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Keeping Quality of Butter in Relation to Its Copper Content*

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ABSTRACT

The cream having 42% fat was pasteurized at 85^0 C for 20 seconds in which copper was added as copper sulphate solution at the rate of zero, 100, 200 and 500 ug/kg. Salted (2%) butter was prepared from the cream having added copper and stored at –10^0 C and 6^0 C. The keeping quality of butter was studied for 20 weeks of storage period by chemical tests like Peroxide Value, FFA content and TBA value. The copper content of butter did not show any effect on FFA development and TBA values of butter during storage but Peroxide value was observed to be in most accordance with the copper content of butter. Similarly butter samples from four Dairies of Gujarat were collected to study its copper content and storagibility.

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INTRODUCTION

Butter is an important dairy product in the diet of Indian people, which not only provides palatability to food but also provides pleasing flavour and aroma. Hence it is necessary to retain desirable qualities of butter for an appreciable length of time as possible. However, quality of butter is affected by several factors among which copper plays most important role in deteriorating the butter quality by oxidative reaction. The extra quantity of the copper could be detected in milk and milk products more than naturally present could be due to insufficient care taken to prevent its contamination to milk and milk products from various sources like animal body, surface including udder, hands of milker, milking pails, seives, cans, milk pipelines, processing equipments to which it comes in contact and packaging materials. Several scientists had seen the effects of added and natural copper on quality of butter. Koops (1964) observed that butter which had low copper content (below 20 ug/kg) showed excellent storage properties while Pont and Britwistle (1966), Lavachev *et al.* (1971) and Luck (1972) observed butters having poor quality during storage were associated with higher copper content. McDowell (1964) and El-sadek *et al.* (1973) observed the effect of added copper on the quality of butter and they concluded that as the addition of copper increased (to cream) the resultant butter showed poor keeping quality. Menger (1964) observed that butter having high natural copper, as high as 100 ug/kg could be stored well for nine months but even addition of 25 ug/

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kg copper during butter making caused oxidative defects. He concluded that the natural copper was bound to the milk constituents in a different manner from that of added copper.

MATERIALS AND METHODS

Pasteurized cream (heated to 85° C/20 seconds and cooled to 4°C) was taken in 400 kg quantity for each trial. The cream was immediately analysed for acidity, fat and storch tests and found that fat (42.0 to 42.1%), Acidity (0.08 to 0.09% L.A.) and Storch (negative) tests were normal for five trials. For each trial cream was divided into four batches each amounting to 100 kg cream. Copper was added as solution of $CuSO_4$; $5H_2O$ (200 ug Cu/ml) at the rate of Zero (Cu_o), 100 (Cu_1), 200 (Cu_2) and 500 (Cu_3) ug Cu/kg of cream. Salted butter (2%) was prepared from these copper treated cream in silkeborg stainless steel butter churn having volumetric capacity of 300 litres. The working of butter was done to get 15% final moisture level in butter. The butter was packed in 250 gm slabs using Silkeborg wooden butter moulder. "Cryovac" was used as a packaging material throughout the study. Butter samples were stored at two different temperatures viz., -10 ± 2°C (T_1) and 6 ± 10 °C (T_2) for 20 weeks storage.

The samples of butter were tested during the storage period of 20 weeks at an interval of 5 weeks for Peroxide value (PeV), Free Fatty Acids ((FFA) content and Thiobarbituric Acid (TBA) value. PeV (m.eq./kg fat) of butter was determined by the "Ferric Thiocyanate Method" of Loftus-Hills and Thiel (1946) modified by Holloway (1966). FFA content (% oleic acid) of butter was determined by "Extraction Titration Method" of Deeth and Fritz Gerald (1976). TBA test used for butter was of El-Negoumy and Hammond (1962). "Spectronic 20" (Bousch and Lomb U.S.A.) was used to determine the optical density of colour developed in the PeV and TBA tests. Copper content of butter was determined as per the standard method prescribed by ISI (IS: 3507-1966) and also by Atomic Absorption Spectrophotometry (AAS) (Atomic Absorption Spectrophotometer, AA-120, Varion Techtron Co., Australia) at 3253 wavelength as per Willis (1964).

