For Reference

NOT TO BE TAKEN FROM THIS ROOM

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex LIBRIS
UNIVERSITATIS
ALBERTAENSIS

Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

<https://archive.org/details/photochemicaloxi00pime>

77
89
892

THE UNIVERSITY OF ALBERTA

PHOTOCHEMICAL OXIDATION OF BUTTER

by

RUFINITA C. PIMENTEL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF MASTER OF SCIENCE
DEPARTMENT OF DAIRY AND FOOD SCIENCE

EDMONTON, ALBERTA

January, 1966.

ABSTRACT

Samples of butter taken at random from grocery stores were subjected to different tests to determine whether the fluorescent light used in the display cases had an oxidizing effect on the butter. Fresh butter samples were exposed to fluorescent light in the laboratory. The state of oxidation after various exposure times was determined by chemical tests and by organoleptic evaluation. The butter samples were exposed at three different distances from the light source. Unwrapped butter and butterfat samples were also exposed to the light. This was done to find out whether the phospholipid fraction of the fat has any effect on the oxidative deterioration of the butter under the light.

The changes in peroxide values and carbonyl values indicate that fluorescent light had a prooxidant effect on the butter. The organoleptic tests correlated with the results of the chemical tests. The butter was also bleached as a result of the light exposure, indicating that the oxidation degraded the carotenes.

The harmful effects of fluorescent lighting in the grocery stores were indicated by the results of the tests performed on the samples taken from the supermarkets.

The use of better packaging materials that would protect the butter against light seems an urgent requirement.

ACKNOWLEDGEMENTS

The writer would like to express her thanks to the National Research Council of Canada for the financial support of this study, in the form of a research assistantship, and to Dr. J.M. deMan for his guidance and advice.

She also expresses her appreciation to the staff and students for their suggestions and constructive criticism.

Finally she wishes to express her deepest gratitude to her parents, Mr. and Mrs. Pablo N. Pimentel, for being her constant source of encouragement and inspiration.

TABLE OF CONTENTS

<u>INTRODUCTION</u>	1
<u>REVIEW OF LITERATURE</u>	3
<u>Factors Affecting Oxidation</u>	3
<u>Metal</u>	3
<u>Air and Oxygen</u>	6
<u>Light</u>	7
<u>Moisture</u>	10
<u>Salt</u>	12
<u>Acid</u>	13
<u>Antioxidant</u>	15
<u>Techniques in Autoxidation Studies</u>	17
<u>Review of Methods for Determination of Autoxidation</u>	
<u>Products</u>	18
<u>Peroxides</u>	18
Iodimetry	18
Polarography	18
Ferric Thiocyanate Method	18
Dichloro-indophenol Method	19
<u>Carbonyl Compounds</u>	19
<u>Thiobarbituric Acid Test</u>	20
<u>Photochemical Methods</u>	21
<u>EXPERIMENTAL METHODS</u>	23
<u>Preparation of Butterfat</u>	24
<u>Organoleptic Evaluation</u>	24
<u>Peroxide Value</u>	25
<u>Carbonyl Value</u>	25
<u>RESULTS</u>	26
<u>DISCUSSION</u>	69
<u>BIBLIOGRAPHY</u>	75

LIST OF TABLES

Table 1.	Measurement of state of oxidation of butter samples obtained from supermarket display shelves	35
Table 2.	Measurement of state of oxidation of butter samples exposed on supermarket display shelves	36
Table 3.	Progress of oxidation of butter exposed to fluorescent light at a distance of 10 inches	37
Table 4.	Progress of oxidation of butter exposed to fluorescent light at a distance of 20 inches	38
Table 5.	Progress of oxidation of butter exposed to fluorescent light at a distance of 20 inches	39
Table 6.	Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 10 inches	40
Table 7.	Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 20 inches	41
Table 8.	Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 30 inches	42

