6-1977

Control of oxidation in butteroil

Dilip Narendra Patel

To the Graduate Council:

I am submitting herewith a thesis written by Dilip Narendra Patel entitled "Control of oxidation in butteroil." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Food Science and Technology.

H.O. Jaynes, Major Professor

We have read this thesis and recommend its acceptance:

S.L. Melton, C.C. Melton

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Dilip Narendra Patel entitled "Control of Oxidation in Butteroil." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Food Technology and Science.

H. O. Jaynes
Major Professor

We have read this thesis and recommend its acceptance:

Curtis C. Melton

Sharon L. Melton

Accepted for the Council:

L. Evans Roth
Vice Chancellor
Graduate Studies and Research

CONTROL OF OXIDATION IN BUTTEROIL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Dilip Narendra Patel

June 1977

ACKNOWLEDGMENTS

The author wishes to express his sincere feeling of indebtedness and gratitude to the chairman of his graduate committee, Dr. H. O. Jaynes, for his valuable guidance, suggestions and friendship during the course of the author's graduate studies. Grateful acknowledgment is also extended to the other graduate committee members, Dr. S. L. Melton and Dr. C. C. Melton, without whose generous assistance and encouragement this thesis would have not been possible.

The author expresses appreciation to Dr. W. I. Sanders for his advice and assistance with the experimental design and statistical analysis of the research data. Appreciation is also extended to Dr. W. W. Overcast for his suggestions and as a graduate committee member for a short time. Special thanks are certainly due to Mrs. Ann Helms for her assistance and suggestions in the laboratory and to Mrs. Ola Sanders for her suggestions in the sensory evaluation of the samples.

The author extends his thanks also to those faculty and staff members and students who participated in the sensory evaluation of the samples.

The author dedicates this thesis to his mother and father.

ABSTRACT

The objective of this study was to evaluate the effectiveness of alpha tocopherol and ascorbyl palmitate as antioxidants for butteroil stored at 45° C.

Butteroil samples were treated with ascorbyl palmitate and alpha tocopherol separately and in combination. Treatment levels were: 100 ppm alpha tocopherol, 200 ppm alpha tocopherol, 500 ppm ascorbyl palmitate, 500 ppm ascorbyl palmitate plus 100 ppm alpha tocopherol and 500 ppm ascorbyl palmitate plus 200 ppm alpha tocopherol. The control was butteroil without any additives. The treated samples were stored at 45° C in an oven which excluded light.

At intervals of 15, 30, 45 and 60 days the samples were tested subjectively and objectively by sensory panels and measuring the peroxide value, respectively.

This study showed that alpha tocopherol did not retard oxidation in the butteroil but acted as a pro-oxidant. Ascorbyl palmitate and combinations of alpha tocopherol and ascorbyl palmitate successfully retarded the oxidation.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER I

INTRODUCTION

The United States of America imports about 1.2 million pounds of butteroil annually (8) which is mainly used in ice cream mix. Some of the Asian countries also import butteroil in large quantities, but due to poor storage facilities it becomes oxidized. Low storage temperature and/or a proper amount of antioxidants in butteroil could retard oxidative changes to a certain extent.

Alpha tocopherol and ascorbyl palmitate have been found to have good antioxidative properties in butterfat (23). High concentrations of alpha tocopherol are pro-oxidative. Therefore, it is necessary to determine an optimum level of this antioxidant required to retard oxidative changes.

Tocopherols, also known as vitamin E, are natural antioxidants found in vegetable oils. They are cyclic compounds with a hydroxyl group and heterocyclic oxygen. Tocopherols are easily oxidized to quinones in the presence of oxygen and thus prevent oxidation of unsaturated fat.

Ascorbyl palmitate functions by oxygen scavenging, an entirely different mechanism. Ascorbyl palmitate is not found in nature even though it is physiologically acceptable and it has been listed as G.R.A.S. (Generally Recognized as

Safe), a category of approved food additives established by the Food and Drug Administration (14).

CHAPTER II

LITERATURE REVIEW

I. BUTTER AND BUTTEROIL

The word butter is used in Genesis, in the Song of Solomon, and in other Biblical writings (22). References are made in ancient writings to the use of butter as a food in India between 2000 B.C. and 1400 B.C. The Greek, Solon, (638-559 B.C.) refers to a peculiar fat obtained by agitating milk (13,20).

Wilster (30) describes ghee, butterlard, butteroil and dry butterfat as the products consisting of butterfat almost completely free from the water, protein, milk sugar (lactose) and mineral substances present in normal butter. In the field of dairy science the terms butterfat, butteroil, milkfat, dry milkfat and anhydrous milkfat are often used interchangeably. McDowall (20) defines butteroil as a commercial designation which is applied to the milk lipids containing 0.5% or less of moisture.

The United States of America imports about 1.2 million pounds of butteroil annually (8), which is mainly used in ice cream mix. Some of the Asian countries also import butteroil in large quantities and it is mainly used in reconstituted milk, but due to poor storage facilities it

becomes oxidized (24). Low storage temperature and/or proper amounts of antioxidants in butteroil could retard oxidative changes to a certain extent.

The methods employed for the production of butteroil as stated by McDowall (20) and Jenness and Patton (15) on a large scale may be divided into four main classes. The first and simplest method is the direct heating of butter till it is free from water. This is accomplished at atmospheric pressure or at low pressure in a vacuum pan. By a second method butter is melted and allowed to stand for some time or until the fat clears. The fat is then decanted off from the top. Centrifugal separation of the melted butter is another method of producing high quality butteroil. Direct centrifugal separation of butteroil from cream is achieved by breaking the cream emulsion. A high speed centrifugal pump and an agitator-heater separates 90-98% of the fat directly from the cream. The remaining water is removed by a second separation or through a dehydrator.

Packing of butteroil is very important in preserving its freshness. Wilster (30) reports the use of 55 gallon steel drums with a sanitary coating as suitable for protection of the product for bulk storage. Wooden barrels of 50-60 gallon capacity are equally good if the headspace air is reduced to minimum. Also tinned steel cans which are hermetically sealed and brown glass jars which exclude ultraviolet light are ideal for small scale packaging (30).

