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Effect of Some Natural Antioxidants on Free Fatty Acid and Peroxide Value of Ghee During Storage

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ABSTRACT

Changes in free fatty acid (FFA) and peroxide value (PV) of ghee samples added with curry, betel and drumstick leaves at 1.0 and 3.0% levels were studied at an interval of one month during a storage period of 12 months at ambient temperatures. Their effects were compared with legally permitted levels of BHA, BHT and their combination. It was observed that only curry leaves could protect ghee from hydrolytic rancidity while betel and drumstick leaves, alongwith BHA, BHT or their combination, gave higher FFA values in comparison to control, the value being maximum in case of drumstick leaves. None of the natural antioxidants studied in the present investigation could protect ghee from oxidative deterioration and on the contrary, gave higher PV than control, while chemical antioxidants were effective in this respect. Lower favour and colour scores and lower colour score were obtained in ghee samples added with curry and betel leaves, respectively.

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INTRODUCTION

Ghee, a clarified butterfat, finds wide acceptance in Indian dietary and at present about one-third of milk produced in India is being converted into ghee (NAC-Report, 1976). The product, once made, is commonly stored at ambient temperature till finally used. During storage, it gets readily oxidized resulting in flavour determination, thereby causing market problems. Attempts have been made to prolong the shelf-life of ghee through addition of chemical antioxidants, (Kuchroo and Narayanan. 1973 : El-Emary *et al*, 1974; Chatterjee, 1977). Addition of BHA or BHT, either singly or in combination, at a maximum concentration of 0.02% has been legally permitted under PFA Rules. However, prolonged use of such antioxidants is reported to cause adverse physiological effects (Patel and Rajorhia, 1979). Therefore, use of a safe antioxidant is very much desired. The leaves of certain plants have exhibited antioxygenic property which has been attributed to the presence of phenolic fraction — 1, 2-dihydroxy 4-allyl benzene (hydroxy chavicol) in betel and curryl eaves (Sethi and Aggarwal, 1956; Soundararajan, 1958), ascorbic acid in betel leaves (Banerjee and Pain,

1936-37) and certain amino acids in curry leaves (Patel and Rajorhia, 1979).

On account of their antioxygenic effect, curry and betel leaves (Soundarrajan, 1958; Patel and Rajorhia, 1979) and drumstick leaves (Soundararajan, 1958) have been tried as natural antioxidants for prolonging the shelf-life of ghee. The results of studies have shown their potential as antioxidants. Therefore, a study was planned to investigate the efficacy of curry, betel and drumstick leaves as antioxidants and compare the same with chemical antioxidants, namely, BHA and BHT.

MATERIALS AND METHODS

Ghee was prepared from buffalo milk cream by creamery-butter method using a clarification temperature of 115° C. During conversion of butter into ghee, curry, betel and drumstick leaves were added at 1.0 and 3.0% levels (w/w). Ghee was filtered, filled in glass bottles upto brim, sealed and stored in dark at ambient temperatures (18 to 33° C) for a period of 12 months. For comparison, ghee samples containing 0.01 and 0.02% BHA, BHT and their combinations (50:50), added in filltered ghee at 70° C, were also prepared, filled and stored similarly. Ghee sample without any additive served as control.

The samples of fresh and stored ghee were subjected to chemical analysis for free fatty acid (FFA) content (ISI, 1966) and Peroxide value (PV) determinations (Holloway, 1966). During storage the samples were analysed at a regular interval of one month. The sample once opened for analysis at a particular month was discarded and not reused for analysis. Fresh ghee was also subjected to sensory evaluation to determine whether the antioxidants (both chemical and natural) impart any off-flavour and colour to ghee and thus affect acceptability of ghee.

