannot meantime be legally added to milk powder, only the smallest practicable batches of powder were prepared. For this purpose 100 gallons of milk were preheated according to the normal procedure at this factory (see Table XIV) and transferred to a small tank from which they could be passed to the large spray-drier.

#### Addition of antioxidants.

When drying began, the first 25 gallons of milk were dried without any addition of antioxidants. This gave the control powder. Successive additions of ethyl gallate, dissolved in a little water, were made after the first, second and third 25 gal. portions of the milk had passed into the drier. The concentrations of ethyl gallate aimed at were control, none: sample 1, 0.05; sample 2, 0.10; and sample 3, 0.20% of the powder. The concentrations actually obtained in samples 1 to 3 were 0.07, 0.07, and 0.20% corresponding to about 0.009, 0.009 and 0.026% of the liquid milk. The divergence from the expected figures for samples 1 and 2 was attributable to the fact that in drying so small a quantity of milk as 25 gal., it is not possible to know exactly when any particular portion of the liquid milk entering the drier emerges again as powder. Sample 1 was apparently collected a little late and sample 2 a little early.

After completion of the run with ethyl gallate, which occupied about 20 minutes, the drier was operated

TABLE XXI.

The moisture and copper content and the solubilities of the various ethyl gallate and ascorbic acid powders

<u>Sample No.</u>	<u>Moisture %</u>	<u>Copper as parts per million</u>	<u>% Solubility</u>	
			<u>20°C</u>	<u>50°C</u>
<u>Ethyl gallate</u>				
Control	2.1	1.2	98	100
1	1.8	1.5	98	100
2	1.9	1.3	98	100
3	1.8	1.1	98	100
<u>Ascorbic acid</u>				
Control	1.8	0.8	96	100
1	1.8	0.7	96	100
2	1.9	0.7	97	100
3	1.8	0.8	96	100

continually for three hours, by which time it was assumed that all traces of ethyl gallate would have been removed. A further 100 gal. of milk were then dried, but with the addition of ascorbic acid in quantities calculated to give the following concentrations: control, none\*; sample 1, 0.10; sample 2, 0.15; and sample 3, 0.30% of the powder. When estimated 15 days after manufacture, the quantities of ascorbic acid found were, control, 0.008%; sample 1, 0.11%; sample 2, 0.14%; sample 3, 0.31%; corresponding to approximately 0.001%, 0.014%, 0.018% and 0.040% of the liquid milk. No trace of ethyl gallate was present in any of the samples.

#### Moisture and solubility.

The moisture content and solubility of the various powders are given in Table XXI. The moisture contents were sufficiently low to ensure that the principal type of deterioration would be fat-oxidation. The solubilities were higher than usual for a full-cream powder prepared on a Gray-Jensen plant.

#### Copper content.

The copper content of the various samples, estimated by the method given in Part I, is shown in Table XXI. None of the powders had very high copper

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\*It was assumed, however, that the control powder would in fact contain small quantities of ascorbic acid derived from the liquid milk.

TABLE XXII.

Time at 47°C and 37°C required for the various ethyl gallate and ascorbic acid powders to reach off-scores of 1.0 and 2.0.

<u>Sample No.</u>	<u>Concentration<sup>1</sup> of antioxidant in the powder as %</u>	<u>Weeks to reach off-flavour score of</u>			
		<u>1.0 2.0</u> <u>at 47°C</u>		<u>1.0 2.0</u> <u>at 37°C</u>	
<u>Ethyl gallate.</u>					
Control	None	8	11	18	23
1	0.07	23	28	49	57
2	0.07	27	29	52	66
3	0.20	25	28	51	72
Mean of 1 and 2	0.07	25	28	50	61
<u>Ascorbic acid.</u>					
Control	0.008	12	14	31	34
1	0.110	15	19	48	57
2	0.140	19	20	45	57
3	0.306	20	24	45	54

<sup>1</sup> To convert these values to the approximate equivalents on the liquid milk basis, divide by 7.7. The ascorbic acid values were estimated 15 days after manufacture.

contents, but it will be seen that the ethyl gallate samples had slightly more copper than the ascorbic acid powders.

#### Storage technique.

The method of packing and storing the powders was identical with that described for the Kestner samples in Part II (a), p.28 .

#### Assessment of flavour.

At intervals during storage the flavour of the reconstituted powders was assessed by the method already described in Part I, p.10 . The results are shown in Figs. 7 and 8, while the times required for off-flavour scores of 1.0 and 2.0 to be reached are recorded in Table XXII.

#### Estimation of ascorbic acid and ethyl gallate.

Since cow's milk is normally a relatively poor source of ascorbic acid, the addition of this vitamin to milk before drying would be of great physiological value, provided the ascorbic acid was not materially reduced during storage. Information on this latter point was obtained by estimating ascorbic acid at intervals throughout the storage period. As already stated, ethyl gallate is itself non-toxic. There appeared, however, to be a remote chance that this compound might be oxidised during storage into harmful substances of unknown constitution. Furthermore, it was of interest to determine whether or not ethyl

Figure 7.

The deterioration in flavour of the ethyl gallate samples during storage at 47° and 37°C. Control, no ethyl gallate; No.1, 0.07%, No.2, 0.07% and No.3, 0.20% ethyl gallate.

● = control powder, and ○ = powders containing ethyl gallate.

Figure 8.

The deterioration in flavour of the ascorbic acid samples during storage at 47° and 37°C. Control, 0.008%; No.1, 0.110%; No.2, 0.140% and No.3, 0.306% ascorbic acid.

● = control powder, and ○ = ascorbic acid powders.



