EFFECT OF pH ON KEEPING QUALITY OF SALTED BUTTER.

By G. G. CRITTALL, Dip. Ind. Chem., A.R.A.C.I., Dairy Research Branch.

SUMMARY.

Twenty-three groups of butters were made over a period of 11 months, each group consisting of three churnings of the same cream neutralized to different pH levels. An examination of the butters after cold storage for six months showed that butters in the more alkaline range (pH 7.8–8.2) had better keeping quality.

I. INTRODUCTION.

It was noticed in butter competitions conducted over several years under the auspices of the Australian Institute of Dairy Factory Managers and Secretaries that there appeared to be a tendency for butters of high pH to have better keeping quality. This is shown in Table 1, where results of five annual competitions have been compounded. Samples which showed such abnormalities as gross underworking, high copper content and high iron content, and abnormal bacteriological counts were excluded from the data because of the possible interference of these factors with keeping quality.

It was apparent, however, that there were many variables contributing to keeping quality and in the absence of their assessment it was difficult to obtain true significance.

The apparent tendency for butters with a high pH to have better keeping quality is contrary to overseas findings. McDowall, Smith and McDowell (1937), after exhaustively reviewing the literature and conducting experiments on butters with serum pH as high as 7·7, concluded that:—

(1) Butters with high pH readings show a high incidence of "neutralizer" flavours.

(2) No improvement in keeping quality is noted when the pH is higher than 7·0.

Experiments by Barnicoat (1947) gave results which showed that, after storage at 14, 35, 45, and 65 deg. F. for various periods up to 12 months, butters of pH 7·0–7·6 with 1·5 per cent. salt were no better than butters of pH 6·6–6·8 with the same salt concentration. Over-neutralized, salted butters tended to develop rancidity after prolonged storage.

In Queensland there has been a gradual tendency in recent years towards the manufacture of butters with higher alkalinity; of the 945 butter samples examined in the routine Butter Improvement Service during the year 1954–55, 247 (26 per cent.) had pH values greater than 7·9 (quinhydrone electrode) and 366 (39 per cent.) were in the range 7·6–7·9. This means that 65 per cent. of butters had pH values greater than 7·5. In spite of these relatively high alkalinities, the incidence of "neutralizer" flavour was negligible.

II. PRELIMINARY COMMERCIAL EXPERIMENTS.

Attempts were made to perform factory trials by subdividing and neutralizing cream to give various pH ranges. It was hoped that this work would provide information regarding the effect of pH on the keeping quality of the resultant butters.

The work was carried out on the following lines:—

(*a*) At three factories with tandem or triple vacreators and a good standard of hygiene, cream was subdivided and neutralized to give acidities corresponding to butter serum pH ranges 6·8–7·2, 7·3–7·7, and 7·8–8·2.

(*b*) Separate churnings were made from each portion of cream. In the manufacture of these butters a uniform rate of salting (1·3–1·5 per cent.) was aimed at, and care was taken to ensure that all butters were well worked.

Seven groups of butters were made in this way, but it was found that practical difficulties made it almost impossible to obtain reliable results. The main difficulties met were:—

(1) Some butters had a high copper and iron content which could have been responsible for any observed difference in keeping quality. Every attempt was made to reduce the metallic contamination of the butters to the same level, but under commercial factory conditions this was not possible.

(2) The attainment of the desired pH was found to be very difficult when using normal types of cream neutralizer. Much greater amounts of neutralizer than would be expected theoretically were found necessary to achieve a pH in the higher alkaline ranges, due probably to the buffering capacity of the cream or to the partial saponification of the fats.

It thus became apparent that a change in experimental technique was necessary in order to overcome the interference due to these factors.

III. EXPERIMENTAL CHURNINGS.

In the later work, smaller quantities of cream were used in one plant only, under circumstances which permitted the control of all factors which were found to interfere with the earlier experiments. Neutralization to give the desired pH in the final butter serum was obtained by preliminary acidity correction to 0·12 per cent. with normal commercial neutralizers, followed by pasteurization and subsequent adjustments with sodium hydroxide to give final acidities. In this way the buffering capacity of the cream was overcome.

Twenty-three groups of churnings were made and boxes of the butter examined after six months' cold storage at 10 deg. F. Three pats were also taken from each churning; two were examined fresh and one after storage for four weeks at approximately 50 deg. F. In order to provide information on the losses of butterfat in churning, fat tests were performed on cream samples taken from the churns and on the corresponding buttermilks.

(1) Methods.

(a) General.