Butter samples from four different co-operative dairies of Gujarat were collected (coded as B_1, B_2, B_3 and B_4) and their copper content as well as storagibility tests were carried test

RESULTS AND DISCUSSION

The natural copper content of cream and butter have been shown in Table 1. The mean natural copper content in cream and butter by colorimetry were 490 and 162 ug/kg while that of by AAS were 403 and 138 ug/kg respectively. The butter prepared from cream added with Cu_1, Cu_2 and Cu_3 copper showed 182, 198 and 282 ug Cu/kg by colorimetry and 158, 183 and 255 ug Cu/kg by AAS respectively. The difference between copper content of butter samples of different treatments was found to be significant indicating that addition of copper to cream results into increased copper content of butter.

Peroxide Value:

The threshold peroxide value of all samples varied from 0.00 to 0.01

TABLE 1

Copper content of cream and butter (ug/kg) as affected by addition of copper to cream d method of analysis. (Mean of five replications).

Cream		*Copper added to cream*	*Butter*	
Colorimetry	*AAS*		*Colorimetry*	*AAS*
		—	162	138
		100	182	158
		200	198	183
490	403	500	282	255

when they were placed in store at −10° C. The PeV increased with the duration of storage period. The rate of increase of PeV was not similar in samples having different copper levels stored at −10° C. The PeV development was highest, 0.00 to 1.00 in the butter samples having Cu_3 level, while it was lowest, 0.00 to 0.36 in samples having Cu_0 level at −10° C during 20 weeks storage. Cu_1 level samples showed negligible difference in PeV that

TABLE 2

Peroxide value of butter as affected by copper content, storage temperature and storage period (m.eq./kg fat). (Mean of five replications).

Storage Period	*Storage Temperature*							
	−10° ± 2°C (T_1)				: 6° ± 1° C (T_2)			
	Copper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
S_1	0.06	0.07	0.07	0.12	0.16	0.18	0.24	0.41
S_2	0.14	0.13	0.20	0.32	0.40	0.43	0.63	1.01
S_3	0.25	0.26	0.37	0.62	0.77	1.01	1.22	1.95
S_4	0.36	0.37	0.64	1.00	1.10	1.39	1.83	3.16

of Cu_0 level. This indicates that if the samples are stored at −10° C, even addition of 100 ug Cu/kg to cream would not cause appreciable deterioration within 20 weeks storage mostly because of low storage temperature. However, when the samples of Cu_2 level were compared with Cu_0 and Cu_1 levels, higher PeV, 0.01 to 0.64 were noticed. But when the samples of Cu_2 level were compared with Cu_3 level, the Cu_3 level showed highest PeV compared to all others indicating significant role of copper in deteriorating the shelf life of butter.

Peroxide Values of Butter at 6° C:

The threshold PeV of all butter samples varied from 0.00 to 0.01. The PeV increased with the duration of storage period. The rate of increase of PeV was not similar in samples having different copper levels stored at 6°C. The PeV development was highest, 0.00 to 3.16 in butter samples having Cu_3 level while it was lowest, 0.00 to 1.10 in samples having

Cu_0 level at 6°C during 20 weeks storage. The Cu_1 level samples showed Cu_0 level samples. This indicates that even addition of 100 ugcu/kg to cream would cause appreciable deterioration within 20 weeks storage at 6°C. Cu_2 level samples showed 0.01 to 1.83 PeV development during 20 weeks. All levels of copper showed different rate of PeV development. The rate of PeV development was increased as the copper content and storage period of samples were increased.