RESULTS AND DISCUSSION

Flavour and colour scores of fresh ghee samples :

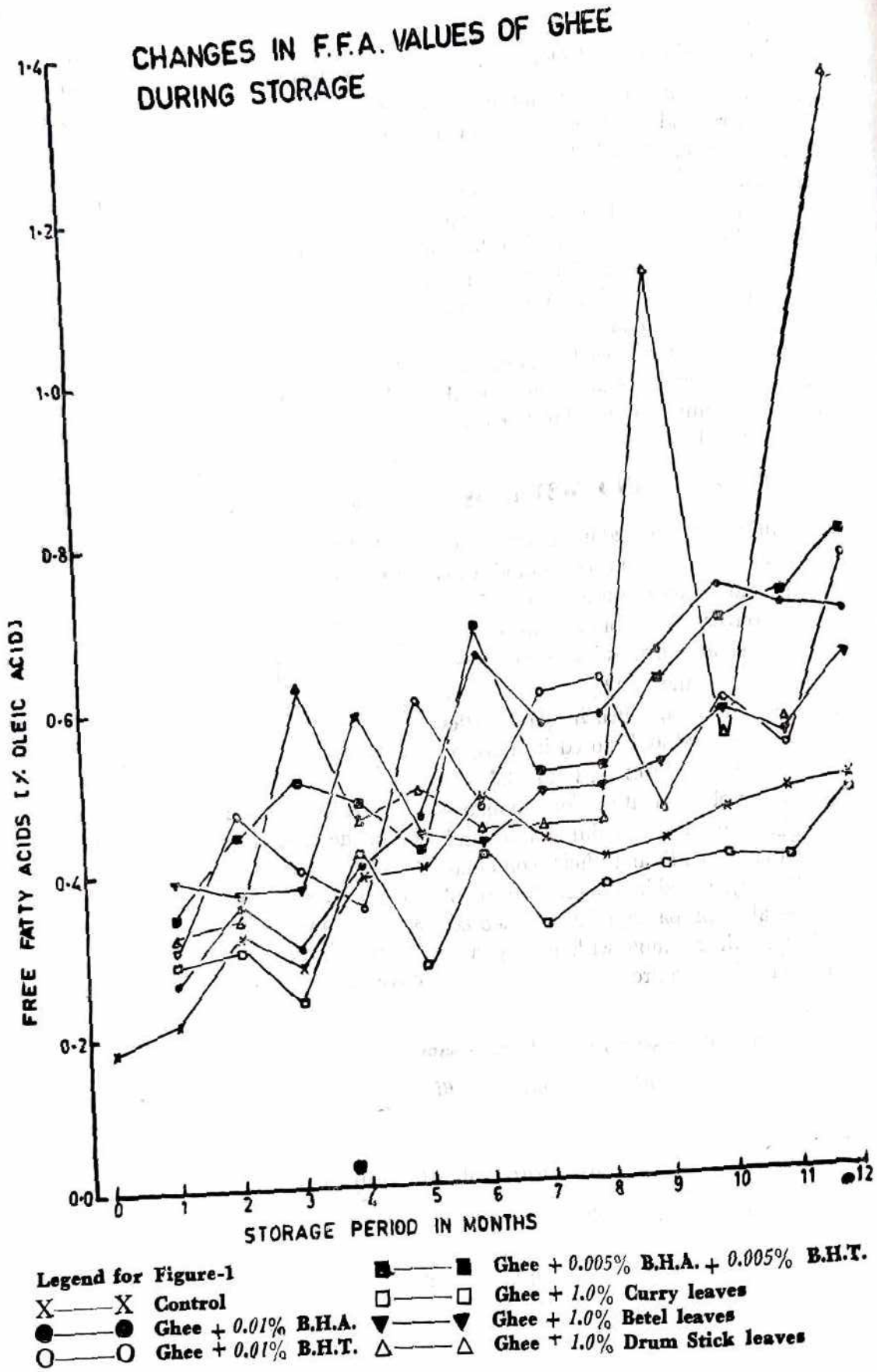
Soon after preparation, ghee samples were subjected to sensory evaluation by a panel of judges so as to know the effect of the additives on flavour and colour scores. The results are presented in Table-1.

It can be seen from the above that both, the control and ghee samples containing chemical antioxidants, were almost similar in their flavour and colour scores. However, flavour as well as colour scores of ghee samples added with curry eaves and colour score of betel leaves

TABLE 1

Flavour and colour scores of fresh ghee samples.

