THE PHYSICAL CHEMISTRY OF CANNED 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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April, 1941.

ACKNOWLEDGEMENT.

I wish to express my grateful appreciation of the facilities accorded to me by the Council of the Hannah Dairy Research Institute, Kirkhill, Ayr. I wish also to thank Dr N.C. Wright and Dr J.A.B. Smith for their interest, advice and helpful criticism in this work.

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Introduction and Summary.

The production of milk in this country depends on the cyclic life of the dairy cow. Taking a typical dairy breed as an example, the Ayrshire cow has a lactation period of from nine to ten months, producing probably 40 lb of milk per day at the start and about 4 lb at the end of this period. The cow will be served in about its second or third month of lactation and as the gestation period is nine months there is a gap of two to three months in which the cow produces no milk, she is technically "dry". During this dry period the animal's food requirements are less than during milk production, the cow is only fed a maintenance ration. In this country dairy cattle do not winter outside but are brought into the byre about November and only allowed out to graze in late March or early April, depending on the locality. Hence for three to four months every year the farmer must feed his cattle indoors. For this he makes great use of his summer hay, any root crops and greenstuffs (kale etc.) he may have grown and, more recently, silage. But to provide an adequate, balanced ration, a considerable amount of concentrates, oil seed cake, oats etc. must be included and these are costly. In this position it is not difficult to realise why the winter months should be arranged to coincide with the dry period of the cows, when their nutritive demands are least. This arrangement is admirable for the farmer but results in a flood of spring calvings which in turn give rise to a huge production of milk, well in excess of the liquid milk demand. For some years past, an attempt, both by advice and price control, has been made to persuade the farmer to spread his herd's calvings more uniformly over the year and although the response has been slow, according to a recent survey by Wright(1) some progress had been made up to 1938. The present war has now reversed the desire for this policy by causing a shortage of the requisite winter feeding stuffs and consequently the large spring and early summer surplus of milk is likely to continue for some years.

In times of peace this surplus of milk is taken by the dairy industry and converted into butter, cheese, condensed milk, milk and whey powders and, to a smaller extent, casein. Of these products only condensed milk and dried milk powder preserve all the milk constituents as a source of human food, although milk from which cheese is made can be considered economically utilised if the resulting whey is dried, particularly if the dried product is of such a quality as to be suitable for human consumption. Since casein is a national necessity for the manufacture of plastics the best use must also be made of the whey resulting from its precipitation.

For many purposes, such as the bakery, confectionery and patent food trades, dried milk powder is preferable to condensed milk. Moreover, for the purpose of storage, the present importance of which needs no stressing, it is obviously an advantage to store a product containing 2-4% of water rather than one containing 40-60%. Unfortunately milk powder, and in particular whole milk powder (or full-cream milk powder as it is also called), is a much more difficult product to store over long periods than condensed milk. It is susceptible to changes in the protein constituent, leading to objectionable flavours and loss of "solubility" and, in the case of whole-milk powders, is even more liable to chemical changes affecting the butter fat, causing rancidity and tallowiness, both of which render the powder most unpalatable.

Rancidity in milk powders is due to the presence of free butyric and other volatile acids and is the result of hydrolysis of the butter fat. This hydrolysis is caused by the action of the enzyme lipase present in the milk and can be successfully controlled by arranging processing temperatures prior to drying sufficiently high to ensure the destruction of this enzyme and by maintaining a low moisture content in the powder(2).

Talloweness is the result of oxidation of the unsaturated fatty acids in butterfat, a reaction which is greatly accelerated by the presence of heavy metals such as copper and iron, exposure to light, particularly the ultra-violet end of the spectrum and exposure to air. By careful factory working and the use of tinned and stainless steel surfaces the amount of heavy metals entering the milk powder can be kept to a safe minimum. Light is excluded by packing the powder in barrels or tins, but air is more difficult to remove. Methods of doing so are by producing a vacuum in the container, by compression into blocks or by replacing the air by an inert gas, such as nitrogen. In the two former methods as applied commercially, the oxygen content would still be relatively high. Lea and Moran(3) have estimated that the highest permissible oxygen content if tallowiness is to be completely avoided is about 0.5-1.5% for spray dried powder and this can only be obtained by packing the powder in an inert gas.

In co-operation with the Low Temperature Research

Station at Cambridge an investigation into this means of preventing storage deterioration in skim and whole milk powders, prepared by a variety of processes, was proceeding when the present work commenced, hence such powders have not been included, attention being paid more to special types of milk powder, although for control purposes, one whole milk powder was also stored.

The course of the oxidation reaction for butterfat shows, in common with many other animal and vegetable oils and fats, a distinct induction period during which the amount of oxygen taken up is very small. This is thought to be due to the presence in the milk of natural fat antioxidants which must first be oxidised before the fat can react. This suggests a further method of prolonging the useful life of whole milk powder, by adding small quantities of substances which, whilst not affecting the flavour or general properties of the milk powder, would reinforce the natural antioxidants. Some work has been done on these lines using oat-flour as an antioxidant in samples of spray-dried whole milk powder prepared on a laboratory machine especially built for the purpose.

In the course of the work it was found that the laboratory tests developed to follow the changes on storage were applicable to both the milk and whey powders and hence the first section deals with the analytical methods employed and, in the case of original work, the experiments leading to their adoption.

The storage of inert gas-packed powders and powders containing antioxidants occupy the second part of this thesis, the third section of which deals with the problems encountered in drying whey by the roller process. This latter section also includes an investigation into the possibility of producing an edible dried material by the same process from the acid whey at present run to waste in the manufacture of casein.

Finally there is a short account of some work on the various factors affecting the solubility of milk powders. These experiments were actually commenced before the other work and were brought to an abrupt and somewhat incomplete conclusion by pressure of more urgent war time problems.

Summary of Results.

Part I. Analytical.

In this section only the determinations of solubility and peroxide value presented any difficulty. The commercial method of determining solubility by measurement of the sediment volume after centrifuging the reconstituted milk was fully examined but rejected as being insufficiently accurate and unsuited to powders of widely differing solubility. A simple method involving the determination of the total solids in the reconstituted milk, prepared under standard conditions, is described.

After considering the various published methods of measuring the peroxide value of fats, that of Smith(15) was used, in which the butterfat is brought into solution by the action of a solvent mixture on the whole milk powder, an aliquot of this solution being used to liberate iodine from a saturated solution of potassium iodide, with subsequent titration against 0.01 or 0.005N sodium thiosulphate.

Part II. A. Air and inert gas storage of milk powders.

In an endeavour to delay the onset of talloweiness by providing a protective covering for the fat in whole milk powder, sucrose was added to the milk before spraying. The results of the storage tests showed that the sweetened powder was slightly more resistant to air oxidation, resulting in an increase in the keeping quality of about ten to twelve weeks at normal temperatures. Greatly increased resistance to oxidative deterioration was obtained by replacing the butterfat in whole milk powder by the much less unsaturated cocoanut oil; such a substitution having little deleterious effect on the taste and appearance of the reconstituted milk. Malted milk powder possessed by far the best keeping quality of all the various types studied. In this powder the malt ingredients caused a reduction in the percentage of butterfat from a normal figure of 26% to about 7.5%. Whether the increased keeping qualities of such powders is due to this dilution of the fat or to the formation of protective protein films is discussed.

In the work on inert gas storage, reduction of the oxygen content within the containers to 1.5% or less was seen to be necessary if butterfat oxidation was to be completely prevented and the technique required to accomplish this is described. The much easier reduction of the oxygen content to between 2-3%, however, is shown to have a very marked beneficial effect in delaying fat oxidation and whole milk powders in such atmospheres would probably remain palatable for at least two years at normal temperatures.

Composite containers of cardboard and impregnated paper wrappers proved to be unsuitable for prolonged storage of milk powder owing to their permeability to moisture vapour, although for short period emergency storage such containers could be used.

Part II. B. The storage of whole milk powders containing antioxidants.

The effect on the keeping quality of the powder of adding oat flour to the whole milk at various stages before spraying was to delay the development of tallowiness in all cases. The best results were obtained by adding the oat flour to the milk before condensing, in which case 0.25% (on the weight of liquid milk) increased the storage time at 37°C before tallowiness occurred by about four weeks and 0.50% by six weeks, equivalent to about four months and six months respectively at normal temperatures. No tallowiness had developed in powders containing hydroquinone after sixteen weeks at 37°C (control tallowy after nine weeks) but the powders possessed a most unpleasant "metallic" taste.

Part III. The drying of cheese whey and of acid casein whey by the roller process.

It was found possible to neutralise the developed or initial acidity in cheese whey, without deleteriously affecting its drying properties when used on the atmospheric roller drying plant, by the addition of a suspension of slaked lime. Any addition of sodium or potassium salts for the purpose of neutralisation caused the whey to behave in an unusual manner on the drying machine, resulting in complete inability to obtain a satisfactory dried product. Hydrochloric acid casein whey could be similarly neutralised with lime, but only partially to a critical limit of acidity, whereas whey from the precipitation of casein by acetic acid required no addition of neutralising agent to produce an easily dried, almost neutral product on the same type of machine.

Part IV. Factors affecting the solubility of milk powders.

In a series of experiments on the interrelation of moisture content, heat treatment and insolubility of milk powders, (work curtailed by more urgent war time problems) the influence of increasing moisture content and storage temperature on protein solubility was examined and the conclusion reached that a critical moisture content exists at which the rate of protein denaturation, leading to insolubility in cold water, is a maximum.

Part I. Analytical Methods.

In judging whether a milk or whey powder is still useable the nature of the use to which it would in practice be put is the deciding factor. For example, in a milk powder which will only be used in the confectionery or bakery trades the solubility does not need to be of the same high order as one that is, after reconstitution, to take the place of the fresh liquid milk. Again, a whey powder which is incorporated in cattle food can be considerably coarser in every respect than one intended for human consumption. But in the comparative examination of dried milk products certain standard methods of analysis, as objective as possible, can be used, although even here in such a matter as testing for fat oxidation, the taste of a powder may be of more guidance in the very early stages than the chemically determined peroxide value.

In the following work the tests which have been applied to milk and whey powders are:-

1. moisture content
2. fat content
3. acidity and pH
4. taste
5. solubility
6. peroxide value.

and of these, only the determination of solubility and

and peroxide value require any discussion, standard methods being employed in the other cases.

1. Moisture Content.

Approximately 1 g. of powder, weighed into a flat aluminium dish provided with a tightly fitting lid, was heated at 98-100°C for three hours in an electric oven. The results are expressed as grams of moisture per 100 g. of original material.

2. Fat Content.

The butterfat in whole milk powders was determined by the modified Röse-Gottlien method recommended in the report of the Milk Products Sub-Committee(9). The fat content of milk used for the production of powder in the section on antioxidants was determined by the usual Gerber method.

3. Acidity and pH.

These measurements were chiefly confined to the whey samples and normal trade practice was followed. This is to titrate 10 ml. of whey (or reconstituted powder, 10 g. in 100 g. solution) with N/9 sodium hydroxide solution, the resultant titre being divided by 10 to give the "acidity" expressed as percentage lactic acid. Actually it does no such thing, since perfectly fresh, sweet milk containing no lactic acid at all gives an apparent figure of 0.12-0.15% lactic acid. The titre really measures two properties of the milk or whey of which the actual acidity due to developed lactic acid may be the lesser. One of these is the buffer action of the salts and proteins and the other the developed acidity, which may only partly consist of lactic acid.

The pH of solutions was measured using a quinhydrone electrode either on the fresh milk or whey or on a 10% solution of the powder in distilled water.

4. Taste.

Milk powder is best tasted when reconstituted in water to the same concentration of solids as is found in normal milk; the palate rapidly becomes clogged and fatigued if the actual powder is tasted. For tasting tests 8 g. of whole milk powder were reconstituted in 64 ml. water and the smell and taste of samples recorded independently by five observers. The samples were numbered and no member of the tasting panel was aware of the identity of particular samples before tasting. It was found expedient, when tallowy flavours began to develop first to place the samples in an agreed order of smell before tasting, since a tallowy taste once in the mouth is not easily removed. In almost every case all observers were able to spot the "control" (0°C) sample and usually there was very good agreement between individual tasters; only where differences of opinion occurred was a system of marks used and the samples graded by this manner.

The taste of reconstituted, good quality, fresh spray dried powder can only with difficulty be distinguished from that of raw milk, usually by its very faintly "cooked" taste. On storage in air for long periods at normal temperatures or for shorter periods at higher temperatures the powder undergoes a series of chemical changes which result in the development of a variety of "off" flavours. Of these, reference has already been made to the rancid taste due to free volatile fatty acids produced by lipase activity and to the talloweiness due to fat oxidation, but in addition there are fishy tastes due to trimethylamine produced by lecithin hydrolysis, and stale and musty flavours believed to be associated with the protein constituents of milk and most likely to develop in powders of high moisture content. But in a well prepared powder the only flavours likely to be met with on storage are talloweiness, which appears first as a "cardboardy" flavour, and what is variously described as "cooked" or "burnt" flavours. This latter defect is most noticeable in powders stored in nitrogen at high temperatures, probably because the tallowy flavours are lacking, and appears to be the result of the high storage temperature on the lactose. This burnt taste is not met with in powders held at room temperature for 2-3 years but, although it is unlikely, might develop on prolonged storage. It is not an unpleasant taste and, in fact is preferred by some observers to the somewhat insipid taste of pure milk. Only samples graded "definitely tallowy" or "very tallowy" would be completely unusable.

5. Solubility.

The "solubility" of milk powder is taken to mean that portion of powder which, when mixed with water to give the approximate composition of raw milk, either goes into true solution (salts and lactose) or forms a stable suspension (protein and fat). Loss of solubility in milk or whey powders is due to the denaturation of the protein and this may be due to exposure of the milk to excessive temperatures either whilst condensing or, more frequently, during the drying operation. It is for this latter reason that the solubility of roller dried powders is so much lower than that of spray dried powders in which the heating effect of the hot air is partially balanced by the cooling evaporative effects.

Milk which has become acid due to the action of bacteria is also said(4) to give a powder of lowered solubility whilst several workers(5) have stressed the importance of a low moisture content in the stored powder.

This protein insolubility has been shown by Wright(6) to be of two types, a reversible type, in which the protein is soluble in hot water, and an irreversible type, where solution temperature has no effect and which is assumed to be true denaturation. Later work by Howat, Smith, Waite and Wright(7) showed, however, that the rate and duration of stirring of the reconstituted milk very materially affected the solubility as measured by the amount of protein present in the supernatant liquor after centrifuging. The explanation of this appeared to lie in a type of mechanical peptisation of the irreversibly insoluble protein and led to the formulation of a very much simpler method of measuring solubilities, using the minimum of necessary shaking.

The American Dry Milk Institute(8) have prescribed a method for use in commercial practice in which the amount of insoluble residue after centrifuging 20 g. powder suspended in 200 ml. water at 16°C is taken as an index of solubility. It was shown by the author in the work already mentioned(7) that whilst this type of determination can supply valuable information regarding the comparative solubilities of powders which are normally highly soluble, such as spray dried powders, its value is questionable when applied to powders of low solubility.

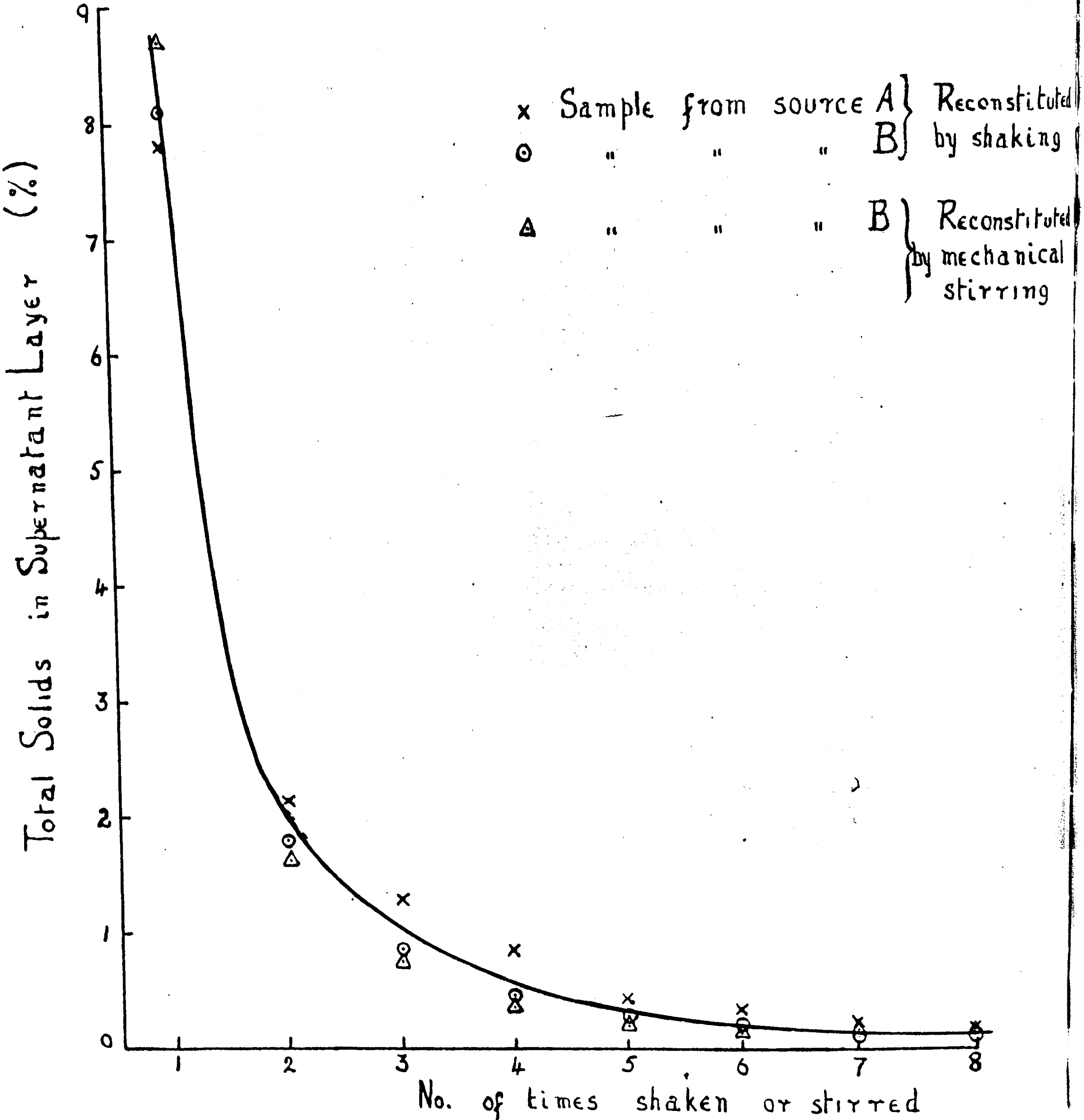
The effect of repeated washings on the volume of sediment.

It has been suggested(53) that the accuracy of the sediment method might be improved by pouring off the supernatant layer after centrifuging, shaking the sediment with a second volume of water, and re-centrifuging. It was felt desirable to investigate this point.

1 g. of a roller dried skim milk powder from source A was weighed into each of eight graduated centrifuge tubes and reconstituted at 20°C with 9 ml. of water according to the rapid method given below for determining solubilities. After centrifuging, the volume of sediment was noted and one tube was used for determining the total solids content of both the supernatant layer and of the sediment. From the other seven tubes the supernatant liquid was removed, water added up to 10 ml., the mixture shaken for 1 min. and then centrifuged. Again one tube was used for the determination of total solids content of the supernatant liquid and the sediment. This process was repeated until all eight tubes had been used, so that the sediment in the last tube had been washed seven times after the first centrifuging. The experiment was repeated with a second sample of roller-dried powder obtained from source B. In order to determine the effect of rapid stirring as distinct from shaking, the experiment was repeated on the first powder (source A) using 45 min. stirring. In this

Fig. 1

The Total Solids Content of the Supernatant Layer after successive shakings or stirrings.



instance it was not found possible, however, to record the volumes of the sediment. [illegible]

The results from these two powders, which show excellent agreement, are illustrated in Figs 1-3. It will be seen (Fig.1) that the total solids content of the supernatant liquid at successive washings falls along a smooth curve from about 8.5% (the solids content of the original reconstituted and centrifuged sample) to less than 1% after four washings. Fig. 2 shows a parallel fall in the total solids content of the sediment from 20% after the initial reconstitution to roughly 10% after four washings. Thereafter both curves remained at an approximately constant level. (It may be noted that the apparent rise in the total solids content of the sediment at the later washings in Fig. 2 is probably attributable to experimental error involved in estimating accurately the very small quantities of sediment present). It was thought possible that the initial rapid fall in both curves might be associated with the "washing out" of that portion of the supernatant liquid which occupies the interstices between the insoluble particles of the powder, while the remaining small quota (indicated in Fig. 2 by the relatively constant level of the curve after the fourth washing) might represent a small but constant peptization of the insoluble particles themselves.

not clear at this stage

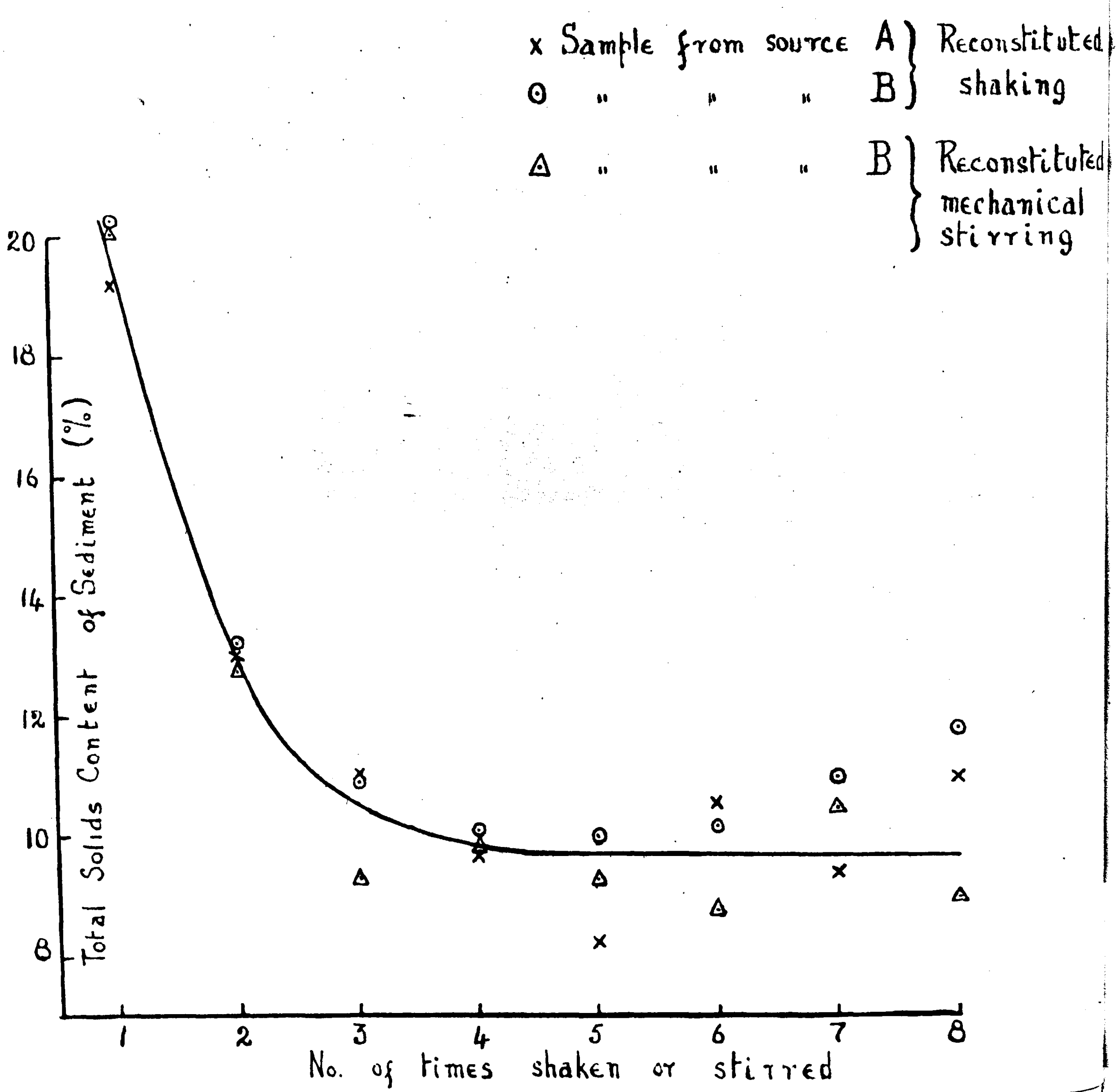


Fig. 2

The Effect of successive shakings or stirrings on the Total Solids Content of the Sediment.

Calculations showed that this assumption was correct. It was found that the weight of solids in the interstitial liquid (i.e. in the liquid between the insoluble particles) after the initial reconstitution was 0.160-0.180 g. for both powders. This value fell at successive washings to 0.035-0.050, 0.015-0.025 and 0.007-0.014 g. After the fifth washing the value was less than 0.002 g. On the other hand, the weight of solids composing the insoluble portion of the sediment after the initial reconstitution was between 0.180 and 0.260 g. and this value fell relatively slowly and at a roughly constant rate throughout the eight successive washings, the value at the final washing still being relatively high (i.e. 0.075-0.080 g.). This gradual decrease is shown diagrammatically in Fig. 3a, where it will be seen that the weights of the insoluble portion of the sediments after successive washings fall along two roughly straight lines.

how obtained

[illegible] assumptions made

only volume sediment measured? JL

The above calculations indicate that, while the total solids content of the initial sediment consists of roughly equal portions of soluble and insoluble matter, that of the final washings contains about forty times as much insoluble as soluble matter. This shows clearly that the major effect of washing sediment is to replace

Fig. 3.

⊙ Sample from Source A
× " " " B

Fig. 3a.

The Effect of successive shakings on the undissolved solids in the sediment.