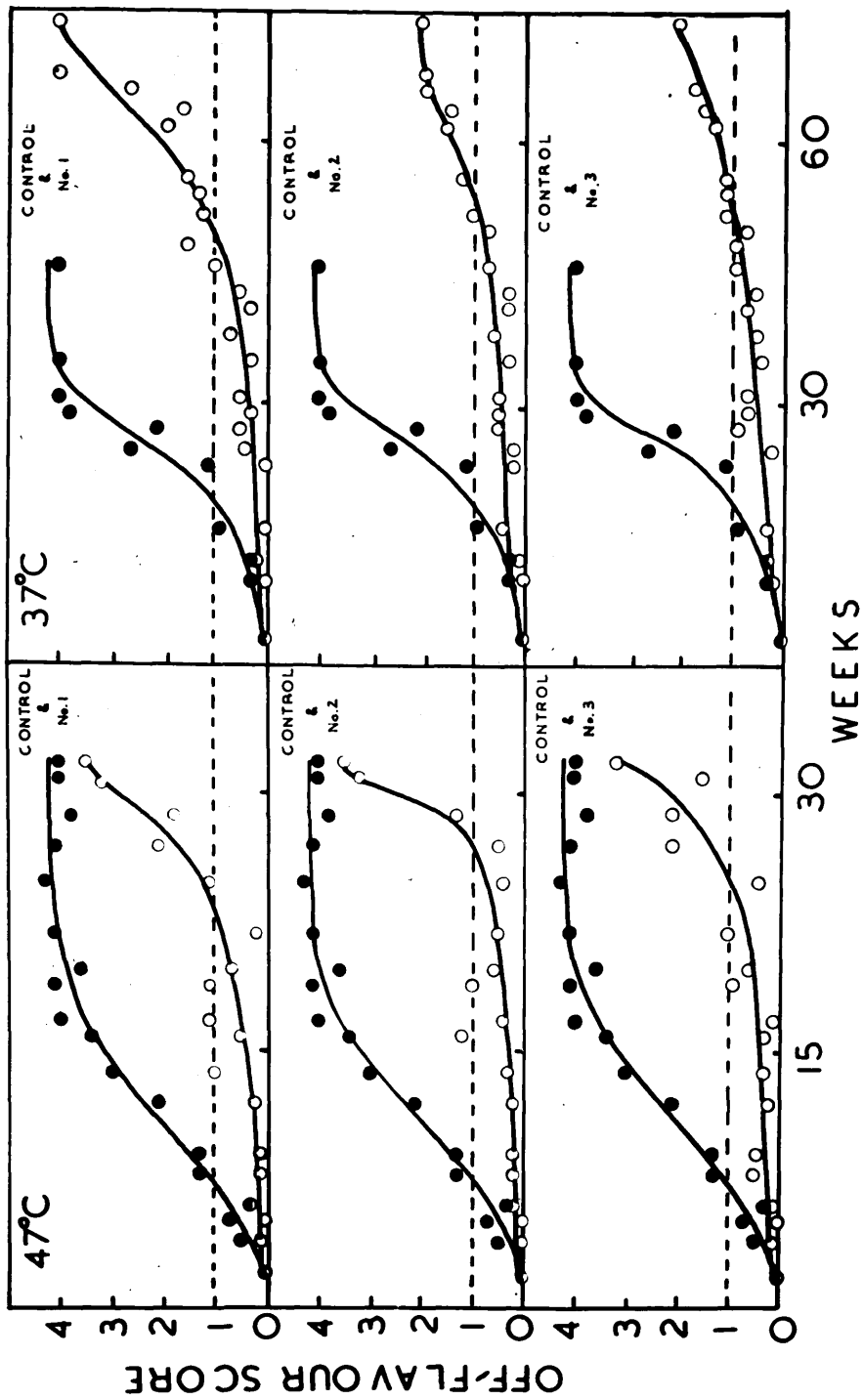
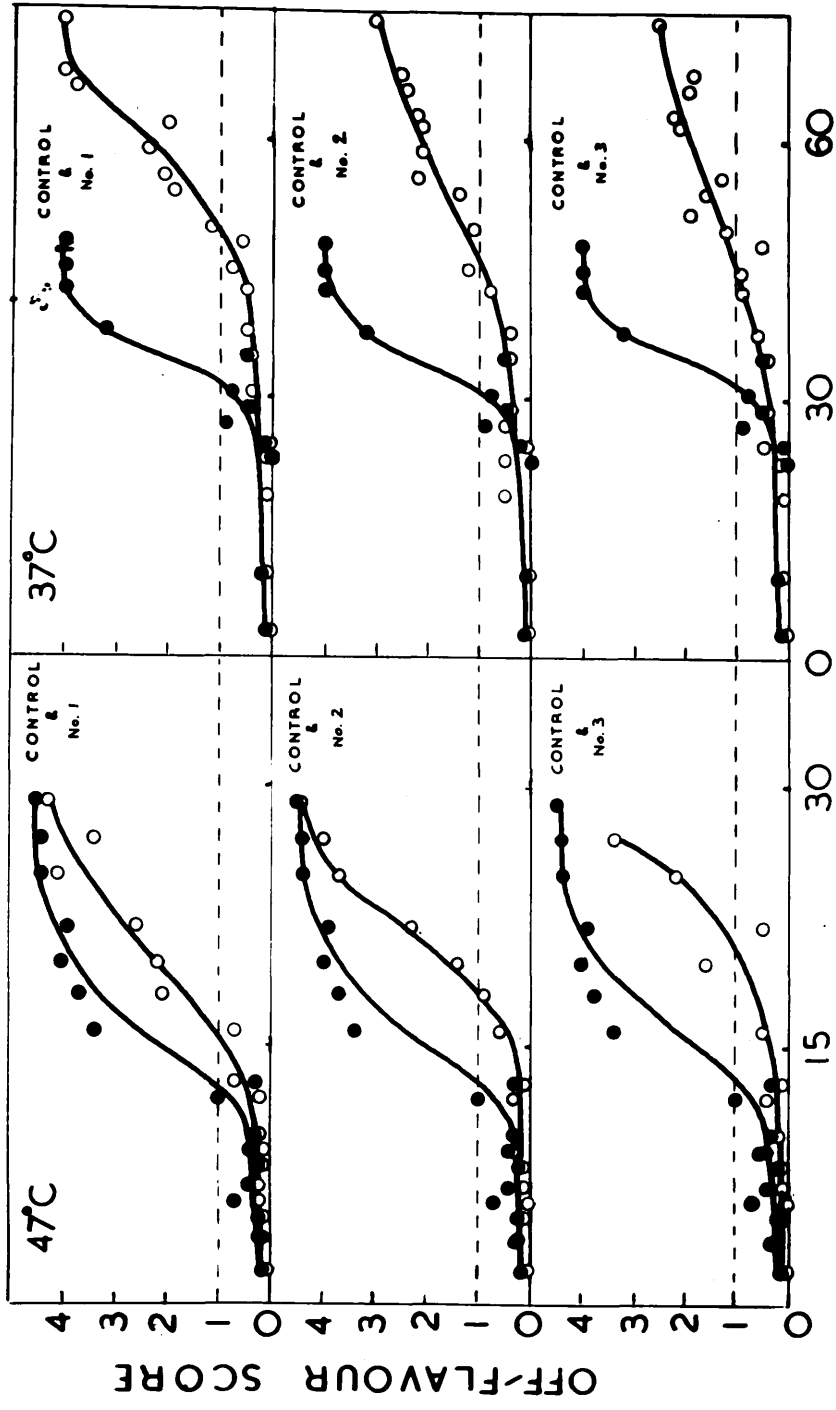


FIG. 7



WEEKS

FIG. 8

gallate owed its antioxidant properties to preferential oxidation (like ascorbic acid) or not. The content of ethyl gallate in the various samples was therefore estimated at intervals during the experiment. The method adopted was that of Radeff (1937) for ascorbic acid and a modification of that of Mitchell (1923) for ethyl gallate.