II. KEEPING QUALITY OF BUTTEROIL

Butteroil free from suspended moisture is immune to microbial attack, but when more than 0.3% of water is present mold growth can develop causing a musty and rancid flavor (28). If butteroil is free from water the only deterioration to which it is readily subject is oxidation with the development of tallowy flavor and frequently bleaching of the color (27).

Butteroil is more subject to oxidative deterioration than butter because a portion of the antioxidants present in the butter, e.g., the phospholipid protein complexes, are lost into the butter serum (15,20).

Butterfat prepared in New Zealand and packed in four-gallon metal containers with zero headspace has been found to remain in good condition over six years at room temperature (21). Oxidative changes are detected by the peroxide and fat aldehyde tests, but usually the human palate is a more sensitive detector of incipient oxidation than are these tests (30). McDowall (20) and Wilster (30) recommend using fresh cream or butter for the production of good quality and long-lasting butteroil.

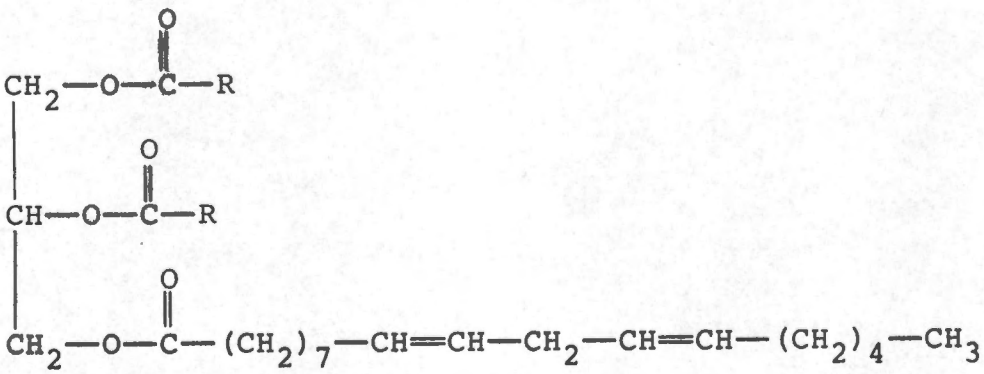
III. OXIDIZED FLAVOR

The most important single flavor defect of milk and a number of its products, including butteroil, is oxidized

flavor (9,12). Such terms as cardboard, metallic, oily, tallowy, painty, fishy and mushroom also are used to describe this off flavor (12,15,27). It seems probable that oxidized flavor is a general term that can be applied to a number of closely related off flavors (11,15). These off flavors have oxidation of lipid materials in common. However, the nature of the specific flavor compounds, their concentrations, their origins or modes of formation must differ. For example, the oxidized flavor of fluid milk is not identical to the oxidized flavor of butteroil (27,28).

Oxidized flavors are the products of autoxidation of the unsaturated fatty acids, mainly oleic, linoleic and linolenic, associated with the phospholipid and triglyceride fractions of milkfat (12,15,28). The autoxidation mechanism is a chain reaction involving the formation of free radicals, then peroxides and hydroperoxides.

The essence of the reaction as it may transpire with a glyceride containing linoleic acid follows (15):



by the mechanism:

$$-CH_2-CH=CH- \rightarrow -\overset{*}{C}H-CH=CH- + H$$

$$-CH-CH=CH- + O_2 \rightarrow -\underset{\underset{OO\ \text{(Peroxide)}}{|}}{CH}-CH=CH- +$$

$$-CH_2-CH=CH- \rightarrow -CH_2-CH=CH- \rightarrow -\underset{\underset{OOH\ \text{(Hydroperoxide)}}{|}}{CH}-CH=CH- +$$

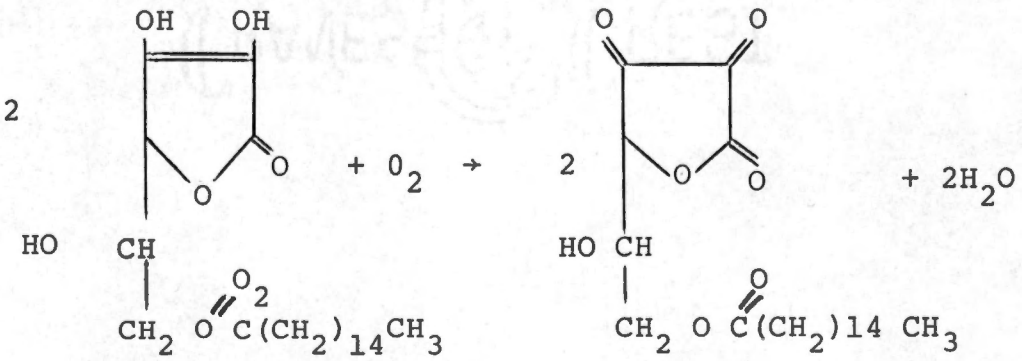
$$-\overset{*}{C}H-CH=CH-$$

The hydroperoxides are unstable and decompose readily to yield saturated and unsaturated aldehydes, ketones and alcohols (15,17,27). Downy (7) describes 1—octene—3—one and malonaldehyde as the two most important products of lipid oxidation from a flavor point of view.

IV. ANTIOXIDANTS

Antioxidants which have been employed in milk and its products fall into three main categories (15,19). First are the phenolic type compounds which interrupt the chain reaction mechanism of lipid oxidation resulting from free radical and hydroperoxide formation (19). Strong reducing compounds, which lower the oxidation-reduction potential to a point unfavorable for lipid oxidation, are a second type, followed by tryptic-type antioxidants, which appear to alter the milk proteins in a manner rendering them antioxygenic (15).