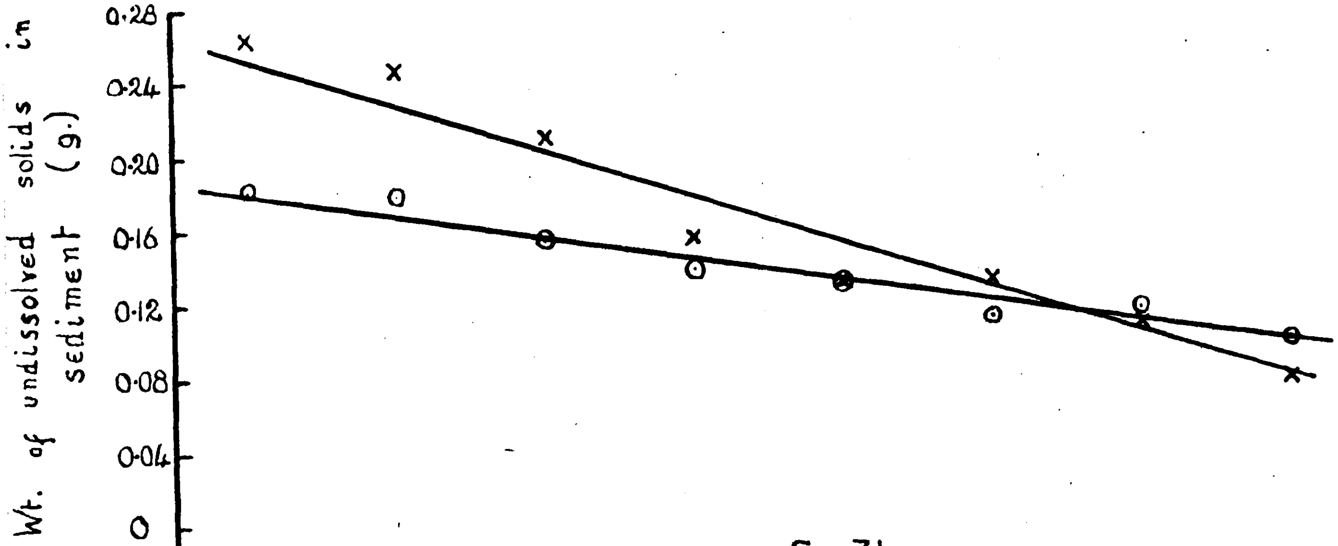
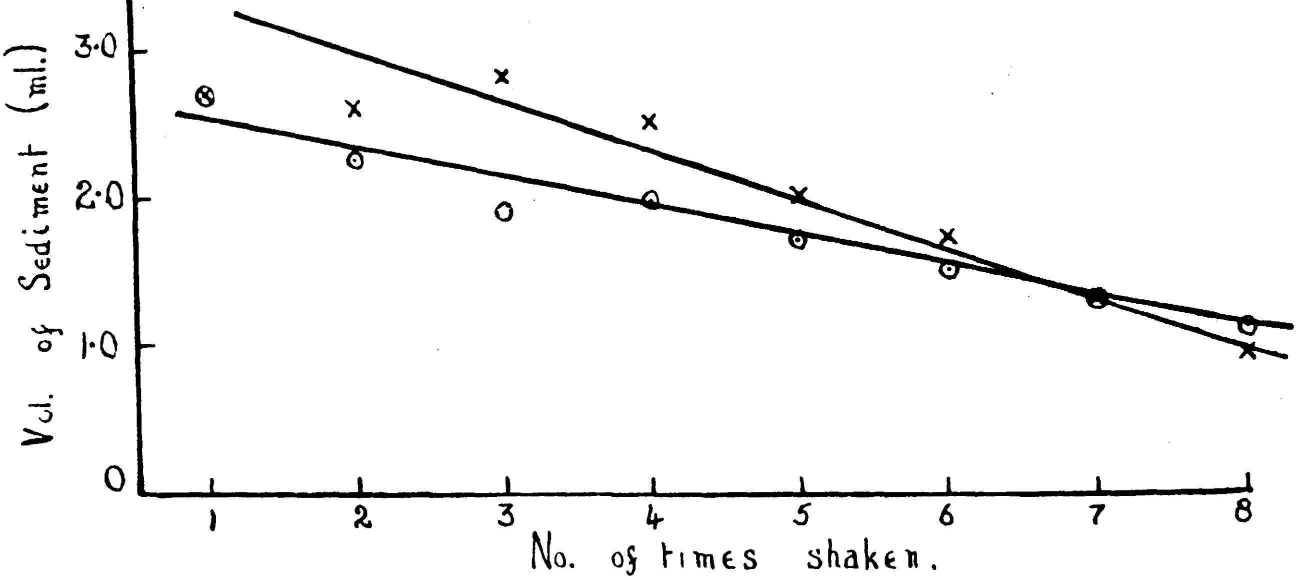


Fig. 3b.

The Effect of successive shakings on sediment volume.



the interstitial liquid with water,

On the other hand Fig. 3a shows that a portion of the insoluble matter is also peptized by washing with the result that there is a constant reduction in the weight of the sediment throughout successive washings. This fact is confirmed by reference to Fig. 3b where the sediment volumes after successive washings are plotted. The reductions in volume run remarkably parallel to the reductions in weight, both being reduced to about 30-50% of their initial values by the eighth washing. It has been found, moreover, that while with some powders washing causes a considerable decrease in sediment volume, with other powders the change in volume may be much less. Thus, of two samples, which showed an initial sediment volume of 2.7 ml., one gave a sediment volume of 2.4 ml. after a single re-washing, while the other showed no change in volume. These facts provide a strong argument against the inclusion of one or more additional washings in any standard method for determining the solubility of milk powders.

were these volumes used in calculations or weights [illegible] [illegible]?

It might, however, be urged that washing will be advantageous in causing the insoluble material to form a more compact sediment and in enabling the boundary between the sediment and the supernatant liquid to be more easily seen. Actually neither of these arguments is tenable. As regards the compactness of the sediment a comparison of Figs 3a and 3b shows that the weights and volumes of the insoluble material run strictly parallel, and that the observed reductions in volume with succesive washings are attributable largely - if not solely - to the reductions in the quantity of insoluble sediment lost through peptization and not to the formation of a more compact layer. As regards the clearness of the boundary between the sediment and the supernatant liquid, observations on a large number of samples of dried milk derived from different sources indicate that this is connected with the physical and possibly the chemical nature of the powder rather than with alterations in the nature of the supernatant liquid, Thus powders which give compact and easily differentiated sediments after initial reconstitution and centrifuging usually exhibit the same properties at subsequent washings, while the loose and indefinite sediments given by other powders frequently show no marked improvement in this respect until they have been subjected to three or more washings - a procedure which would involve excessive peptization of the insoluble sediment and which would in any event be impracticable under commercial conditions.

The method which was worked out in this laboratory and the one which has been adopted in all solubility measurements recorded in this thesis, is as follows:-

A rapid method for solubility determinations. 1 g. of the powder to be tested is weighed into a 15 ml. centrifuge tube. About 2 ml. of water are added from a burette and the mixture stirred well with a glass rod which has been previously wetted. When all the powder has become thoroughly moistened, more water is added until a total of 9 ml. has been run in, the stirring rod being washed with the last few ml. of water. The tube is then stoppered and kept in a water bath at 20 or 50°C for 5 min. and is then shaken rapidly for 1 min. The shaking speed will affect to some extent the solubility finally obtained, but if the process be carried out as vigorously as possible, involving some 4-6 complete double excursions per second, very close agreement is obtained by different workers for the same sample. If it is desired to estimate the solubility at 50°C the tube is shaken inside a container lined with cotton wool to conserve the heat. The tube is then cooled to room temperature and centrifuged, the supernatant layer poured off as completely as possible (including the fat if the same is a whole-milk powder), and its total solids content estimated by the rapid method of Golding(52). The ratio of the dissolved solids to the solids initially present (expressed as a percentage) is taken as an index of the solubility. The initial solids must be corrected for moisture content. Golding's method has been found most convenient and reliable provided phosphorous pentoxide be used as a drying agent in the dessicators. Without such an efficient drying agent the results tend to be slightly high.

From data given in the paper by Howat et al.(7) it is evident that for spray-dried milk powders, (with which the present work deals) this short method gave very similar results to the much more elaborate mechanical stirring method.

6. Peroxide Value.

In 1903 Kreis(10) put forward a test for the qualitative determination of oxidation in fats which consisted in heating the fat with an ethereal or alcoholic solution of phloroglucinol and hydrochloric acid, a characteristic pink colour developing. Later workers endeavoured to put this test on a quantitative basis and several modifications and improvements have been suggested. The technique of Walters, Muers and Anderson(11) in which a solution of phloroglucinol in amyl acetate and trichloracetic acid replaces the original constituents, possesses the great advantage of providing a single phase solution in which the colour is estimated using a tintometer. Despite such improvements the method is still considered by many workers(12 & 13) to have many disadvantages, of which non-specificity is the greatest, aldehydes and ketones not normally present in tallowy fats also producing the same colour with phloroglucinol. Lea and Moran(3) also state that even when rigid, standard conditions are adhered to "a change of observer at the tintometer could introduce a great difference" (in reproducibility of results). In the case of milk powder a still further and perhaps the greatest disadvantage arises. Here the butter fat must first be extracted before the method can be used and although with roller-dried whole-milk powders straight-forward solvent extraction removes between 92-96% of fat, similar treatment only results in the removal of a small proportion of fat (ca 10-15%) from spray dried whole milk powders. This is thought to be due to the orientation of the lactose molecules in the spray dried particles shielding the fat from the solvents. Lampitt and Bushill(14) found, however, that when the moisture content of the spray dried powder had been raised from its normal value of 2-3% to 9-12%, the fat could be readily solvent extracted. Lea and Moran(3) in their measurement of the peroxide values of spray dried whole milk powders expose the powder in petri dishes over water for 12-15 hours at 1°C in the absence of light, followed by extraction with peroxide free ether. It seemed more desirable, if at all possible, to use some method which did not involve such lengthy treatment, with its possibility of further oxidation, and Smith(15) in 1939 published such a method. This was a modification of Wheeler's(16) method in which the fat was dissolved in a mixture of glacial acetic acid and chloroform (60-40). Smith showed that such a solvent could extract all the fat from spray-dried whole milk powder in roughly five minutes at 35°C and the resulting filtrate could be used to liberate iodine from a saturated solution of potassium iodide, using 0.01 or 0.005 N sodium thiosulphate in the subsequent iodine titration. Such a method gave only about 90% of the true peroxide value but where only comparative values were required, as in storage experiments, the ease and speed of the determination outweighed the disadvantage of its relative nature. Prior to adopting this method, with its rather difficult end point, an attempt was made to utilise the acetic acid-chloroform filtrate in the method of Yule and Wilson(17), where organic peroxides are used to oxidise ferrous ions to ferric in the presence of ammonium thiocyanate, the colour so formed being titrated with titanous chloride or estimated colorometrically as suggested by Young _et al._(18). Unfortunately the other constituents of milk powder also extracted by this solvent mixture caused the formation of a precipitate, filtration of which afforded opportunity for atmospheric oxidation of the fat solution, thus making the method impracticable. An attempt to increase the sharpness of the end point in Smith's method by the addition of a known quantity of dilute iodine solution or biiodate solution was unsuccessful, some of the excess free iodine combining with the unsaturated fat before the titration could be made. Hence it was decided to use the method as given by Smith, although in the antioxidative experiments, where storage was entirely at a high temperature and reasonable peroxide values might be expected, only five, in place of ten grams of powder were taken. To avoid any possible acceleration of oxidation by light, the whole operation was carried out in a dimly lit room and the titration made by the light of a 60 watt "daylight" lamp.

In the tables recording the results of storage tests the peroxide value is given as the volume of N/100 sodium thiosulphate necessary to reduce the iodine liberated by the fat in 10 g. of powder. When the actual volume of oxygen absorbed is required this can be obtained by the following simple calculation.

The basic equation is

$$O + 2HI \longrightarrow H_2O + I_2$$

i.e. 1 atom of oxygen liberates 2 atoms of iodine $\equiv$ 2 litres N sodium thiosulphate

i.e. 200,000 ml. N/100 $Na_2S_2O_3$ are equivalent to the absorption of $\frac{1}{2}$ x 22.4 litres of oxygen.

Hence X ml. N/100 $Na_2S_2O_3$ (the "peroxide value") $\equiv \dfrac{0.5 \times 22400 \times X}{200,000}$ ml. O_2

and if the can contents weight Y grams

then the total volume of oxygen absorbed $= \dfrac{0.5 \times 22,400 \times X}{200,000} \times \dfrac{Y}{10}$ ml. O_2

PartII.A. The Technique of Inert Gas Packing And the Storage of Whole Milk Powders.

It has long been known that on storage in air roller dried whole milk powder will resist the development of tallowy flavours much longer than spray dried powder. Average times at normal temperatures are from 9-12 months for the former and 3-6 months for the latter. This has been ascribed to the difference in physical structure of the particles of the two types of powder. In the roller drying process the dried milk leaves the rollers as a thin paper-like sheet, falling into a trough from which it is removed and broken up in the same operation; it is then finely ground and sieved. Thus the particle consists of solid material and its size depends upon the fineness of the grinding process. Spray-dried powder, made either by the pressure spray or the disc atomising process, consists of roughly spherical particles which are said to consist of a shell of solid material enveloping a central air cell, since the liquid globule first dries on its outer surface as it meets the stream of hot air. It is the presence of this internal air cell together with the greater specific area which is held to account for the poor keeping quality of spray whole milk powder, although the general arrangement of the milk constituents (which have been seen already to affect the ease of fat extraction) also probably plays a part. The more uniform size of the spray dried particles allows much closer packing than roller dried powder and into any given volume, roughly one and a half times as much spray dried powder can be packed as roller dried.

In studies of the prevention of tallowiness in milk powders it was obvious that the best type of powder to be used was the one most likely to suffer from this defect, and consequently spray dried powders have been used throughout the following experiments.

In their work on the inert gas storage of whole and skim milk powders Lea and Moran(19) have shown that the possession of this internal air cell by spray dried whole milk powder constitutes a marked disadvantage. Even when the oxygen content of a can of spray-dried whole milk powder has been reduced to 1% or less, in about seven to ten days it will have risen to as much as 3-4% although the can seams are entirely gas-tight. This phenomena had also been noted in preliminary packing experiments in the research laboratories of the

Metal Box Co. Ltd., London(20). This rise in oxygen concentration occurs even when the time to which the powder is exposed to vacuum is considerably increased and can only be due to some type of desorption of the air from within the granule which tends to equalise oxygen pressure inside and outside the powder. ✓

This desorption effect had also been investigated by the author, prior to the circulation of Lea and Moran's paper and one experiment may be worth mentioning. In order to eliminate any chance errors due to faulty can seams specially designed glass gas sampling tubes of 100 ml. capacity were used. These resembled ordinary sampling tubes except that one end carried the usual two-way tap on a ground-glass stopper instead of directly attached to the main body, so that powder could be easily filled and emptied. The stopper was greased with vacuum-tap grease and held firmly to the tube by two small springs. Three tubes were taken, in duplicate, and filled with different amounts of spray-dried powder so that they were one-third, two-thirds and completely full respectively. A vacuum of 60 mm. (equivalent to the 28 inches of mercury vacuum obtained on commercial plants) was applied to each tube for four minutes and then released by the admission of specially purified nitrogen.

Samples of gas were removed at intervals over two days and analysed in a Haldane apparatus; this was the ordinary apparatus fitted with a 10 ml. burette (of which 3 ml. was in the bulb) surrounded by an air agitated water jacket. Table 1 gives the results of these analyses:-

Table 1.

Desorption of Air from Spray Dried Whole Milk Powder.

Hrs. stored (lab. temp.)	Oxygen Concentration % Wt. of powder 17g.	34g.	54g.
1	0.09	0.15	0.14
24	0.13	0.48	1.16
48	0.36	0.79	1.75

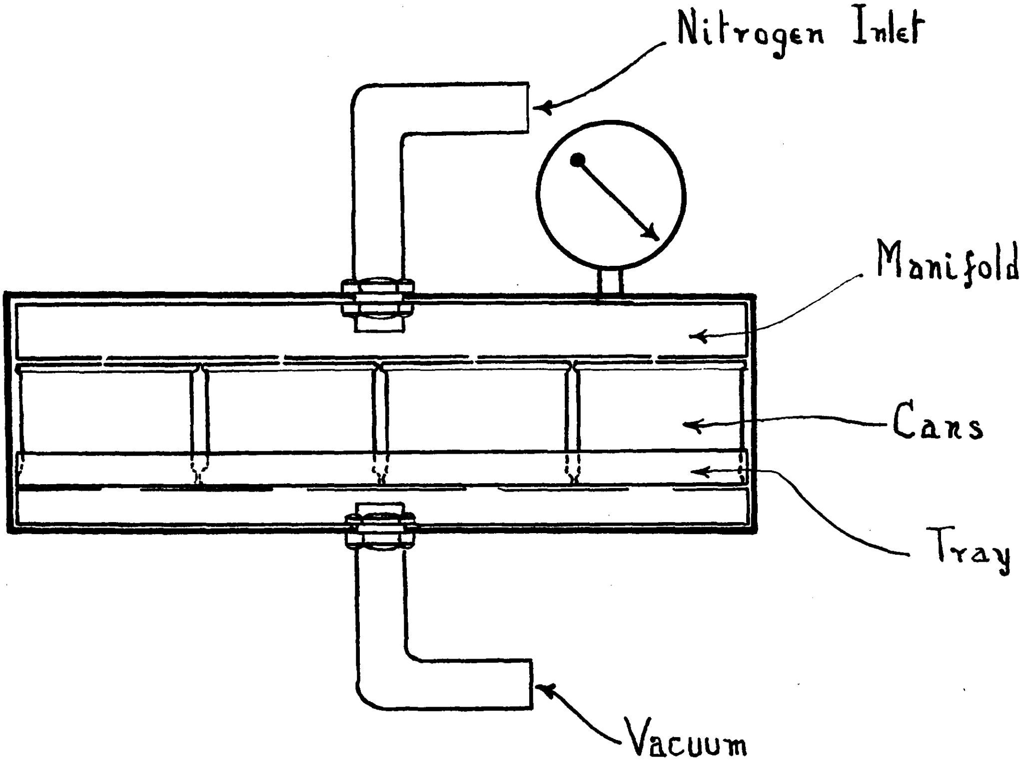
These figures show that considerable desorption had already occurred within twenty-four hours and was still increasing after forty-eight hours. As would be expected if rise in oxygen concentration was due to the powder, larger amounts of powder gave rise to higher oxygen concentrations, that in the full tube increasing about twelve-fold whilst that in the tube only one-third full increased four-fold. In comparison it may be of interest to give comparative figures for a roller dried powder. Full tubes of roller dried skim milk powder were given one cycle of inert gas filling and examined for oxygen content after 1, 24 and 48 hours, when the oxygen contents were 2.19, 2.77 amd 2.71%. After the slight initial rise, no desorption of oxygen occurred, supporting the view that the roller dried milk powder particle is solid and contains no interior air-cell. Lea and Moran(3), as a result of experiments on butterfat, concluded that talloweness could only be avoided on storage if the oxygen concentration was of the order of 0.01 ml. per gram of fat, which, they suggest is probably equivalent to an oxygen concentration of 0.5-1.5% for spray-dried whole milk powder when allowance has been made for the oxygen absorbing capacity of the non-fatty constituents. In subsequent work by Lea and Smith(21) these figures were confirmed, 0.5-1% of oxygen being the necessary concentration if tallowiness in whole milk powder was to be prevented over an indefinite period, although it was thought that reduction of the atmospheric oxygen content to 3-6% of oxygen "should still have a very marked effect in retarding the development of tallowiness".

Thus it appeared that to maintain an oxygen content of 1% or less in cans of spray-dried powder, the gas packing cycle would have to be repeated after sufficient time had been allowed to elapse for complete desorption to take place. The commercial disadvantages of this are at once obvious, not only does it mean increased labour and time but also duplication of plant and provision of large warehouses for storage during the desorption phase. It seemed, therefore, more practicable to investigate the limitations of an inert gas packing technique which involved only one series of operations and would probably leave the final oxygen concentratiom of spray dried powders in the order of 2-3%.

Description of Apparatus and Gas Packing Technique.

By courtesy of the Metal Box Co. Ltd., London, the Institute was already in possession of a machine for closing open-top cans. This machine was of the ordinary double-seaming type, power driven and was adjusted to close cans of the 6 oz. cream can size (volume 185 ml.). Prior to commencing operations empty cans were closed and sent to the Metal Box Company for checking of the seams. From Lea and Moran's(19) conclusions and from personal experience it was decided that Wood's metalling of the rolled-on can seams to prevent leakage was unnecessary; a roller dried separated

Fig. 4.



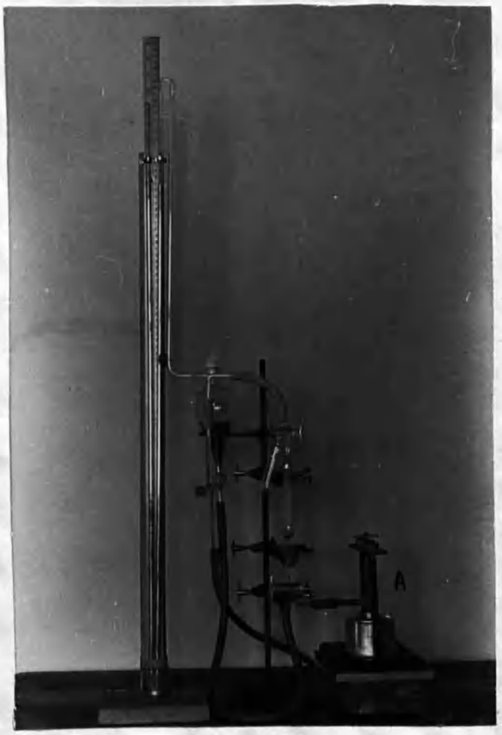
Gas-Packing Unit

powder which had an oxygen concentration of 0.74% when packed had fallen to 0.51% after five weeks and remained at that figure even after eighteen months. The inert gas packing unit consisted of a shallow rectangular cast-iron box measuring 18" x 12" x 4½", closed with a hinged door at one end which was fitted with thumb-screws and a rubber gasket to prevent leakage. Originally the inlet and outlet valves for vacuum and gases were located down one of the long sides but from previous experience it was known that this arrangement gave unsatisfactory results, the oxygen content of cans largely depending on their position with respect to the nitrogen inlet. Consequently the unit, a cross-section diagram of which is shown in Fig. 4, was altered as follows. The nitrogen inlet was shifted to the centre of the top of the chest and led into a manifold lying closely against the top inner wall of the chamber. The manifold consisted of a tinplate box the same size as the chamber but only ½" deep. Holes ⅜" in diameter were drilled in the lower surface in positions corresponding to the centres of the cans to be gas packed. This arrangement was found to give reasonably uniform gas packing when batches of twenty-four cans were packed at one time, the oxygen content of different cans being within 0.1-0.2%. The vacuum outlet was also shifted to the centre of the bottom of the chest, this precluded any "tidal" effect on admitting the nitrogen. An electrically driven oil pump produced a vacuum of about 10-15 mm. when the chest was filled with cans of spray-dried powder.

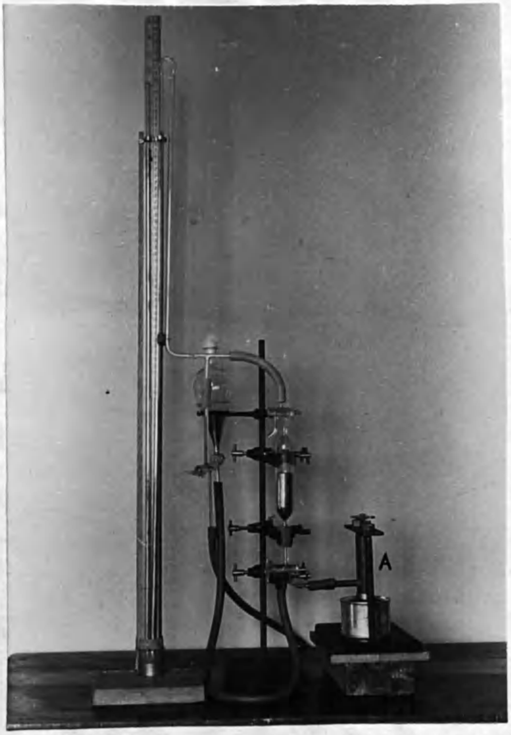
Theoretically, if a 28" vacuum is produced in a vessel when the barometric pressure is 30" and pure nitrogen is admitted to restore the pressure to atmospheric, then the oxygen concentration should be only one-fifteenth that of air,, i.e. 1.4%. If the cycle is again applied, the oxygen concentration should have fallen to 0.09% and similarly to 0.006% when the cycle is applied for the third time. In practice, however, with cans of milk powder these very low concentrations are never achieved. This is due to the difficulty of removing all interstitial air, to leaks in the apparatus and to oxygen in the "pure" nitrogen. It was found by experience that subjecting the cans to more than three cycles of operations had little or no effect and that the order of oxygen concentration so obtained with spray-dried powder was initially about 0.7-1.0% which rose to 2.5-3.3% on storage.

The method of gas packing the cans was as follows:

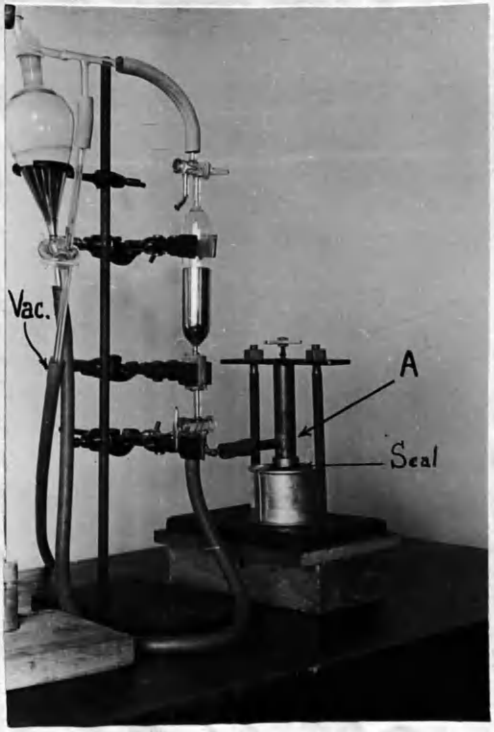
6 oz. plain, i.e. unlacquered, cream cans (volume 185 ml.) were filled to within a quarter of an inch of the top with powder settled by tapping the can on the bench. This resulted in a weight of 100 g. per can for spray dried whole milk powder. The end was then seamed on and a hole about 1/16" punctured in the top of the can. Twenty-four cans were placed on a metal tray and the tray put into the gas-packing chest, which left a minimum of dead-space between the can tops and the nitrogen manifold. The chamber was closed and a vacuum of 10-15mm. applied for three minutes, which was then released by the admission of purified nitrogen to a positive pressure of 8 lb/□" and held for one minute. This cycle was twice repeated, after which the trayful of cans was removed quickly from the chest and the puncturedholes soldered over. Twenty-four cans could be soldered in 40-50 seconds. It had been found in the research laboratories of the Metal Box Company that no appreciable amount of air entered cans treated in this manner. Table 2 gives the oxygen concentrations within empty cans left for various time intervals in the air after gas packing.



1. **Before puncturing.**



2. **After puncturing.**



increase in powders kept at 47°C. It will be seen later that these estimates are quite well borne out.

Withdrawal for Gas Sample for Analysis.