Attribute	*Control*	*BHA* %		*BHT* %		*BHA + BHT* %		*Curry leaves* %		*Betel leaves* %		*Drumstick leaves* %	
		0.01	0.02	0.01	0.02	0.01	0.02	1.0	3.0	1.0	3.0	1.0	3.0
Flavour Score (Max. 50)	46	46.5	46.5	46.5	46.5	45.5	45.5	42	38	46	46	45	45
Colour Score (Max. 10)	9.2	9.2	9.2	9.2	9.2	9.0	9.0	8	6	8.5	8.0	9.0	9.0


CHANGES IN F.F.A. VALUES OF GHEE DURING STORAGE
FREE FATTY ACIDS (% OLEIC ACID)
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0
1
2
3
4
5
6
7
8
9
10
11
12
STORAGE PERIOD IN MONTHS
Legend for Figure-1
X——X Control
●——● Ghee + 0.01% B.H.A.
O——O Ghee + 0.01% B.H.T.
■——■ Ghee + 0.005% B.H.A. + 0.005% B.H.T.
□——□ Ghee + 1.0% Curry leaves
▼——▼ Ghee + 1.0% Betel leaves
△——△ Ghee + 1.0% Drum Stick leaves

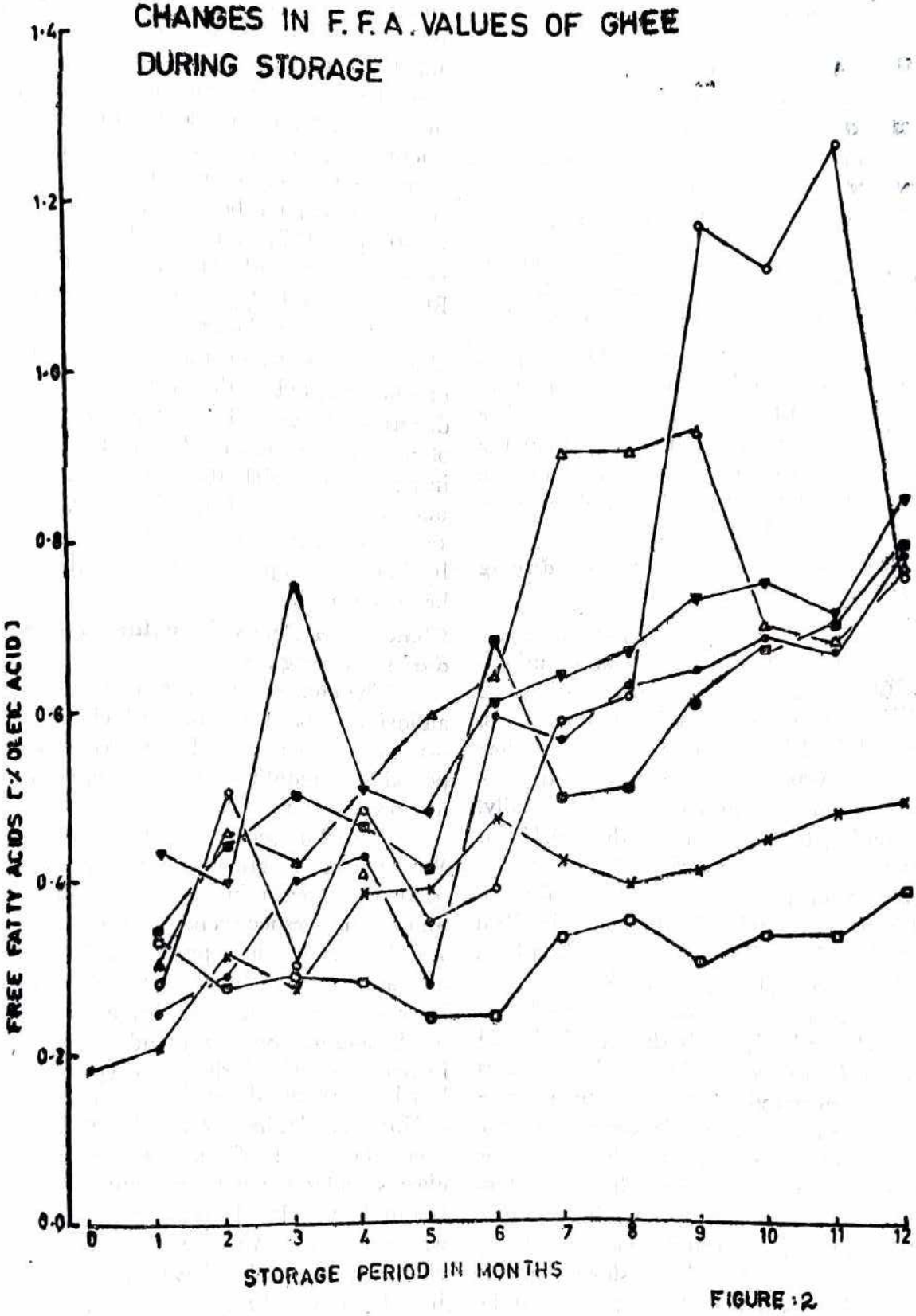

CHANGES IN F.F.A. VALUES OF GHEE
DURING STORAGE
FREE FATTY ACIDS (% OLEIC ACID)
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0·0
0
1
2
3
4
5
6
7
8
9
10
11
12
STORAGE PERIOD IN MONTHS

FIGURE : 2

Legend for Figure 2

X—X **Control**
●—● **Ghee** + *0.02%* **B.H.A.**
O—O **Ghee** + *0.02%* **B.H.T.**
■—■ **Ghee** + *0.01%* **B.H.A.** + *0.01%* **B.H.T.**
□—□ **Ghee** + *3.0%* **Curry leaves**
▼—▼ **Ghee** + *3.0%* **Betel leaves**
△—△ **Ghee** + *3.0%* **Drum Stick leaves**

—added with ghee samples were lower. This was attributed a typical flavour and yellowish to yellowish green tinge imparted by these leaves to the ghee samples. However, Soundararajan (1958), who studied addition of curry leaves to ghee at lower concentration (0.5%) than the present study, found no such adverse effect on flavour of ghee and samples had acceptable aroma.

Changes in FFA levels during storage:

Figure 1 and 2 delineate the changes in FFA levels of control and antioxidant-treated ghee samples during 12 months storage at ambient temperatures. The initial FFA content of all the ghee samples was 0.18% (oleic acid). In control sample the value increased gradually, reaching to slightly more than 0.4% at the end of storage period. Such increasing trend in FFA content of the untreated samples has been reported by Paul *et al.