The experiments were conducted at regular intervals from April 1954 to March 1955 at the Queensland Agricultural High School and College, Lawes. The cream used was a blend of choice and first quality, and the initial acidities varied from 0·16 to 0·47 per cent. Approximately 250 gal. of cream was neutralized to 0·12 per cent. acidity with sodium sesquicarbonate or sodium bicarbonate, pasteurized in a "Junior" vacreator at approximately 200 deg. F. (vacuums 14 and 27 in., water temperature rise 40 deg. F.), cooled in a heat exchanger, and held overnight in a stainless steel holding vat.

Prior to churning, all the cream was neutralized with 10N sodium hydroxide to 0·10 per cent., and one-third of this treated cream was churned. The remaining two-thirds of the cream was further neutralized with sodium hydroxide to approximately 0·04 per cent. and half this quantity was churned. Sodium hydroxide neutralizing solution was then added to the balance until it gave a faint pink colour with phenolphthalein indicator. This cream was then run into the same churn as was used for the previous two portions and churned in a similar manner. In this way three comparative churnings were made, each yielding about six boxes of butter. No break-water was used during churning, and efforts were made to keep the moisture and salt content uniform in each group.

Three pats were hand-cut from the butter during packing, two being used for grading and analyses while fresh, and one being stored at 50–55 deg. F. for one month. A box of 56 lb. from each churn was held in cold storage at 5–10 deg. F. for six months before examination.

(b) Analytical.

pH estimations were made on the centrifuged serum, using both a glass electrode and a quinhydrone electrode.

Peroxide values were determined, using the ferric thiocyanate method of Loftus Hills and Thiel (1946), with a chloroform-methanol solvent and a photoelectric colorimeter.

Moisture and salt were determined by the Kohman (1919) method.

Bacteriological analyses were carried out on duplicate samples by methods specified by Muller and Nichols (1950).

Microscopic examination, to give a measure of butter working by estimation of the number of moisture droplets larger than 30μ in diameter, was carried out, using the method of Muller (1952).

Copper and iron were estimated by the wet-ashing method of McDowell (1947).

(2) Results.

(a) Butter Flavour.

The losses in flavour points of butter in the three pH ranges are set out in Tables 1 and 2. These results show a marked trend in flavour score in that the neutral butters lost three times as many points as the very alkaline butters, and the slightly alkaline butters lost twice as many as the very alkaline butters. These differences were apparent after four weeks in storage and were maintained after six months' storage. It is significant that the neutral butters lost an average of more than three full points for flavour over the six months' storage period.

Table 1.

COMPARISON BETWEEN pH AND LOSS IN FLAVOUR SCORE AFTER COLD STORAGE FOR THREE MONTHS. (COMPETITION BUTTERS.)

—	pH Range (Glass Electrode).		
	6·8–7·2.	7·3–7·7.	7·8–8·2.
No. of Samples	48	61	44
Average Loss in Flavour Points	0·67	0·44	0·31

Table 2.

INFLUENCE OF pH ON BUTTER FLAVOUR AFTER COLD STORAGE.

—	pH Range (Glass Electrode).		
	6·8–7·2.	7·3–7·7.	7·8–8·2.
Average Loss in Flavour Score After 4 Weeks (pat)	2·3	1·5	0·8
Average Loss in Flavour Score after 6 months (box)	3·1	2·0	1·0

(b) Fat Losses.

Table 3 gives the results of butterfat estimations on the cream samples taken from 15 churnings and their corresponding buttermilks. Most of the fat tests on cream were determined by volumetric analysis, which, though not as accurate as the gravimetric method, does provide a useful guide. Although

Table 3.

INFLUENCE OF pH ON BUTTERFAT LOSSES.

—	pH Range (Glass Electrode).		
	6·8–7·2.	7·3–7·7.	7·8–8·2.
Average Fat Percentage in Creams	32·9	32·1	30·9
Average Percentage Fat Losses in Buttermilks	1·45	1·40	1·67

there was some evidence of a slightly greater dilution in the lower testing, more alkaline creams, appreciable differences in fat losses were recorded; these appeared to be related to pH. The fat losses were calculated from the Udy formula (McDowall 1953), and varied from 1·45 per cent. for nearly neutral creams to 1·67 per cent. for very alkaline creams.

(c) Peroxide Values.

Metallic contamination was in the ranges 0·10–0·20 p.p.m. copper and 0·7–1·5 p.p.m. iron. Peroxide values of butter of various pH values after six months' storage are shown in Table 4. No explanation of the wide range in peroxide values is offered. No correlation is apparent between pH and degree of oxidation. These findings confirm those of Muller and Ferricks (1953).