LIST OF FIGURES

Fig. 1.	Typical butter display shelf in a supermarket	43
Fig. 2.	Butter in parchment wrap for exposure test	44
Fig. 3.	Butter exposed for one week at a distance of 10 inches from the light, side (a)	45
Fig. 4.	Butter exposed for one week at a distance of 10 inches from the light, side (b)	46
Fig. 5.	Butter exposed for one week at a distance of 20 inches from the light, side (a)	47
Fig. 6.	Butter exposed for one week at a distance of 20 inches from the light, side (b)	48
Fig. 7.	Butter exposed for one week at a distance of 30 inches from the light, side (a)	49
Fig. 8.	Butter exposed for one week at a distance of 30 inches from the light, side (b)	50
Fig. 9.	Butter exposed for two weeks at a distance of 10 inches from the light, side (a)	51
Fig. 10.	Butter exposed for two weeks at a distance of 10 inches from the light, side (b)	52
Fig. 11.	Butter exposed for two weeks at a distance of 20 inches from the light, side (a)	53
Fig. 12.	Butter exposed for two weeks at a distance of 20 inches from the light, side (b)	54
Fig. 13.	Butter exposed for two weeks at a distance of 30 inches from the light, side (a)	55
Fig. 14.	Butter exposed for two weeks at a distance of 30 inches from the light, side (b)	56
Fig. 15.	Butter exposed for three weeks at a distance of 10 inches from the light, side (a)	57
Fig. 16.	Butter exposed for three weeks at a distance of 10 inches from the light, side (b)	58
Fig. 17.	Butter exposed for three weeks at a distance of 20 inches from the light, side (a)	59

No.	Description	Amount
1	...	...
2	...	...
3	...	...
4	...	...
5	...	...
6	...	...
7	...	...
8	...	...
9	...	...
10	...	...
11	...	...
12	...	...
13	...	...
14	...	...
15	...	...
16	...	...
17	...	...
18	...	...
19	...	...
20	...	...
21	...	...
22	...	...
23	...	...
24	...	...
25	...	...
26	...	...
27	...	...
28	...	...
29	...	...
30	...	...
31	...	...
32	...	...
33	...	...
34	...	...
35	...	...
36	...	...
37	...	...
38	...	...
39	...	...
40	...	...
41	...	...
42	...	...
43	...	...
44	...	...
45	...	...
46	...	...
47	...	...
48	...	...
49	...	...
50	...	...
51	...	...
52	...	...
53	...	...
54	...	...
55	...	...
56	...	...
57	...	...
58	...	...
59	...	...
60	...	...
61	...	...
62	...	...
63	...	...
64	...	...
65	...	...
66	...	...
67	...	...
68	...	...
69	...	...
70	...	...
71	...	...
72	...	...
73	...	...
74	...	...
75	...	...
76	...	...
77	...	...
78	...	...
79	...	...
80	...	...
81	...	...
82	...	...
83	...	...
84	...	...
85	...	...
86	...	...
87	...	...
88	...	...
89	...	...
90	...	...
91	...	...
92	...	...
93	...	...
94	...	...
95	...	...
96	...	...
97	...	...
98	...	...
99	...	...
100	...	...

Fig. 18.	Butter exposed for three weeks at a distance of 20 inches from the light, side (b)	60
Fig. 19.	Butter exposed for three weeks at a distance of 30 inches from the light, side (a)	61
Fig. 20.	Butter exposed for three weeks at distance of 30 inches from the light, side (b)	62
Fig. 21.	Butter exposed for four weeks at a distance of 10 inches from the light, side (a)	63
Fig. 22.	Butter exposed for four weeks at a distance of 10 inches from the light, side (b)	64
Fig. 23.	Butter exposed for four weeks at a distance of 20 inches from the light, side (a)	65
Fig. 24.	Butter exposed for four weeks at a distance of 20 inches from the light, side (b)	66
Fig. 25.	Butter exposed for four weeks at a distance of 30 inches from the light, side (a)	67
Fig. 26.	Butter exposed for four weeks at a distance of 30 inches from the light, side (b)	68

PHOTOCHEMICAL OXIDATION OF BUTTER

INTRODUCTION

The autoxidation of edible oils adversely affects the flavour quality and the vitamin and essential fatty acid contents. The ingestion of oxidized fats also has toxic effects.

For these reasons, the study of oxidative deterioration of edible oils or fats has been the subject of numerous investigations. Ways and means for evaluating the keeping quality and incipient rancidity of fats have given rise to the development of various methods of accelerated tests. These methods were primarily used for evaluating the resistance of fat to oxidation and also for evaluating the effectiveness of antioxidants. The general characteristics of these tests are that fats and oils are subjected to accelerated conditions of oxidation under carefully controlled environmental factors.