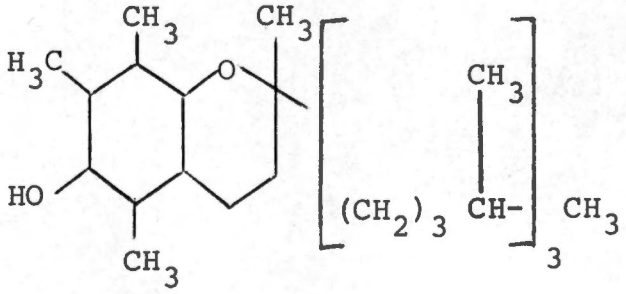
Ascorbic acid has good antioxygenic properties but it is insoluble in fats and oils. The ester of ascorbic acid and palmitic acid, ascorbyl palmitate, retains the antioxygenic properties of ascorbic acid and is soluble in fats and oils. Ascorbyl palmitate is also a good source of vitamin C (14). Ascorbic acid and ascorbyl palmitate, which function by oxygen scavenging, are used as antioxidants, particularly in a closed system, to remove oxygen in the headspace and in solution. Ascorbyl palmitate is considered physiologically acceptable and it has been listed as G.R.A.S., a category of approved food additives established by the Food and Drug Administration (5,6,14). The mechanism of oxygen scavenging by ascorbyl palmitate follows:



Ascorbyl palmitate Dehydro ascorbyl palmitate

The International Union of Pure and Applied Chemistry and the International Union of Biochemistry recognize and

name eight naturally occurring tocopherols. These belong to two series of methyl-substituted chromanols with either a saturated or unsaturated side chain (26).



Alpha Tocopherol (5,7,8—Trimethyltocol)

Tocopherol is vitamin E, and is abundant in wheat, rice germ and vegetable oils. Whether added by nature or as a food additive, tocopherol can act as an antioxidant (14,29, 31).

Antioxidative activity of the tocopherol has been observed mainly in animal fat which contain little natural antioxidants. The optimal effect is seen with 200 ppm tocopherol; higher concentrations are pro-oxidative. The antioxygenic efficiency of the tocopherol isomers is in the following order at 20-60° C: Alpha > Gamma > Beta > Delta (23).

Cort (5) successfully used alpha tocopherol to retard peroxides development in chicken, pork and beef fats. Pongracz's (23) study on butter fat showed that the peroxide

value in controls (no tocopherol added) at 80° C after 3 days was 265 (Meq. O_2 per kilogram of fat) and with 200 ppm alpha tocopherol added at the same conditions it was only 9.9.

CHAPTER III

MATERIALS AND METHODS

I. SOURCE

Two separate lots of butter, each 36 pounds, were purchased from Breakstone Sugar Creek Foods, Knoxville, Tennessee. Butteroil was prepared from each lot of butter separately.

II. PREPARATION

Butter was melted slowly in a 3 liter glass beaker at atmospheric pressure. An electric hot plate was used as a heat source. The temperature was gradually raised to 105-106° C with continuous stirring. Stirring was accomplished by a magnetic stirring bar which also helped in scraping the glass bottom and thus prevented excessive burning of curd particles. All the visible water was boiled out of the butter. The residual butterfat was allowed to stand about 15 minutes until all curd particles settled. The top layer of melted fat was then decanted from the curd. The time required for boiling down a batch varied from one to three hours, according to the difficulties experienced in controlling the foam.

For each lot of butter, all batches of butteroil which had been prepared in a glass beaker were mixed in a stainless steel container at the end to obtain homogeneity in the final sample. The two lots of butteroil marked as 1 and 2 were stored at -28° C in brown glass bottles until used for the study.

III. FAT OXIDATION STUDY

Samples of each of two lots of butteroil were treated as follows:

One hundred grams of butteroil in glass bottles with enamel lids were subjected to six different treatments (Control—No additives, 100 ppm alpha tocopherol, 200 ppm alpha tocopherol, 500 ppm ascorbyl palmitate, 100 ppm alpha tocopherol + 500 ppm ascorbyl palmitate and 200 ppm alpha tocopherol + 500 ppm ascorbyl palmitate) and stored at 45±2° C in a temperature controlled oven which excluded light. The stored treatment lots were sampled at 15, 30, 45 and 60 days. The alpha tocopherol and ascorbyl palmitate were provided by Hoffman-La Roche Inc., Nutley, New Jersey. The glass bottles had a total capacity of 370 ml, leaving 270 ml headspace.

IV. PEROXIDE VALUE

Each treatment was analyzed for peroxide value (milliequivalents of oxygen per kilogram of fat) at the end

of each specified time interval. Peroxide value was measured by the method given in A.O.A.C. (1). Each test was done twice and the average of two measurements was used to calculate peroxide value. Analysis of variance was performed and differences among means were partitioned into specific linear, quadratic and cubic polynomials.

V. ASCORBYL PALMITATE

The author followed the method by Budslawski and Poyorzelski (3) for the determination of ascorbyl palmitate in butterfat. It was observed that the recovery of ascorbyl palmitate was very poor; hence a standard curve could not be established.

VI. ALPHA TOCOPHEROL

The method described by Sharon and Armstrong (25) was followed for the determination of alpha tocopherol in milk fat. Poor recovery of alpha tocopherol resulted in inconsistent readings which did not give a linear standard curve.

Hence the fate of the antioxidants during storage could not be followed.

VII. SENSORY EVALUATION

A group of 25 people was chosen from among professors, graduate students and staff in the Institute of Agriculture

who indicated that they would participate in sensory evaluation of butteroil.

The group was familiarized with oxidized flavor by conducting two training taste panels. Four samples of butteroil, oxidized to different degrees as indicated by peroxide values (2.68, 4.00, 5.04 and 6.58) were homogenized twice into skim milk with a hand homogenizer to get 4% fat in the resultant reconstituted milk. The group was given these four samples and a reference 'R'. Reference 'R' was a reconstituted, homogenized mixture of skim milk and butteroil with zero peroxide value at a level of 4% fat. The panel was asked to indicate the dgreee of intensity of the oxidized flavor of the samples in comparison to the reference. Each sample was coded with a three digit random number and presented in random order to the panel.