* (1949), Ramamurthy *et al.* (1968), Chatterjee (1977) and Wadhwa *et al.* (1979). The ghee samples treated with all the additives, both chemical and natural, showed higher FFA values than untreated control except in case of curry leaves. Curry leaves, at both the levels (1.0 and 3.0%), showed lower values than control throughout the storage period except in the initial stages. In contrast, durmstick leaves at 1.0% and BHT at 0.02% levels showed maximum FFA value of 1.3% at 12 and 11 months, respectively. The observations of the present study, barring those related to curry leaves, suggest that type and levels of antioxidants studied do not accord any protection to gradual increase in FFA content of ghee during storage at room temperature. Similar observations have been reported by Chatterjee (1977) and Lalitha and Dastur (1953) in ghee treated with 0.01% BHA and 0.02% ethyl gallate, respectively. Soundararajan (1958) has also reported small increase in acidity of ghee treated with curry, betel and drumstick leaves. The protective effect of curry leaves observed in this study is in accordance with the results of Patel and Rajorhia (1979). However, protective effect of betel leaves as reported by Patel & Rajorhia (1979) could not be confirmed.

Changes in Peroxide value of ghee during storage:

The changes in PV of control and antioxidant (both natural and chemical) —treated ghee samples stored for a period of 12 months at room temperature are presented in Table-2.

It can be seen from the table that PV of control ghee sample increased gradually, becoming almost double and triple respectively at the end of 7 and 9 months, then progressively increased at faster rate showing an eight-fold increase over fresh samples at the end of 12 months. Similar trend in rate of increase in PV of ghee during storage has been reported by Gaba and Jain (1975) and Wadhwa *et al.* (1979). However, the trend of increase in PV of ghee samples treated with antioxidants (natural and chemical) in present study was irregular. An irregular trend of change in PV of ghee has been reported by Chatterjee (1977).