In sampling a can of milk powder for gas analysis it is desirable to know not only the analysis of the gases present but also their volume, to enable calculations of actual amounts of oxygen consumed to be made. For this purpose the sampling outfit illustrated in Plates 1-3 was employed. "A" is the puncturing device. It consists of a short metal barrel fitted with a steel rod threaded at one end where it passes through a spring loaded vacuum gasket at the end of the barrel and sharply pointed at the other; a side arm is soldered into the barrel about $\frac{3}{4}$" above the open bottom end. The puncturing unit is placed on the flat centre panel of the can end with the point just in contact with the can. Apiezon Vacuum Sealing-compound "Q" is firmly pressed round the flanged base of "A" and the can, and the special clamp for holding the puncturing unit against the can adjusted. The side arm is then connected to the 50 ml. gas sampling tube which is fitted with a mercury reservoir, the mercury of which is held at the bottom tap. The top of the sampling tube is connected to a mercury manometer and a "Cenco" vacuum oil pump. The vacuum is brought to 1-2 mm. and the tap connecting the unit and the pump closed, to test for leaks. The pointed screw is then given about six rapid turns, which punctures the can top and allows the gases to diffuse into the evacuated sampling tube, at the same time causing a drop in vacuum equivalent to the volume of gas in the can. By previous calibration, this rise of pressure in the system gives the total gas volume within the can. When the system has reached equilibrium, usually in about 10-15 seconds, the top tap of the sampling tube is closed and mercury allowed to enter to restore atmospheric pressure. The sampling tube is disconnected from the pump and the puncturing unit and connected to the Haldane apparatus. In this way a sufficient gas sample is obtained for more than one determination, if necessary; due allowance being made for the very slight residual pressure of oxygen in the sampling tube prior to puncturing.

The Storage of Milk Powders. I.

(a) Sweetened Whole Milk Powder.

It has frequently been mentioned that addition of sucrose helps to prevent the development of tallowiness in whole milk powders. Hunziker[23] gives the case of a roller-dried powder containing 14% of sucrose remaining free of oxidation for three years and suggests that this may be due to a film of sugar covering the fat globules. No quantitative data has, however, been published on this question and since the introduction of sugar into milk powder has another beneficial effect, namely increase in wettability, it was decided to investigate this problem more fully.

To determine the amount of sugar to be added to the milk a series of powders were prepared on a laboratory spray drying machine, the construction and performance of which is described later, containing 0,10, 20,30,40 and 70% sucrose. The final choice was guided by considerations of increased wettability since the amount required for optimal conditions in this case seemed adequate to protect the fat, if such was to be the function of the sugar during storage. By a rough qualitative test it was found that the time required by a constant weight of sweetened powder to sink through a constant area of water surface decreased almost linearly with increasing sucrose content of the powder up to 40%. Beyond 40% sucrose there seemed little increase in wettability. Thus it was decided to prepare a spray-dried whole milk powder containing about 40% sucrose for storage purposes.

By the kindness of the directors, the Gray-Jensen spray drying plant of a local factory was placed at our disposal and the sweetened powder was made together with normal whole milk powder from the same bulk sample of milk to act as a control.

The working conditions of the plant were:-

Total solids in milk before spraying - 30%

Drying temperature - 120°C

Spraying pressure - 3800/lbs/inch^2

and the two powders had the following compositions:-

	Control	Sweetened	
Moisture	2.3%	2.6%	
Fat	26.2%	16.4%	
Protein	24.5%	15.7%	
Lactose	39.8%	23.9%	
Sucrose	-	36.3%	
Ash	7.0%	4.5%	
Bacterial count/g.	22x10^3	5x10^3	(by Dr C.H. Higginbottom).
Wt. per 6 oz. can	105 g.	120 g.	

The two powders were very similar in physical appearance, the granule size being essentially the same.

The powder was packed in 56 lb cans and removed to the laboratory where it was stored at 10°C overnight

TABLE 3.

Cans Stored in Air.

		WHOLE MILK POWDER (2.25% H_2O)				SUGAR POWDER (2.47% H_2O)			
Storage Temp. °C.	Length of Storage in weeks	Solubility Index 20°C.	Solubility Index 50°C.	Peroxide Value ml. N/100 Thioxulphate	Taste	Solubility Index 20°C	Solubility Index 50°C	Peroxide Value ml. N/100 Thiosulphate	Taste
0°C.	0	97	100	Nil	Good	100	100	Nil	Good
	1	96	101	Nil	Good	102	102	Nil	Good
	2	96	100	Nil	Good	100	100	Nil	Good
	3	96	102	Nil	Good	102	102	Nil	Good
	4	95	101	Nil	Good	102	102	Nil	Good
	5	98	103	Nil	Good	102	102	Nil	Good
	6	96	102	Nil	Good	102	102	Nil	Good
	7	95	103	Nil	Good	102	103	Nil	Good
	8	97	101	Nil	Good	102	102	Nil	Good
	9	98	102	Not deter.	Good	102	102	Nil	Good
	12	96	102	Nil	Good	103	103	Nil	Good
	16	97	101	Nil	Good	102	102	Nil	Good
	20	97	101	Nil	Good	103	102	Nil	Good
	24	97	102	0.05	Good	101	101	Nil	Good
Lab. 17°C.	0	97	100	Nil	Good	100	100	Nil	Good
	1	96	102	Nil	Good	102	102	Nil	Good
	2	96	100	Nil	Good	100	100	Nil	Good
	3	96	101	0.05	Good	101	102	Nil	Good
	4	95	102	0.05	Good	102	102	Nil	Good
	5	96	103	0.05	Good	102	102	Nil	Good
	6	95	102	0.08	Good, very slightly cardboardy	102	103	Nil	Good, very slightly cardboardy
	7	97	102	0.08	Good, very slightly cardboardy	101	102	Nil	Good, very slightly cardboardy
	8	96	102	0.08	Good, very slightly cardboardy	101	102	0.05	Good, very slightly cardboardy
	9	98	102	Nil	Good, very slightly cardboardy	102	103	Nil	Good, very slightly cardboardy
	12	97	102	Nil	Good, very slightly cardboardy	103	103	Nil	Good, very slightly cardboardy
	16	95	101	Nil	Very slightly tallowy	100	101	Nil	Slightly cardboardy
	20	96	102	Nil	Very slightly tallowy	103	103	Nil	Slightly cardboardy
	24	95	100	0.15	Slightly tallowy	102	102	Nil	Good
37°C.	0	97	100	Nill	Good	100	100	Nil	Good
	1	95	101	Nil	Very slightly cooked	102	102	Nil	Good
	2	95	100	Nil	Slightly cardboardy	100	100	Nil	Good, very slightly cardboardy
	3	94	101	0.10	Slightly tallowy	102	102	0.05	Good, very slightly cardboardy
	4	94	101	0.08	Cooked and slightly tallowy	101	101	Nil	Cardboardy
	5	96	102	0.15	Tallowy	101	102	0.02	Cardboardy
	6	95	101	0.20	Definitely tallowy	102	102	0.08	Slightly tallowy
	7	96	102	0.38	Very tallowy	102	103	0.09	Very tallowy
	8	93	100	0.52	Very tallowy	102	102	0.18	Very tallowy
	10	96	102	0.09	Very tallowy	102	102	0.10	Very tallowy
	14	94	101	0.65	Very tallowy	101	102	0.31	Very tallowy
	24	97	101	0.98	Very tallowy and slightly burnt	102	102	0.31	Very tallowy and cooked
47°C.	0	97	100	Nil	Good	100	100	Nil	Good
	1	96	100	Nil	Very slightly cooked	100	100	Nil	Very slightly cardboardy
	2	93	101	0.17	Slightly tallowy	102	102	0.08	Very slightly cardboardy
	3	95	102	0.12	Slightly tallowy	102	102	0.05	Very slightly tallowy
	4	96	102	0.15	Cooked and tallowy	102	102	0.05	Very slightly tallowy
	5	93	101	0.35	Very tallowy	102	102	0.10	Slightly tallowy
	6	94	102	0.57	Very tallowy	102	103	0.12	Cooked and tallowy
	7	96	101	0.40	Very tallowy	102	102	0.30	Very tallowy
	9	96	101	0.23	Very tallowy	102	103	0.24	Very tallowy
	13	93	99	0.30	Very tallowy	100	102	0.55	Very tallowy
	24	93	98	1.15	Very tallowy and cooked	102	102	0.55	Very tallowy and cooked

and canned next day, approximately 16-20 hours after production. Half of each powder was inert gas packed by the method described and the remainder packed in air. A quarter of the number of each set of cans was then stored at each of the four temperatures, 0, 17, 37 and 47°C. As a matter of interest, a few of the nitrogen filled cans at each temperature were given a second gas packing operation a fortnight after the original packing.

For examination, air packed cans were taken in duplicate each week from each batch and examined for oxygen content, moisture, solubility, peroxide value and taste; similar tests were carried out on duplicate gas packed cans at less frequent (roughly monthly) intervals.

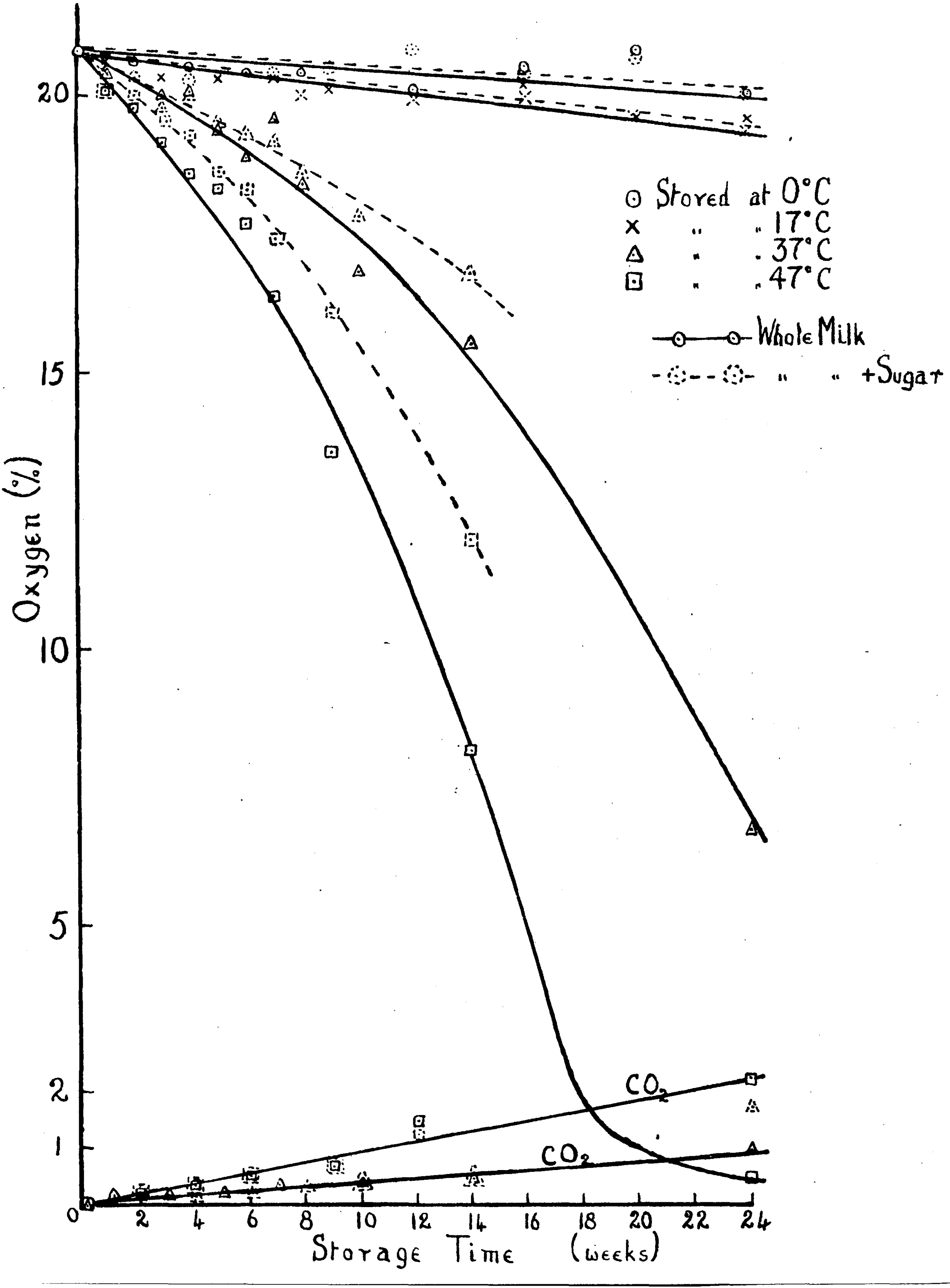
Table 3 sets out the data for the samples stored in air for six months, Table 4 for the nitrogen packed powders and Table 5 for the nitrogen packed powders regassed after fourteen days.

Examining first the results of the air-packed powders (Table 3) it is apparent that in all samples, both control and sweetened, there has been no decrease in solubility. This was not surprising since the moisture content of both powders was well below that at which protein denaturation might be expected to take place. The peroxide values and the records of the tasting tests give some measure of the progress of fat oxidation. At 0°C over the whole period of six months both powders when reconstituted tasted as fresh as when first made. In the laboratory stored samples (17°C) there was a slight but definite difference in favour of the sweetened powder, the control powder becoming slightly tallowy towards the end of four months. At 37°C, the control samples were slightly tallowy after three weeks and recognisably so after five weeks whereas the sweetened powders were only showing slight tallowiness after six weeks. At 47°C this time gap might be expected to be smaller and it will be seen that the control and the sugar powder were both slightly tallowy after two and three weeks respectively. Thus the reaction factor of 2 for every 10°C. increase in temperature is approximately borne out in the tasting tests. It may be worth mentioning here that the very early stages of fat oxidation can frequently be detected organoleptically before any appreciable result is shown by chemical tests. This view appears to be held by some other workers but by no means all.

The peroxide values at both 0°C and 17°C are mainly absent; at 37°C they agree with the tasting tests, those

FIG. 5a

Absorption of Oxygen by Powders packed in Air.



for the whole milk being appreciably higher than for the whole milk plus sugar, whilst at 47°C this relation is again manifested in the early stages, with less difference occurring as both powders become very tallowy.

Thus it may be said that in cases where no preventive gas packing is used, inclusion of sucrose into whole milk powder does delay, to some slight extent, the onset of talloWiness, but whether this is due to the sugar, *per se*, or simply to the lower fat content of the sweetened powder, requires further examination. It probably means that, at normal temperatures, this amount of sugar will lengthen the storage life of whole milk powder by three to four months.

Fig. 5a shows the gradual absorption of oxygen from the air and the rise in carbon dioxide in cans of control and sweetened powders respectively. The two sets of curves are substantially similar, absorption proceeding more slowly in the sweetened powders, which agrees with the peroxide values and the tasting tests. The curves for production of carbon dioxide are almost identical and do not rise very high.

Turning to the data for nitrogen stored samples, Table 4, it will be seen that again there has been no fall in solubility of either powder. Also that in no case was any measurable peroxide value observed so that the only

TABLE 4.

Cans stored in Nitrogen.

		WHOLE MILK (2.25% H_2O)					SUGAR POWDER (2.45% H_2O)				
Storage Temp. °C.	Length of Storage weeks	$\%O_2$	$\%CO_2$	Sol. Index 20°C.	Sol. Index 50°C.	Taste	$\%O_2$	$\%CO_2$	Sol. Index 20°C	Sol. Index 50°C	Taste
0°C.	1 day	1.40	0.06	96	102	Good	0.75	0.05	-	-	Good
	2	2.91	0.08	94	102	Good	1.90	0.05	102	102	Good
	6	2.77	0.05	96	102	Good	1.38	0.05	102	102	Good
	10	2.34	0.10	96	101	Good	1.14	0.06	102	102	Good
	24	2.92	0.03	98	102	Fairly good	1.44	0.06	102	101	Good
Lab. 17°C.	2	2.74	0.08	94	102	Good	1.98	0.11	101	101	Good
	6	2.31	0.10	96	102	Good	1.02	0.07	102	103	Good
	10	2.31	0.12	96	101	slightly cardboardy	0.92	0.13	102	102	Good
	24	2.50	0.14	98	102	cardboardy	1.30	0.09	102	102	Good
37°C.	2	2.44	0.09	94	102	very slightly cooked	1.15	0.11	102	102	Good
	6	2.30	0.20	94	102	slightly cardboardy	1.20	0.25	102	103	slightly cooked
	10	1.59	0.22	96	101	cardboardy	0.80	0.27	102	103	slightly cardboardy
	24	0.87	0.38	96	100	very slightly tallowy	0.8	0.49	102	102	cooked
47°C.	2	2.30	0.18	96	101	very slightly cooked	1.06	0.17	102	103	fairly cooked
	5	2.24	0.22	93	101	slightly cooked and slightly cardboardy	1.09	0.27	102	102	cooked
	10	1.25	0.27	98	102	cardboardy	1.09	0.50	104	104	slightly cooked
	24	0.71	0.52	96	100	very slightly tallowy and cooked	0.69	0.71	102	103	cooked and cardboardy

Peroxide Value for all samples - NIL

evidence of changes occurring within the cans lies in the tasting tests and gas curves. As before, the taste of the reconstituted samples stored at 0°C was good over the whole period and this was so also for the sugar powders stored at 17°C, although cardboardiness, the forerunner of tallowiness, was becoming apparent after three months in the whole milk samples at 17°C. At 37°C the control samples had become slightly tallowy after about five months, whereas the sweetened powders were still very palatable although showing the slightly "cooked" flavour associated with high temperature storage. At 47°C these defects had become rather more obvious and the whole milk samples were slightly cardboardy after five weeks, becoming tallowy and cooked by the end of six months. The sweetened samples at the same temperature although possessing a cooked and cardboardy taste were not tallowy.

From these figures it would appear that one inert gas packing operation, reducing the oxygen concentration in a 6 oz. can of spray dried powder to between 2-3%, will considerably prolong the life of whole milk powder, from a normal time of 3-4 months to 16-20 months. In the case of sweetened powder it would be sufficient to prevent the development of tallowiness for at least 2-4 years.

Fig. 5b

Absorption of Oxygen by Powders packed in Nitrogen.

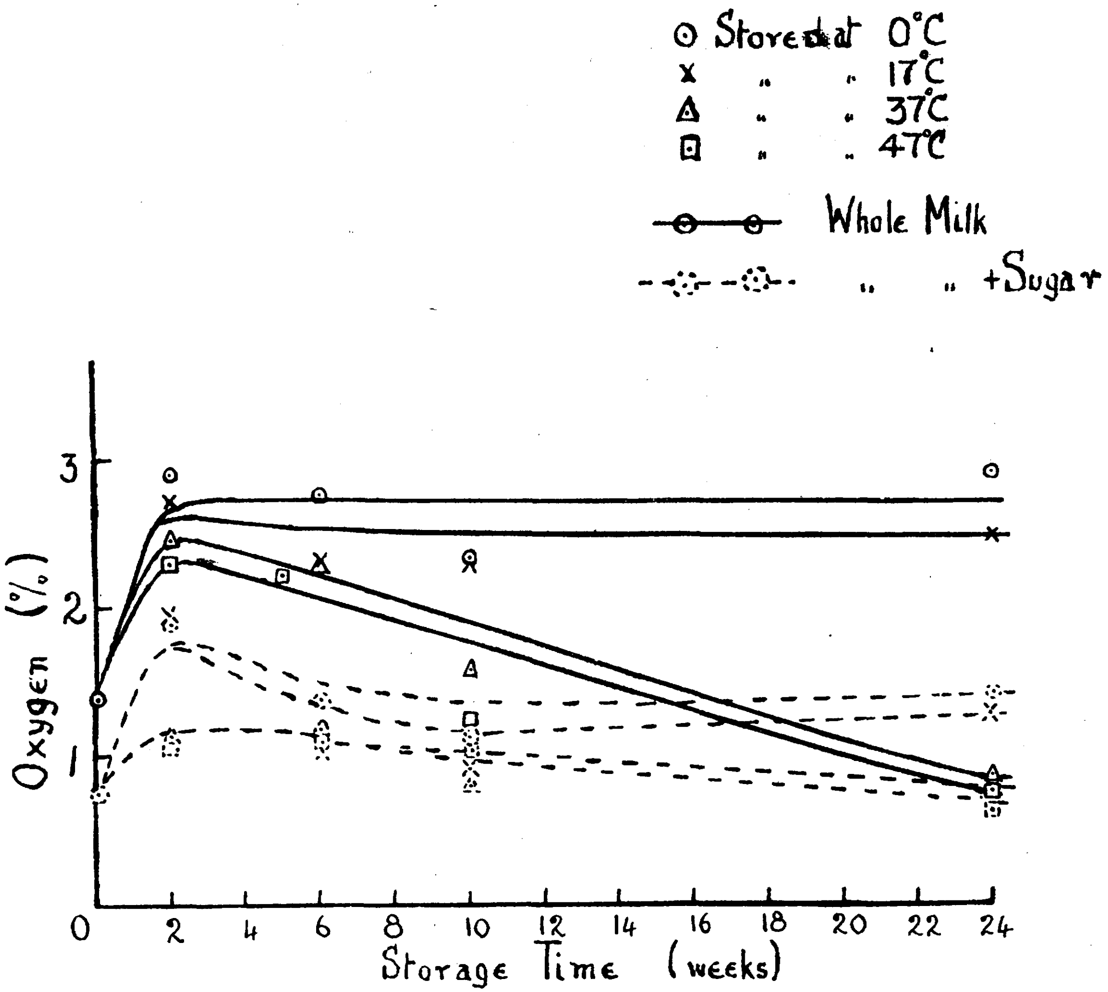


TABLE 5.

Re-gassed Samples in Nitrogen.

(14 days at respective temps. before re-gassing)

Storage Temp. °C.	Length of Storage weeks	WHOLE MILK (2.25% H_2O)					SUGAR POWDER (2.45% H_2O)				
		%O_2	%CO_2	Sol. Index		Taste	%O_2	%CO_2	Sol. Index		Taste
				20°C.	50°C.				20°C.	50°C.	
0°C	4	0.56	0.08	96	102	Good	0.23	0.06	102	103	Good
	8	0.51	0.05	96	102	Good	0.62	0.05	102	103	Good
	12	0.63	0.08	94	102	Good	0.72	0.07	102	104	Good
	20	0.80	0.13	96	102	very slightly cardboardy	0.82	0.25	102	102	very good
	24	0.36	0.11	97	102	Good	0.56	0.05	102	102	Good
17°C.	4	1.28	0.05	96	102	Good	0.97	0.08	101	103	Good
	8	0.44	0.06	98	102	good, very slightly cardboardy	0.50	0.08	102	102	Good
	12	0.83	0.06	96	102	slightly cardboardy	0.37	0.09	103	104	Good
	20	-	-	-	-	-	-	-	102	102	Good
	24	-	-	-	-	-	-	-	-	-	-
37°C.	4	0.49	0.11	95	103	slightly cooked	0.66	0.13	103	103	very slightly cardboardy
	8	0.27	0.11	96	101	very slightly cardboardy	0.38	0.11	102	103	good, slightly cardboardy
	12	0.35	0.20	96	100	slightly cardboardy	0.58	0.22	102	102	slightly "off"
	20	-	-	-	-	-	0.55	0.34	102	102	slightly cooked
	24	0.12	0.65	96	102	slightly cardboardy and cooked	0.04	0.25	97	101	slightly cardboardy and cooked
47°C.	3	0.73	0.14	93	102	slightly cardboardy	0.44	0.22	103	102	slightly cardboardy
	7	0.18	0.22	95	101	slightly cooked and cardboardy	0.55	0.18	103	102	slightly cardboardy
	11	0.21	0.52	99	98	cooked	0.29	0.55	103	102	cooked
	19	0.30	0.48	95	100	cooked	0.20	0.58	101	102	definitely cooked
	24	nil	0.72	95	98	cooked	nil	0.63	100	102	definitely cooked

Peroxide Values for all samples - NIL.

The figures in Table 5 for the regassed cans confirm the need for second gas packing operation if complete absence of tallowiness over indefinite periods is required. Again there was no decrease in solubility and no measurable peroxide values were obtained. No tallowiness was detected by taste although "cardboardiness" was apparent in some samples and at the higher temperatures the cooked flavour was again noticeable.

Fig. 5b gives the corresponding curves for the absorption of oxygen by powders in the nitrogen packed cans. It will be seen that the curves for the sweetened powder start lower and do not reach such a high level of oxygen concentration as those for the whole milk powder but that the curves follow very similar courses over the six months. The values for the 0°C are highest due to little or no absorption of oxygen taking place. Hence to prevent tallowiness completely, a second gassing operation must be given to the inert gas packed cans.

(b) Ice-cream Powder.

The manufacture of a certain type of milk powder, intended largely for use in making ice-cream, presented an interesting continuation of the storage of sweetened whole milk powder. This particular ice-cream powder was a spray dried product, made on the same plant as the previous powders, from separated milk to which had been added sufficient de-odourised cocoa-nut oil to replace the butter fat, together with 25% sucrose for sweetening purposes. In short, its composition, given below, was similar to the sweetened whole milk powder used in the previous experiment except that cocoa-nut oil replaced the original butter fat and the fat content more nearly approached that of normal whole milk powder. This seemed an excellent opportunity to determine the effect of the presence of a more saturated fat in the milk powder with respect to the development of tallowiness on storage.

The composition of the ice cream powder was as follows:-

	%
Moisture	2.5
Fat	30.8
Protein	15.6
Lactose	24.3
Sucrose	23.3
Ash	3.4

According to the analyses of cocoanut oil and butter fat given by Collin and Hilditch(24) and quoted by Channon, Jenkins and Smith(25) the constituent fatty acids are considerably different, both with respect to the proportion of saturated to unsaturated acids and also as regards the composition of the unsaturated acids. Below is given the detailed analysis of the unsaturated acids:-

	Butter	Cocoanut Oil
Total saturated acids	55.0%	92.2%
Unsaturated acids.		
Oleic	41.9	5.7
Linoleic	4.1	2.6
C_{20} unsaturated acid	-	-
C_{22} " "	-	-
Total unsaturated acids	46.0	8.3

More recently, Smith and Dastur(58) have shown that there is also present in butter fat about 0.8% of "arachidonic" acid, a C_{20} unsaturated acid possessing four double bonds, and that such an acid would oxidise with the utmost readiness. From the above figures it will readily be appreciated that the chance of oxidation occurring in butter fat is considerably greater than in cocoanut oil. When this is taken in conjunction with the fact that very minute traces of oxidised fat are capable of producing a tallowy flavour in such a product as milk powder (as will be calculated later), there seemed every chance that the ice-cream powder, with its substituted fat would possess better keeping qualities than normal whole milk or sweetened whole milk powder. In manufacturing this powder, the sucrose was first dissolved in the skim milk, the calculated amount of cocoanut oil added and the temperature raised to 75°C in a tubular heater. The mixture was then homogenised at 70°C and condensed to about 30-33% total solid content before spraying. The working conditions of the plant were the same as those operating during the production of the sweetened whole milk powder. The resultant powder was very similar in appearance to ordinary milk powder and could not be easily distinguished from the sweetened whole milk powder of the previous experiment. The reconstituted "milk", however, had a slightly different appearance than that from normal milk powder in that it looked more like skim milk, being slightly "blue" in colour. This no doubt, is due to the absence of carotene in the deodourised cocoanut oil, the presence of which in butter fat gives milk its typical colour. Another difference was in the taste of the reconstituted ice-cream powder, which appeared to lack the body and creaminess of whole milk; it was described as feeling "thin" on the tongue. As before, the powder was removed from the factory in 56 lb cans

Table 6.