After each member completed tasting, they were given correct answers and were instructed to taste the samples again to learn and memorize the level of oxidized flavor associated with scoring levels.

Butteroil samples to be evaluated at each period in the storage study were homogenized twice with a hand homogenizer into skim milk in such a proportion so as to get 4% fat in the resultant reconstituted milk. Skim milk contained less than 0.1% fat which was not taken into consideration. Samples of the six butteroil treatments, so reconstituted,

were presented to a sensory panel. A reference sample, marked 'R' and reconstituted with unoxidized butteroil, was used as a base for comparisons. The panel was asked to indicate preference on the basis of multiple comparison difference among the treatments compared to 'R', using a 0 to 5 point hedonic scale (0—No difference, 1—Slight difference, 2—Some difference, 3—Moderate difference, 4—Much difference and 5—Extreme difference). Analysis of variance was performed and differences among means were partitioned into specific linear, quadratic and cubic polynomials.

CHAPTER IV

RESULTS AND DISCUSSION

I. PEROXIDE VALUE

Table 1 presents the analysis of variance of the peroxide value development. Treatment, time and their interaction had a significant effect. The longer the storage time the higher will be the peroxide value in butteroil. The interaction indicated that different treatments behaved differently over time.

Treatment 1 (Control) showed a gradual increase in the peroxide value over storage time (Table 2); however it was statistically not significant. This leads to the conclusion that oxidation of butteroil at 45° C for 60 days may not be as serious a problem as anticipated. Figure 1 presents graphically the small, nonsignificant linear (see Appendix for the equation) increase in peroxide value of treatment 1 (Control). Treatment symbols for Figure 1 are listed in Table 3.

Treatment 4 (500 ppm ascorbyl palmitate) showed a peroxide value of 0.11 and 0.49 at 45 and 60 days respectively (Table 2). However the increase was not significant, but in comparison with Treatment 1 (Control) the increase of peroxide value in Treatment 4 (500 ppm ascorbyl palmitate) is less (Table 2). Figure 1 presents the small, not

TABLE 1

ANALYSIS OF VARIANCE FOR THE PEROXIDE VALUE IN BUTTEROIL TREATED WITH ANTIOXIDANTS

Source	D.F.	S.S.	M.S.	F-Ratio
Treatment	5	52.71	10.54	21.28**
Error A[1]	5	2.48	0.49	
Time × Treatment	15	37.90	2.53	16.79**
Tmt-1 Linear	1	0.45	0.45	2.98
Quadratic	1	0.02	0.02	0.11
Cubic	1	0.01	0.01	0.06
Tmt-2 Linear	1	9.54	9.54	63.38**
Quadratic	1	0.94	0.94	6.24*
Cubic	1	0.05	0.05	0.32
Tmt-3 Linear	1	43.77	43.77	290.76**
Quadratic	1	4.21	4.21	27.99**
Cubic	1	0.01	0.01	0.09
Tmt-4 Linear	1	0.25	0.25	1.68
Quadratic	1	0.07	0.07	0.48
Cubic	1	0.01	0.01	0.01
Tmt-5	-	-	-	-
Tmt-6	-	-	-	-
Time	3	21.43	7.14	47.46**
Error B[1]	18	2.71	0.15	
Total	47	119.06	2.53	

*Statistically significant at the 0.05 level of probability.

**Statistically significant at the 0.01 level of probability.

[1]Error A is Treatment × Rep., and Error B is Treatment × Time × Rep.

TABLE 2

THE EFFECT OF STORAGE ON THE PEROXIDE VALUE OF BUTTEROIL CONTAINING ANTIOXIDANTS

Antioxidants	Peroxide values[1,2]			
	15 Days	30 Days	45 Days	60 Days
	Meq. O_2/Kg. Oil			
Control	0.13[a]	0.50[b]	0.62[c]	0.80[c]
100 ppm Alpha Tocopherol	0.34[a]	0.77[ab]	1.54[b]	3.34[b]
200 ppm Alpha Tocopherol	0.45[a]	1.17[a]	3.15[a]	6.76[a]
500 ppm Ascorbyl Palmitate	0.00[a]	0.00[c]	0.11[d]	0.49[d]
500 ppm Asco. Palm. + 100 ppm Alpha Toco.	0.00[a]	0.00[c]	0.00[d]	0.00[e]
500 ppm Asco. Palm. + 200 ppm Alpha Toco.	0.00[a]	0.00[c]	0.00[d]	0.00[e]

[1]Means of 2 replicates.

[2]Means in columns followed by the same letter are not different at the 5% level of significance using Duncan's multiple range test (18).