The changes occurring during the oxidation of fats are characterized by an induction period which is followed by rapid oxidation. The factors that speed up oxidation are metals, light, oxygen, moisture and high temperatures. The presence of natural and added antioxidants alters the relationship between the pro-oxidants and the lipid system. The study of oxidative deterioration of a given lipid system is complex because of the various factors enumerated above which often operate simultaneously.

THE HISTORY OF THE

REIGN OF

CHARLES THE FIRST

BY JOHN BURNET

IN TWO VOLUMES

The first part of this history contains the reign of Charles the First, from his accession to the throne in 1625, to his execution in 1649. The second part contains the reign of Oliver Cromwell, from his death in 1658, to the restoration of Charles the Second in 1660. The third part contains the reign of Charles the Second, from his restoration in 1660, to his death in 1685. The fourth part contains the reign of James the Second, from his accession to the throne in 1685, to his flight to France in 1688. The fifth part contains the reign of William the Third, from his accession to the throne in 1689, to his death in 1702. The sixth part contains the reign of Anne, from her accession to the throne in 1702, to her death in 1702.

The history of the reign of Charles the First is a very interesting one, and is full of many interesting events. The reign of Oliver Cromwell is also a very interesting one, and is full of many interesting events. The reign of Charles the Second is also a very interesting one, and is full of many interesting events. The reign of James the Second is also a very interesting one, and is full of many interesting events. The reign of William the Third is also a very interesting one, and is full of many interesting events. The reign of Anne is also a very interesting one, and is full of many interesting events.

Studies on the oxidative deterioration of fats and oils under normal conditions of storage have shown that there is still room for improvement in so far as the keeping quality of foods are concerned. Recent investigations (43, 44, 127, 134) concern the effect of artificial lighting in retail stores on lipid containing foods. This arises from the fact that supermarkets are always intensely lighted and foods are sometimes no more than a few inches away from the source of light while on the display shelf.

The purpose of this study was to find the effects of fluorescent light on butter and the butterfat as shown by the results of chemical and organoleptic tests.

REVIEW OF LITERATURE

Factors Affecting Oxidation

Metal - In 1917, Hunziker and Hosman (72) found that copper as well as iron catalyzed the development of tallowy flavour in butter. Either an iron nail or a copper wire imbedded in the butter caused bleaching and tallowiness. The addition of colloidal hydroxides of iron and copper in minute quantities to butter (4 drops per 180 grams of butter) was tried with the result that the copper-contaminated sample became tallowy in 8 days, whereas the iron-contaminated sample did not show this defect after two months in storage at 32°F. Pure butterfat emulsified with casein and a slight excess of alkali showed slight tallowiness and bleaching after 5 days at room temperature in the presence of iron, copper and brass. These samples were intensely tallowy and bleached after 28 days. Samples containing nickle and tin, which were normal after 5 days, had turned slightly tallowy without bleaching, and the butterfat of normal lactose content emulsified without acid, alkali or metal addition remained normal. The iron-contaminated sample containing alkali became fishy. It was observed further by these workers that in all cases of tallowiness the defects appeared first at the surface of the butter and then inward.

In 1922, Emery and Henley (35) found that copper and iron containers caused oxidative defects in lard, corn oil and cottonseed oil. They recommended lacquering as a preventive measure. Thome

General Notes

1. The following notes are for the purpose of providing a general overview of the project and its objectives.

2. The project is a multi-phase study designed to investigate the effects of various factors on the growth and development of the organism. The phases are as follows:

- a. Phase I: Initial growth and development under standard conditions.
- b. Phase II: Growth and development under conditions of stress (e.g., temperature, nutrient availability).
- c. Phase III: Growth and development under conditions of competition (e.g., with other organisms).

3. The results of the study will be presented in a series of reports, each corresponding to one of the phases. The reports will include data on the following parameters:

- a. Growth rate (measured as the increase in length or weight over time).
- b. Developmental stage (measured as the appearance of specific morphological features).
- c. Survival rate (measured as the percentage of organisms that survive under the given conditions).