Ice-Cream Powder.

Temp. of Storage	Time of Storage (months)	Moisture Content	Stored in Air. %O$_2$	%CO$_2$	Sol. Index at 20°C	50°C	Perox.Val. ml.N/100 Na$_2$S$_2$O$_3$	Taste	Stored in Nitrogen %O$_2$	%CO$_2$	Sol. Index 20°C.	50°C	Perox.Val. ml. N/100 Na$_2$S$_2$O$_3$	Taste
0°C	0	2.54	20.8	0.05	99	102	nil	Good	3.2	0.02	99	102	nil	Good
	3	-	20.8	0.08	97	101	"	"	3.8	0.02	101	102	"	"
	8	2.61	20.3	0.16	101	102	"	"	3.3	0.01	100	101	"	"
	11	2.57	20.8	0.09	101	102	0.15	"	2.4	0.07	101	102	"	"
	14	2.66	19.8	0.09	102	102	0.04	"	3.4	0.04	99	102	"	"
	17	2.66	19.8	0.10	101	101	nil	"	3.4	0.09	102	101	"	"
17°C	0	2.54	20.8	0.05	99	102	nil	Good	3.0	0.02	99	102	nil	Good
	3	-	20.8	0.08	102	103	"	"	2.9	0.02	100	102	"	"
	8	2.55	19.8	0.13	100	101	"	slightly cardboardy	2.9	0.02	100	101	"	"
	11	2.46	19.7	0.12	103	103	0.25	Good	3.4	0.03	101	101	"	"
	14	2.56	19.7	0.15	101	102	0.06	slightly cardboardy	2.8	0.06	101	102	"	"
	17	2.50	19.3	0.18	102	101	0.15	very slightly tallowy	3.0	0.08	102	101	"	"
37°C	0	2.54	20.8	0.05	99	102	nil	Good	3.2	0.02	99	102	nil	Good
	3	2.88	20.8	0.05	99	102	"	"	3.1	0.02	101	102	"	"
	8	2.38	19.4	0.05	101	101	0.06	slightly tallowy	3.8	0.11	100	101	"	slightly cooked
	11	2.47	20.6	0.29	102	103	0.20	tallowy	3.1	0.24	101	102	0.10	"
	14	2.63	18.4	0.38	100	101	0.10	"	2.8	0.22	101	102	nil	cooked
	17	2.50	17.3	0.23	102	103	0.30	"	2.2	0.30	101	102	"	"

and stored overnight at 10°C. It was packed next day (approximately 20 hours after manufacture) in 6 oz. cream cans, half of which were gas packed with purified nitrogen in the manner previously described and the various batches stored at three temperatures only 0°C, 17°C, and 37°C. Table 6 records the results of storage experiments carried on for seventeen months.

It will be seen that the solubility of the powder did not decrease over this period. By far the most striking result, however, was the general resistance to oxidation of the air stored samples. Considering the peroxide determinations, in none of the samples, even those at 37°C, is there any measurable value up to the end of eight months. Only in the samples examined after a storage period of eleven to seventeen months at 37°C in air is there a definite peroxide value. In view of this, it is not surprising that none of the inert gas packed samples, where the oxygen content had been reduced to 3.0-3.5%, showed any measurable value over the whole period. These results are borne out by the tasting tests where talloviness was distinguishable only in the samples in air at 37°C after storage for eight months. This compares most favourably with the behaviour of the whole milk control powder of the previous experiments, the results of the storage of which were given in Table 3. In that powder, tallowiness was apparent in the air-stored samples at 17°C after four months and in the samples at 37°C after three weeks. Such a comparison is, perhaps, not quite justified due to the inclusion of sucrose in the ice-cream powder, but that this increased resistance to fat oxidation is due largely to the less unsaturated nature of the cocoanut oil is apparent from a comparison with the sweetened whole milk powder. This is best seen in the powders stored in air at 37°C, which, in the case of the sweetened whole milk powder became slightly tallowy after six weeks, compared with the eight months required by the ice-cream powder to reach the same state. This difference of twenty-six weeks at the elevated temperature of 37°C probably represents a storage life in air of about two to two and a half years at normal temperatures before the taste of the powder becomes objectionable although the "cardboardy" flavour will have developed before that time, as seen in the laboratory-stored samples. Nevertheless, replacement of butter fat by deodourised cocoanut oil substantially increases the keeping quality of milk powder and provides that added resistance to oxidation which would make one operation of nitrogen packing entirely adequate for storage over an indefinite period.

In Table 6 are also included the figures for the oxygen concentrations of both the air and nitrogen packed cans. It will be seen that in the air packed cans no appreciable uptake of oxygen had occurred even after a year and a half at 37°C, in contrast with the previous whole milk powder and the sugar powder which utilised approximately 14% of the oxygen in the can within six months at the same temperature.

(c) Horlick's Malted Milk.

Continuing the work of storage of special milk powders, an apportunity was afforded to study the effect of a much more complicated system on keeping quality under storage conditions similar to those previously described, in the form of a malted milk powder, provided by Messrs. Horlick's Ltd., Slough, Buckinghamshire.

Before giving details of the storage tests it may be advisable to describe briefly the manufacturing process by which the powder is produced(26).

Malted milk is a prepared food made by combining whole milk with the liquid filtered from a mash of barley malt and wheat flour and removing the water by some dehydrating process, usually vacuum drying. High grade barley grain is completely wetted, a process occupying 24-48 hours, and then spread on to a germinating floor. The germinating process requires five to seven days during which time a temperature of 24°C is maintained in the barley mass. During this time the enzyme diastase is being produced and when this has been carried to the right point, further germination is arrested by a drying process, usually in kilns, at 27-43°C rising later to 49°C. This barley malt contains more diastase than is required to invert the starch of the barley itself so that wheat flour is used as an additional source, which at the same time introduces the protein gluten. In preparing the mash, the wheat flour is first gelatinised in hot water and then cooled before the addition of the crushed barley malt. The temperature of the liquid is then raised first to 45°C for half an hour and then to 70°C over 25 minutes and held there for one hour. Various additions such as sodium chloride, sodium bicarbonate and potassium bicarbonate are sometimes added at this stage. With all the starch converted to dextrins and maltose the husks are allowed to settle and the liquid run off. The mash extract is then mixed with fresh whole milk, usually in the proportion of 55 parts:45 parts and dried. In the case of Horlick's

Malted Milk this is done in two stages. The mixed mash liquor and milk are condensed to a high solids content, about 60%, in vacuum condensers and then transferred to a second high-vacuum condenser fitted with powerful mechanical beaters. Here the remaining water is removed whilst at the same time the beaters agitate the doughy mass until it rapidly swells and becomes porous. Great care is taken to control the temperature at this stage and Hunziker(26) states that a temperature of 135°F is not exceeded. The finished product is dug out of the pans in brittle honeycombed masses which are immediately ground and packed to prevent absorption of mixture.

The chemical composition of the malted milk used in the storage experiments was:-

Moisture	2.76%
Fat	7.52%
Protein	13.22%
Ash	3.47%
Sugars (by diff)	73.0%

This, as will be seen by comparison with the data given on p. 40 , is a product with roughly only a quarter the amount of butter fat, one-half the protein and twice the sugar content of whole milk powder. Hence in any question of keeping quality the considerably

Table 7.

Horlicks Malted Milk Powder "B".

		Stored in Air							Stored in Nitrogen						
Storage Temp. °C	Time of Storage (mths.)	Moisture Content	$\%CO_2$	$\%O_2$	Solubility Index. 20°C	50°C	Perox.Val. ml.N/100 $Na_2S_2O_3$	Taste	Moisture Content	$\%CO_2$	$\%O_2$	Solubility Index 20°C	50°C	Perox.Val. ml.N/100 $Na_2S_2O_3$	Taste
0°C	0	2.76	0.05	20.8	97	97	Nil	Good	2.76	-	-	97	97	Nil	Good
	6	2.51	1.03	20.2	96	96	0.10	"	2.24	1.26	2.55	97	97	"	"
	12	-	1.30	19.6	97	97	0.07	"	-	1.52	1.48	96	97	"	"
	16	3.50	1.00	19.9	99	99	Nil	Lack of maltiness	2.44	1.53	2.03	97	97	"	"
	19	2.93	1.19	19.2	98	99	"	cardboardy	2.21	1.80	1.66	95	99	"	Very good
17°C	0	2.76	0.05	20.8	97	97	Nil	Good	2.76	-	-	97	97	Nil	Good
	6	2.50	2.85	19.3	96	96	"	"	2.34	2.75	3.07	95	96	"	"
	12	-	2.74	18.3	97	98	"	cardboardy	-	3.42	1.81	98	98	"	"
	16	2.53	3.87	18.6	97	98	0.13	**Slightly cardboardy, lack of maltiness**	2.40	3.76	2.20	97	97	0.05	"
	19	2.12	3.77	18.6	98	99	0.05	Very slightly cardboardy	2.09	4.31	1.49	97	98	Nil	Very good
37°C	0	2.76	0.05	20.8	97	97	Nil	Good	2.76	-	-	97	97	Nil	Good
	6	2.56	6.63	16.6	95	97	"	"	2.52	6.15	2.26	97	97	"	"
	12	-	8.87	15.0	98	97	"	Cardboardy and slight suspicion of talloweiness	-	9.51	0.81	96	98	"	"
	16	3.26	15.68	11.5	99	98	0.20	Slightly tallowy	2.46	11.51	0.94	98	97	0.10	Good, more malty than air stored sample
	19	2.10	16.19	11.6	99	99	0.15	Tallowy	2.15	14.21	0.47	99	99	0.10	Slightly "off", lacking maltiness

smaller amount of fat present to be oxidised might be expected to check the deterioration due to tallowiness, whilst the high sugar content, on previous evidence, should also asist in producing a product of excellent keeping quality. Powder which had been freshly prepared was filled into six ounce cream cans, half of which were packed in nitrogen by the method previously described, and one-third of each of the air and nitrogen packed cans stored at 0°C, 17°C (laboratory) and 37°C.

In testing for taste, the malt flavour made discernment of very slight "off" flavours, such as "cardboardiness", difficult but good agreement was found between various members of the tasting panel. Table 7 gives the results of storage tests, extending over 19 months.

Once again storage over this period, even at 37°C has had no effect on the solubility of the powder, due, of course, to the correct low moisture content. In air, appreciable peroxide values developed only after sixteen months whilst in nitrogen no significant value was recorded. On the other hand, tasting tests, as has been seen previously in the case of the ice cream powder, indicated slight tallowy flavours before the chemical test could be said to show any appreciable oxidation. The results are similar to those of the air-stored ice cream powder; at 17°C a "cardboardy" flavour appearing after 12 months in the Horlick's powder compared with 11 months for the ice cream powder. At 37°C the differences appears rather greater, no tallowiness being apparent before the end of 12 months in the malted milk but after only eight months in the case of the ice cream powder. These results indicate that the keeping quality of the malted powder is very much better than a sweetened or unsweetened whole milk powder.

The malted milk powders stored in nitrogen, with an initial oxygen concentration of ca. 3%, showed no sign of deterioration at all, except a slight diminution of the malty flavour after 19 months at 37°C which again shows a better keeping quality than any of the powders dealt with so far.

Apart from the excellent keeping qualities of this product, the most striking feature of the storage data is the behaviour of the gases within the can. Normally, the absorption of oxygen by whole milk powder is slow at first increasing as the induction of the fat is passed, at the same time evolving a small amount of carbondioxide, which presumably arises from complete oxidation of hydrocarbon. As will be seen from the curves for carbon dioxide evolution in Fig.3, in 6 months this value at 37°C had reached only one per cent CO_2 for normal whole milk powder, and 1.8% CO_2 for the sweetened powder. Since the slope of the curve appears to be constant this would amount to some 3% and 5.4% respectively in 18 months. From Table 7 it will be seen that in a similar period the carbon dioxide contents in the cans of malted milk stored in air had risen to 1.19%, 3.77% and 16.2% at 0°C, 17°C and 37°C respectively. In the nitrogen packed cans the figures were similar, 1.80%, 4.31% and 14.2% CO_2 at the three temperatures over the same length of time.

Closer examination of these figures shows that this generation of carbon dioxide is quite different from that occurring in cans of whole milk powder since it can be shown mathematically that the actual amounts of carbon dioxide formed in the cans at 37°C exceeds the amounts of oxygen originally present. Let the data in Table 8, for the samples stored at 37°C and examined after 19 months be considered. Actually two batches of the malted milk powder were stored, but since no significant difference in keeping quality was shown, the data in Table 7 refers only to one powder. The only

Table 8.

Malted Milk Powder Stored in Air 19 Months at 37°C.

	Powder A.		Powder B.	
	In air	In N_2	In air	In N_2
Weight of powder in cans	140 g.			
Vol. $\overset{\text{gas}}{\text{air}}$ in cans when packed	100 ml.			
Vol. gases after 19 months	210 ml.	240 ml.	115 ml.	120 ml.
% oxygen after 19 months	4.02%	0.10%	11.6%	0.47%
% carbon dioxide	40.9%	38.8%	16.2%	14.2%
Vol. O_2 after 19 months	8.45 ml.	0.24 ml.	13.3 ml.	0.56 ml.
Vol. CO_2 after 19 months	86.0 ml.	93.0 ml.	18.6 ml.	17.0 ml.
Vol. O_2 when packed	20.8 ml.	3.0 ml.	20.8 ml.	3.0 ml.
Vol. O_2 utilised in fat-oxidation (from peroxide value)	0.3 ml.	0.05 ml.	0.15 ml.	0.10 ml.
Maximum vol. which could have gone to Co_2 = 20.8 - (resid.O_2 + perox. O_2).	12.0 ml.	2.7 ml.	7.3 ml.	2.3 ml.
Volume of CO_2 unaccounted for	$\underline{\underline{74.0}}$ ml.	$\underline{\underline{90.3}}$ ml.	$\underline{\underline{11.3}}$ ml.	$\underline{\underline{14.7}}$ ml.

difference in behaviour of the two samples was in the evolution of carbon dioxide on storage, which is well shown in Table 8. In both cases a positive pressure existed in the cans, those containing the "A" sample having their ends bulged outwards and, as will be seen from the data given, both contained in the enclosed gases far more carbon dioxide than could be accounted for by normal oxidation processes. This suggests that carbon dioxide must either have been evolved by chemical decomposition or by some form of desorption. The sodium bicarbonate added to malted milk is not a very likely source of the excess carbon dioxide since the pH of the reconstituted powder after storage showed no change from that of the fresh powder and 37°C is not a high enough temperature to cause thermal decomposition. A possible explanation might be that during the mashing process carbon dioxide was either adsorbed by or formed a loose compound with the protein present and that on continued storage at 37°C this combination was broken and the carbon dioxide released. Whether this carbon dioxide comes wholly or in part from bicarbonate and/or fermentation processes, there seems little doubt that it will assist in prevention of the development of tallowiness; if due to fermentation, by the utilisation of oxygen which would otherwise be available for fat oxidation. Opinion seems divided as to whether replacement of air by carbon dioxide in containers storing whole milk powder prevents development of tallowiness. Holm, Wright and Greenbank(27) consider that since carbon dioxide will hydrolyse soaps in the presence of water it will probably act similarly on the glycerides of butterfat, but at the low moisture contents normally prevailing this seems doubtful. Schatzel and Clausen(28) actually found that whole milk powder stored in an atmosphere of carbon dioxide after seven months at 20° and 40°C was better than controls stored in air. At the risk of exaggerating small differences, it may be noted that whereas the quality of the malted milk powder and the ice cream powder were very similar when stored in air at 17°C, at 37° the malted milk powder, which by this time was producing a fairly high concentration of carbon dioxide, resisted the development of tallowy flavours for four months longer than the ice cream powder.

The gluten constituent has also been credited(26) with producing the excellent keeping quality of malted milk powder, the action being due to a film of this protein, together possibly with sugar, enveloping the fat globules, although why this protein in particular, rather than normal milk proteins is not apparent.

Whatever the reason, either low fat content, the presence of large amounts of sugar, evolution of carbon dioxide or protective protein films, from the data presented it is evident that the combination of a mash of barley malt with whole milk produces a dry product of exceptionally good keeping quality.

Table 9 summarises the keeping qualities in air of the four milk powders dealt with, taking as a criterion the time of storage at 37°C required for the development of the first signs of tallowiness in the taste of the reconstituted powder.

Table 9.

Keeping Quality of Milk Powders.

Powder	Time to develop tallowiness when stored in air at 37°C
Whole Milk Powder	3 weeks
Whole Milk Powder + 35% sucrose	6 weeks
Skim Milk Powder + 25% sucrose +30% cocoanut oil	8 months
Horlick's Malted Milk	12 months

(d) The Keeping Quality of Spray-Dried Whey Powder.

Whey from the manufacture of cheese was brought almost to neutrality (0.05% lactic acid) by the addition of sodium bicarbonate and the carbon dioxide gas allowed to escape during the pre-heating and pre-condensing. The whey was condensed to about 24-28% total solids and then spray dried in the same plant and under similar conditions to those already set forth in the production of the sweetened whole milk powder.

It is well known that dried whey powder, which has an analysis of

Moisture	3-5%
Butterfat	0.5-1.0%
Protein	12.3%
Lactose	70.0%
Ash	7.5%

normally keeps extremely well, as a product consisting mainly of sugar might be expected to, and that deleterious flavours are only likely to occur if the product is allowed to absorb moisture, as it is extremely prone to do. Such an absorption causes the product to become sticky, gummed together and will ultimately cause loss of solubility due to denaturation of the protein, which is largely albumin and globulin. In this particular product, however, an experiment had been made in order to control frothing in the storage tanks. To increase the surface tension of the whey, 0.25% (by weight) of cocoanut oil was added as the whey was piped in, resulting in approximately 2.5% of fat

Table 10.

The Storage of Spray-Dried Whey Powder.

Temp. of Storage °C	Time stored in weeks	Moisture Content %	Solubility Index at 20°C	Solubility Index at 50°C	Perox. Val. ml N/100 $Na_2S_2O_3$	Taste
0°C	0	3.11	101	102	Nil	Good, sweet and salty. No tallowiness.
	2	-	100	99	"	
	4	-	99	99	"	
	6	3.17	101	102	"	
	8	3.11	99	100	"	
	10	3.11	101	101	"	
	12	3.11	97	101	"	
	13	3.04	100	100	"	
37°C	0	3.11	101	102	Nil	Good, sweet and salty.
	2	-	100	101	"	Good, saltiness less pronounced
	4	-	99	101	"	"
	6	3.11	101	103	"	"
	8	3.11	101	101	"	"
	10	3.11	100	100	"	Good, no tallowiness.
	12	3.11	99	99	"	"
	13	3.13	99	99	"	"
47°C	0	3.11	101	102	Nil	Good, sweet and salty.
	2	-	100	100	"	Good, saltiness less pronounced.
	4	-	99	100	"	"
	6	3.09	102	103	"	"
	8	3.11	101	101	"	Good, saltiness less pronounced and slightly burnt. No tallowiness.
	10	3.11	98	99	"	
	12	3.11	99	99	"	
	13	3.13	99	98	"	

in the dried product, which was a white, fined-grained powder. As already mentioned, the total fatty acids in cocoanut oil contain only some 8% of unsaturated acids and it was not anticipated that in the small quantities used this would cause talloweness to develop on storage or necessitate nitrogen packing but in order to confirm this point (which had an obvious value in the commercial storage of whey powder) the powder was kept in air-packed cans for 16 weeks at three temperatures, 0°, 37°C, and 47°C.

Table 10 gives the results of these experiments. From this table it can be seen that no tallowiness or other objectionable flavours developed up to the end of 16 weeks, even at the maximum storage temperature of 47°C, equivalent approximately to about three years at normal temperatures. It is interesting to note, however, that the typical saltiness of liquid whey and markedly present in the fresh powder and the samples kept at 0°C appeared to decrease in the samples stored at 37°C and 47°C and that in the case of the latter, the usual cooked or burnt taste associated with high temperature storage was again noticeable. Whether this apparent lack of saltiness is due to masking by the flavours resulting from very slight caramelisation of the lactose at 47°C is difficult to say. As would be expected in such a product with a moisture content of only 3%, no change in solubility appeared over this length of storage.

(e) The Storage of Whole Milk and Sweetened Whole Milk Powders in Composite Containers.

From the experiments already described it can be seen that the ordinary, plain (i.e. non-lacquered) "tin" can is an extremely useful container for milk powder in that it is robust enough to withstand packing and transporting whilst at the same time excluding light and moisture from the contents. Moreover, when the adjustment of seaming rollers is correct the closed can is virtually air-tight and can be used successfully in inert gas packing. There are, however, two disadvantages to the all-metal can, if storage is only required over short periods, such as six months to a year. The first of these is the relatively high cost of tin-plate and the machines required to form it into cans and secondly, due to war conditions, the utilisation of so much iron and tin. In view of these two facts an experiment was made to determine whether another type of container, although less durable than the metal can, might be suitable for packing with milk powder. The type investigated was of the class known as composites. These composite containers, as the name suggests, are composed of two dissimilar metals, usually a cardboard body, closed top and bottom by a flat, metal end which can be seamed on to the body just as the ends are seamed on metal cans. In the following experiment two types of composite were used, (a) a wound cardboard body, lined with parchment paper, and (b) a wound cardboard body, coated internally with waxed paper. The first type is known as a parchment finish and the second as a glassine finish.

Since the type of product to be packed in these two containers would be consumed in some period under 12 months, and more probably in under six months (troop and emergency rations, etc.) no attempt was made to study the possiblity of inert gas packing, which in any case, would have been limited by the mechanical strength and air permeability of the cardboard body.

The necessity for this experiment arose about the same time as the question of the oxidation protective power of sugar in milk powder was being investigated and as moreover, the sugar powder was noticeably more hygroscopic than ordinary milk powder, thus making the packing test in composites more rigorous, the opportunity was taken to pack half of each type of composite with normal whole milk powder and half with sweetened milk powder. Batches of each were then stored at 0°C, 17°C (laboratory) 37°C and 47°C. At each temperature each batch consisted therefore of:-

Table 11.

COMPOSITES STORED IN AIR.

Whole Milk.

Storage Temp. °C	Length of Storage in weeks	Parchment % H_2O	Parchment Solubility Index 20°C	Parchment Solubility Index 50°C	Parchment Perox.Val. ml.N/100 sod.thio.	Parchment Taste	Glassine % H_2O	Glassine Solubility Index 20°C	Glassine Solubility Index 50°C	Glassine Perox.Val. ml.N/100 sod.thio.	Glassine Taste
0°C	1	3.75	96	102	Nil	Good	2.77	96	100	Nil	Good
	2	4.61	101	102	"	"	2.43	95	102	"	"
	3	5.73	96	101	"	"	2.54	95	102	"	"
	4	6.70	97	102	"	"	3.16	96	101	"	"
	5	6.65	98	102	"	"	3.74	98	103	"	"
	9	7.03	96	100	"	Slightly cardboardy	4.95	98	102	"	"
	13	8.20	91	98	"	Very slightly tallowy	5.36	100	101	"	"
	17	8.26	84	94	"	Cardboardy	6.56	96	101	"	"
	21	7.93	90	97	"	Slightly cardboardy	6.23	97	102	"	Fairly good.
17°C	1	2.86	97	102	Nil	Good	2.40	97	103	Nil	Good
	2	3.04	97	102	"	"	2.33	97	101	"	"
	3	5.25	96	102	"	"	2.55	96	101	"	"
	4	3.16	96	101	"	"	2.67	96	101	"	"
	5	3.22	97	102	0.08	"	2.27	95	101	0.08	"
	9	5.56	98	104	0.05	Slightly cardboardy	3.27	93	97	0.05	Very slightly cardboardy
	13	6.05	97	101	Nil	Good	3.67	97	102	Nil	"
	17	5.83	96	101	0.05	Slightly tallowy	4.40	97	101	0.05	Slightly tallowy
	21	6.94	97	103	Nil	Slightly cardboardy	4.46	96	101	Nil	Slightly cardboardy
37°C	1	2.73	97	102	Nil	Slightly cooked	2.67	96	102	Nil	Slightly cooked
	2	2.68	97	102	"	cooked	2.42	95	101	"	cooked
	3	2.85	95	102	"	Very slightly tallowy	2.66	96	102	"	Very slightly tallowy
	4	2.72	95	102	0.05	Slightly tallowy	2.71	94	102	0.05	Slightly tallowy
	5	2.81	98	101	0.10	Slightly tallowy	2.75	96	102	0.10	Slightly tallowy
	21	2.59	94	97	0.52	Slightly tallowy and burnt	2.43	95	97	0.28	Slightly tallowy and burnt
	30	2.66	94	96	1.85	"	2.85	93	96	2.77	"
47°C	1	2.75	96	101	Nil	Very slightly tallowy	2.30	96	101	Nil	Slightly cardboardy and cooked
	2	2.36	94	101	"	Slightly tallowy	2.25	94	100	"	cardboardy
	3	2.50	94	102	"	Tallowy	2.34	95	102	"	Slightly tallowy
	4	2.46	95	101	0.10	Tallowy and cooked	2.22	94	101	0.10	Tallowy and cooked
	5	2.49	95	101	0.15	Tallowy	2.19	95	100	0.15	"
	21	2.01	96	97	1.27	Tallowy and cooked	2.01	93	98	1.00	"
	30	1.49	93	96	10.57	Very tallowy and cooked	1.68	94	94	10.10	Very tallowy and cooked
As packed		2.25	97	100	Nil	Good	2.25	97	100	Nil	Good

(a) Whole milk powder in parchment lined composite containers

(b) Whole milk powder in glassine composites

(c) Whole milk powder + 35% sucrose in parchment lined composites

(d) Whole milk powder + 35% sucrose in glassine composites.

Two composites of each batch were opened at intervals, weekly for the first five weeks and then less frequently, over seven months and the powders examined for moisture content, solubility, peroxide value and taste. The results of these examinations are given in Tables 11 and 12.