Table 4.

COMPARISON OF pH AND PEROXIDE VALUES.

	pH Range (Glass Electrode).						
	6·5–6·7.	6·8–7·0.	7·1–7·3.	7·4–7·6.	7·7–7·9.	8·0–8·2.	8·3–8·4.
No. of Samples	9	11	10	15	4	11	6
Range of Peroxide Values	·08–·52	·13–·63	·09–·50	·08–·45	·21–·35	·11–·32	·10–·32
Average Peroxide Value ..	0·22	0·28	0·25	0·25	0·28	0·21	0·20

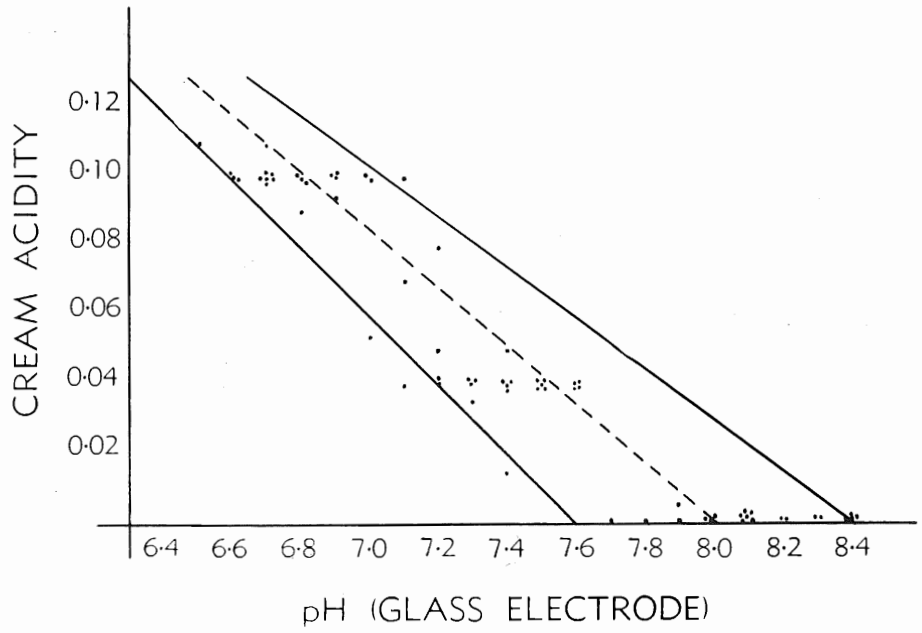

Fig. 1.

Relationship Between Final Cream Acidity and pH of the Butter Serum.

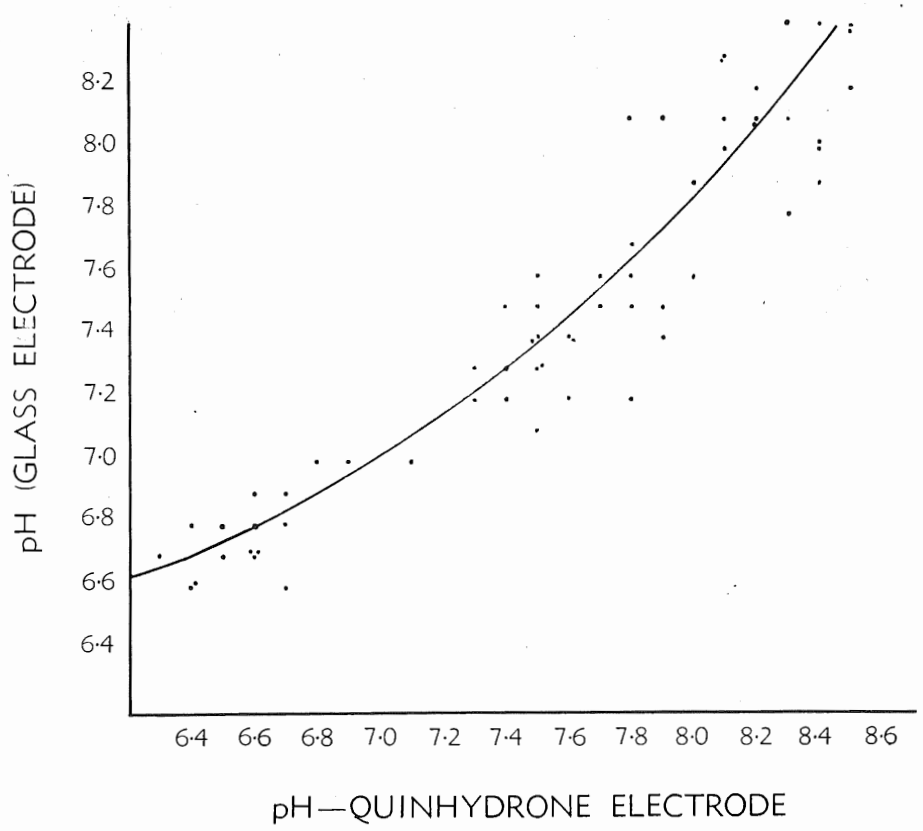

Fig. 2.