#### Ascorbic acid.

Approximately 0.01N dichlorophenolindophenol solution was prepared by mixing 0.15 or 0.20 g. of the dye with warm water and diluting the mixture to 500 ml. The next day it was filtered and standardised against a freshly prepared ascorbic acid solution of known strength. 1-3 g. of milk powder (according to the content of ascorbic acid) was thoroughly mixed with 25 ml. of water in a 100 ml. flask. 5 ml. of 20% sulphosalicylic acid were added and the mixture made up to the 100 ml. mark. It was then well shaken and filtered and 20 ml. aliquots of the filtrate titrated with the dye solution contained in a 5 ml. burette graduated to 0.01 ml. The titration had to be completed within 1-2 minutes.

#### Ethyl gallate.

Approximately 2 g. of milk powder were accurately weighed into a 100 ml. flask and thoroughly shaken with 50 ml. water at 55°C. The mixture was allowed to stand at room temperature with occasional shaking for half an hour. 10 ml. of 10% trichloroacetic acid were then added and the volume made up to the 100 ml. mark with water. The flask was again vigorously shaken and allowed to stand for a further half-hour with further occasional shaking. The mixture was then filtered through a Whatman No.42 paper to give a water-clear filtrate. A 75 ml. aliquot was removed to a 100 ml. flask and treated with 5 ml. of 10% NaHCO<sub>3</sub> and 5 ml. of ferrous reagent containing 1.0 g. ferrous sulphate and 5.0 g. sodium potassium tartrate per litre. The volumes were then made up to 100 ml. 1 hour later the colours were read in a Spekker absorptiometer which had previously been calibrated using the colour filter No.5.

The Spekker absorptiometer was calibrated by preparing some milk powder filtrate from 10g.

TABLE XXIII.

The calibration of the Spekker absorptiometer for the estimation of ethyl gallate.

<u>Ethyl gallate</u> <u>mg. per 100 ml.</u>	<u>Absorptiometer</u> <u>reading</u>
0.00	0.012
0.50	0.064
0.75	0.092
1.50	0.168
2.50	0.244
3.50	0.298

TABLE XXIV.

Temperature coefficients (10°C) for the ethyl gallate and ascorbic acid powders.

<u>Sample</u> <u>No.</u>	<u>Antioxidant</u> <u>%</u>	<u>Temperature coefficients for</u> <u>37°C-47°C calculated from the</u> <u>off-flavour score of</u>	
	<u>Ethyl gallate</u>	<u>1.0</u>	<u>2.0</u>
Control	None	2.3	2.1
1	0.07	2.1	2.0
2	0.07	1.9	2.3
3	0.20	2.0	2.6
Mean of 1 and 2	0.07	2.0	2.3
	<u>Ascorbic acid</u>		
Control	0.008	2.6	2.4
1	0.110	3.2	3.0
2	0.140	2.4	2.8
3	0.306	2.3	2.3
Mean		2.6	2.6

of typical Gray-Jensen powder by the same method as that employed for the 2 g. lots of powder. To 75 ml. aliquots of the filtrate in 100 ml. flasks, sufficient ethyl gallate was added to cover the range, and the  $\text{NaHCO}_3$  and ferrous reagent added. Table XXIII gives typical calibration figures.

The ferrous reagent used in these estimations was the same as that described by Mitchell (1923). Mitchell in 1924 suggested the use of osmic acid but this reagent was found to offer no advantage in the present study.

In using this modification of Mitchell's method applied to dried milk three points are to be noted. Firstly, sulphosalicylic acid cannot be used as the precipitating reagent since it gives a colour with the ferrous reagent. Secondly, the strength of the reagents must be exact since the colour develops only if the solution is alkaline and deepens with increasing alkalinity. The same amounts of the same reagents must therefore be used for the actual estimation as for the calibration. Thirdly, the colour must be read within 1 hour of its development as it deepens with time.

The ascorbic acid results are shown in Fig.9 and the ethyl gallate results in Table XXVI.

#### Discussion.

##### Ethyl gallate.

From Fig.7 and Table XXII, it will be seen that the presence of ethyl gallate caused a very marked increase in the storage life of the powder. Whereas