It was not anticipated that the keeping qualities of the two powders would be any better in the composite containers than in cans but the point to be determined was whether it would be as good, or if inferior, by how much? Taking the result for the whole milk powder first (Table 11) it will be seen that as far as peroxide value and taste are concerned there is no difference whatever between the powders stored in the parchment lined container and those in the glassine type. Since the oxidation of the butterfat is carried on by the air already within and around the particles this result was to be expected. With regard to the moisture contents, however, there is a small, though well marked difference between the two types, both of which differ considerably from the results for powders packed in cans. Both kinds of composite showed themselves to be permeable to moisture vapour, the parchment lined type more so than the wax lined glassine. This had the effect of not only increasing the moisture content of the powders stored at 0°C and in the laboratory (17°C) but also of decreasing that of the powders at 37°C and 47°C. This change in original moisture content is shown to the greatest extent in the powders stored at 0°C in parchment lined containers. It will be noted that when packed, the whole milk powder had a moisture content of 2.25% but that even by the end of the first week it had risen to 3.75% at 0°C, 2.86% at 17°C, 2.74% at 37°C and 2.75% at 47°C. This is the result of two similar effects. The powder had of necessity to be packed in the laboratories of the Metal Box Company Ltd., London, as the double seamer in use at this Institute had not the necessary seaming chucks for seaming composites, consequently the filled containers had to be sent back to Scotland by rail, during which time, although themselves packed in boxes, they would be subjected to atmospheres of relatively high humidity. Hence even the powders stored at the higher temperatures, where the tendency was to lose moisture, started their storage period possessing a higher moisture than the than the freshly manufactured powder. The relative humidity of air in the incubators at 0°C, 17°, 37°C and 47°C was 85, 47, 37 and 30% R.H. respectively and these differences are reflected in the behaviour of the moisture content of the powders. At 0°C and 17°C the relative humidity of the atmosphere was considerably greater than that of the air within the containers, and since both types of container were permeable to air and moisture vapour, the powders absorbed water. This tendency to bring about humidity equilibrium is the second effect contributing to the recorded increased moisture contents of the powders after one week's storage and is the controlling factor in the subsequent storage. As would be expected, the absorption of moisture is greatest at 0°C where, in the case of the parchment lined containers, it increases from 2.25% to a moderately constant figure of about 8.2% whilst in the glassine composites the highest figures reached is 6.6%. This difference is even greater at 17°C where the excess of moisture in the surrounding air over that in the container is not so great, thus enabling the wax lining more effectively to play its part and to prevent absorption better, whilst the parchment still offers little or no protection. (It may be recalled that leaving spray dried whole milk powder over water for 20 hours, as in Lea's method for the extraction of fat (see p. 24) increased the moisture content to about 10%). At 37°C, within fairly broad limits, the moisture contents are reasonably constant, suggesting that an equilibrium existed between the relative humidity of the air within the composite and that of the surrounding atmosphere. At 47°C, the reverse process to that at 0° and 17°C appears to have taken place; starting with a moisture content of between 3.0-3.4% the powders in both types of container after 30 weeks storage had fallen to 1.5% and 1.7% respectively.

For the first time in these storage experiments there are some slight changes in the solubility of the stored powders which, as will be shown in a later section, are due to the combined effects of moisture and temperature. This is greatest at 0°C in the parchment lined containers, where the moisture content reached its highest value. Here the solubility index of the powder, after 13 weeks was beginning to show a definite decrease when determined both at 20°C and 50°C. It may be noted that at the apparent maximum moisture contents reached by the powder in the glassine composite, 6.6%, no such fall in solubility had occurred, either in those containers or in the parchment type at the same moisture content and that the moisture content must first exceed some critical figure (in the order of 8%) before such deterioration occurs at this temperature. Consequently powders stored at other temperatures were not affected by this type of deterioration, but nevertheless there was some loss of solubility at 47°C in both types of container where the moisture content was, in fact, lower than normal. This decrease is hard to account for, unless it is that extreme tallowiness is a contributory factor, the peroxide value having risen to 10 by the end of 30 weeks. This same decrease was found with the whole milk powder stored in cans at 47°C to about the same extent.

Comparing Tables 3 and 11 it will be observed that, apart from the variations in moisture content noted above, there was very little difference between the general keeping qualities of the powder, whether stored in cans or composites. The exception to this was at 0°C in the case of powder stored in parchment lined containers, which developed a cardboardy flavour after nine weeks. This may very likely be the result of the increasing moisture content on the protein constituent of the powder. For the rest, tallowiness was noticeable after storage periods very similar to those for powders packed in cans, e.g. 16-17 weeks at 17°C, 3-4 weeks at 37°C and after 1-2 weeks at 47°C.

Hence for the storage of spray-dried whole milk powder, composite containers which are likely to meet

Table 12.

COMPOSITES STORED IN AIR.

Sugar Powder.

Storage Temp. °C	Length of Storage in weeks.	Parchment %H20	Solubility Index 20°C	Solubility Index 50°C	Perox. Val. ml. N/100 sod. Thio.	Taste	Glassine %H20	Solubility Index 20°C	Solubility Index 50°C	Perox. Val. ml. N/100 sod. thio.	Taste
0°C	1	4.18	102	102	Nil	Good	2.91	102	102	Nil	Good
	2	4.53	101	100	"	"	2.58	101	100	"	"
	3	5.30	102	103	"	"	2.92	102	103	"	"
	4	5.94	102	102	"	"	2.61	102	101	"	"
	5	6.68	103	103	"	"	3.01	101	101	"	"
	9	8.11	104	101	"	"	3.79	100	100	"	"
	13	9.97	98	101	"	"	4.36	102	101	"	"
	17	9.82	101	101	"	Slightly "off". Cardboardy?	5.45	102	102	"	"
	21	8.99	101	101	"	Slightly cardboardy	6.37	102	102	"	Very slightly cardboardy
20°C	1	3.55	103	103	Nil	Good	2.58	104	103	Nil	Good
	2	3.27	103	103	"	"	4.25	102	102	"	"
	3	3.51	101	102	"	"	2.47	102	101	"	"
	4	3.31	103	101	"	"	2.82	103	101	"	"
	5	3.80	102	104	0.03	"	2.74	103	102	"	"
	9	5.83	101	102	0.10	"	3.89	102	101	"	"
	13	6.93	99	103	0.05	Very slightly cardboardy	4.48	105	102	0.05	Very slightly cardboardy
	17	6.76	103	103	0.05	Good	4.11	103	102	0.05	Good
	21	7.97	102	100	0.05	Slightly cardboardy	3.62	101	101	0.05	Slightly cardboardy
37°C	1	3.27	102	103	Nil	Very slightly cooked	2.61	103	103	Nil	Good
	2	3.54	102	102	"	Cooked	2.54	102	103	"	Slightly cooked
	3	3.14	101	102	"	Slightly tallowy	3.08	101	102	"	Slightly tallowy
	4	2.93	102	103	"	"	2.47	102	101	"	"
	5	3.10	102	102	0.08	"	2.57	102	102	0.08	"
	21	2.53	100	101	0.43	Tallowy and burnt	3.29	102	102	0.05	Cooked and tallowy
	30	3.14	102	103	0.60	"	3.16	101	103	1.70	"
47°C	1	3.41	103	103	Nil	Very slightly cardboardy	2.62	101	103	Nil	Slightly cooked
	2	2.94	103	103	"	Very slightly tallowy and cooked	3.00	103	103	"	Cooked
	3	3.05	101	102	"	"	2.49	102	101	"	Tallowy
	4	2.69	103	102	0.05	Tallowy and cooked	2.31	101	103	0.05	Slightly cooked and tallowy
	5	2.79	102	102	0.10	"	2.50	103	105	0.10	"
	21	2.09	100	102	0.86	"	1.96	100	102	0.70	Cooked and tallowy
	30	1.55	101	100	2.33	"	1.72	102	104	1.50	"
As packed		2.45	100	100	Nil	Good	2.45	100	100	Nil	Good

extremes of temperature and humidity are less suitable than cans, but for short period storage, up to the limit of tallowiness imposed by air storage, (i.e. four to six months) composites could quite well be used in place of the all-metal containers.

In the sweetened whole milk powder, where the relative proportion of protein is less, due to the 35% sucrose, it might be expected that, whilst the absorption of moisture might be greater, on account of the more hygroscopic nature of the powder, the relative effect on solubility would be less. Table 12 confirms such deductions.

As with normal whole milk powder, there is very little difference between the keeping properties of sweetened milk powder stored in parchment or glassine lined composite containers. Such difference as there is, resulted in the cardboardy flavour developing slightly earlier in the parchment lined containers stored at 0°C, but the difference is not so marked as with whole milk powder. At the other storage temperatures cardboardiness or tallowiness developed about the same time in each type of container. In no case did the peroxide value rise as high as for unsweetened whole milk powder and this is particularly noticeable after thirty weeks at 47°C, where from the high values given by the whole milk powder, it is evident that the induction period is well passed whereas in the sweetened powder oxidation has only just overcome this initial stage. This confirms the previous finding of the protective power of sugar in the powder against that oxidation.

The moisture contents for the two types of container at each temperature follow very similar trends to the unsweetened powder, the general level of absorption being slightly higher, whilst the reduction at 37°C and 47°C brought the final moisture content after 30 weeks to almost exactly the same value as in the case of the unsweetened powder. Since in this latter case the resultant moisture content of the powder is due to the equilibrium between moisture vapour in the can and in the outer air, this similarity would be expected.

Compared with the sweetened powder stored in cans, the only practical differences lies in the absorption of water by the powder in composites stored at 0°C and 17°C, which led to the formation of a cardboardy taste at 0°C which did not develop in the can powder. Despite the higher moisture content of powders stored in composites at these two temperatures, the presence of added sucrose was sufficient to prevent any protein denaturation which may have occurred from manifesting itself as a decrease in solubility index, neither did such a fall appear in the longer stored, high temperature powders.

Thus the conclusions arrived at for the storage of whole milk powders in composite containers holds equally well for the sweetened powder.

Discussion.

From the data presented it will be seen that the only method of preventing the development of tallowiness in spray dried milk powders containing an appreciable proportion of the natural butter fat is in almost completely removing the oxygen from the container, and, as far as possible, from within the powder itself. That this removal of oxygen need not be carried to such a stage as would make the process commercially impracticable is indicated by the resistance to oxidation of the powders in cans still containing 2-3% oxygen. Inclusion of sugar does not in itself appear sufficient to do more than delay for a short period the development of tallowy flavours. This suggests that no enveloping surface film of carbohydrate covers the powder granule, or if it does, oxygen can readily permeate it and reach the fat globules. Staining spray dried whole milk granules with osmic acid vapour gives a uniform brown colour over the whole surface. If the butter fat was spread as an even outer layer this colour should be black and consequently it is more likely that the fat exists in a very finely divided state amongst the other constituents. From the fact that 55% of the fatty acids in butter fat are saturated it would not be expected that monomolecular surface films of fat would readily form as the liquid globules dry; it seems more likely in light of recent developments in this type of work that such a function would be assumed by the protein constituents, confirmation of which is to be found in the difficulty of direct fat extraction from spray dried whole milk powder. Hence it is regarded as far more likely that whole milk products in which the protein to fat ratio is higher than normal, such as malted milks, represent a better method of prolonging the storage life than by addition of carbohydrate.

In a later section the influence of moisture content on the spoilage of milk powder is fully considered but it may be remarked here that in any storage of milk powders in moisture permeable containers great care is obviously necessary to avoid extremes of humidity conditions in the store. From the approximate constancy in moisture content of the powder stored in composite containers at 37°C and the changes recorded at both higher and lower storage temperatures, it would appear that an equilibrium existed between the pressure of moisture vapour in the containers and in the incubators.

The relative humidity in the 37° incubator recorded over several days was about 37%. From data given by Holm and Greenbank.(55) the vapour pressure in equilibrium with spray dried powder containing 3% moisture content was about 3 mm., the temperature at which this equilibrium was reached is not given but if 20°C is assumed, this vapour pressure corresponds to a relative humidity of 17%, considerably lower than that of the 37°C incubator mentioned above. A possible explanation of this is that although the composite containers were permeable to moisture vapour, a considerable difference between the vapour pressures within and without the containers had to exist before any appreciable transfer of moisture took place either way. In this way the powder stored at 0°C contained only 8-9% moisture after 24 weeks, although the relative humidity in the chamber was 85%. This pressure effect explains also the lower moisture content reached by the powder stored in the less porous, wax lined containers.

A line of approach to the problem of air storage of fat-containing milk powders appears to be indicated by the results obtained in the storage of ice-cream powder. The use of a completely saturated fat would presumably impart even better keeping qualities than the cocoanut oil actually used, which possessed some 8%

unsaturated fatty acids. Further work on these lines is envisaged. In a recent paper, Brown, Dustman and Weakley(56) have shown that feeding one pound of cocoanut oil in the ration per animal per day to cows decreased slightly the iodine number of the resultant butterfat and reduced the intensity of the oxidised flavour on storage. Here, as in the ice cream powder, the more saturated cocoanut oil is replacing a certain amount of butterfat and retarding the development of talloweness.

Summary.

1. Addition of 35% sucrose to whole milk powder delays the onset of tallowiness when the product is stored in air.
2. Substitution of cocoanut oil containing only 8% unsaturated fatty acids for butterfat in spray dried milk powder results in a product possessing excellent keeping qualities.
3. Malted milk powders possess the best keeping qualities of the various milk powders examined.
4. Spray dried whey powder containing 2.25% of cocoanut oil has excellent keeping properties.
5. Composite containers are inferior to tin cans for the prolonged storage of milk powders but could be used over short periods of 3-6 months.

6. Complete prevention of tallowiness in spray dried whole milk powder stored over long periods can only be obtained by reducing the oxygen content within the container to a value not exceeding 1,5%, but a reduction to 2.5-3.0% oxygen greatly increases the keeping quality of the powder.

Part II. B. The Storage of Whole Milk Powders. containing Antioxidants.

In storage experiments described so far the prevention of butterfat oxidation has been mainly by physical methods, e.g. addition of sugar to form a protective coating, addition of barley malt for the same purpose, at the same time diluting the fat content, or by inert gas packing, thereby removing the oxygen necessary for the development of talloweiness. In the present section a series of experiments is described in which a chemical method of prevention was investigated. This consisted of an attempt to extend the induction period of the butterfat oxidation reaction by the use of substances which may broadly be classed as anti-oxidants and whose function appears to be the provision of a more easily oxidised molecule.

Much of the work done on antioxidants and the anti-oxidation of fats comes from Mattill and his co-workers. From 1930 onwards this team has published some dozen or so papers thoroughly investigating the various types of chemical compounds, including naturally occurring ones, which function either as anti- or pro-oxidants for animal and vegetable fats, together with quantititive estimations of the products formed in these processes. In 1930 Mattill and Crawford(29) noticed that as corn oil was progressively purified during manufacture it became increasingly susceptible to oxidation. This they attributed to the removal of sterols amongst which they decided were antioxidative substances. Acetylation or exposure of the sterols to high temperatures destroyed their efficiency as antioxidants. The following year Mattill(30) investigated a series of compounds to secure information on the chemical nature of antioxygenic substances which occur in natural oils by measuring their ability in a concentration of 0.02% to prolong the thermal oxidation induction period of a standard mixture of lard and cod liver oil at 70°C. The results suggested that the antioxygenic capacity lay in the possession of two hydroxyl groups in ortho and para positions attached to the benzene nucleus. Hydroxyl in the meta position was very much less effective, α-napthol having roughly twenty times the antioxidative effect of β-napthol. The most effective compound studied was hydroquinone, with pyrogallol and pyrocatechol next. Further work by Olcott (31) showed that hydroxy-hydroquinone and 1.8. napthalenediol were also effective. French, Olcott and Mattill(32) then endeavoured to put this work on a quantitative basis and found that for two wheat oil fractions, containing the unsaponifiable lipids, the degree of inhibition was directly proportional to the amount of inhibitor used. With hydroxyaromatic compounds such as hydroquinone this linear relation did not hold until a threshold value of about 0.2%-0.3% had been passed, and then only approximately. The effectiveness of one of the wheat oil fractions varied inversely with the amount of peroxides already present in the fat and under such conditions there appeared to be a mutual destruction of antioxidant and peroxide. Investigating the antioxidative properties of lecithin, Olcott and Mattill(33) concluded that commercial preparations possessed only moderate antioxygenic action on refined cotton seed oil, little effect on lard and none at all on lard-cod liver oil mixtures and that the true inhibitor was not lecithin but cephalin, present as an impurity. The particular portion of the cephalin molecule responsible for this property appeared probably to be the monobasic phosphoric acid radical. Studying the mode of action of antie and pro-oxidants, Hamilton and Olcott(34) concluded that phenolic inhibitors caused no change subsequent to the end of the induction period and that they exert their effect solely by inhibiting the formation of the initial active moloxide, the precursor of peroxide formation, in the unsaturated fat molecule and that such inhibitors are entirely destroyed before the start of the rapid oxidation which characterises the end of the induction period. The action of pro-oxidants such as perbenzoic acid and copper oleate would thus be to decrease the induction period by virtue of their destruction of naturally occurring inhibitors. Later Olcott and Mattill(35) extracted the fractions of vegetable oils possessing antioxygenic properties and showed that their structure was closely allied to that of Vitamin E and that although they acted as inhibitors in the oxidation of several easily oxidisable substances, e.g. fatty acid esters, they were not inhibitors for the vegetable oils in which they occur. In activity these compounds appeared to be about the same level as α-hapthol and well below that of hydroquinone. Studying the course of oxidation of several pure, unsaturated compounds Hamilton and Olcott(36) concluded that in the intial reactions at the double bonds each molecule of methyl oleate absorbed four atoms of oxygen rather than the two or three atoms usually assumed. Recent work by Deatherage and Mattill(37) analyses the reactions and end products occurring during the oxidation of fats and shows that after the addition of oxygen to form peroxides at the ethylenic linkages, these peroxide may cleave to give two moles of ethylene oxide or they may aid further oxidation of the carbon chain or themselves autoxidise to form acids and peracids. This accounts for the rise in the measured peroxide value of butterfat to a definite maximum followed by a fairly rapid fall.

Lea(38) investigating the preservation of edible fats mentions, amongst other substances, that proteins have a considerable antioxidative activity and this finds experimental confirmation in the work of Corbett and Tracy(39). These authors found that condensed skim milk added to cream to produce a milk of 4% fat content had the effect of preventing tallowiness even when 3 p.p.m. of copper were added. Barnicoat and Palmer(40) also found that milk plasma substances had a slight antioxygenic effect.

Of more definite nature appears to be the evidence relating to the effect of cereals as protective agents for butterfat. Davies(41) in an article reviewing its applications, mentions oat flour being used either directly, as an ice cream mixtures, or in the form of an aqueous extract incorporated in butter or impregnated in the paper wrappers used for butter. It had also been used as a suspension in wax for spraying on to the inner surface of paper milk bottles where it is suggested that the active antioxygenic principle is an organic phosphorous compound - probably something similar to that suggested by Olcott and Mattill as occurring in cephalin. In these papers, as in that of Peters and

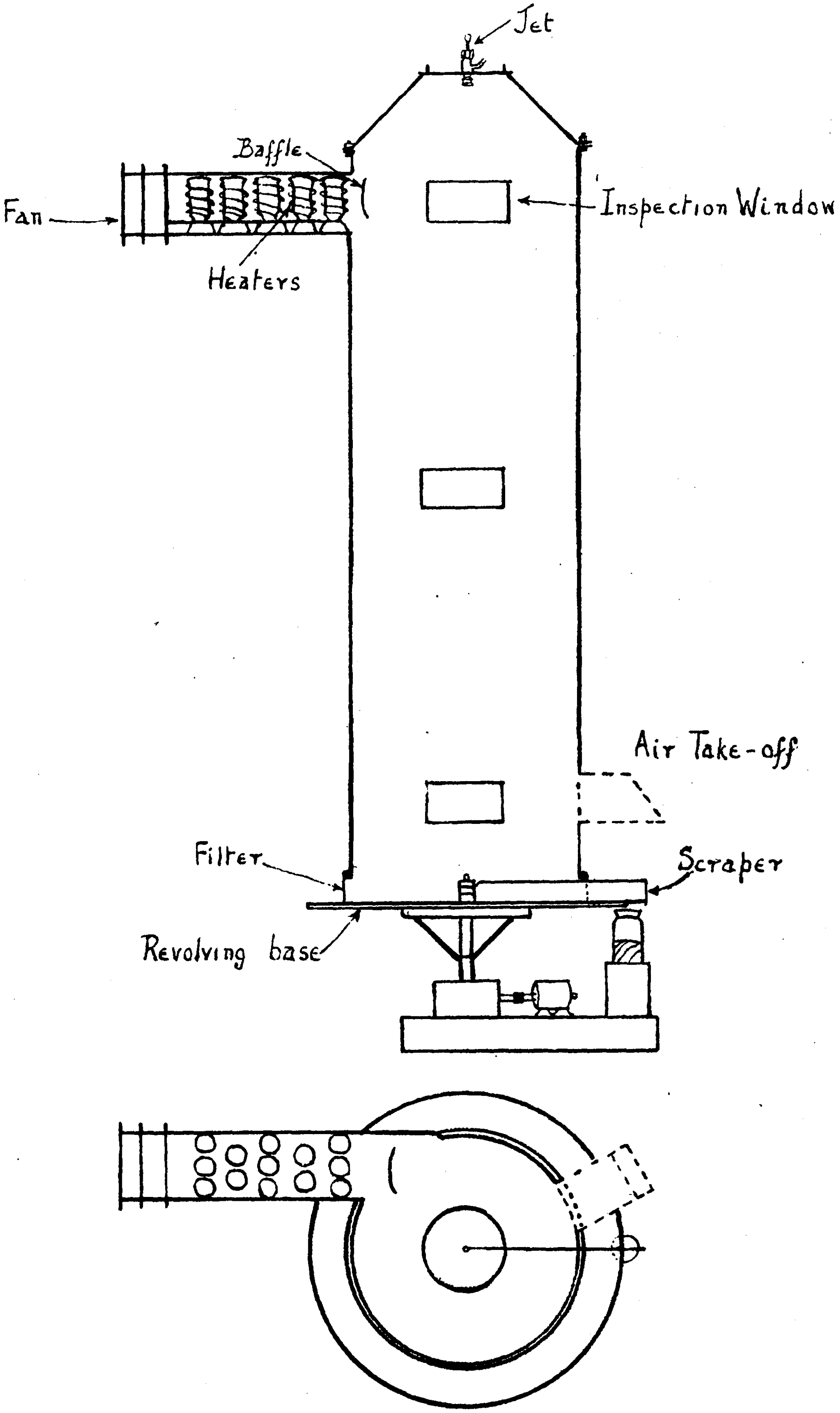
Musher[42] the addition of small quantities of oat flour to milk or milk products is said not to be noticeable, whilst at a concentration of 0.5% the milk is said to possess a slight, but not unpleasant, taste of oats.

It is obvious that if any addition is to be made to milk or milk powder with a view to increasing its keeping quality such a substance must, above all, be harmless when ingested and preferably one which does not alter the normal flavour of milk. The first of these two conditions rules out all the various aromatic polyhydroxy compounds such as hydroquinone, α-napthol etc. but it leaves the wide field of the cereal germ oil class which was mentioned in the above investigations. The second condition however now rules out any highly flavoured fractions and so the number of possible substances is again reduced. Oat flour would appear to be one of the best of the remaining possibilities, as it is said to be more protective than other cereal flours[42] whilst at the same time, being itself a normal foodstuff, its harmlessness and palatability is assured. Thus it was decided to incorporate oat flour in milk before drying and to determine what effect this had on the keeping qualities of the stored powder.

Experimental.

Since the only guide to the concentration suitable for use was the statement already referred to, that of 0.15% (by weight) caused a definite oat flour flavour in milk, it was apparent that a range of concentrations would require investigation. Moreover, being essentially a starch containing product, oat flour gelatinises above a temperature of about 62°C and as the antioxygenic properties might conceivably be reduced by gelatinisation and prolonged heating (such as would be received in the pre-condensing stage of powder manufacture, if added to raw milk), these new factors had to be considered. This made it apparent that a fairly large number of samples prepared under varying conditions would be necessary; at the same time, quite small amounts, suitable for short period, high temperature storage, would be sufficient. Such samples would be difficult and costly to obtain on the commercial plant by which the previous powders had been prepared and hence it was decided to construct a spray drying machine suitable for use in the laboratory, capable of producing the required samples. As the machine includes some original features it is proposed to give a short description of its construction and performance together with a few characteristics of the milk powder produced.

Fig. 6.

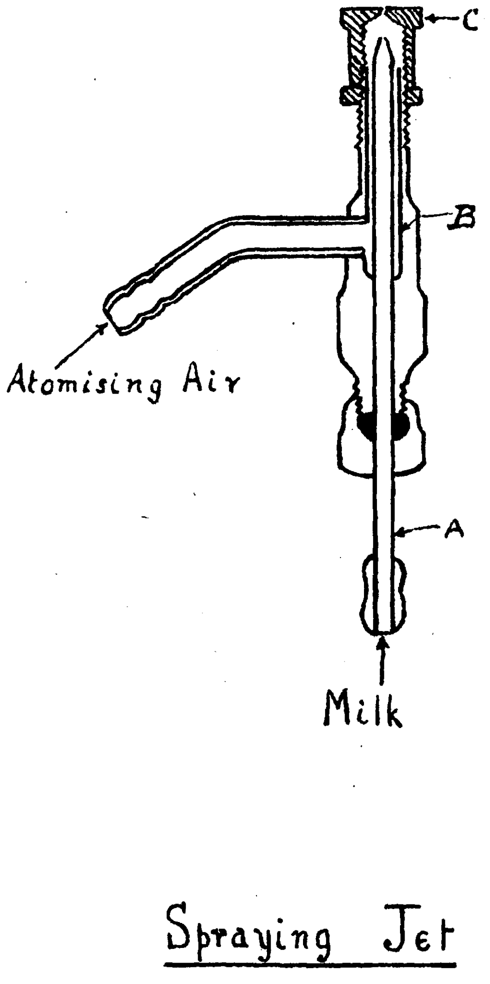


Spray Dryer

The commercial plant previously used employed a pressure in the milk line of 3,800 lb/sq.inch but Scott(43) has shown that for small scale purposes pressures of 2-4 lb/sq.inch used on the atomising principle, are sufficient to give a fine, mist like spray.

Fig. 6 is a diagrammatic sketch of the machine; milk is sprayed from a jet at the top of a cylindrical drying chamber into a stream of hot air entering tangentially. Powder forms in the upper half of the chamber and about four-fifths of it falls on to a revolving base plate, where it collects against a stationary scraper arm and can be raked into a suitable container. The outgoing air as it passes through a metal guaze filter fitted to the bottom of the chamber wall deposits the remainder of the powder. Periodic tapping of the filter causes the powder to fall on to the base where it is collected with the other material. Since theoretically it is undesirable that the relatively humid outgoing air should leave the drier at the point of deposition of the powder, experiments have been made in which the air left the chamber six inches above the base plate. These showed that there was no improvement, either in the amount or quality of powder recovered, although the temperature of the base plate was lowered

Fig. 7.



Spraying Jet

by 20°C.

Constructional Details.