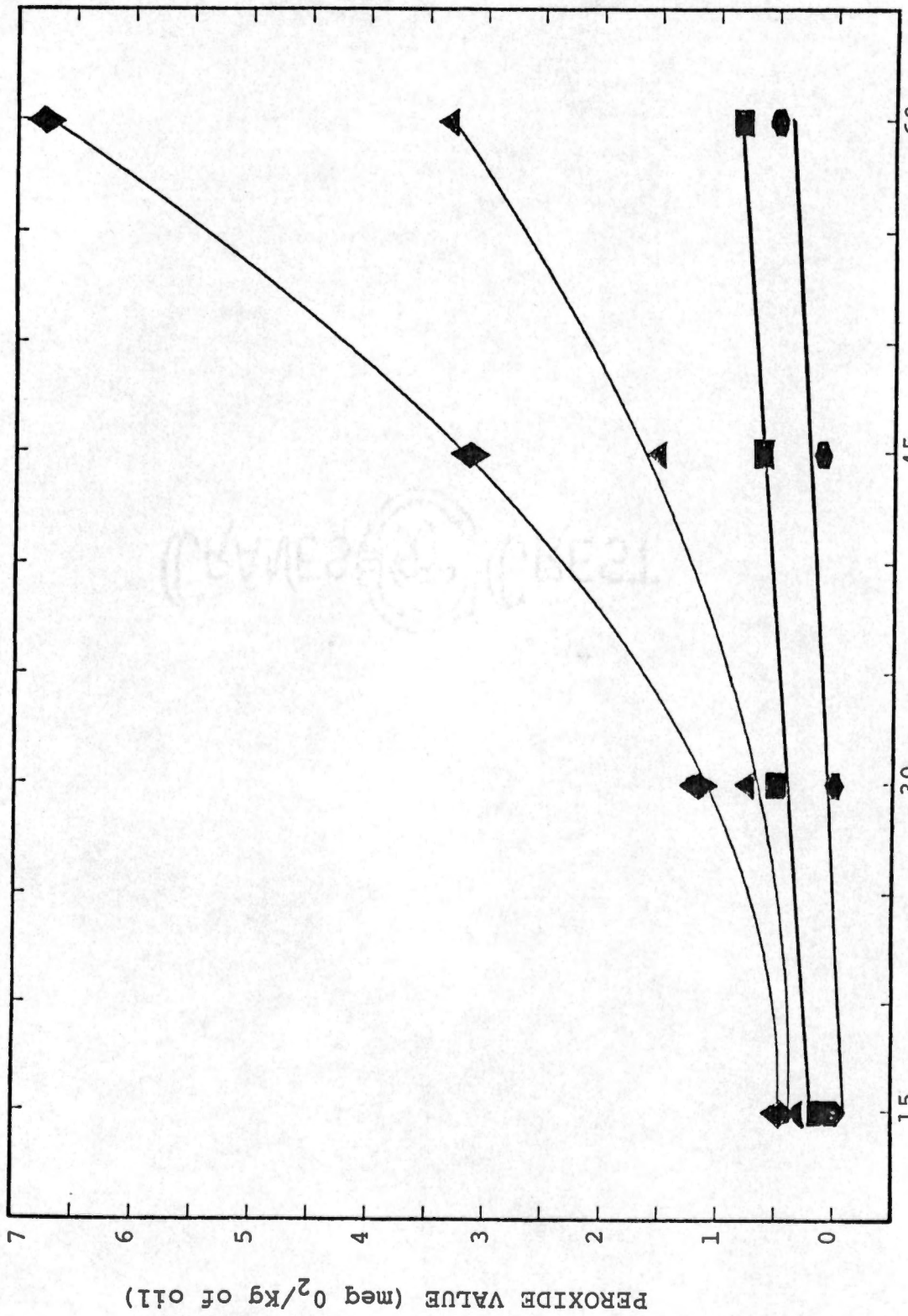


Figure 1. Changes in peroxide values in butteroil over days storage.

TABLE 3

SYMBOLS USED IN FIGURE 1 AND 2 FOR REPRESENTING THE CORRESPONDING TREATMENTS

Number	Treatment	Symbol
1.	Control	■
2.	100 ppm Alpha Tocopherol	▲
3.	200 ppm Alpha Tocopherol	◆
4.	500 ppm Ascorbyl Palmitate	⬢
5.	500 ppm Asco. Palm. + 100 ppm Alpha Toco.	▼ [1]
6.	500 ppm Asco. Palm. + 200 ppm Alpha Toco.	◆ [1]

[1]Not shown in Figure 1 since all values from these treatments were 0 P.V.

significant linear (see Appendix for equation) increase in the peroxide value of Treatment 4 (500 ppm ascorbyl palmitate). It is below the line of Treatment 1 (Control) indicating lesser peroxide value than in Treatment 1. This finding supports the assumption that using ascorbyl palmitate in butteroil will retard peroxide development.

Treatment 5 (500 ppm ascorbyl palmitate + 100 ppm alpha tocopherol) and Treatment 6 (500 ppm ascorbyl palmitate + 100 ppm alpha tocopherol) showed no measurable peroxide value within 60 days (Table 2), indicating the combination of ascorbyl palmitate and alpha tocopherol should be better in retarding peroxide development than ascorbyl palmitate alone in the butteroil. As the peroxide value was zero, there is no equation for the curve.

Treatment 3 (200 ppm alpha tocopherol) and Treatment 2 (100 ppm alpha tocopherol) had 6.76 and 3.34 peroxide value (P.V.) respectively at the end of 60 days (Table 2). One may conclude that, instead of retarding oxidation, alpha tocopherol accelerated the peroxides development, i.e., it worked as a pro-oxidant. Since alpha tocopherol worked as a pro-oxidant, higher peroxide values in Treatment 3 (200 ppm alpha tocopherol) could be expected due to higher alpha tocopherol concentration. Treatment 3 (200 ppm alpha tocopherol) and Treatment 2 (100 ppm alpha tocopherol) showed significant peroxide value increase over storage time,

indicating alpha tocopherol cannot be used in butteroil to retard peroxide development. Our assumption of using alpha tocopherol in butteroil as an antioxidant does not stand true. The peroxide value increase in Treatment 3 (200 ppm alpha tocopherol) and in Treatment 2 (100 ppm alpha tocopherol) was quadratic in nature (see Appendix for the equations) and statistically significant. Figure 1, page 19, presents the respective curves in relation to increase in peroxide value over storage time.

There was an apparent increase in the P.V. of Treatment 1 (Control) but it was not significant. An explanation for the slow P.V. increase in Treatment 1 (Control) could possibly be the absence of light in the oven. Since the butteroil was stored in glass bottles with lids there may not have been enough oxygen in the headspace to promote the oxidation process in the butteroil. Natural antioxidants like -SH groups might have developed in butteroil during its preparation. These factors are suggested as possibilities.