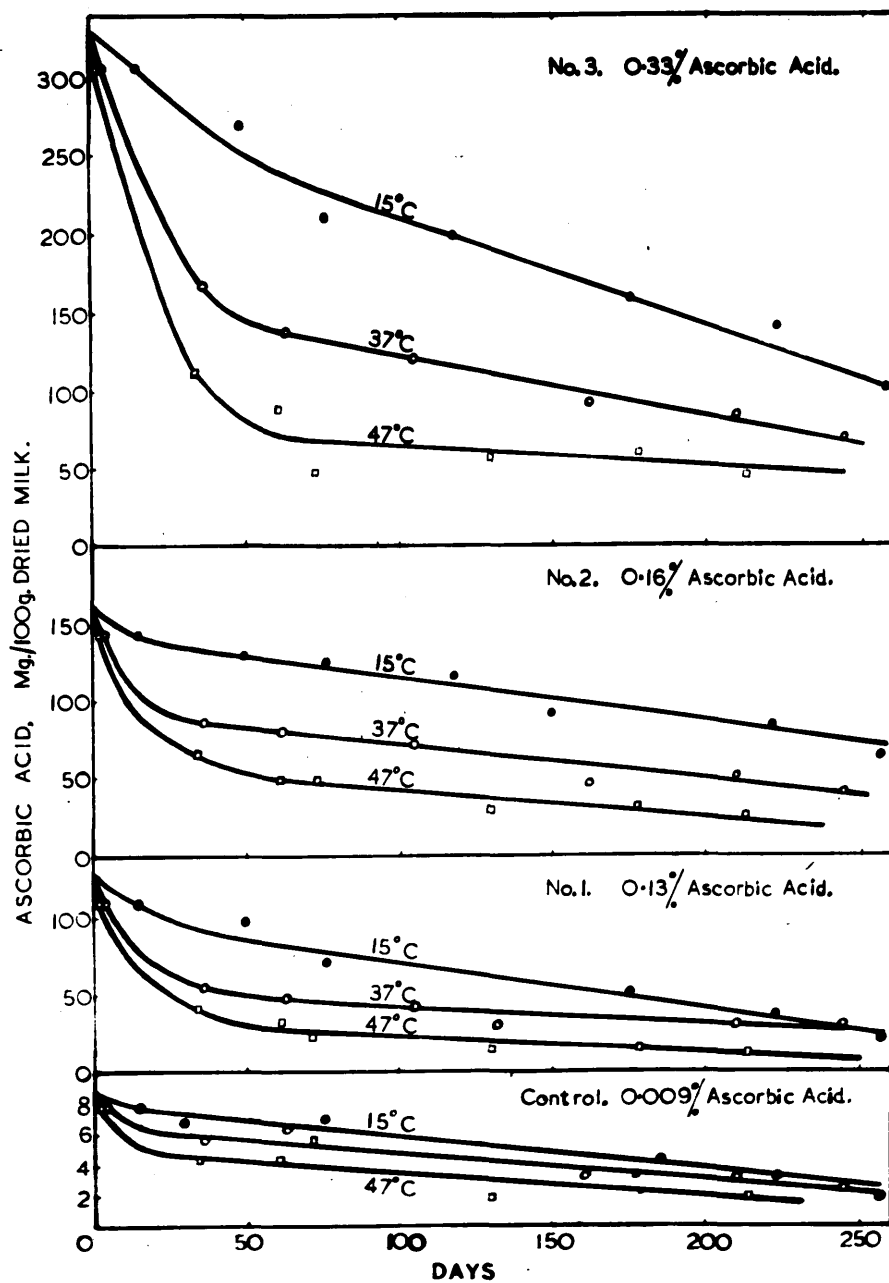


FIG. 9

TABLE XXV.

Estimated storage life of the powders containing ethyl gallate and ascorbic acid.

<u>Sample No.</u>	<u>Antioxidant %</u>	<u>Estimated storage life in years at 15°C calculated+ from the time at 37°C required to reach off-flavour score of:</u>	
	<u>Ethyl gallate</u>	<u>1.0</u>	<u>2.0</u>
Control	None	1.9	2.0
1	0.07	4.8	4.9
2	0.07	5.1	5.7
3	0.20	5.0	6.2
Mean of 1 and 2	0.07	4.9	5.3
	<u>Ascorbic acid.</u>		
Control	0.008	3.0	3.0
1	0.110	4.7	4.9
2	0.140	4.4	4.9
3	0.306	4.4	4.7

+ The temperature coefficient for 22°C used is 1.7 at off-flavour score 1.0 and 1.6 at off-flavour score 2.0 (see text on p. 62 ).

TABLE XXVI.

The ethyl gallate content of the various samples during storage at 47°C, 37°C and room temperature.

<u>Age of powder Weeks</u>	<u>Temperature of storage</u>	<u>Concentration of ethyl gallate as %</u>			
		<u>Control</u>	<u>1</u>	<u>2</u>	<u>3</u>
0	-	None	0.07	0.07	0.20
9	47°C	None	0.07	0.07	0.22
9	37°C	None	0.07	0.07	0.21
9	Room	None	0.07	0.07	0.21
35	47°C	None	0.06	0.06	0.18
35	37°C	None	0.06	0.06	0.20
35	Room	None	0.06	0.06	0.20
54	47°C	-	0.07	-	0.20



the control kept for some 8-11 weeks at 47°C and 18-23 weeks at 37°C, the powders containing ethyl gallate kept for two and a half to three times as long, the lower concentration of 0.07% ethyl gallate being almost as effective as the higher concentration of 0.20%. This was accomplished without any foreign flavour being perceptible in the milk.

The temperature coefficients for the 37-47°C range are shown in Table XXIV. They are of the same order as those already found for the same ranges of temperature for Gray-Jensen powders as recorded in Table XX. If it may be assumed that the coefficients of 1.7 and 1.6 recorded in Table XX for the room temperature to 37°C range also hold in the present experiment, the probable storage life of the ethyl gallate samples should be between 5 and 6 years as compared with just under two years for the control (Table XXV). Room temperature storage has not yet progressed sufficiently far for this assumption to be confirmed, but after 92 weeks the ethyl gallate samples are still in excellent condition, while the control is beginning to be very slightly tallowy.

The ethyl gallate content of the various powders is shown in Table XXVI. Within the limits of the method of estimation, no change in concentration was detected. Ethyl gallate therefore acts as an antioxidant without itself becoming decomposed even after the powder has

become extremely tallowy. The stability of ethyl gallate is interesting since the majority of antioxidants that have been used in milk powder behave as such by being preferentially oxidised. It would appear that the ethyl gallate acts as a true catalyst in retarding the oxidation of the fat. Much of its efficiency may be due to its higher solubility in fat as compared to water, thus allowing intimate contact with the medium it is protecting. While the mode of action of ethyl gallate has not yet been elucidated, it seems probable that its antioxidant properties have a physical basis.

#### Ascorbic acid.

The results in Fig.8 and Table XXII show that ascorbic acid also exhibited antioxidant properties. At 47°C the extension of storage life over that of the control increased with increasing concentrations of ascorbic acid. At 37°C, however, concentrations of 0.140 and 0.306% were no more effective than 0.110%. At both 37° and 47°C the maximum increase in storage life as a result of adding ascorbic acid was about 70%.

From the temperature coefficients for the room temperature to 37°C range recorded for Gray-Jensen powders in Table XX, the various powders may be expected to have the storage lives indicated in Table XXV, i.e. 4½ to 5 years as compared with 3 years for the control. After 92 weeks at room temperature all the powders including the control are still in

excellent condition.

It will be observed that there was a marked difference in the storage life of the two controls, the ascorbic acid control keeping longer than the ethyl gallate control. This was in part due to the higher copper content of the ethyl gallate control. Ethyl gallate has thus been even more effective than might have appeared at first sight, since it produced a greater extension in storage life than was conferred by ascorbic acid, and this extension was moreover produced in powders which might have been expected, because of their copper content and by comparison with the control, to have had poorer keeping qualities.

The estimation of ascorbic acid (Fig.9) showed that the content of ascorbic acid decreased during storage, particularly at the higher temperatures, - very rapidly at first, and then more slowly. Physiologically, therefore, much of the advantage of adding ascorbic acid to milk powder would be lost during storage. This observation, together with the fact that ascorbic acid is relatively scarce and expensive and that it is not so effective an antioxidant as ethyl gallate, justifies the conclusion that the latter would in practice be a more suitable substance for extending the storage life of milk powders.