Relationship Between pH Determined by the Glass Electrode and pH Determined by the Quinhydrone Electrode.

(d) pH of Butter Serum.

The difficulties of neutralization to a desired pH level can be seen in Fig. 1. Cream acidities of 0·10 per cent. resulted in butters with serum pH readings varying from 6·6 to 7·1; in the highly alkaline ranges the variation is even greater.

pH determinations were made on all butters by using both glass and quinhydrone electrodes. The relation between the two is shown in Fig. 2. The quinhydrone electrode gives results fairly comparable with the glass electrode in the pH range 7·0–7·8, but results are somewhat lower than the glass electrode in the lower ranges and slightly higher in the more alkaline ranges.

(e) Bacteriological.

No correlation between pH and bacterial development after storage was evident. With butters in the low pH range a significant increase in plate count on milk agar was found in three cases, and in three other cases there was a significant decrease. In the case of butters in the alkaline ranges, five showed an increase in bacterial population after storage, and five a decrease.

(3) Discussion.

The results show a better keeping quality for salted butters in the alkaline pH range. It is significant that butters in this range lost an average of only one point for flavour after prolonged storage, while butters in the slightly alkaline and neutral ranges lost an average of 2 and 3 points, respectively. As good keeping quality is desirable for the United Kingdom market, it would seem preferable to produce a butter of high alkalinity, to stand up to the long storage periods necessary during shipment, provided, of course, that the butter is of sound quality initially. However, it also appears that some increases in fat losses occur during the manufacture of highly alkaline butter, and the extent of these losses may well militate against such manufacture.

It was thought before these experiments were commenced that severe neutralization might destroy some of the typical butter flavour, but no apparent significant difference in initial quality was found by the graders. The average flavour scores for the low, medium and high pH ranges were 92·1, 92·2 and 92·3 respectively. One case of "soda" flavour was noticed, but this was very slight and no loss in points score was sustained.

It is recognized that neutralization with sodium hydroxide is not a usual commercial practice. This alkali was used during the experiments for the sole purpose of ensuring more accurate neutralization for the higher pH ranges. The results did show an appreciable benefit in keeping quality for butters neutralized to "zero" with sodium hydroxide, and experiments are now being performed to find out if the usual neutralizing agents have a similar effect.

IV. ACKNOWLEDGEMENTS.

Thanks are due to Mr. L. L. Muller, B.Sc., formerly of this Department, now Technologist for the Downs Co-op. Dairy Association Ltd., and to Mr. W. D. Mitchell, B.Sc.Agr., of this Department, who co-operated in the initial field work; to Mr. D. F. Keith, of this Department, for grading the experimental butter; to the Queensland Cold Storage Co-operative Federation Ltd., for storing the butter; and to the Queensland Butter Marketing Board for purchasing the butters after storage. The assistance of the dairy factory staff at the Queensland Agricultural College in the manufacture of these butters is gratefully acknowledged.

REFERENCES.

BARNICOAT, C. R. 1947. N.Z. J. Sci. Tech. A29: 199.

KOHMAN, E. F. 1919. J. Industr. Engng. Chem. 11: 36.

LOFTUS HILLS, G., and THIEL, C. C. 1946. J. Dairy Res. 14: 340.

MCDOWALL, F. H. 1953. The Buttermaker's Manual, Vol. 2. p. 882.

MCDOWALL, F. H., SMITH, T. W. and MCDOWELL, A. K. R. 1937. N.Z. J. Sci. Tech. 19: 345.

MCDOWELL, A. K. R. 1947. J. Dairy Res. 15: 70.

MULLER, L. L. 1952. Aust. J. Dairy Tech. 7: 44.

MULLER, L. L., and FERRICKS, M. B. 1953. Aust. J. Dairy Tech. 8: 94.

MULLER, L. L., and NICHOLS, L. E. 1950. Aust. J. Dairy Tech. 5: 7.