The drying chamber is made of 20's S.W.G. tinplate in the form of a cyliner 6 ft. long by 2 ft. in diameter, lagged outside with a ½ in. thickness of magnesite cement over the top half and supported on three legs of inch angle iron. Closing the top is a truncated cone of 8 in. vertical height, carrying the spraying jet in a flat top plate. Both cone and jet are easily detachable from the chamber for cleaning. The jet shown in Fig. 7 is essentially similar to that used by Scott(43), and is made throughout of stainless steel to prevent metallic contamination of the milk. Milk under a pressure of 2 lb/sq. inch enters through the capillary tube, A, whilst at the same time atomising air at the same pressure enters the annular space B and is caused by the shape of the cap C to impinge on the liquid stream, dispersing it into a fine mist about 6 in. below the jet. The capillary tube A is attached to the barrel of the jet by a locking nut and packing gland to facilitate substitution of tubes of different orifice diameter. Four tubes have been used varying from 0.25 mm. to 1.00 mm. in orifice diameter. Increasing the atomising air pressure results in a finer spray, but owing to a rising back pressure, a lower rate of liquid flow; if, however, the milk-line pressure is increased proportionally a rate of liquid flow can be found which will result in complete liquid drying at any given inlet air temperature. Table 13 gives an example of this for water at 20°C.

Table 13.

Inlet Air Temperature 100°C   Outlet air Temperature 80°C

Water at 20°C.

Atom. press. lb/sq.ins.	Milk press. lb/sq. in.	Liq. flow ml./min.	Condition of base plate
0.5	0.65	8.5	very wet
1.0	1.4	8.2	wet
1.5	2.0	8.0	fine drops
2.0	2.5	7.1	few drops
2.5	3.1	6.3	dry
3.0	3.8	6.0	dry

The air-heating unit consists of a fan delivering 45 cubic feet of air per minute over twelve 600-watt elements controlled in groups of three. Hence the temperature of the top of the chamber, which controls the rate of drying, can be varied over a wide range for different products. The air filter at the bottom of the chamber wall is stainless steel gauze of 40's mesh, 3 inches deep, with an asbestos ring interposed to

Table 14. Whole Milk condensed to 20% Total Solids.

Inlet air temperature 126°C. Outlet air temperature 100°C. Milk temperature 20°C.

Sample	Jet orifice diam.mm.	ml. per min.	g. per min.	Powder recovery effic.	Moisture %	Sol. Index		% collected on		
						20°C.	50°C.	Plate	Filter	Take-off
(a)										
Raw	0.25	4.0	0.09	19	3.11	-	-	90	10	-
	0.50	5.5	0.37	54	1.42	96	101	65	35	-
Whole Milk	0.75	10.0	0.62	50	1.36	99	101	69	31	-
	1.00	13.5	0.70	42	2.05	95	99	67	33	-
(b)										
Condensed whole	0.25	4.0	0.27	31	2.63	95	-	85	15	-
milk	0.50	5.0	0.67	63	1.58	95	97	78	22	-
21% total solids	0.75	9.0	1.24	65	2.54	95	97	78	22	-
	1.00	11.5	1.30	54	2.27	96	102	76	24	-
(c)										
Condensed whole	0.25	4.0	0.2	41	-	97	-	50	20	30
milk	0.50	6.2	0.70	54	2.59	96	98	70	15	15
	0.75	8.5	0.89	53	3.41	98	100	76	11	13
	100	12.5	1.52	62	4.61	94	103	79	11	10

Air take-off fitted.

prevent direct heat conduction. There is about ⅛th inch clearance between the filter and the ¼ inch thick plate-glass base-plate which rests upon a turntable driven by an eighth horse power, variable-speed motor through a reduction gear. The scraper arm is also made of ¼ inch plate glass, with a ground edge riding on the base-plate.

Performance.

The weight of powder produced in a given time depends chiefly on the total solids content of the liquid. Thus for milk containing 12.5%, 20% and 35% total solids, using the same spraying jet, the rate of powder collection was 0.6 g, 1.0 g, and 1.8 g per minute. Table 14 gives the performance for the four jets for (a) untreated whole milk of 12.5% total solids and (b) whole milk condensed to 21% total solids, when the outgoing air left the chamber solely through the surrounding filter gauze and (c) for whole milk condensed to 20% total solids when the outgoing air left through both the auxiliary take-off above the base-plate and the filter gauze. Comparison of (a) and (b) shows the effect of condensing the milk and of (b) and (c) the effect of the auxiliary air take-off.

It will be seen that pre-condensing lowers very slightly the solubility of the product at 20°C, but this decrease is not sufficient to make worth while the spraying of raw milk, with its much lower rate of powder recovery. No improvement either in efficiency of powder recovery or in the quality of the product is produced by removing most of the outgoing air at a level above the powder collection, probably because the high outlet temperature and large air volume avoid any recondensation of moisture on the powder; indeed the powder collected on the cooler base-plate appears to have suffered from this very fault. The powder losses incurred are due to two factors, both arising from the heterogeneous nature of the globule size of the spray. The very fine globules dry to a powder capable of passing through the filter into the outer air whilst occasional large globules are incompletely dried when they reach the base-plate and become spread over it as a film. It will be seen that the smallest jet is too fine for practical use, since most of the powder is carried off in the outgoing air.

Incidentally, it may be noted that the temperature of the liquid to be sprayed appears to have little effect on its drying properties. This would be expected from the sonsiderable heat surplus in the drying air and from the fact that cold atomizing air is used to prevent the clogging of the jet and cap orifices*.

Particle Size.

Fresh whole milk was condensed under vacuum in two batches at 60°C until the concentration of total solids was 27% and 35%, the original milk containing 13% solids. Each of these three batches of milk was then sprayed under the conditions given in Table 14 (without the air take-off), through the three larger jets and an attempt made to determine the effect of milk concentration and jet orifice diameter on particle size of the powder. It is obvious that the smaller the particle size the greater will be the surface area over which any weight of butterfat must be spread and hence be expected to oxidise more readily, although the closer packing of the granules would militate against this to some extent.

The method of obtaining the counts of particle size was as follows. An aluminium clip holding four ordinary

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*This machine has been used at the request of colleagues to dry a variety of liquids other than milk, amongst which have been egg yolk, grass juice, blood and blood plasma, serum and fruit juices. All have been successfully dried, some with more difficulty than others and in general it can be said that liquids having a low total solid content are most difficult to dry and collect on account of the large volume of water to be avaporated and the fineness of the resulting powder. Liquids such as blood, egg yolk and condensed fruit juices containing 20-40% solids with not too much sugar as a constituent are by far the easiest.

microscope slides was placed on the revolving glass base-plate and pushed to the centre whilst the milk was being sprayed. Due to the rotation of the plate the clip came up against the stationary collector arm where centrifugal force immediately caused it to move out of the chamber. In this way powder falling over half the diameter of the chamber, which, as the spraying jet is located centrally, should give a fairly representative sample, alighted on the four microscope slides, without sufficient being collected to cause individual particles to cover one another. To measure every particle on each of the four slides would have required excessive time, so that a very arbitrary selection had to be made. It was decided to take each slide and measure the particles on a very narrow strip along the length of the slide. This was done by setting one end of the slide under the microscope objective and measuring each particle coming within the field of a 10 times micrometer eyepiece as the slide was moved along until its opposite end was under the objective. Although the limitations of this method are clearly recognised, the figure ultimately obtained represents the average of roughly six hundred measurements for each milk concentrations and jet size. The minimum particle size found was 0.007 mm. and the maximum 0.17 mm. but by far the largest number fell within much narrower bands and the range 0.007 mm. to 0.070 mm. can be said to contain about 90% of all the particles. When the actual particle sizes had been tabulated they were collected into five broad groups whose ranges increased progressively by 0.035 mm. and finally expressed as a percentage of the total number counted. Table 15 gives the result of this rather arbitrary grouping and in the last column of this table a further "average" has been calculated. This is the "average" particle size at each concentration and jet size, it is a purely imaginary figure as the other data in the table demonstrate, but it may serve to give a more readily grasped idea of the size of the milk powder particle produced by this small scale machine. This figure has been arrived at in the usual manner by multiplying the number of particles at each group size by the arithmetical mean of that size, summing the figures so obtained and dividing by the number of particles.

Table 15.

Effect of Milk Concentration and Jet Diameter on Particle Size.

Concn. of Milk %	Jet Size mm	% Between					"Average" Particle size mm.
		0 and 0.035 mm.	0.035 and 0.070 mm.	0.070 and 0.105 mm.	0.105 and 0.140 mm.	0.140 and 0.175 mm.	
Raw 13.4	0.25	82	17	1			0.023
	0.50	77	21	2			0.026
	0.70	73	21	5			0.028
	1.00	74	24	2			0.027
27.4	0.50	66	29	2	2		0.031
	0.75	61	35	3	1		0.032
	1.00	46	35	15	4	1	0.049
34.5	0.50	53	30	14	3		0.039
	0.75	35	32	23	10		0.054
	1.00	54	32	12	1	2	0.038

From these results it will be seen that despite the arbitrary methods of counting and grouping there is a fairly rational shift in the figures, with the exception of those for 34.6% solids sprayed through the 0.75 mm. jet. Concentration of the milk has considerably more effect than variation in the orifice diameter of the spraying jet, but on the whole the sizes of the various particles do not differ widely and, as already mentioned lie mostly within the first two groups, between 0.007 and 0.070 mm. Hunziker(44) mentions that the size of the particle produced by the pressure spray of the Gray-Jensen type is of the order of 0.05 mm. Whole milk powder actually made by this plant varied in particle size from 0.01 to 0.09 mm. with an "average" size of 0.04 mm. Thus from the table, a whole milk condensed to about 20-25% total solids would give a product of particle size about 0.03 to 0.04 mm. As the time taken to condense in the laboratory the quantity of milk required in the following experiments to this concentration was about the same as is taken in commercial practice on the Gray-Jensen plant (ca. 1 hr) this concentration was chosen in order to equalise as far as possible the heat pretreatment of the milk used in the experimental drier and in the manufacture of the powder employed in the previous storage experiments.

Preparation of Whole Milk Powder containing Oat Flour as Antioxidant.

In an experiment to determine the relative keeping qualities of samples of milk powder it was essential that the various samples should be uniform and that the milk from which they were prepared would change as little in composition as possible. In deciding whether to take milk from the daily bulked sample of the whole herd or from one individual cow, two factors had to be considered, the fat content and the general constitution of the milk. It is well known that milk from different cows has very different keeping qualities and that this can be influenced by the amount of unsaturated compounds in the feed. This difference may be due to the presence in amounts varying from animal to animal of the antioxidants present in the milk plasma, as suggested by the authors mentioned previously. Bulked milk will probably have a more constant fat content, but over a short period such as a fortnight that of the milk of a single cow, in the middle of a lactation period, would not be expected to change too radically whilst the anti- or pro-oxygenic constituents might be expected to remain more constant in the milk from a single cow. On these grounds it was decided to use the milk from a single Ayrshire cow about two-thirds way through its fourth lactation.

According to the data for several types of whole milk powder given by Hunziker(45) 26-27% is an average fat content and in some specifications for whole milk powder, 26% butterfat is layed down as the desirable figure. In a powder containing 2.5% moisture this corresponds to a fat percentage in the liquid milk of 3.3%, assuming a total solids content of 12.5%. For these reasons it was decided to standardize the raw milk at 3.3% butterfat. In batches where the fat content was higher, some of the milk was partially skimmed in the centrifuge to adjust the final value of the whole batch. Condensing was carried out in a glass vessel under a vacuum of 25 inches at 60°C since lowering the temperature to 40°C enabled lipase hydrolysis to become active, giving a rancid product.

The oat flour used gelatinised at 60-65°C, hence if added to the milk before condensing it would, during that process, be just on the point of gelatinisation and some proportion of the granules would probably swell and burst. In deciding whether the oat flour should be added before or after condensing, gelatinised or unswollen, the chief factor to be considered was the effect of such heat treatment on the antioxygenic constituents and, of secondary importance, which method would be more practicable in commercial milk drying, if such an addition proved to be advantageous. As no data appeared to have been published on this question, all previous additions of oat flour having apparently been made in the cold or in melted wax, each method was tried in turn, including one series in which oat flour was added directly to the dried milk powder and mixed mechanically before storage. The use of an aqueous extract as mentioned by Davies(41) was rejected on account of the large volumes necessary to incorporate the requisite amount of oat flour. A 0.5% addition of oat flour on the weight of raw milk was taken as a maximum to avoid imparting too strong a taste of oats to the milk powder; two other concentrations, 0.1% and 0.25% were used in most of the series together with a control powder containing no oat flour. Five series in all were stored, originally at 37°C, later being transferred to 47°C. The powder was packed into a number of uniform amber coloured, screw-top, glass bottles containing just sufficient in each for the weekly examination of solubility, taste and peroxide value. In this way the amount of air available for oxidation by a constant weight of powder remained the same for all samples over the period of the experiment. The peroxide value was determined on 5 g. of powder, using half the normal quantities of reagents and 0.005 N sodium thiosulphate solution, as quite high values were expected, but the results have been calculated back to the same basis as those in the previous storage experiments.

The five series consisted of:-

(1) oat flour in 0.1, 0.25, 0.50% concentration added to the milk before condensing.

(2) oat flour in 0.1, 0.25, 0.50% concentrations added to the milk after condensing.

(3) oat flour in 0.1 and 0.5% concentration gelatinised in a minimum of water and added to the milk after condensing.

(4) oat flour in 1.0, 2.5, 5.0% concentration added to a dried milk powder.

(5) hydroquinone in 0.5% concentration, calculated on the weight of butterfat, added to the milk (a) before and (b) after condensing.

A control powder was made for each series.

The last series, in which hydroquinone was added, was included so that the storage results on this powder could act as a base line for the oat flour results. Hydroquinone has probably received the widest recognition as a fat antioxidant and as it was known that oat flour was not so active, comparison of results for the two additions would give some measure of the action of antioxidants in general as applied to milk powder. It was, of course, recognised that hydroquinone could not be used in practice.

The powders were first stored at 37°C, a temperature chosen because of the reaction accel eration which occurs without much intrusion of the burnt or cooked taste. At the end of five weeks' storage however, the control powders had not developed any real tallowiness, as might have been expected from the previous experiments, so the bottles were transferred to the 47°C incubator for the remainder of the storage period. In presenting the results the time of storage has been given in terms of weeks at 37°C, using a reaction factor of 2.0 for the 10°C rise from 37o to 47° since this appeared justified by the results of the previous work. This increased keeping quality of the whole milk control powders may be attributable to the fact that the condensation of the milk before spraying was done under vacuum, whereas in the commercial Gray-Jensen plant producing the previous powders which became tallowy after five weeks at 37°C, condensing is carried out by spraying and recirculating the pasteurised milk through the hot outgoing chamber air until the desired concentration is reached. This latter process may conceivably shorten the induction period of the fat in the resultant powder. Storage in glass bottles, as opposed to tin cans, may also be a contributory factor to the increased resistance to oxidation.

One difficulty experienced in drying the milk with an oat flour addition was the tendency of the coarser fragments in the flour to settle to the bottom of the milk container. The amount of this sediment was determined by collection and drying after centrifuging and amounted to some 10-15% of the oat flour added and, as might be expected, was most in the series in which the unswollen oat flour had been added to the condensed milk. This trouble would also be experienced in commercial practice where the condensed milk is usually stored in some kind of tank before spraying; finer grinding of the flour would

Table 16.

Series 1 Oat Flour added to Milk before Condensing.

% Oat Flour in the raw milk	Time of Storage at 37°C (weeks)	Av. Moisture Content %	Solubility Index at		Perox. Val. ml. N/100 $Na_2S_2O_3$	Taste
			20°C	50°C		
0	0	2.24	103	101	Nil	Good
	2		100	102	"	Slightly cardboardy
	3		94	101	"	"
	4		97	101	"	"
	5		98	102	"	"
	7		93	100	"	"
	9		100	101	0.10	Slightly tallowy
	13		100	101	0.40	"
	15		100	102	0.96	Tallowy
0.10	0	2.76	92	98	Nil	Good
	2		100	102	"	"
	3		95	100	"	"
	4		97	100	"	"
	5		98	104	"	Slightly cardboardy
	7		99	102	"	"
	9		98	101	"	Very slightly tallowy
	13		98	102	0.24	Cardboardy
	15		100	100	0.66	Slightly tallowy
0.25	0	2.74	-	-	Nil	Good
	2		99	102	"	"
	3		93	102	"	Slightly"cardboardy
	4		99	100	"	"
	5		99	102	"	"
	7		97	100	"	Cardboardy
	9		96	100	"	"
	13		99	99	0.10	"
	15		100	103	0.30	Very slightly tallowy
0.50	0	2.83	100	98	Nil	Good
	2		98	100	"	"
	3		98	98	"	"
	4		98	99	"	Slightly cardboardy or faintly oatmealy
	5		96	97	"	"
	7		95	97	"	"
	9		96	98	"	"
	13		96	100	0.10	Oat flour flavour just distinguishable.
	15		96	98	0.24	Fairly good, oat flour flavour just distinguishable.

Table 17.

Series 2 Oat Flour added to Milk after Condensing.

% Oat Flour in the raw milk	Time of Storage at 37°C (weeks)	Av. Moisture Content %	Solubility Index at		Perox. Val. ml. N/100 $Na_2S_2O_3$	Taste
			20°C	50°C		
0	0	2.04	104	99	Nil	Good
	2		100	101	"	"
	3		96	98	"	Slightly cardboardy
	4		101	102	"	"
	5		100	102	"	"
	7		102	101	"	Very slightly tallowy
	9		102	102	"	Cardboardy
	13		101	101	0.60	Slightly tallowy
	15		101	100	0.70	"
0.10	0	2.10	-	-	Nil	Good
	2		98	99	"	"
	3		97	99	"	Slightly cardboardy
	4		100	101	"	"
	5		101	100	"	"
	7		95	101	"	"
	9		101	101	"	Very slightly tallowy
	13		93	100	0.70	Slightly tallowy
	15		101	101	0.40	"
0.25	0	2.35	-	-	Nil	Good
	2		99	99	"	"
	3		99	99	"	Slightly cardboardy
	4		100	100	"	"
	5		97	98	"	"
	7		99	100	"	"
	9		99	100	"	Slightly tallowy
	13		97	100	0.26	"
	15		98	101	0.30	"
0.50	0	2.01	-	-	Nil	Good
	2		-	-	"	"
	3		98	100	"	Good, slight oat meal flavour
	4		94	100	"	Slightly cardboardy or oat meal flavour
	5		94	99	"	"
	7		96	100	"	Good, oatmeal flavour
	9		97	100	"	"
	13		95	100	0.30	"
	15		98	99	0.20	"

Table 18.

Series 3 Oat flour gelatinised and added to milk after condensing.

% Oat Flour in the raw milk	Time of Storage at 37°C (weeks)	Av. Moisture Content %	Solubility Index at		Perox. Val. ml. N/100 $Na_2S_2O_3$	Taste
			20°C	50°C		
0	0	2.18	103	101	Nil	Good
	2		100	102	"	Slightly cardboardy
	3		94	101	"	"
	4		97	101	"	"
	6		98	102	"	"
	8		93	100	"	"
	12		100	101	0.10	Slightly tallowy
	14		100	101	0.40	"
	16		100	102	0.96	Tallowy
0.10	0	2.50	-	-	Nil	Good
	2		90	100	"	"
	3		98	101	"	"
	4		100	102	"	Slightly cardboardy
	6		99	101	"	"
	8		97	103	"	Slightly tallowy and slightly cooked
	12		99	101	0.70	Tallowy and slightly cooked
	14		100	103	1.10	"
	16		104	104	0.90	"
0.50	0	2.88	95	103	Nil	Good, oatmeal flavour
	2		93	94	"	"
	3		94	102	"	"
	4		92	101	"	Slightly cardboardy, oatmeal less noticeable
	6		93	102	"	"
	8		93	102	"	Very slightly tallowy, no oatmeal flavour
	12		94	100	0.60	Slightly tallowy
	14		94	99	0.30	"
	16		96	100	0.50	"

Table 19.

Series 4 Oat flour added to commercial spray dried whole milk powder.

% Oat Flour in the powder	Time of Storage at $37^{\circ}C$ (weeks)	Av.Moisture Content %	Solubility Index at		Perox.Val. ml. N/100 $Na_2S_2O_3$	Taste
			$20^{\circ}C$	$50^{\circ}C$		
0	0	3.25	93	101	Nil	Good, slightly burnt
	2		92	99	"	"
	3		92	100	"	"
	4		94	100	"	Very slightly cardboardy
	6		91	96	"	"
	10		95	98	"	"
	12		91	94	0.20	Slightly tallowy
	14		91	95	0.20	"
	16		89	93	0.30	"
1.0	0	3.13	-	-	Nil	Good, slightly burnt
	2		91	99	"	"
	3		91	99	"	"
	4		92	99	"	Slightly cardboardy
	6		89	97	"	"
	10		90	94	"	"
	12		90	94	0.10	"
	14		92	94	0.10	"
	16		90	92	0.20	"
2.5	0	2.71	-	-	Nil	Good, slightly burnt, slight oatmeal flavour
	2		93	99	"	"
	3		93	99	"	"
	4		99	99	"	"
	6		91	97	"	Slightly cardboardy
	10		92	95	"	"
	12		90	95	0.10	"
	14		91	96	0.10	"
	16		91	97	0.15	"
5.0	0	3.13	88	98	Nil	Good, slightly burnt, oatmeal flavour
	2		90	97	"	"
	3		91	97	"	"
	4		91	97	"	"
	6		90	97	"	"
	10		88	93	"	"
	12		89	93	0.24	Good, very slightly cardboardy
	14		90	94	0.10	Good, definite oatmeal flavour
	16		87	91	0.20	"

help considerably to overcome this difficulty.

Results.

Tables 16-20 give the results of the tests made on samples stored at 37°C. As already mentioned, all the control powders, including the commercial sample, remained free of tallowy flavours for double the length of time of the previous untreated whole milk powder. The freshness of the winter milk may have helped in this respect, but the true cause is not as yet known. The average moisture content of the powders produced in the laboratory was lower than that of the commercial sample and no changes in solubility arose from this factor. The solubility index of the powders at each reconstitution temperature as a whole did not change significantly although greater irregularity than usual appeared in several samples. These slight variations may be due to the presence of oat flour constituents, which are virtually insoluble but may be held in suspension in varying amounts according to the fineness of the particles.

In assessing the taste of the powders containing oat flour a difficulty hitherto not encountered appeared as a result of the rather "cardboardy" or "flat" flavour of the oat flour itself in low concentrations. This made the first stages of the development of tallowiness difficult to establish and in the tables where a sample containing oat flour is marked as "cardboardy" it should be remembered that this may be due either to the flour or to the beginning of tallowiness. Agreeing with previous workers, it was found that oat flour up to 0.25% on the weight of liquid milk did not produce any distinct taste of oats but that a concentration of 0.5% did. This taste was most noticeable in the samples in which the oat flour had been mechanically mixed with the dry powder, least in the powders made from milk to which the flour had been added prior to condensing and intermediate in the powders from milk to which the gelatinised flour or the flour after condensing had been added. Possibly some of the volatile constituents which produce the characteristic taste of oats had been removed during the vacuum condensing. Where it was definitely discernible as an oat flavour, the taste was quite pleasant but the lower concentrations only resulted in a slightly stale flavour. Hydroquinone in an amount approximating to 0.12% on the weight of dry powder, (0.5% on the weight of fat in the raw milk) had a most unpleasant effect on the taste, producing a rather "metallic" flavour which remained in the mouth for some time even when the reconstituted milk had not been swallowed.

In none of the series does the oat flour show any very marked antioxidative effect although in every case the powders containing most oat flour had developed least tallowiness as measured both by the peroxide value and by the taste of the reconstituted milk at the end of the storage period. The difference in resistance to oxidation between the various series is small but appears to show that the best results are obtained when the oat flour is added to the milk prior to condensing, with addition after condensing and to the powder direct next in efficiency, whilst gelatinisation of the flour before adding to the condensed milk gave definitely the worst results. Hydroquinone behaved as a much better antioxidant than the oat flour and even at the end of the storage period, no tallowiness was discernible. It is possible that a slight tallowy flavour might have been masked by the foreign flavour introduced by the hydroquinone but this is not very likely since the two tastes were quite dissimilar. Moreover, no appreciable peroxide values had developed in the hydroquinone samples in this time. The addition of hydroquinone to the milk before or after condensing resulted in no difference in the keeping qualities of the two powders.

Discussion.

The use of oat flour as an antioxidant for the butterfat in whole milk powders appears to have possibilities, the value of which requires further investigation. The surprising resistance to oxidation of the control powders didnot allow the significance of the oat flour addition to be clearly brought out and in future work the advisability of using the higher storage temperature throughout will be considered. The use of an accelerator such as copper is unsound since this introduces the complication of whether the rate of reaction of the antioxidant with the copper is the same as the rate of the antioxidant and the milk alone and whilst comparative results might be obtained these would have no direct relation with the practical problems. It is interesting to note the greater efficiency of hydroquinone as an antioxidant, which agrees with the work of Mattill and his co-workers already reviewed. The objectionable flavour and the possible deleterious physiological effects probably make the use of this reagent impossible in practice but it would be of interest to determine the lowest concentration of hydroquinone necessary to protect the butterfat in whole milk powder from oxidation. This in turn raises the question as to whether very much smaller amounts of the active antioxygenic principle of oat flour, similar to that isolated by French _et al._(32) from wheat, might not be more effective antioxidants than the whole flour. At least 0.25% of oat flour must be added to the milk, preferably before condensing, in order to delay tallowiness for any appreciable time and at normal temperatures this would amount to an increase in keeping quality of about four months, although if there was no objection to a definite oat meal flavour, 0.5% oat flour would prolong this additional period to about six months. More experiments on powders of different manufactures will be necessary before any conclusive estimates of the effect of oat flour additions on the keeping quality of spray dried whole milk powders can be given.

Summary.

1. Addition of oat flour to whole milk before spraying delays the development of talloweness in the resultant powder when stored in air at 37°C.
2. Resistance to oxidation was proportional to the amount of oat flour present.
3. Milk to which oat flour had been added before condensing gave powders possessing the best keeping quality.
4. A definite oat flavour was only recognisable in powders from milk containing 0.5% by weight of oat flour.
5. Hydroquinone, used in a concentration of 0.5% on the weight of fat present in the liquid milk, was more effective as an antioxidant in the resultant powder than oat flour, but produced an objectionable

taste in the reconstituted milk.

Part III The Drying of Cheese Whey and of Acid Casein Whey by the Roller Process.

Just as the summer flush of milk causes most of a year's supply of milk powder to be produced within the period of a few months, thus involving the question of storage, so also it raises various problems in an allied industry, the drying of whey. In early summer creameries in normal times produce large amounts of butter and cheese, which in turn give rise to large volumes of skim milk and whey. Both of these products must be used immediately to prevent bacterial spoilage. Skim milk is used either by direct drying to give a separated milk powder, or in the manufacture of casein for the plastic and paper trades. In the latter case, acid is added in sufficient quantity to precipitate all the casein after which the clear liquid is run off. This acid whey has formerly been run largely to waste, since it cannot be fed to pigs in the usual manner and its drying presents difficulties. The whey resulting from cheese manufacture, whilst being similar in composition to the acid whey except in acidity and nature of the acid, can readily be dried and large quantities are produced annually. Much of the whey is dried by means of the drum or roller process since a large part of the product goes into animal feeding stuffs and the higher quality, more costly spray dried powder is not required. For certain purposes, however, such as dried whey intended for the bakery trade it is necessary to produce a roller dried product from cheese whey which has been brought as near as possible to the neutral point. The first part of this section deals with problems involved in drying such neutralised cheese whey. The second part deals with the parallel problem of the neutralisation and drying of the whey formed as a by-product in the manufacture of casein.