#### Summary.

1. Of a number of substances tested for antioxidant

activity in laboratory-made spray-dried powders, ascorbic acid and ethyl gallate proved most promising. Both these substances materially increased the resistance of the powder to the development of tallowiness without producing any foreign flavour in the milk.

2. The activity of both substances has been tested on factory-made powders using a Gray-Jensen plant. Ethyl gallate was found to be considerably more powerful than ascorbic acid. At a concentration of 0.07% it increased the storage life of the powder in accelerated tests two-and-a-half to three-fold, while the maximum increase brought about by ascorbic acid was 70%.

3. Ethyl gallate remained unchanged during storage of the powder but the concentration of ascorbic acid decreased.

4. Ethyl gallate is sufficiently plentiful and cheap to make its use as an antioxidant in dried milk feasible. It is non-toxic and would be tasteless in the amounts required.

PART IV.THE STORAGE LIFE OF SPRAY-DRIED FULL-CREAM MILK  
POWDER IN DIFFERENT TYPES OF CONTAINERS.Introduction.

In their work on the storage of vacuum roller-dried milk powder Hollender and Tracy (1942) found that powder packed in lacquered tinfoil showed a significantly better keeping quality than that stored in ordinary tinfoil. Similar results were obtained by Lea (1944a)\* in storage tests with butterfat, while certain evidence in the earlier storage experiments carried out jointly at Cambridge and the Hannah Institute appeared to confirm the findings of Hollender and Tracy, - though the results were not clearcut. It was therefore decided to include in the present study a preliminary investigation of the effect of the type of container on the storage properties of spray-dried milk powder.

Experimental.

Spray-dried milk powders made on a Krause plant, on two Gray-Jensen plants, and on a Milkal plant were used in these preliminary trials. The powders were stored in four types of container, i.e. (i) acid-washed glass bottles, (ii) plain tinfoil cans, (iii) plain tinfoil cans which had previously been washed with alcohol and ether, and (iv) lacquered tinfoil cans. The storage tests were carried out on the same

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\* also in communications of 1941.

TABLE XXVII.

The storage life of the powders made on the Krause  
plant as judged by flavour.  
Stored in acid washed glass bottles.

<u>Trial No.</u>	<u>Preheating temperature OF</u>	<u>Weeks to reach off-flavour score of:</u>					
		<u>1.0 2.0</u> <u>at 47°C</u>		<u>1.0 2.0</u> <u>at 37°C</u>		<u>1.0 2.0</u> <u>at room temperature</u>	
1	160	5.2	6.4	7.6	10.0	17.2	22.8
2	170	3.6	4.8	6.8	9.2	20.0	24.0
3	180	7.2	8.8	16.0	18.0	46.0	50.0
4	190	12.4	15.6	28.0	30.0	*	*
5	200	12.0	13.6	26.8	30.0	*	*

Relative storage life expressed as a  
multiple of the storage life of the  
shortest-lived powder

1	160	1.4	1.3	1.1	1.1	1.0	1.1
2	170	1.0	1.0	1.0	1.0	1.2	1.0
3	180	2.0	1.8	2.4	1.9	2.7	2.2
4	190	3.4	3.3	4.1	3.3	*	*
5	200	3.3	2.8	3.9	3.3	*	*

\* Storage at room temperature has not progressed sufficiently far for these values to be obtained.

TABLE XXVIII.

The keeping quality of Krause powders stored in glass bottles compared with the keeping quality in tinfoil cans.

<u>Sample No.</u>	<u>Preheating temperature</u> °F	<u>Glass:plain tinfoil ratio where the storage life in the plain tinfoil is taken as 1.0.</u>					
		<u>Off-flavour score</u>		<u>Off-flavour score</u>		<u>Off-flavour score</u>	
		<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>	<u>1.0</u>	<u>2.0</u>
		<u>47°C</u>		<u>37°C</u>		<u>Room temp.</u>	
1	160	0.8	0.7	1.3	1.1	1.1	1.2
2	170	0.8	0.7	1.1	1.1	1.3	1.2
3	180	0.8	0.7	1.1	1.1	1.1	1.1
4	190	1.2	1.3	1.3	1.3	*	*
5	200	1.3	1.2	1.4	1.4	*	*

\* The results at room temperature are not yet available for these powders.

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lines as those recorded in Parts II and III, deterioration being judged by assessment of off-flavours (tasting tests) and - where feasible - by gas analyses on the can contents. Since the details of the trials varied with the different powders, it will be convenient to discuss the results for each type of powder separately.

1. Milk powder made on a Krause plant.

The samples used were identical with those employed in the storage tests described in Part II(b). The results there detailed referred only to powders stored in plain tinsplate cans. A parallel series was, however, also stored in acid-washed glass bottles. It was not feasible to obtain gas samples from the bottles for determining oxygen absorption; it was therefore necessary to rely on flavour tests to measure the comparative rates of deterioration.

The results for the powders stored in plain tinsplate cans have already been recorded in Table IX; the results for those stored in glass bottles (which have been interpolated from Fig.10) are contained in Table XXVII. By comparing these two sets of results the relative keeping qualities of the powders in the two types of container can be calculated (Table XXVIII).

This table shows that for all samples stored at 37°C and for the three samples stored at room temperature for which results are available, the



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**Figure 10.**

**The deterioration in flavour of the Krause samples stored in acid washed glass bottles at 47°<sup>o</sup>, 37°<sup>o</sup> and room temperature.**