II. SENSORY EVALUATION

Table 4 presents the analysis of variance for the taste panel scores of butteroil reconstituted in skim milk. The treatment component was significant at the 1% level of confidence indicating that the panel members were able to detect a significant difference in their judgment for

TABLE 4

ANALYSIS OF VARIANCE OF TASTE PANEL SCORES
OF BUTTEROIL RECONSTITUTED IN SKIM MILK

Source		D.F.	S.S.	M.S.	F-ratio
Treatment		5	21.46	4.29	163.21**
Error A[1]		5	0.13	0.263	
Time-Treatment		15	10.91	0.73	9.49**
Tmt 1	Linear	1	0.01	0.01	0.15
	Quadratic	1	0.004	0.004	0.05
	Cubic	1	0.002	0.002	0.02
Tmt 2	Linear	1	0.65	0.65	8.60**
	Quadratic	1	1.11	1.11	14.53**
	Cubic	1	0.66	0.66	8.64**
Tmt 3	Linear	1	5.74	5.74	74.97**
	Quadratic	1	2.31	2.31	30.18**
	Cubic	1	0.05	0.05	0.75
Tmt 4	Linear	1	0.14	0.14	1.85
	Quadratic	1	0.02	0.02	0.32
	Cubic	1	0.01	0.01	0.25
Tmt 5	Linear	1	0.20	0.20	2.66
	Quadratic	1	0.01	0.01	0.18
	Cubic	1	0.04	0.04	0.53
Tmt 6	Linear	1	0.62	0.62	8.13*
	Quadratic	1	0.004	0.004	0.06
	Cubic	1	0.67	0.67	2.75**
Time		3	1.39	0.47	6.09**
Error B[1]		18	1.38	0.08	
Total		47	35.49	0.76	

*Statistically significant at the 0.05 level of probability.

**Statistically significant at the 0.01 level of probability.

[1]Error A is Treatment × Rep., and Error B is Treatment × Time × Rep.

oxidized flavor among the treatments. The time component was also significant at the 1% level of confidence, as was the time-treatment interaction, indicating that the panel members scored different treatment samples differently over time.

Figure 2 presents the regression curves for the mean panel scores of skim milk reconstituted with butteroil over time. The appendix includes the regression equations used to produce these curves. The regression curves were drawn from the composite means of 2 replicates.

Treatment 2 (100 ppm alpha tocopherol) and Treatment 3 (200 ppm alpha tocopherol) had the highest P.V. (Table 2, page 18) as well as highest scores after 60 days (Table 5). The regression curve for Treatment 2 (100 ppm alpha tocopherol) was cubic in nature and that for Treatment 3 (200 ppm alpha tocopherol) was quadratic. The flavor score increased in both these treatments up to 45 days, but at 60 days it decreased, even though the P.V. at 60 days was higher than at 45 days. This inconsistency could be attributed to poor training of panel members. Instead of 2 training sessions, 4 or 5 sessions might have made the panel more aware of relative oxidized flavor levels. Some of the panel members might have forgotten the actual oxidized flavor levels and that would have made them under-score. Frequent tasting of oxidized milk might have made them reluctant to reach objective decisions. These factors could have contributed in the low scoring at 60 days.

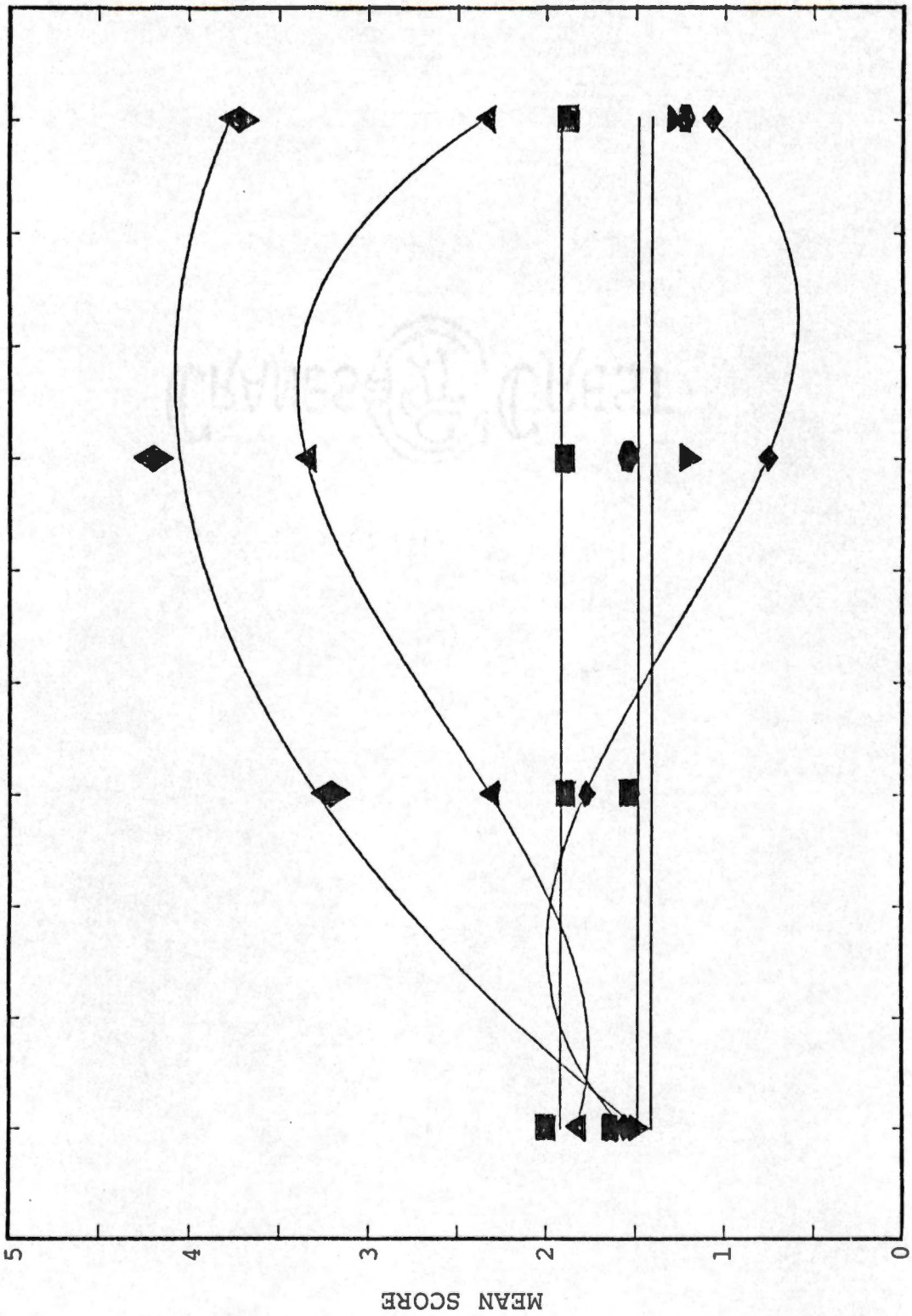


Figure 2. Regression curves of mean flavor score over days storage.