Effect of Storage Temperature on PeV of Butter :

Storage temperature showed definite effect on keeping quality of butter as indicated by PeV of butter samples. All samples stored at -10°C showed lower PeV development than the samples stored at 6°C. The control (Cu_o) samples of butter stored at 6° C showed even higher PeV development, 0.00 to 1.10 compared to the PeV development, 0.00 to 1.00 in butter samples having Cu_1 level at -10° C during 20 weeks stroage period. The control butter did not show any difference in PeV development to that of Cu_1 level at -10°C but this was not the case at 6°C. This indicates that copper plays an important catalytic role in deterioration of samples stored at higher temperatures. While this effect can be minimized if the samples are stored at low temperatures.

Pont and Britwistle (1966) reported that as storage period of butter increased the P_eV of butter fat also increased. Jebson *et al.* (1974) observed that butter stored at 4°C showed higher PeV than the butter stored at -4°,-10" and -18°C. El-Hagarway *et al.*(1970) found that butter at 14°F (-10°C) was most suitable as determined by PeV. McDowell (1964) found that as the copper content of butter increased the rate of PeV development was also increased and the rate of PeV development was proportional to copper content. He observed that control butter showed 0.1 PeV and butter containing 0.6 ppm copper (added to cream) showed 1.8 PeV after eight months storage.

Free Fatty Acids (FFA)Content (% Oleic Acid) FFA Content of Butter at -10°C:

The threshold value of FFA content of all butter samples varied from 0.14 to 0.15%. The FFA content in butter samples increased with the duration of storage period. The rate of development of FFA in all butter samples stored at -10°C showed very small variation during storage of 20 weeks. The samples having Cu_o, Cu_1, Cu_2 and Cu_3 copper

TABLE 3

Free fatty acids content (% oleic acid) of butter as affected by copper content, storage temperature and storage period. ((Mean of five replications).

Storage Period	*Storage Temperature*							
	$-10^0 \pm 2^0$ C (T_1)				$6^0 \pm 1^0$ C (T_2)			
	Copper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.15	0.14	0.15	0.14	0.15	0.14	0.15	0.14
S_1	0.17	0.17	0.18	0.18	0.27	0.27	0.28	0.26
S_2	0.20	0.20	0.21	0.22	0.40	0.39	0.37	0.40
S_3	0.24	0.24	0.22	0.24	0.48	0.49	0.52	0.50
S_4	0.25	0.26	0.24	0.25	0.59	0.63	0.60	0.61

content showed FFA content of butter from 0.15 to 0.25%, 0.14 to 0.26%, 0.15 to 0.24% and 0.14 to 0.25% respectively after 20 weeks storage indicating copper content did not have any effect on FFA develpment in butter but the storage period showed definite effect on FFA content of butter samples.

FFA Content of Butter at 6°C:

The FFA content of freshly prepared butter samples varied from 0.14 to 0.15%. The FFA content of butter samples increased with the duration of storage period. The rate of increase in FFA content of all butter samples stored at 6°C showed very small variation during storage period. The increase in FFA content of butter samples during 20 weeks at 6°C were from 0.15 to 0.59%, 0.14 to 0.63%, 0.15 to 0.60% and 0.14 0.61% having Cu_o, Cu_1 Cu_2 and Cu_3 levels respectively indicating FFA development in butter was not affected by copper content.

Effect of Storage Temperature on FFA Content of Butter :

The rate of development in FFA content of butter was found to be higher at 6°C than at -10°C. This indicates that at higher temperature lipolysis of butter fat occurs at greater rate than at lower temperature, which indicates better shelf life at low storage temperature of butter.

Ibrahim *et al.* (1975) studied the effect of storage temperature on keeping quality of butter in relation to development of FFA and concluded that when butter was stored at -18°C and -10°C, the development of FFA was reasonably less compared to butter stored at 5°C. O'Connell *et al.* (1975) stated that though there was two fold increase in FFA at 5°C at 3 months storage of butter but at low storage temperature FFA level of buter was not increased significantly during storage.