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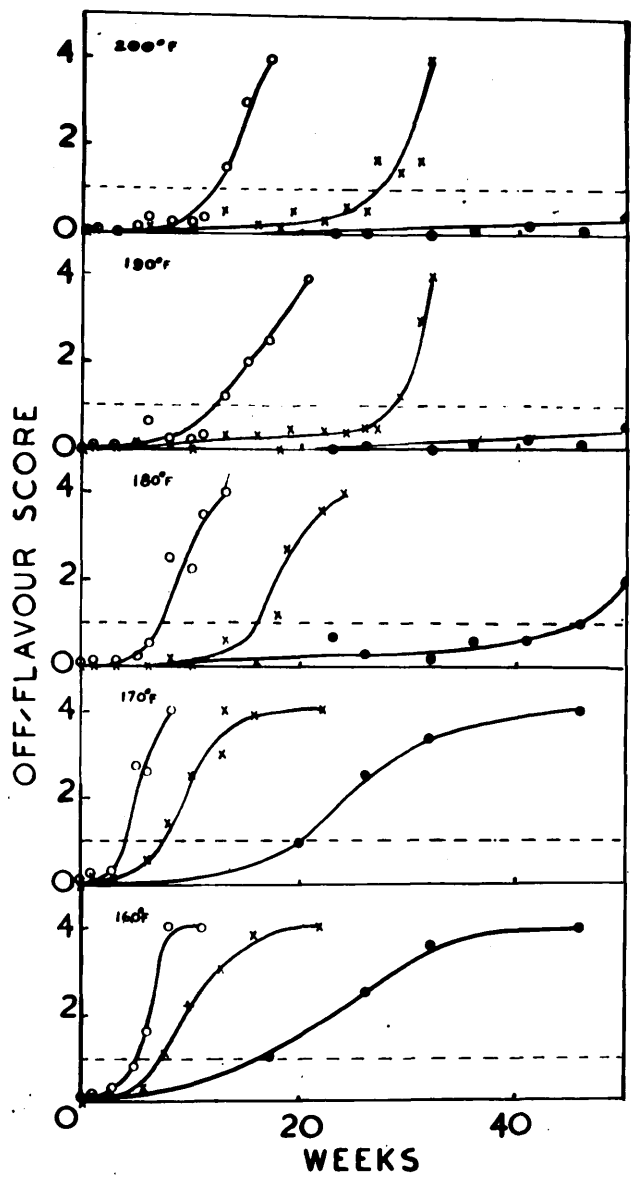


FIG. 10

TABLE XXIX.

The moisture content and solubility of the Gray-Jensen powders (Plant A) stored in different containers.

<u>Sample No.</u>	<u>Preheating temperature of</u>	<u>Moisture %</u>	<u>Solubility</u>	
			<u>20°C</u>	<u>50°C</u>
6	190	3.75	89	98
7	160	2.96	91	99

storage life in glass was some 10 to 40% longer than that in plain tinplate. At 47°C, however, a similar difference (20-30%) was only found with powders made from high temperature preheated milk: with powders made from low temperature preheated milk, storage in plain tinplate was better than storage in bottles.

Another point emerges from a comparison of the results in Fig.10 with those in Fig.4. With plain tinplate (Fig.4) there was no significant difference as judged by flavour between the storage life at 47°C and that at 37°C for the samples made from milk which had been preheated to 160°F, but with glass the difference was quite well marked. In both types of container the difference between storage at 47°C and 37°C increased as the preheating temperature of the liquid milk increased.

Differences between individual samples of only 10 to 20% cannot of themselves be regarded as significant: when however, as in this experiment, there is an increase of from 10 to 40% in 10 out of the total of 13 samples examined, it seems safe to assume that acid-washed glass gives a slightly extended storage life as compared with ordinary tinplate.

## 2. Milk powder made on Gray-Jensen plant A

Two different samples of powder from Gray-Jensen Plant A were available. The moisture contents and solubilities of the two powders are shown in Table XXIX. Owing to circumstances outwith the control of the

writer, the moisture contents of these powders were above 2.5%. At these levels of moisture content deterioration due to protein-lactose changes would tend to mask the off-flavours produced by fat oxidation. Reliable comparisons of the extent of fat oxidation could not therefore be made by flavour tests. Gas analyses had, therefore, to be used as the sole criterion of the rate of deterioration.

90 g. of powder were packed in 6 oz. cans, all of which were of identical size and made by a single manufacturer. The types of can used were plain tinfoil, plain tinfoil washed with alcohol and ether, and tinfoil coated with 'meat' lacquer (a commercial lacquer the composition of which has not been published but which may be a phenol-formaldehyde thermo-setting resin\*). The results for these three types of container are recorded in Fig.11 and Table XXX. The curves in Fig.11 show that for powders at 47°C the rate of deterioration as measured by oxygen absorption was greatest in plain tinfoil, slightly less in washed tinfoil, and least in 'meat' lacquered tinfoil. At 37°C the lacquered cans again gave the longest storage life, but the difference between the

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\* Experiments were also carried out with blackplate cans, but gas analyses showed that leaks were present in most of these cans, - due to the fact that the seams of blackplate cans cannot be soldered.

... of oxygen by the Gray-Jensen powders A at 47° and 37° C stored in 'meat' lacquer, (M), washed tinplate (W) and plain unwashed tinplate cans.

**Figure 11.**

The rate of absorption of oxygen by the Gray-Jensen powders A at 47° and 37° C stored in 'meat' lacquer, (M), washed tinplate (W) and plain unwashed tinplate cans.