TABLE 5

THE EFFECT OF STORAGE ON THE TASTE PANEL SCORES[1] OF BUTTEROIL[2] RECONSTITUTED IN SKIM MILK

Antioxidants	Flavor score after x days[3]			
	15 Days	30 Days	45 Days	60 Days
Control	2.00[a]	1.89[c]	1.90[c]	1.88[c]
100 ppm Alpha Tocopherol	1.83[ab]	2.32[b]	3.35[b]	2.34[b]
200 ppm Alpha Tocopherol	1.53[c]	3.21[a]	4.20[a]	3.73[a]
500 ppm Ascorbyl Palmitate	1.63[bc]	1.53[e]	1.55[d]	1.23[d]
500 ppm Asco. Palm. + 100 ppm Alpha Toco.	1.63[bc]	1.53[e]	1.20[e]	1.26[d]
500 ppm Asco. Palm. + 200 ppm Alpha Toco.	1.56[c]	1.78[cd]	0.75[f]	1.07[d]

[1]Means of 2 replicates.

[2]Butteroil was reconstituted (4%) in pasteurized skim milk.

[3]Means in columns followed by the same letters are not significantly different at the 5% level by Duncan's multiple range test (18).

Treatment 4 (500 ppm ascorbyl palmitate) developed measurable peroxide value at 45 and 60 days, but in comparison to Treatment 1 (Control), Treatment 2 (100 ppm alpha tocopherol) and Treatment 3 (200 ppm alpha tocopherol), they were low. The flavor score change was not significant and decreased in general, supporting the assumption of using ascorbyl palmitate as an antioxidant in butteroil. Figure 2 presents the effect of score over time in a linear, nonvarying fashion for Treatment 4.

The decrease in flavor score of Treatment 1 (Control) was not significant. The P.V. in Treatment 1 (Control) increased, but the increase was not significant. Even though the flavor score decreased numerically, it too was not a significant change. The decrease in scoring could have resulted from bias introduced by the high scores of Treatment 2 (100 ppm alpha tocopherol) and Treatment 3 (200 ppm alpha tocopherol).

Treatment 5 (500 ppm ascorbyl palmitate + 100 ppm alpha tocopherol) did not develop peroxides during the 60 days storage period. The flavor score decreased in general; however, ideally the flavor score should be zero for Treatment 5 (500 ppm ascorbyl palmitate + 100 ppm alpha tocopherol). But the higher score of Treatment 1 (Control), Treatment 2 (100 ppm alpha tocopherol) and Treatment 3 (200 ppm alpha tocopherol) may have caused panel members to impart

some score to Treatment 5. Of course poor training of the panel members, or their forgetfullness and fatigue, are possible causes in scoring Treatment 5. The flavor score did not change significantly and it is presented in Figure 2, page 25, as a straight line.

Treatment 6 (500 ppm ascorbyl palmitate + 200 ppm alpha tocopherol) had a significant linear and cubic variation. The lowest score was at 45 days and then it increased. This could have resulted from bias introduced by the high scoring of Treatment 2 and Treatment 3 at the same time. Figure 2, page 25, shows the curvilinear nature of Treatment 6 (500 ppm ascorbyl palmitate + 200 ppm alpha tocopherol) which is different from Treatment 2 and Treatment 3.

This study showed that there was no measurable peroxides in the butteroil stored at 45° C for 60 days with 500 ppm ascorbyl palmitate + 100 ppm alpha tocopherol and 500 ppm ascorbyl palmitate + 200 ppm alpha tocopherol added to butteroil.

Ascorbyl palmitate alone in the butteroil retarded the production of peroxides to some degree but when alpha tocopherol was mixed with it both showed an additive effect on retarding the peroxides.

Alpha tocopherol alone in butteroil accelerated the peroxides development.

CHAPTER V

SUMMARY

An antioxidant system composed of ascorbyl palmitate and alpha tocopherol was added to butteroil which was stored in glass bottles with enamel lids. The bottles were held at 45±2° C in an oven which excluded light. At intervals of 15, 30, 45 and 60 days butteroil was examined by an objective and a subjective method, by sensory evaluation and measuring the peroxide value.

Butteroil was reconstituted with fresh skim milk at a level of 4% and was presented to taste panels who were asked to indicate their preference on the basis of multiple comparison and difference analysis. A reference was a blend of butteroil having zero peroxide value.

The peroxide value increase was found not significant in control butteroil containing no antioxidants held for 60 days at 45° C. Alpha tocopherol accelerated the peroxides development in butteroil. Ascorbyl palmitate and mixtures of alpha tocopherol and ascorbyl palmitate retarded peroxides development in the butteroil, hence indicating a good possibility for using them as antioxidants for commercial butteroil.

REFERENCES

REFERENCES

1. A.O.A.C. 1970. "Official Methods of Analysis." 11th ed. Association of Official Agricultural Chemists, Washington, D.C.

2. Berger, K. G. 1975. Catalysis and inhibition of oxidation process. Chemistry and Industry 5(1):194.

3. Budslawski, J. and Poyorzelski, K. 1964. Dosage colorimetrique du palmitate d'ascorbyle dans les matieres grasses. Le Lait 44(437):378.

4. Cerutti, G. 1956. "Sull mantenimmento dello stats di freschezza dialcuni prodotti lattierocaseari. Nota 2. Stabilizzazione del burro: risultati sperimentali" in "Preservation of dairy products. 2 butter." Latte 30 (4):267.