4. The study is expected to provide valuable information on the role of the various factors in the growth and development of the organism. This information will be used to develop a more complete understanding of the organism's biology and to identify potential areas for further research.

5. The project is supported by the following grants:

- a. Grant #12345 from the National Science Foundation.
- b. Grant #67890 from the Department of Education.

and Olsson (148) also mentioned the prooxidant effect of copper in a pump used to prepare butter. This is because small amounts of copper pass into solution when the pump was used to circulate the cream. Koops (79) also reported that oxidative deterioration of butter from cultured cream during cold storage is strongly promoted by copper contamination. He recommended the use of anti-oxidants in addition to copper elimination.

Several factors influence the dissolution of the metal of containers. Whitfield (158) observed that greater corrosion occurred at 144°F than at 60°F. Increased solubility of copper up to 158°F was observed (47).

Copper containers with oxidized surfaces showed increased corrosion (118). The presence of oxygen has been shown to increase the rate of copper corrosion. However, the presence of carbon dioxide decreases it (46, 47, 48, 94, 118).

Since off-flavours are believed to be due to oxidation, the factors affecting the oxidation of butterfat received increasing attention. Briggs (8, 9) showed that certain metallic catalysts hasten the oxidative reaction. Parodi (105) studied the types of butter boxes and cartons and the chemical nature of the vegetable parchment wrapping. It was found that when the copper content of the parchment is kept below 5 ppm there was no evidence of surface oxidation after storage at 10°F for 6 months. With increasing amounts of copper, surface grades deteriorated. The effect of metals

on washed cream was also studied (144). It was observed that flavour defects were fishy and metallic. Tarassuk et al. (145) suggested that the possible origin of trainy flavour in the fat globule membrane is produced by the oxidation of the unsaturated fatty acids of the phosphatides and is accelerated by metals, increased temperature and pH. They indicated that if the membrane protein-bound copper is removed by a copper binding antioxidant no oxidation will occur.

Milk and milk products have natural copper as part of their constituents. Several investigators have shown that copper combines with proteins. It is their belief, however, that the combination is a matter of adsorption rather than direct chemical combination (102, 149, 150).

Because of the importance of copper in milk, a test for copper was developed (121) based on the peroxidase reaction. The reagents used are p-phenylenediamine, alpha naphthol and hydrogen peroxide. When these are added to freshly pasteurized milk or cream, the rapidity of formation of a blue color is proportional to peroxidase content and since copper acts as a catalyst in the reaction, the test can be used as the measure of copper content. This test was modified by Turgeon et al. (152) who also found that vitamin C complicated this application. Later, Herrington and Brereton (68) developed a flame test for determining the presence of copper in metals or alloys. A polarographic determination of copper and iron in fats was developed by deMan and Engelhardt (30).

Air and Oxygen - In 1910 Nestrelayev (97) observed the difference in susceptibility to oxidation by air and light of different butter samples. He learned that the larger the content of unsaturated acid present the greater the effect of light.

Browne (12) studied the decomposition of butterfat and found a marked increase in free and volatile acids and a considerable decrease in the content of insoluble acids. He reasoned that disintegration of the fats was primarily due to the action of active oxygen, one atom of which was liberated for each atom absorbed at the points of unsaturation. Greenbank (52) found that butterfat did not undergo oxidation when free fatty acids were removed by steam distillation and when stored under vacuum in diffused light for three years. He found that the oxidation of fats in the presence of heat and air, and in the absence of light, reduced the induction period after three months of storage from 248 minutes to 41 minutes.

Greenbank (51) suggested packing butter in evacuated containers and then releasing the vacuum by inert gas to prevent oxidative deterioration. Prucha et al. (113) reported that storage of butter in an atmosphere of carbon dioxide in tightly sealed cans improved its keeping quality.

Sommer (136) found that presence of air caused fishiness in butter. Overworking of butter resulted in increased air content and therefore increased oxygen available for the oxidative deterioration.

Giermak (49) stated that a smoothly finished surface permits

good contact between the butter and wrapper which aids against surfact taints, off-flavour, mold development and oxidation. He believed that uneven surface results in the failure of the treated liners to adhere to the butter surface thus permitting air pockets to form which may cause development of defects. Columbic et al. (23) examined the flavours produced during light reversion of soybean oil under atmospheres of different oxygen concentrations. No decrease in the tendency to revert under different conditions was observed.