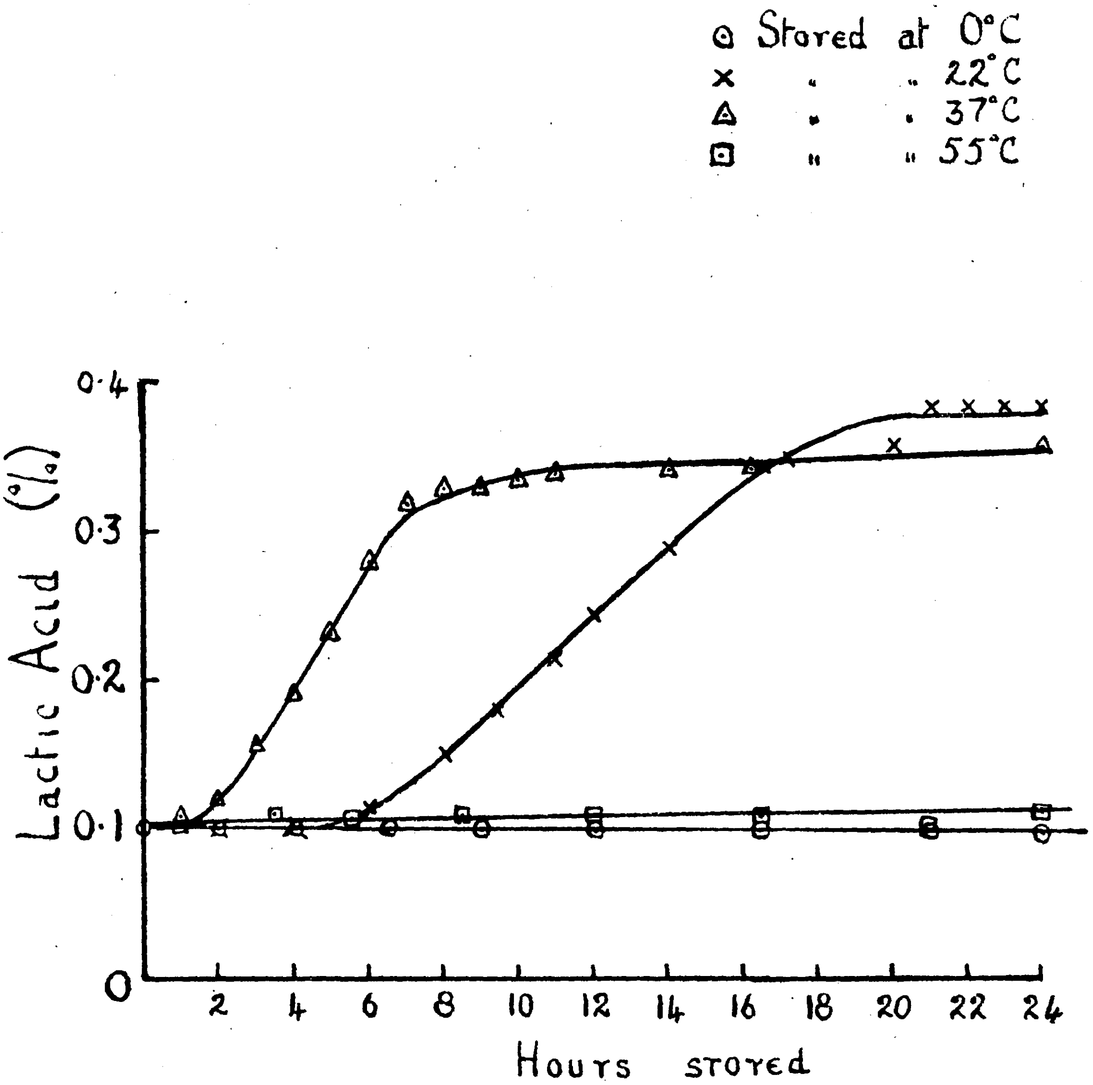
1. The Drying of Neutralised Cheese Whey.

(a) Prevention of acid development.

Whey which has been freshly drawn from the cheese vats usually has an acidity of 0.15%-0.20% expressed as lactic acid. In large creameries considerable volumes of whey may be drawn off from the vats many hours before it can be dried. Due to the large innoculation of lactic acid forming bacteria in the whey, acid development during storage will be rapid unless special precautions are taken, acidities up to 0.30% and even 0.40% being not uncommonly encountered in practice. The rate of acid development will depend on the temperature of storage and the initial extent of the bacterial contents. Fig.8 shows the rate of acid development in a typical

Fig. 8.

Development of Acidity in Stored Whey.



sample of Cheddar whey stored at temperatures from 0 to 55°C. The shapp rise in acidity of the samples stored at 22°C and 37°C showed that storage either at low temperatures or relatively high temperatures is necessary. Here it may be mentioned that the curve for storage at 55°C may be somewhat misleading. At such temperatures there is always the risk of chance infection by a strongly acid forming thermophilic bacterial strain and although in this particular sample this did not occur, the bacterial count - made by Dr C.H. Higginbottom - increased from ten per ml. to one hundred thousand per ml. in 24 hours. Another diaadvantage of high temperature storage is the recorded commercial experience that whey kept for any length of time at 55°C is difficult to dry. Hence a low storage temperature is to be preferred. Another method of reducing the initial number of bacteria would be by appropriate heat treatment of the whey as it is drawn from the cheese vats and for this purpose either of the two methods generally used for milk pasteurisation could be used. Both the "flash" method of pasteurisation of raising the temperature of the whey rapidly to 70°C and holding it there for 30 seconds and the "holding" method, 30 minutes at 62.5°C, were carried out on samples of cheddar whey and batches stored at 0, 22, 37 and 55°C along with an untreated control.

Table 21 gives the results of these tests.

Table 21.

Effect of Pasteurisation on Acidity Development.

C = Untreated Control

F = Sample "flash" pasteurised

H = Sample pasteurised by "holding"

Hours incubated	% Acidity											
	0°C			22°C			37°C			55°C		
	C	F	H	C	F	H	C	F	H	C	F	H
0	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
1							0.11	0.10	0.10			
2	0.10	0.10	0.10	0.12	0.12	0.11				0.11	0.12	0.12
3							0.19	0.11	0.11			
4	0.13	0.11	0.10	0.17	0.10	0.11	0.22	0.12	0.11	0.12	0.12	0.12
5	0.12	0.11	0.11	0.19	0.11	0.12	0.27	0.11	0.11	0.11	0.11	0.11
22	0.12	0.11	0.11	0.39	0.11	0.11	0.38	0.36	0.32	0.11	0.11	0.11
38							0.43	0.38	0.35			

These figures show clearly the beneficial effect of such heat treatment in preventing the rapid development of acidity, provided that a subsequent storage temperature around 37°C is avoided. No significant difference appears between the results of the two types of pasteurisation. It must be emphasised at this point that the value of pasteurisation, as well as of regulation of the storage temperature would be largely negatived unless the storage tanks were adequately cleaned and sterilised between runs.

An alternative method to pasteurisation for controlling the development of acidity might be that of continuous neutralisation, as practised in the manufacture of lactic acid. This would involve either the intermittent addition of alkali or the presence of an excess of a relatively insolubule alkaline salt such as calcium carbonate, which would neutralise the acidity as it develops. Both these methods were tried on a laboratory scale and found to be unsuitable. In one case lime water was added in sufficient quantity to neutralise the developed acidity of a sample of whey after one, eight and twenty hours at 37°C whilst an untreated sample was stored as a control. The net result was that acid development was actually stimulated, more acid being produced in the intermittently neutralised sample than in the control. This is due to the fact that increasing acidity tends ultimately to inhibit the action of the bacteria, with the result that additions of alkali from time to time afforded further opportunity for bacterial reproduction. In the second method, solid calcium carbonate was added to the whey at 37°C and the contents vigorously stirred. Table 22 gives the results of this treatment.

Table 22.

Hours at 37°C	% Acidity		
	Control	Whey + $CaCO_3$	
0	0.12	0.12	Stirred vigorously
1	0.18	0.15	
2	0.19	0.15	
4	0.34	0.16	
21	0.37	0.36	Stirring stopped
28	0.43	0.42	

It will be seen that acid development was effectively controlled so long as vigorous stirring was continued but when this ceased the acidity rapidly rose to that of the control sample. In large volumes of whey e.g. 3,000-4,000 gallons, the difficulties of adequate stirring would be considerable and there would be the possibility of the finer particles of alkali being carried over with the drawn-off whey, resulting in an alkaline product. Moreover, continuous neutralisation with an insoluble salt would also stimulate acid production, although such acidity would not be detected. In this connexion it is important to realise the extent of the breakdown of lactose which accompanies the development of acidity by bacteria.

Table 23 records the lactose and acidity contents of a sample of whey stored at 37°C for 17 hours.

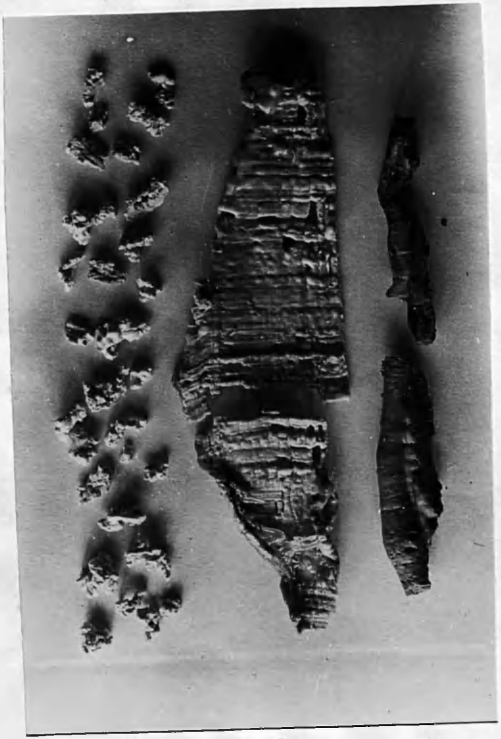
Table 23.

Effect of Acid Development on Lactose Content.

Hours at 37°C	% Acidity	% Lactose*
0	0.10	5.22
3½	0.18	4.94
6	0.28	4.82
8½	0.33	4.73
11	0.34	4.75
17	0.35	4.77

*By the method recommended in Report on Milk Products No.2 1930, Analyst, 55.

Thus it is apparent that an increase of 0.25% in acidity results in the destruction of almost 10% of the weight of lactose originally present in the whey. Continuous neutralisation which resulted in the formation of double the amount of acid normally produced would, in this way, break down 20% of the lactose originally



4.

Dried Whey

present, which would be detrimental both to the drying properties of the whey and to the composition of the dried product.

(b) Neutralisation of Normal Whey.

Even when excess acid development is prevented, as by pasteurisation, there still remains the question of how best to neutralise the acidity of the original whey.

The chief difficulty in this connexion is to neutralise the whey without affecting its drying properties on the rollers. Normally, with whey having an acidity between 0.15 and 0.25%, the scraper knife collects a molten mass, which quickly forms a dry skin, breaks up and drops off in the form of small irregular pieces, somewhat resembling popcorn in shape and size (see Plate 4a). Preliminary experiments carried out on roller drying machines at two creameries in Scotland showed, however, that, if the whey was previously neutralised with sodium bicarbonate it behaves in a very different manner; the molten material collecting at the knife failed to form a dry outer coat and remained as a continuous liquid strip which revolved continuously against the knife and consequently became abnormally brown and caramelised. Moreover the evolution of large volumes of carbon dioxide caused such vigorous frothing in the roller trough that the normal rate of flow of whey could not be maintained.

It was decided to transfer experimental work to a small scale roller drier. For comparison, data for a commercial plant and for this model drier are given below:-

	Model	Factory
Steam pressure lb/sq.in.	40	50
Roller speed revs/min.	15	16
Length of rollers, ins.	24	80
Diameter of rollers, ins.	12	28
Relative area of rollers	1	8½
Rate of whey, galls/hr.	7	120
Pre-heating temperature of whey, °F	140	140

It was found in practice that, whereas on a commercial machine the dried whey is normally pushed off the knife by the bulk of following material, on the model machine, due to the thinner layer of drying material, the product usually formed a gradually broadening strip, separated from the rolls (and therefore not heated) but adhering at its upper end to the knife edge (see Plate 4b). The colour, taste, texture and moisture contents of the two types of material did not, however, differ appreciably.

Table 24

Cheese Whey.

Neutralising agent added to skimmed whey	Original acidity %	Acidity reduced to %	Moisture content of dried whey	Drying properties	Taste of dried whey	Reconstituted whey (10 g. in 100 ml.)				
						pH	Acidity	Colour	Solubility Index 20°C	Solubility Index 50°C
No addition	0.22	-	5.31	Good	Good	5.13	0.30	Good	99	100
$NaHCO_3$	0.20	0.12	6.34	Very bad. Browning at knife and violent frothing in trough	Burnt, rather lacking in taste	6.93	0.05	Muddy	102	102
NaCl(0.12%)	0.23	0.23	5.21	Bad effect, but somewhat better than bicarbonate. No frothing.	Very salty	5.57	0.25	Good	100	100
K_2CO_3	0.18	0.03	5.97	Very bad. Violent frothing, not drying at knife.	Burnt, rather lacking in taste.	7.05	0.04	Muddy	101	101
K_2HPO_4	0.37*	0.12	-	Very bad, similar to bicarbonate, but no frothing.	Better	6.56	0.15	Dark	-	-
"	0.11+	0.06	-	" "	"			Very dark	-	-
$Ca(OH)_2$	0.10+	0.01	5.04	Good, similar to untreated whey	Good	7.19	0.04	Dark	100	101
"	0.17	0.05	-	" "	"	6.91	0.04	"	-	-
"	0.17	0.10	4.58	" "	"	6.37	0.11	Good	101	101
"	0.18	0.05	-	" "	"	7.12	0.02	Dark	-	-
"	0.20	0.06	-	" "	"	6.50	0.05	"	-	-
"	[illegible]	[illegible]	[illegible]	" "	[illegible]	6.70	0.03	"	98	101
"	0.30	0.06	3.66	" "	"	6.70	0.02	"	99	100
"	0.33*	0.05	-	Bad, similar to bicarbonate, but no frothing	Sour and burnt	6.28	0.10	Very dark	-	-
" (to over-neutralise)	0.20	Alkaline	-	Bad, black product.	Unpalatable	7.25	0.01	Black	-	-
CaCl(0.12%)	0.18	0.19	4.51	Rather worse than with line, not as bad as bicarbonate or sodium chloride	Very salty	5.52	0.25	Good	96	98

*Whey kept 24 hours at 20°C (68°F).

+Drawn early.

Using a small scale drier, a number of different salts were added to different batches of whey of varying acidities and the resultant liquid dried under the standard conditions noted above. The batches of whey employed varied from fresh whey of very low acidity (0.10%) to stored whey of very high acidity (0.37%). The results are summarised in Table 24. The following comments may be made.

The control samples dried satisfactorily. The addition of sodium bicarbonate confirmed the results already obtained on the large scale plant. The product dried badly, was severely burnt, and frothed violently in the trough. In order to determine whether the faulty drying was due to the sodium ions <u>per se</u>, a similar run was made in which the sodium bicarbonate was replaced by sodium chloride. Apart from the absence of frothing, the effect was little better than with the bicarbonate.

It was considered possible that certain potassium salts might give a more satisfactory results than the sodium salts. Two such salts were used, i.e. potassium carbonate and di-potassium hydrogen phosphate. Both salts gave results at least as bad as with the sodium compounds.

Experiments were then made with calcium hydroxide in the form of a suspension of finely ground slaked lime.

The results were in striking constast to those obtained with the sodium and potassium salts, the drying properties, appearance and taste of the product made from the neutralised whey being as good as that made from the freshly drawn whey of low acidity. This held for acidities which had been reduced from as high as 0.3% to 0.02%. With only one sample (original acidity 0.33%) was a poor product obtained and this may have been due to some abnormal property of the whey itself, which had been stored at 20°C for 24 hours. A check test with calcium chloride showed that calcium ions had a less deleterious effect than sodium ions.

Finally, one trial was made in which the whey was markedly over-neutralised with calcium hydroxyde, i.e. was made actually alkaline. The resulting dried whey (which is illustrated in Plate 4c) was an inedible, black product, in the drying of which the abnormalities experienced with partial neutralisation by sodium bicarbonate were intensified (i.e. adherence to the knives, no formation of dry outer coat, and continuous 'burning' on the rollers).

These experiments show, therefore, that (i) the use of sodium or potassium salts for neutralisation produces with the roller process a very inferior dried whey, difficult to dry and consequently adversely affected in both appearance and taste; (ii) over-neutralisation intensifies these effects; but (iii) correct neutralisation with calcium hydroxide has no adverse effect either on the drying process or the quality of the dried whey. It may, however, be noted that neutralisation below an acidity of 0.05% resulted in a slightly darker product.

2. The Roller Drying of Acid Casein Whey.

Two types of whey were used, one from casein precipitated with hydrochloric acid and the other from the acetic acid precipitation of casein. The wheys were prepared on a small scale, using the accepted procedure outlined in Suttermeister and Browne(46). The proximate composition of the two types of whey was almost identical, as shown by the following typical figures:-

	Hydrochloric acid. %	Acetic Acid %
Total solids	7.1	6.9
Water	92.9	93.1
Lactose	5.5	5.2
Protein and salts	1.6	1.7
Fat	nil	nil
Acidity (as lactic acid)	0.47-0.50%	0.40-0.42%

The reactions of these two types of whey to roller drying were, however, very different. Each type will therefore

Table 25

Hydrochloric Acid Whey.

Original acidity %	Reduced with lime to: %	Moisture content of dried whey %	Drying properties	Reconstituted whey (10 g. in 100 ml. water)					
				Acidity %	pH	Taste	Colour	Solubility Index 20°C	50°C
0.48	-	4.69	Bad, burning at roller	0.50	4.12	Very acid	Brown	100	101
0.47	0.37	-	Fairly good	0.36	5.12	Acid and Bitter	Yellowish-white	-	-
0.48	0.32	4.09	Good	0.31	5.27	" " "	" "	95	95
0.49	0.18	3.61	Very good	0.17	5.89	Slightly acid and bitter	" "	100	101
0.49	0.16	-	Fairly good, slight tendency to revolve at knife	-	-	" " "	" "	-	-
0.44	0.14	-	Moderate, tendency to revolve at knife. Slight precipitate.	-	6.00	" " "	" "	-	-
0.49	0.10	5.17	Bad precipitate, revolving at knife edge and burning.	-	6.31	" " "	Increasingly burnt appearance	91	92
0.49	0.06	-	Not attempted, large precipitate	-	-	-	-	-	-

be dealt with separately.

(i) Hydrochloric Acid Casein Whey.

Preliminary trials shows that, as with strongly acid cheese whey, the unneutralised whey of 0.47-0.50% acidity could not be successfully dried by the roller process. Following the work already described, sodium or potassium salts were avoided and attempts were made to neutralise the liquid prior to drying with calcium hydroxide.

It was found, however, that complete neutralisation with lime resulted in the flocculation of a bulky precipitate, the composition of which when dried was as followes:-

Water	3.9%
Ash	17.4%
Protein	60.5%
Lactose	15.7%

It may be noted that Richter(51) obtained a similar precipitate when neutralising sulphuric acid casein whey. It has been suggested that this dried by-product might be used as a supplementary form of feeding stuff for poultry and other stock.

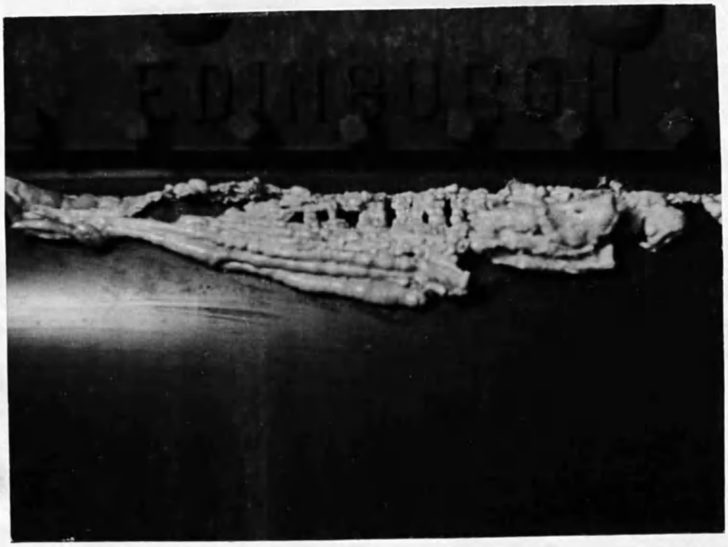
The effect of the presence of this precipitate during roller drying was very unfavourable. Table 25 gives the results of a series of trials in which varying quantities of lime were added to the whey. It will be seen that

Table 26

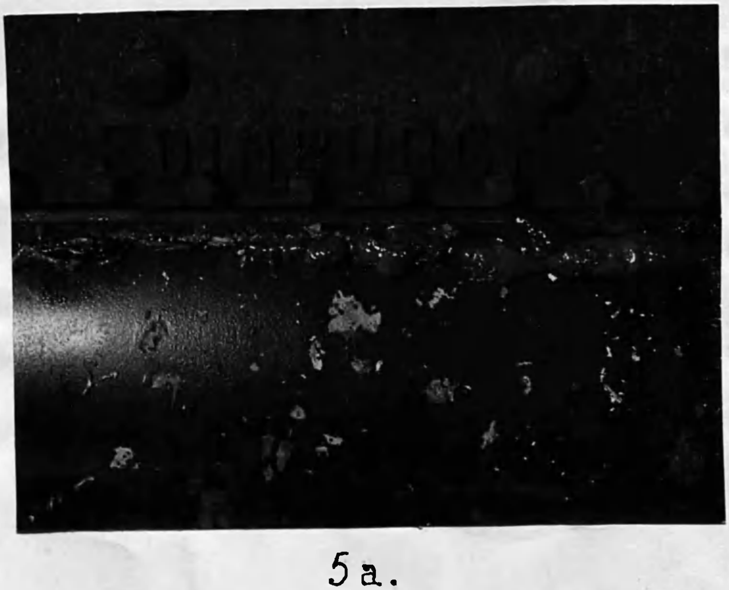
Acetic Acid Whey.

Original acidity %	Reduced with lime to: %	Moisture content of dried whey %	Drying properties	Reconstituted whey (10 g. in 100 ml. water)					
				Acidity %	pH	Taste	Colour	Solubility Index 20°C	50°C
0.42	-	4.12	Excellent	0.06	6.73	Very good	Greyish-brown at first; on standing, yellow.	99	99
0.40	-	-	"	0.08	6.63	"		-	-
*0.40	-	-	"	0.08	6.61	"		-	-
0.40	0.29	6.18	"	0.02	6.98	Good, but slightly stale		96	96
0.42	0.25	5.54	"	Alkaline	7.70	"		97	98
0.42	0.15	-	"	"	7.70	"		-	-

*kept 24 hours before drying.



5b.



5a.

progressive neutralisation to an acidity of 0.18% gave increasingly satisfactory drying properties. Further neutralisation was, however, accompanied by precipitate formation and a marked deterioration in drying properties. The flocculent precipitate passed from the roller trough on to the roller surfaces, covering them with irregular flocks or patches of white coagulated material. At the same time the whey film collected and revolved at the knife edge without drying, becoming progressively darker in colour (see Plate 5a).

It will be noticed from Table 25 that the reconstituted product invariably had an acid and bitter taste. In general it can be described as definitely unpalatable, although it may be relished by live stock when masked in a food mixture.

(ii) Acetic Acid Casein Whey.

It has already been noted that the proximate composition of whey from acetic acid casein is practically identical with that from hydrochloric acid casein. The drying properties were, however, found to be entirely different as will be seen from Table 26. Although the initial acidity of the whey was 0.40% to 0.42%*

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*With acetic acid this acidity was found to be sufficient for precipitating all the casein from skim milk at 110°F (44°C). With hydrochloric acid the acidity required was 0.45%-0.50%. Slow pre-heating of the acid whey above 80°C causes precipitation of the protein.

no difficulty was experienced in drying without the addition of a neutralising agent (Plate 5b), and the final acidity (determined in the reconstituted product) was found to have fallen to 0.06%-0.08%. The acetic acid had apparently been vapourised by contact with the heated rollers during the period of heating in the roller trough, so that the liquid behaved in a manner similar to low acidity cheese whey. This explanation receives interesting confirmation in the fact that when calcium hydroxide was added prior to drying in order to reduce the initial acidity of the whey the dried product was found to be markedly alkaline, i.e. vapourisation of free acetic acid had taken place and the presence of excess of the undissolved suspension of lime had resulted in the over-neutralisation of the powder.

It would appear possible, from the results shown in Table 26, to arrange for the addition of lime in quantities just sufficient to neutralise the residual (non-volatile) acidity. It was in fact found that the addition of 0.04% of lime to whey of 0.40% acidity produced an exactly neutral dried whey. A further point of interest is that the samples of the acetic acid casein whey which had been kept for 24 hours before drying showed as good drying properties as the fresh whey. Moreover the lactose content had not fallen, as was the case with hydrochloric acid casein whey.

The reconstituted whey from all the acetic acid casein whey powders (particularly from the unneutralised whey) was quite palatable and the taste very similar to that of ordinary cheese whey. The usual saltiness of cheese whey was, however, naturally lacking.

Thus it will be seen that it is very much easier to dry the whey obtained by precipitating casein with acetic acid than that resulting from the hydrochloric acid precipitation. With the former, unneutralised whey can be fed directly to the rollers to give an easily dried product of good appearance, very low acidity and palatable taste. With hydrochloric acid whey lime must be added to reduce the acidity to a critical limit (which is easily overstepped) below which a precipitate is formed and the drying properties ruined, while the taste of the partially neutralised dried whey is distinctly acid and bitter.

General Properties of the Casein.

In general appearance the casein produced by acetic acid precipitation is essentially similar to the hydrochloric acid casein and the viscosity of a 0.1% solution in N/100 sodium hydroxide of the two types was very similar (1.29 and 1.23 c.p. respectively, at 18°C). The ash content of the casein precipitated by acetic acid was considerably higher (4.38%) than that of the hydrochloric acid casein (2.28%), which is probably due to the more flocculent nature of the latter on precipitation, allowing more thorough washing.

The Utilisation of Dried Acid Casein Whey.