Thiobarbituric Acid (TBA) Value:

TBA values of butter at -10°C.:

The threshold TBA values of all butter samples placed at -10°C varied from 0.30 to 0.31. No definite trend was noticed regarding TBA values for butter samples throughout the storage period. On the other hand, there was decrease in TBA value from fresh samples (0.31) to samples kept for 5 weeks (0.11). The TBA values were increased at the end of 10 weeks stroage period ranging from 0.33 to 0.47. The TBA values were again decreased, ranging from 0.14 to 0.24 at the end of 15 weeks and again increased at the end of 20 weeks ranging from 0.32 to 0.54. The TBA values showed inconsistent relation with that of storage period, but at definite storage period levels, TBA values were increased as the copper contents of butter samples were increased. Cu_0 level showed 0.11, 0.33, 0.14 and 0.32 TBA values and Cu_3 level showed 0.17, 0.47, 0.24 and 0.54 TBA values at the end of 5, 10, 15 and 20 weeks storage period respectively. This shows that TBA value of butter is affected by copper content.

TAB Values of Butter at 6°C:

The threshold TBA values of butter samples varied from 0.30 to 0.31. No definite trend in TBA values was observed for samples stored at 6°C. At the end of 5 weeks, TBA values were decreased, ranging from 0.18 to 0.27 and at the end of 10 weeks storage period, TBA values were increased ranging from 0.29 to 0.47. The TBA values were again decreased at the end of 15 weeks storage period ranging from 0.17 to 0.29 and again increased at the end of 20 weeks

TABLE 4

TBA value of butter as affected by copper content, storage temperature and storage period. (Mean of five replications).

Storage period	*Storage temperature*							
	$-10^0C \pm 2^0C$ (T_1)				$6^0 \pm 1^0C$ (T_2)			
	Copper treatment to cream							
	Cu_0	Cu_1	Cu_2	Cu_3	Cu_0	Cu_1	Cu_2	Cu_3
S_0	0.31	0.31	0.30	0.31	0.31	0.31	0.30	0.31
S_1	0.11	0.14	0.15	0.17	0.18	0.21	0.23	0.27
S_2	0.33	0.36	0.41	0.47	0.29	0.37	0.41	0.47
S_3	0.14	0.18	0.19	0.24	0.17	0.23	0.24	0.29
S_4	0.32	0.40	0.47	0.54	0.36	0.42	0.51	0.65

storage period ranging from 0.36 to 0.65. The TBA values showed inconsistent relation with that of storage period but at definite storage period levels, TBA values were increased as the copper content of butter samples increased. Cu_0 level showed 0.18, 0.29, 0.17 and 0.36 and Cu_3 level showed 0.27, 0.47, 0.29 and 0.65 TBA values at the end of 5, 10, 15 and 20 weeks storage period respectively. This shows that copper content of butter samples has definite effect on TBA values of butter.

Effect of Storage Temperature on TBA Values of Butter:

Storage temperature showed positive effect on TBA values of butter. Most of the butter samples stored at 6°C showed higher TBA values at respective copper level compared to -10°C.

Copper content in all butter samples of four co-operative dairies of Gujarat ranged from 150 to 170 ug/kg by colorimetry and 125 to 145 ug/kg by AAS.

FFA Content of Butter :

Collected samples of butter showed 0.23 to 0.42 % FFA. Samples B_1, B_3 and B_4 showed negligible difference (0.23 to 0.26) but B_2 showed 0.42% FFA content. There was negligible (0.29 to 0.58%) increase in FFA value for samples stored at -10°F but there was appreciable increase in FFA for those samples stored at 6°C (0.58 to 0.93%).

PeV of Butter :

Collected samples showed PeV from 0.3 to 0.16 but at the end of 15 weeks storage samples showed PeV ranging from 0.26 to 0.36 samples stored at 6°C PeV development from 0.69 to 1.20 in 10 weeks. The rate of increase in PeV was not similar in all butter samples at 6° C.

TBA Value of Butter :

TBA value of butter showed erratic fluctuations during 15 weeks storage period at both storage temperatures indicating limitations of TBA test as an index to measure oxidation of fat.

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