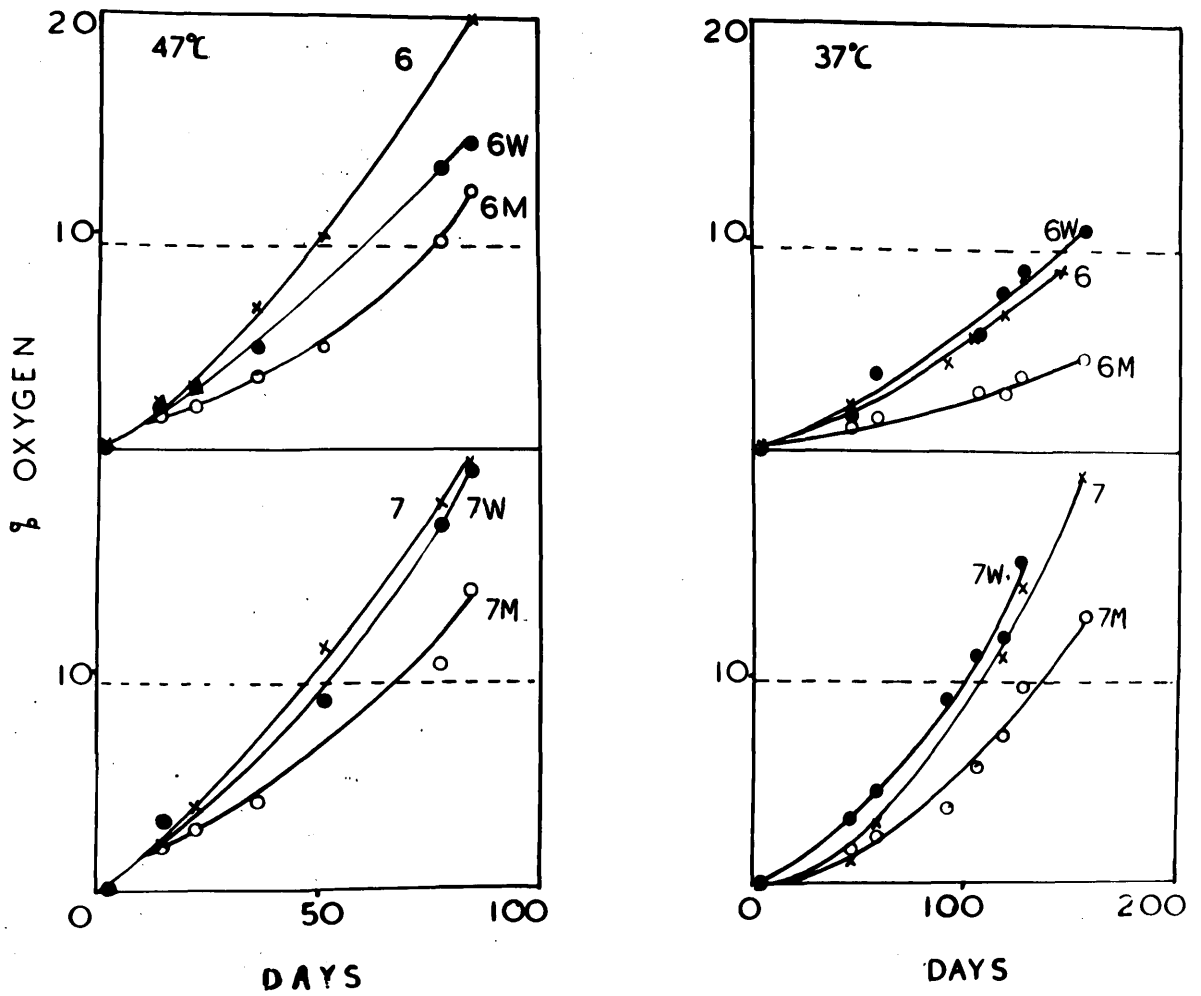


FIG. II

TABLE XXX.

Rate of absorption of oxygen by Gray-Jensen powders (Plant A) stored in different types of cans.

<u>Sample No.</u>	<u>Preheating temperature</u> OF	<u>Days required for the amount of oxygen in the gas of the can to decrease to 10% at</u>					
		<u>47°C</u>			<u>37°C</u>		
		<u>P</u>	<u>W</u>	<u>L</u>	<u>P</u>	<u>W</u>	<u>L</u>
6	190	49	61	76	160	144	*
7	160	47	53	69	112	96	136

Relative merits of containers expressed as ratios

	<u>Preheating temperature</u> OF	<u>L/P</u>	<u>L/W</u>	<u>P/W</u>	<u>L/P</u>	<u>L/W</u>	<u>P/W</u>
		6	190	1.4	1.2	0.8	*
7	160	1.4	1.3	0.9	1.3	1.4	1.2

\* Experiment discontinued before this sample decreased to 10% (200 days).

NOTE: P, plain tinfoil can; W, washed tinfoil can; and L, 'meat' lacquered can.

TABLE XXXI.

The storage life of Gray-Jensen powder (Plant B) in lacquered and plain tinfoil cans.

<u>Days to reach off-flavour score of 1.0</u>		<u>Days to absorb 0.2 mg. oxygen per g. of powder</u>	
<u>Plain cans</u>	<u>Lacquered cans</u>	<u>Plain cans</u>	<u>Lacquered cans</u>
45	51	47	50
<u>Ratio of lacquer:plain</u> 1.1		<u>Ratio of lacquer:plain</u> 1.1	



plain and washed tinplate was scarcely significant, - the advantage, if any, being in favour of the plain tinplate rather than the washed tinplate. The figures in Table XXX show that the lacquered tinplate gave an increase in storage life of some 20-40% as compared with the ordinary plain tinplate.

### 3. Milk powder made on Gray-Jensen Plant B.

A sample of milk powder from Gray-Jensen Plant B was also available. This sample had been made from milk preheated to 170°F and had a moisture content of 1.9%. The solubility was 92% at 20°C and almost 100% at 50°C. It was stored in cans of plain and lacquered tinplate at 47°C. The results for the absorption of oxygen and the development of off-flavour, which are recorded in Fig.12, show that the lacquered cans gave a slightly longer storage life than the plain tinplate cans. It will be seen from Table XXXI, however, that the increase was only of the order of 10% by flavour and 20% by oxygen absorption. The difference between lacquered and plain tinplate with powder made on Gray-Jensen Plant B was therefore not so marked as with the powder made on Plant A. Estimations made on the two sets of samples showed that this might be attributable to their different copper contents. The sample from Plant B contained 2.0 p.p.m. of copper, as compared with only 0.6 p.p.m. for the powders from Plant A. It is not unlikely that a powerful pro-oxidant such as copper

**Figure 12.**

**The deterioration of the Gray-Jensen powders  
B at 47°C measured by flavour and the rate  
at which oxygen was absorbed in plain tinfoil  
and lacquered tinfoil cans.**

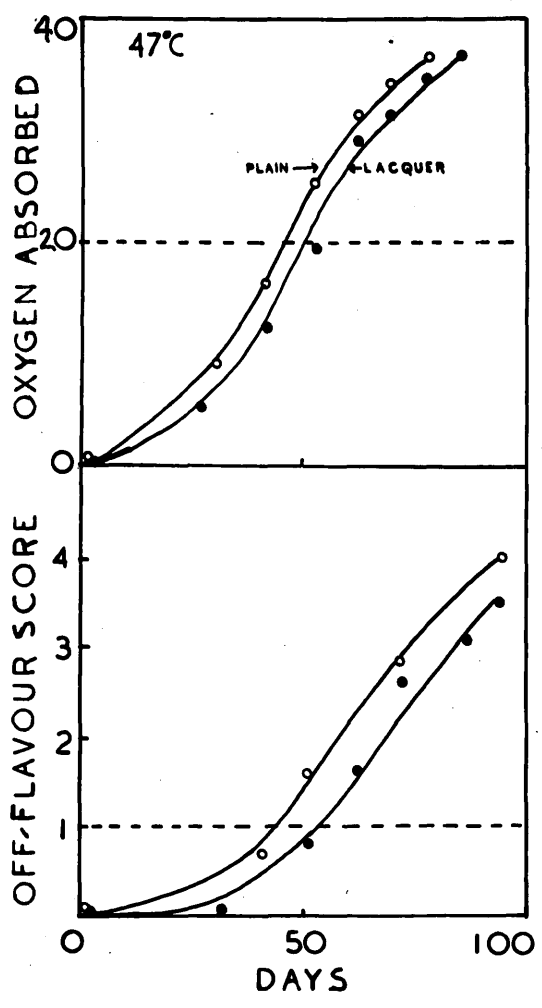


FIG. 12

TABLE XXXII.