5. Cort, W. M. 1974. Antioxidant activity of tocopherols, ascorbyl palmitate and ascorbic acid and their mode of action. J. Am. Oil Chem. Soc. 51(7):321.

6. Cort, W. M.; Scott, J. W. and Harley, J. H. 1970. Proposed antioxidant exhibits, useful properties. Food Technol. 29(11):20.

7. Downey, W. K. 1969. Lipid oxidation as a source of off-flavor development during the storage of dairy products. J. Soc. of Dairy Technol. 22(3):154.

8. Economic Research Services, U.S.D.A. 1975. "Dairy Situation," Washington, D.C. December, 1975.

9. El-Negoumy, A. M. and Hammond, E. C. 1960. The characterization of the oxidized flavor in butteroil. J. Dairy Sci. 43(6):840.

10. Farmer, E. H. and Sutton, D. A. 1943. The isolation and constitution of photochemically formed methyl oleate peroxide. J. Chem. Soc. 3:119.

11. Forss, D. A. 1971. The flavors of dairy fats—A Review. J. Am. Oil Chem. Soc. 48:702.

12. Greenbank, G. R. 1948. The oxidized flavor in milk and dairy products: A Review. J. Dairy Sci. 31:913.

13. Hunziker, O. F. 1940. "The Butter Industry." 3rd ed. Published by the author, La Grange, Illinois.

14. Jacobson, M. F. 1972. "Eater's Digest." Doubleday and Company, Inc. Garden City, New York.

15. Jenness, R. and Patton, S. 1976. "Principles of Dairy Chemistry." Robert E. Krieger Publishing Company, Huntington, New York.

16. Johnson, J. C. 1975. Antioxidants for foods. In "Antioxidants Synthesis and Application." P. 294. Noyes Data Corporation, Park Ridge, N.J.

17. Lampert, L. M. 1970. "Modern Dairy Products." Chemical Publishing Company, Inc. New York.

18. Larmond, Elizabeth. 1970. "Methods of Sensory Evaluation of Food." Canada Department of Agriculture, Pub. 1284, Ottawa, Ont. 88, Canada.

19. Lea, C. H. 1958. Some nutritional and allied problems confronting the food manufacturer: Technological aspect of antioxidants. J. Sci. of Food and Agri. 9 (10):621.

20. McDowall, F. H. 1953. "The Butter Maker's Manual." New Zealand University Press, Wellington, New Zealand.

21. McDowall, F. H.; Dolby, R. M.; Beatson, E. and O'Dea, J. J. 1945. New Zealand dries butterfat. Food Ind. 17(4):78.

22. McKay, C. L. and Larsen, C. 1922. "Principles and Practice of Butter-Making." 3rd ed. John Wiley and Sons, Inc., New York.

23. Ponyracz, C. 1973. Antioxidant mixtures for use in food. International Journal for Vitamin and Nutrition Research. 43(4):57.

24. Rangappa, K. S. and Achaya, K. T. 1974. "Indian Dairy Products." 2nd ed. Asia Publishing House, Bombay 1, India.

25. Sharon, K. S. and Armstrong, J. C. 1968. A modification of the Emmerie-Engle procedure for the determination of vitamin E in butter. J. Canadian Inst. of Food Technol. 1(1):1.

26. Slover, H. T.; Shelley, L. M. and Burks, T. L. 1967. Identification and estimation of tocopherols by gas-liquid chromatography. J. Am. Oil Chem. Soc. 44:161.

27. Webb, B. H. and Johnson, A. H. 1965. "Fundamentals of Dairy Chemistry." The A.V.I. Publishing Company, Inc., Westpoint, Connecticut.

28. Webb, B. H. and Whittier, E. O. 1970. "By products from Milk." 2nd ed. The A.V.I. Publishing Company, Inc., Westpoint, Connecticut.

29. Weiss, T. J. 1970. "Food Oils and Their Uses." The A.V.I. Publishing Company, Inc., Westpoint, Connecticut.

30. Wilster, C. H. 1966. "Practical Buttermaking." 9th ed. O.S.U. Book Stores, Inc. Corvallis, Oregon.

31. Witting, L. A. 1975. Vitamin E as a food additive. J. Am. Oil Chem. Soc. 52:54.

APPENDIX

TABLE A-1

REGRESSION EQUATIONS OF CURVES DRAWN FOR PEROXIDE VALUES IN BUTTEROIL

Treatment No.	Equation
1.	$Y = -0.01425 + 0.014137\ T^{1}$
2.	$Y = 0.7685 - 0.04913\ T + 0.001523\ T^{2}$
3.	$Y = 1.27825 - 0.102353\ T + 0.003224\ T^{2}$
4.	$Y = -0.2470 + 0.010613\ T^{1}$
5.	Peroxide value is zero.
6.	Peroxide value is zero.

[1]Not significant at the 5% level.

TABLE A-2

REGRESSION EQUATIONS OF CURVES DRAWN FOR MEAN SCORE IN BUTTEROIL

Treatment No.	Equation
1.	Time-Treatment interaction is not significant.
2.	$Y = 4.458608 - 0.335973\ T + 0.012636\ T^2 - 0.000127\ T^3$
3.	$Y = -1.359066 + 0.224226\ T - 0.002310\ T^2$
4.	Time-Treatment interaction is not significant.
5.	Time-Treatment interaction is not significant.
6.	$Y = -2.488179 + 0.455741\ T - 0.01428\ T^2 + 0.000128\ T^3$

VITA

The author was born in July, 1950, in Ahmedabad, India. He was graduated in 1967 from D. N. High School, Anand, Gujarat, India. In January, 1975, he received the B.S. degree in the field of Dairy Technology from Gujarat Agricultural University, India. In March, 1975, he enrolled in the graduate school of the University of Tennessee and since that time has been working to complete the requirements for the degree of M.S. in the department of Food Technology and Science.