TABLE 2

Changes in peroxide value of ghee during storage.

Sr. No.	*Type of sample*	*Peroxide value (Mililequivalent per kg of fat)*												
		Storage period in months												
		0	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*
1	Control	0.342	0.467	0.556	0.431	0.503	0.407	0.527	0.659	0.959	1.001	2.253	2.241	2.924
2	Ghee + 0.01% BHA	0.342	0.359	0.731	0.515	0.623	0.479	0.671	0.911	0.910	0.863	1.809	1.893	1.318
3	Ghee + 0.02% BHA	0.342	0.431	0.611	0.444	0.754	0.395	0.431	0.767	1.003	1.001	1.702	1.896	1.510
4	Ghee + 0.01% BHT	0.342	0.503	0.623	0.551	0.761	0.551	0.647	0.718	1.001	0.863	1.768	1.560	1.069
5	Ghee + 0.02% BHT	0.342	0.479	0.575	0.503	0.671	0.395	0.611	0.935	1.281	1.078	1.870	1.676	1.222
6	Ghee + 0.05% BHA 0.005% BHT	0.342	0.527	0.586	0.522	0.562	0.503	0.556	0.671	0.935	0.982	1.702	2.025	1.38
7	Ghee + 0.01% BHA + 0.01% BHT	0.342	0.455	0.658	0.546	0.575	0.503	0.743	0.743	0.959	0.994	1.582	1.534	1.126
8	Ghee + 1.0% Curry leaves	0.342	1.486	1.798	2.564	2.219	1.761	3.571	3.608	4.428	3.786	—	—	—
9	Ghee + 3.0% Curry leaves	0.342	2.492	4.001	4.457	4.457	2.230	4.014	4.290	4.457	4.457	—	—	—
10	Ghee + 1.0% Betel leaves	0.342	1.174	1.473	1.534	1.941	1.126	3.075	2.157	4.050	3.457	—	—	—
11	Ghee + 3.0% Betel leaves	0.342	1.941	1.516	3.068	3.092	1.701	4.014	4.230	4.113	4.457	—	—	—
12	Ghee + 1.0% Drumstick leaves	0.342	0.911	1.042	1.436	1.210	1.248	3.014	1.834	3.571	3.125	—	—	—
13	Ghee + 3.0% Drumstick leaves	0.342	1.030	1.378	1.582	1.462	1.318	3.127	2.780	3.787	3.451	—	—	—

The PV of ghee samples treated with natural antioxidants was higher than the control throughout the storage period of 12 months. This shows that the natural antioxidants studied in the present investigation were ineffective in protecting the ghee from oxidative deterioration. Soundararajan (1958) reported almost same PV in control as well as betel (0.2% and drumstick (0.5%) leaves - treated ghee samples after a storage period of 140 days at room temperature. However observations regarding efficacy of curry leaves as antioxidant are contrary to the result of Soundararajan (1958) and Patel and Rajorhia (1979). This could probably be attributed to differences in the temperature of clarification used in the present study. Soundararajan (1958) clarified ghee at 130°C while treating it with 0.5% curry leaves in comparison to control which was only heated to 122°C. It is possible that the higher temperature might have contributed to the increased shelf-life of curry leaves treated ghee samples over the control. Patel and Rajorhia (1979) clarified ghee at 120° C. The higher temperature of clarification has been reported to improve the shelf-life of ghee through increased phospholopids content (Ramamurthy *et al.* 1968) and carbonyl contents (Singh *et al*, 1979).

In contrast to natural antioxidants, the chemical antioxidants used in the present study have superior performance with regard to protection against oxidation. BHA and BHT, when added singly or in combination at both the levels, showed almost equal effect in protecting the ghee. However, upto about 9 months storage, increase in PV of control and ghee samples added with these antioxidants were almost parallel. Subsequently, the PV of control sample increased at faster rate than the samples treated with chemical antioxidants. The PV of chemical antioxidants — treated samples at the end of 12 months storage were almost half than that of untreated sample showing its beneficial effect on long storage. Similar protective effect has been reported by Kuchroo and Narayanan (1973). However, superiority of BHT and its combination with BHA over BHT alone could not be confirmed.

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