The moisture content and solubility of the Milkal powders

<u>Powder</u>	<u>Moisture</u> %	<u>Solubility</u>	
		<u>20°C</u>	<u>50°C</u>
174°F	2.5	97	98
168°F	2.2	98	99

TABLE XXXIII.

The storage life of Milkal samples stored in lacquered and plain tinplate.

<u>Sample</u>	<u>Days to reach off-flavour score of 1.0 at</u>				<u>Days to absorb 0.10 mg. oxygen per g. powder at</u>			
	<u>47°C</u>		<u>37°C</u>		<u>47°C</u>		<u>37°C</u>	
	<u>P</u>	<u>L</u>	<u>P</u>	<u>L</u>	<u>P</u>	<u>L</u>	<u>P</u>	<u>L</u>
168°F	36	51	66	88	30	40	74	96
174°F	37	46	74	100	37	49	68	100
	<u>Lacquered:plain tinplate ratio</u>							
	<u>47°C</u>		<u>37°C</u>		<u>47°C</u>		<u>37°C</u>	
168°F	1.3		1.3		1.3		1.3	
174°F	1.2		1.3		1.3		1.4	

P = Plain tinplate.  
L = Lacquered tinplate.

would tend to minimise the difference in storage life which would otherwise have been obtained with the two types of container.

4. Milk powder made on a Milkal Plant.

The powders used in this experiment were manufactured by the Milkal spray-drying process, which has been described by Hunziker (1935) and Scott (1932). Two samples were available. They differed mainly in the fact that the preheating temperature of the liquid milk was 165°F for one sample and 174°F for the other. Their moisture contents and solubilities are shown in Table XXXII. The moisture contents were both below 2.5% and the solubilities practically 100%. The two powders were stored in plain and lacquered tinfoil at 47°C and 37°C, the rate of deterioration being measured by both gas analyses and flavour tests.

The results, which are shown in Fig.13 and in Table XXXIII, demonstrate that for both powders the use of lacquered tinfoil extended the storage life at both 47 and 37°C by some 20 to 30% when measured by flavour and by 30 to 40% when measured by oxygen absorption.

Summary to Part IV.

Preliminary experiments have been carried out to determine the relative keeping qualities of milk powders stored in different types of container\*. With one

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\*In order to obtain results within the time limit available, the experiments in Part III had to be limited to accelerated storage tests at 47°C and 37°C, except with the Krause samples.

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**Figure 13.**

**The deterioration of the Milkal powders in lacquered (●) and plain tinfoil (○) cans measured by flavour and oxygen absorption at 47° and 37°C.**

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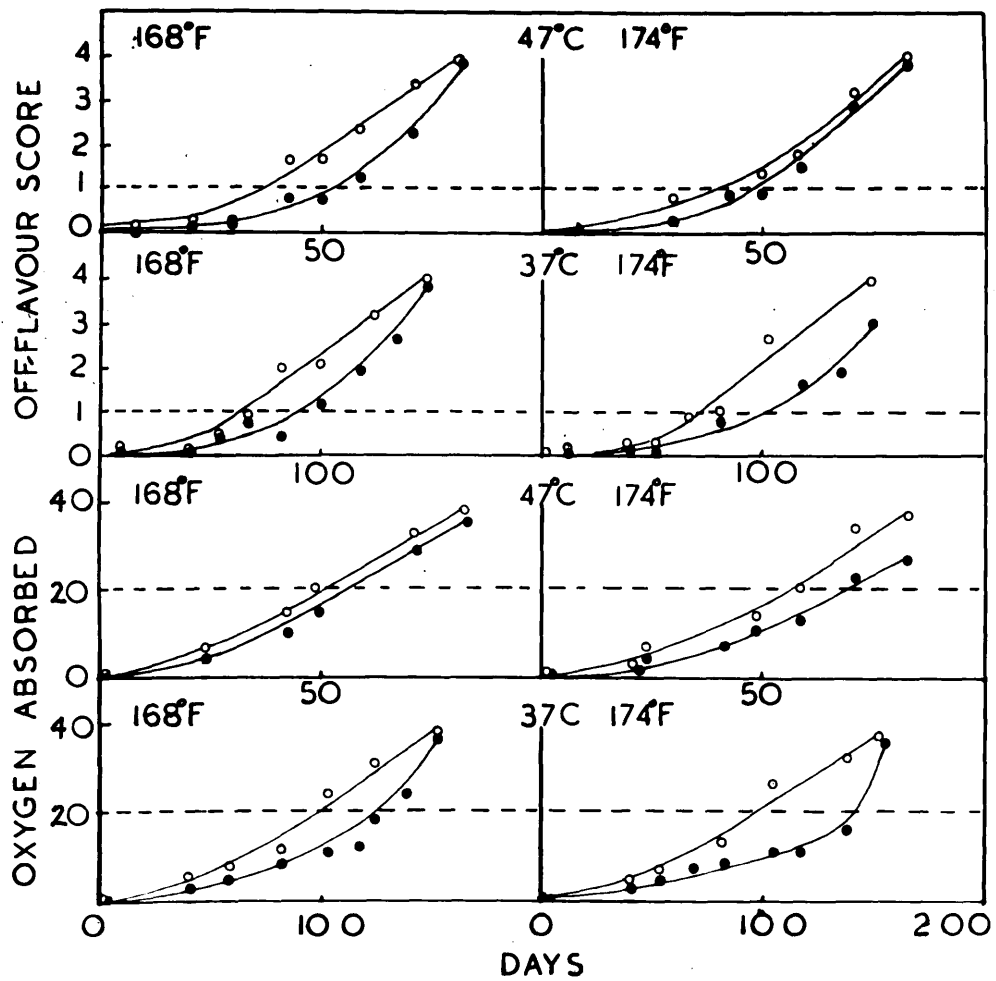


FIG 13

type of powder (Krause) the keeping quality in acid-washed glass bottles was 10 to 40% better than in plain tinfoil. With other samples (from two Gray-Jensen plants and one Milkal plant), the keeping quality in lacquered tinfoil was some 10 to 40% better than in plain tinfoil. It is pointed out that the magnitude of this difference may be affected by the copper content of the powder.

\* \* \* \*



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### ACKNOWLEDGMENT.

The author desires to record his indebtedness to the Directors and Managements of the various factories where the powders were manufactured, both for the facilities placed at his disposal and the willing cooperation extended to him. He is also indebted to his colleagues at the Hannah Institute who, as a tasting team, assisted in assessing the palatability of the many hundreds of samples investigated.