If the casein is precipitated by means of the acetic acid, there seems no reason why the dried whey should not take its place beside dried cheese whey as a product suitable for human consumption. Unfortunately the casein used by certain industries must be precipitated by hydrochloric acid and so the dried whey, if partially neutralised with lime and dried as outlined above, would possess a bitter taste unsuitable for inclusion in food for human consumption but probably palatable to animals. (Witness the feeding of acid silage and urea to dairy cattle). Apart from this outlet there seems no reason why acid whey could not be used in the manufacture of lactose since a neutraliser is always added at an early stage and any protein precipitate removed by filtration. It has in fact been suggested(47.48) that this protein-salt precipitate is itself a suitable cattle food.

In Germany a considerable amount of work has been done on the utilisation of dried whey as an animal food. Several workers(49,50,51) give data for such experiments, usually on pigs, and agree that a quantity up to as much as 75% of the cereal constituent of the feeding ration can be replaced by dried whey.

Thus if acid casein whey was dried instead of at present run to waste a valuable by-product suitable for either human or animal consumption, according to its method of manufacture, would be available.

Summary.

1. Experiments have been carried out in order to determine the best method of neutralising cheese whey prior to drying by the roller process. The use of sodium or potassium compounds leads to difficulties in drying and the production of an unpalatable product of poor quality. Neutralisation with calcium hydroxide gives a satisfactory product. Over-neutralisation must be avoided.
2. Complete neutralisation of hydrochloric acid casein whey results in the formation of a flocculent precipitate and deterioration in the drying properties; reduction of the acidity from 0.48% to 0.18% by the addition of calcium hydroxide allows successful drying and yields a reasonably satisfactory product. The latter is, however, definitely unpalatable.
3. Acetic acid casein whey can be dried without any previous neutralisation to yield an excellent,

palatable product.

4. The casein precipitated by acetic acid had a similar viscosity in dilute sodium hydroxide solution to that precipitated by hydrochloric acid but a considerably higher ash content.
5. Dried acid casein whey could probably be incorporated in the feeding ration of pigs, cattle and poultry as a substitute for cereals.

Part IV. Factors Affecting the Solubility of Milk Powders.

The Effect of Temperature and Moisture Content.

This work was planned to continue and supplement that begun by Wright(6) and reported in 1932. In that paper, the results of an enquiry into the effect of heat on the solubility of milk proteins were given, with special reference to their applicability to the process of roller drying. By raising the moisture content of the spray dried skim milk powder to 13.3% and storing it at temperatures ranging from 16-64°C it was possible to establish a curve showing the effect of temperature on that denaturation of the protein which leads to insolubility in milk powder. The conclusion reached was that, as heating temperature increased the length of time required to produce protein insolubility decreased logarithmically. Moreover, although these results were obtained from storage experiments there was reason to believe that they were entirely applicable to the roller drying process of milk powder manufacture. Since in this process it is likely that a certain amount of heating of the already dried milk film occurs, Wright next studied the protein denaturation occurring in spray dried skim milk powder of normal moisture content

(3%) when held for varying times at temperatures ranging from 100-140°C, which represent the maximum likely to be met with in roller drying practice. Again it was found that as the temperature of storage increased, the time necessary to produce protein insolubility decreased logarithmically but at this normal moisture content of 3%, the process was much slower. Thus, at 100°C 50% protein insolubility was produced in the powder of 87% total solids (13% moisture) in less than one second whereas with 97% solids (3% moisture) 20 hours heating was necessary. In a preliminary experiment Wright had found that with only 28% solids, at 100°C the same degree of protein insolubility had occurred in 30 minutes. Hence there are two conflicting trends, in one, as the total solids content rises (20-87%), the time at any one storage temperature required to produce a given protein insolubility decreases, whilst on the other hand, a further increase of total solids from 87% to 97% led to an increase in the length of heating time required. This suggests the existence of some critical total solids concentration (or moisture content) at which the rate of reaction of protein denaturation undergoes an abrupt reversal of sign. Although the changes noted above are taken to be physical rather than chemical such a change obviously required further investigation and a further series of experiments, described below, were designed to produce more information on this subject. Various workers had previously noted the accelerating effect which increased moisture content produced on insolubility of milk powders and Lampitt and Bushill$^{(54)}$ had concluded that a moisture content of 12-15% produced the maximum rate of protein denaturation. The temperature range (15-30°C) used by these authors did not rise to anything like the temperatures likely to be met with in the roller drying process. It thus appeared that a series of total solids concentrations ranging from that of the normal dried powder to some value overlapping the 87% used by Wright required to be stored over a wide range of temperatures to elucidate this problem.

Experimental.

To obtain a moisture content of 13.3%, Wright passed cold air previously saturated with steam over the dry milk powder for one and a half hours. So long as the temperature of the powder was not allowed to rise the gradual increase in moisture would not cause any appreciable amount of protein denaturation prior to storage, but in the present experiments, where moisture contents up to 20% were desired the length of time required by this method made it necessary to adopt a slightly different technique.

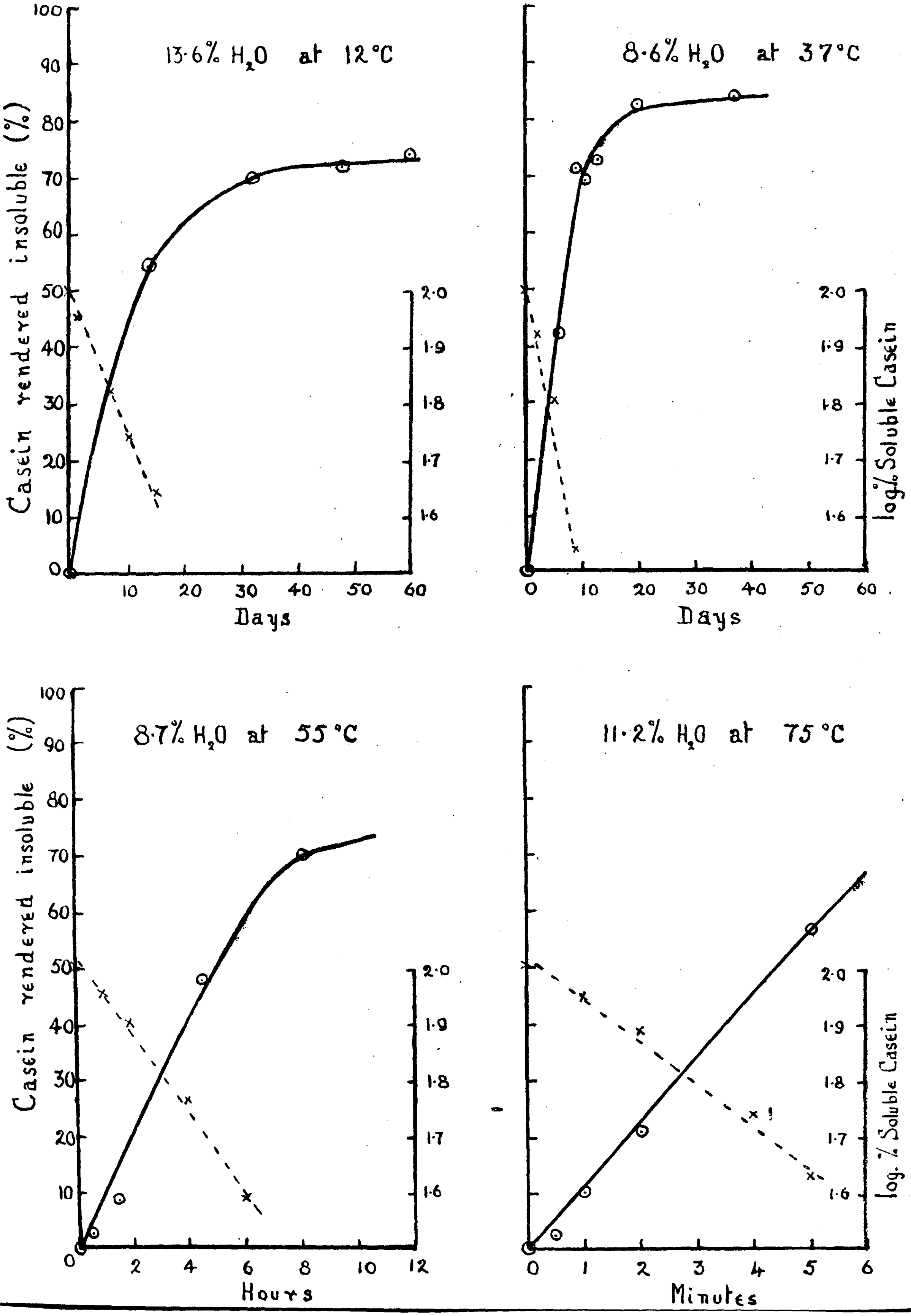
Steam was passed into the base of a rectangular chamber fitted at the top with an outlet connected to a water vacuum pump in order to cause regular circulation of the steam from bottom to top. A series of metal shelves, perforated with a number of half inch holes, caused the steam to diffuse regularly throughout the whole chamber. The powder, in 20 g. lots, was spread in a thin even layer over a tinned metal tray of surface area 300 sq. cm. The metal tray was pressed firmly on to the surface of a salt ice freezing mixture contained in a porcelain photographic developing dish, which was then placed on a shelf near the top of the steam chamber. Preliminary experiments showed that by suitable regulation of the amount of steam entering the chamber and by stirring the thin layer of powder at five minute intervals uniform moisture contents ranging from 5-20% could be obtained in from five to forty minutes, during which time the temperature of the powder did not rise above 4°C. The powder after being exposed to the steam for the requisite time (determined roughly by previous calibration) was transferred to a six ounce bottle, (rejecting the powder round the extreme edges of the plate) and shaken for three to five minutes by hand to provide complete mixing and, in the case of the high moisture content powders, to prevent any tendency of the powder to lump together. This technique produce powders of uniform moisture content which varied within quite small limits, typical figures for duplicate samples being 7.56 and 7.58% for a medium and 14.40% and 14.48% for a high moisture content powder.

In storing the powders, the very wide range of temperatures employed, from 12-100°C, necessitated the use of two techniques. For temperatures up to 37°C, the length of storage time before protein denaturation commenced was sufficient to allow the 20-30 minutes necessary for the powders to reach temperature equilibrium to be neglected. For storage at 47° and 55°C, the powder was brought rapidly to the storage temperature by vigorous agitation in the six ounce bottle in which it had been mixed in a water bath at a temperature higher than that required and then filled in equal amounts into small glass bottles for storage. This operation took about five minutes, and each bottle contained sufficient powder for one determination. At each examination of the powder, the bottle was removed from the incubator and placed in a beaker of water at the storage temperature until the sample had been weighed out. Above 55°C, a technique similar to that employed by Wright in the second part of his paper(6) was used. Briefly, this was to raise the temperature of a weight of powder equivalent to 2 g. of dry material to the desired storage temperature by placing it in the form of a thin layer between two substantial iron blocks (which acted as heat reservoirs) in an electric oven. Since the method of measuring solubility index requires only one gram of powder and a knowledge of its moisture content the method actually used was as follows. About 2 g. of the moistened powder was spread on a sheet of copper foil in a thin layer, covered by a similar piece, and heated for the correct length of time between the iron blocks. The blocks had previously been kept in the electric oven at the desired storage temperature for about 15-20 hours. After withdrawing the copper sheets from the oven the powder was immediately poured into a 15 ml. centrifuge tube and stoppered, all the powder in excess of 1 g. being used for a moisture determination in the usual manner. In this way any loss of moisture by the powder during the short heating period was known and could be allowed for.

In the first 50 or so examinations of powders of varying moisture contents, mostly at the lower storage temperatures, each sample was examined for moisture content, total nitrogen and casein solubilities of the powder reconstituted in water and the normal solubility index by the total solids method. Both Wright(6) and

Lampitt and Bushill(54) found no appreciable change in the solubility of the non-casein nitrogen constituents over the range of temperatures studied, and a similar result was reached from the samples examined to determine this in the present experiments, all the protein insolubility being attributable to the casein. By plotting casein insolubilities against solubility index, a straight line relationship was seen to exist. As will be seen from the analaysisof the powder, given later, the amount of casein present was 32.5%. If the whole of this casein became denatured and insoluble then the solubility index of the powder would be expected to fall to about 67.5%, so long as no other constituents were adversely affected. Similarly, in the untreated, completely soluble powder, all the casein was soluble and hence, plotting casein solubility against solubility index, a straight line connecting these two extreme points would give the relationship for intermediate states. The data gathered by actual protein analysis, when plotted in this manner was found to give a line almost coincident with the theorectical line. Actually for complete casein insolubility it indicated a solubility index of 65.0 instead of 67.5 which may be due to the slight insolubility of non-nitrogenous solids mentioned by Wright(6). This was so for powders of all moisture contents at a variety of temperatures.

Fig. 9a.


13·6% H₂O at 12°C
8·6% H₂O at 37°C
8·7% H₂O at 55°C
11·2% H₂O at 75°C
Casein rendered insoluble (%)
log % Soluble Casein
Days
Hours
Minutes
0
10
20
30
40
50
60
70
80
90
100
1·6
1·7
1·8
1·9
2·0
2
4
6
8
12
0
1
2
3
4
5
6
!

Thus the analytical work was considerably simplified in the powders stored at higher temperatures where the short period storage was more difficult due to the tendency to lose moisture, by reducing the examination of the powder to moisture content and solubility index in water at 20°C. 20°C was chosen in preference to reconstitution at 50°C as it gives a more delicate test of total protein denaturation, as previously mentioned (see p. 16).

Since the object of the experiment was to cause solubility changes, a powder of high initial solubility was necessary and a spray dried skim milk powder of the following composition was used:-

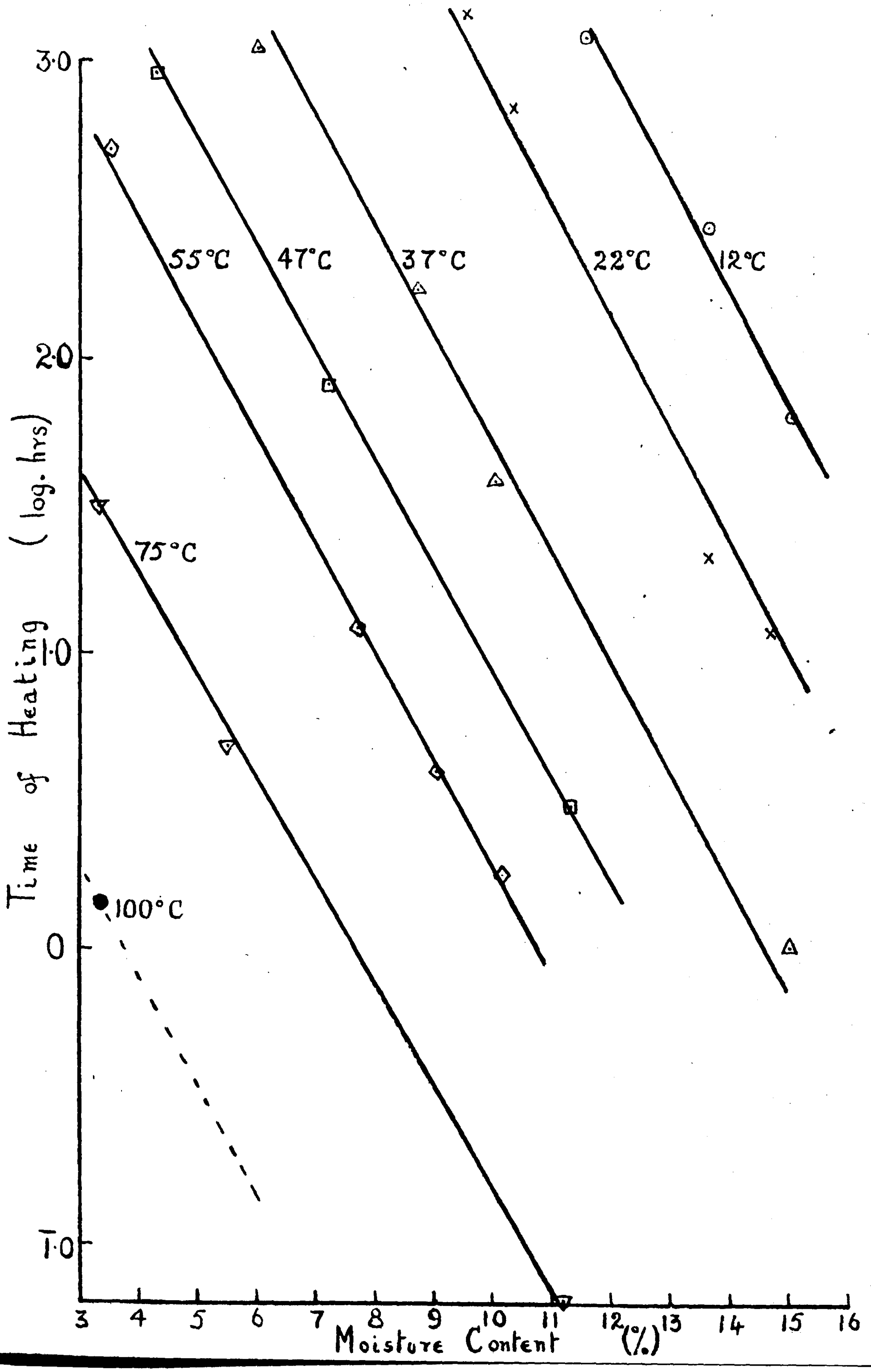
Moisture		3.3%
Fat		1.4%
	Casein	32.5%
Protein	Albumin + Glob.	4.4%
	Non-prot. N x 6.38	2.1%
Lactose (by diff.)		48.3%
Ash		8.0%

Solubility Index at 20°C = 102.

Results.

Following the example of the previous work the results for each sample were first plotted as a curve relating percentage casein insolubility to length of

Fig. 9.b


3·0
2·0
1·0
0
$\bar{1}$·0
Time of Heating (log. hrs)
55°C
47°C
37°C
22°C
12°C
75°C
100°C
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Moisture Content (%)

storage time for each moisture content and storage temperature. Typical curves for this, chosen at random, are given in Fig. 9a, and as would be expected, the length of time required to produce no further change in protein insolubility varied enormously; it will be seen, moreover, that the maximum casein insolubility produced was only 75-80%, agreeing with the results of previous workers(54 & 6). Since all the curves followed the same general trend, no attempt has been made to reproduce them, instead the length of time necessary to cause 50% casein insolubility has been read off and plotted on a graph the ordinates of which represent the logarithm of this storage time and the abscissae the moisture content of the powder. In this way a series of straight line curves have been obtained, each curve corresponding to one storage temperature. These are shown in Fig. 9b. It was found that heating powders of fairly high moisture content at 100°C by the hot block tenchnique caused very great loss of moisture within 10-15 seconds, so that a true casein insolubility - storage time curve could not be drawn. The only point obtainable at this high temperature was for the untreated powder of 3% moisture content which was stored in small stoppered bottles; here the time required for the powder to reach temperature equilibrium was not too great in relation to that required for 50% casein denaturation.

In Fig. 9b it will be seen that the slope of all curves is approximately the same, indicating that the acceleration of protein insolubility at all temperatures over the range studied for any given increase in moisture content is constant. From this data, 1% increase in the moisture content of a powder causes rather more than a halving of the time required for denaturation of half the casein; actually, the factor for the rate of reaction is 2.19.

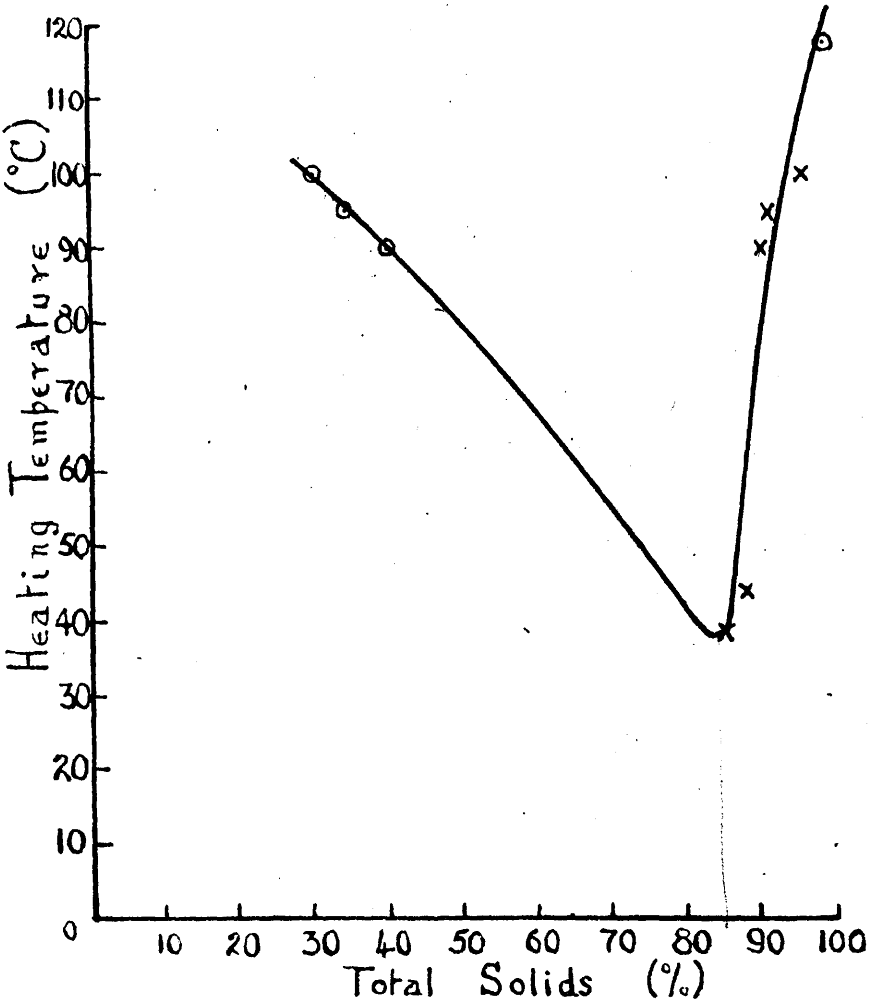
In order to make a comparison with the curve obtained by Wright for the effect of temperature on the time required to produce 50% insolubility in the casein constituent of a spray dried skim milk powder containing 13.34% moisture, a further series of curves have been constructed from the data embodied in Fig. 9b. Taking moisture contents at 3% intervals, starting from the moisture content of a normal powder, 3%, the time required to produce 50% casein insolubility has been read off each temperature curve, thus providing the data for a series of curves similar to that experimentally obtained and deduced by Wright(6). These are shown in Fig.10, where a comparison is made between the present curve interpolated for a powder containing 13.3% moisture and that previously found by Wright (broken line). It will be seen that the two curves, although not far apart are not coincident, the earlier curve fitting better the data for a powder containing 14% moisture.

This discrepancy may find an explanation quite outside the influence of moisture content.. It is well known that different batches of powder produced on the same plant may vary slightly in their physical and chemical characteristics due to the difficulty of maintaining identical working conditions from day to day in commercial plants. Hence if the powder used by Wright had suffered slightly more heat treatment during production than the one now in use, this would account for its greater ease of protein denaturation, and although both powders were made on the same plant, over seven years have elapsed, during which time slight improvements have definitely been made in powder manufacture. Probably of more importance than the actual position of the two curves in the series is the slope of the curves. The slope of each curve shows the effect of temperature on the rate of protein denaturation and below are given the factors for a 10°C rise in temperature for the series of moisture contents illustrated in Fig.10.

Fig. 11.

The Effect of Concentration on the Temperature required to produce 50% Casein insolubility in 30 minutes.

⊙ Wright. J. Dairy Res. 1932. IV. 122.



Moisture Content %	Acceleration due to 10°C rise in temp.
3	3.53
6	3.81
9	4.58
12	4.89
15	5.36
13.3	4.58
13.3 (Wright)	4.46

These figures indicate a definite increase in the effect of a 10° rise in temperature as the moisture content increases, a point which will be dealt with later. The reaction factors for the two curves at 13.3% moisture are substantially the same.

Discussion.

In the introduction to this section mention was made of the two apparently contradictory effects of rising total solids content on the rate of protein denaturation. A composite curve has been drawn in Fig.11 from all the data available on this problem, i.e. from Wright's (6) paper and that now reported. It shows the effect of total solids content on the temperature required to produce 50% insolubility of the casein in a heating period of 30 minutes. It is a curve singularly lacking in experimental points, particularly in the important minimal region but it is given as an aid to the possible explanation of the problem.

In Fig. 9a the broken line in each of the four figures shows the relation between logarithm of the concentration of residual soluble casein and the time of heating. In every case this was a straight line over the first part of the denaturation curve, indicating that the reaction is of the first order; similar results were obtained by Chick and Martin(57) for the denaturation of haemoglobin by heat. This confirms the analytical evidence that denaturation affects only the single constituent casein and since the changes in ionic concentration, which might in themselves lead to protein denaturation, are extremely small, the type of denaturation is probably that of complete re-arrangement of molecular structure. In the above experiments the three factors to be taken into account are the casein, water and temperature. There seems no doubt that it is the reaction between casein and water which causes the denaturation and that changes in temperature merely serve to change the rate of these reactions. Now if it be assumed that the casein molecule or micelle has to enter into some specific combination with the water molcules, the amount of protein denaturation at very low or very high total solids contents becomes more explicable. In liquid milk, the dispersal of the casein is at a maximum and although water is present in excess, the effect on the total solubility of the milk, even if all the casein becomes denatured, is small. At the other extreme, in the normal powder containing only 3% moisture the availability of water molecules to the casein to promote denaturation is at a minumum and at normal storage temperatures, as has already been shown does not produce any insolubility. As the storage temperature rises, the mobility of the molecules will be increased, offering more contacts between the casein and water resulting in increased insolubility. At intermediate concentrations of total solids in the milk or milk powder the chance of reaction between the two types of molecules in the dry powder will be greater and will have a proportionately greater effect on the solubility than in liquid milk, until at some critical concentration the effect of the combination of casein and water molecules on the solubility of the powder is a maximum. At this concentration the increased mobility of molecules arising from increased temperature is unnecessary and denaturation will occur at a minimal temperature. This then is a possible explanation of the curves shown in Fig. 11 where the standard amount of casein insolubility has occurred at a minimum temperature of about 40°C at a total solids concentration of about 15%. It may be recalled that Lampitt and Bushill(54) found a maximum rate of protein insolubility in milk powders containing 12-13% moisture.

In the above experiments little or no mention has been made of the difference in solubility of milk powders when reconstituted at 20 and 50°C. Wright(6) attributed this difference to two types of insolubility, reversible and irreversible. At 20°C the insolubility was a combination of the two, whilst at 50°C only the irreversibly denatured protein caused insolubility. It had been intended to investigate this theory more fully in the above experiments, but with the outbreak of war, more urgent problems arose and this somewhat academic work had to be curtailed.

Conclusions.

1. Increase in moisture content in milk powder leads to decreased solubility at all storage temperatures.
2. For any given moisture content, rise in storage temperature leads to increased insolubility, the rate of which varies with the moisture content of the powder.
3. A critical moisture content, probably about 15%,

exists at which rate of protein denaturation and consequent insolubility is at a maximum at all storage temperatures.

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