Light - Early workers (8, 11, 35, 38, 52, 65, 123, 124, 126, 131) have established the important accelerating effect of light on fat oxidation. Nestrelayev (97) found that butter from different parts of the country differed in their susceptibility to oxidation when exposed to air and light depending on the content of unsaturated acids. de Vleeschauwer et al. (154) found that the oxidation of ascorbic acid in both water and milk was increased by the presence of riboflavin and light. The estimation of steam volatile monocarbonyl compounds from oleate, linoleate and linoleate esters was carried out by Gaddis et al. (45) after exposing the esters to ultraviolet light. Pedersen and Andersen (109) found that during storage of ascorbic acid-enriched milk in darkness, the ascorbic acid content decreased slowly and no off-flavour could be detected after 2 days of storage. On exposure to daylight, the ascorbic acid was decomposed rapidly and a marked tallowy flavour was produced. In a strong daylight noticeable changes took place when the milk was exposed for only 15 minutes. Radema (115) found that skim milk is most sensitive to light-induced oxidation.

Different studies on the autoxidation of fats show that shorter wavelengths are mainly responsible for the initiation of the chemical reaction. In 1932, Coe and LeClerc (20) reported that ultraviolet light is more effective in promoting oxidation than sunlight. Greenbank and Holmes (55) reported that the lower wavelengths are more effective in their study of different oils. In 1947 McConnell and Eoselen (92) also reported on the more effective action of the lower wavelengths. Soldberg and Reidar (135) found that off-flavour in milk is caused by light of wavelengths below 500 millimicrons. Brown glass bottles, although providing good protection are not completely effective in preventing the detrimental effect of exposure to light.

Fifteen years later a study of the effect of different wavelengths present in fluorescent light was made by Scott (127) who concluded that the wavelengths in the ultraviolet portion of the spectrum had a definite effect on the quality of butter. His evaluations were based on organoleptic tests. In 1965 Moser et al. (95) published a paper describing the development of off-flavours in oils and other food products while on the shelves when exposed to fluorescent light. They devised an accelerated test apparatus wherein the oils are exposed to fluorescent light and the samples tested at regular intervals.

Malm and Hildington (91) made a study of the effect of lighting in cold storage cabinets in retail stores. The yellow light from filament lamps and the blue-white and warm light from tubular

lamps were equally active. An exposure of even one hour to any of these sources of light caused a rise in peroxide number. They found that an aluminum foil wrapper was effective protection against the effect of light. Futschik and Aigner (43) made a similar study. They exposed prints of butter wrapped in aluminum foil, parchment and unwrapped. They used a filament lamp of 40 watts or an ultra-violet lamp of 30 watts for 24 hours at a temperature of 15°C. Taste, smell and appearance of butters wrapped in aluminum foil were satisfactory irrespective of the type of light, but unwrapped samples and those wrapped in parchment showed a marked deterioration in quality.

Futschik and Aigner (44) studied the effect of light on the quality of milk, whipping cream, butter and cheese. Thirteen types of fluorescent tubes made by 4 manufacturers and giving white and yellow light (100 - 260 lux) were compared at a distance of 1.5 meters from the products enclosed in a cabinet at 10° - 12°C; the controls were kept in darkness under similar conditions. The changes in the quality of the product were assessed organoleptically after 24 hours and 72 hours illumination. They found that with the exception of Edam cheese the illumination of unwrapped products gave rise to the development of off-flavours, the intensity of which depended on the product and the colour of the light. White light was found to be more harmful than yellow light. Milk in clear glass bottles became defective after 24 hours while those in brown bottles remained unchanged irrespective of the colour of the light. Whipping cream was more sensitive to yellow light than to white light. With butter white light was found to be most harmful. Aluminum foil was found to

protect the butter from deterioration whereas parchment paper was ineffective. The deterioration was most pronounced in unwrapped butter. Edam Cheese was hardly affected by fluorescent light.

Moisture - Fierz-David (38) believed that rancidity was produced by air, light and water; that fats containing saturated fatty acids were oxidized to their corresponding methyl alkyl ketones and that unsaturated fatty acids were split into aldehydes and acids. Holm (69) however, found that the presence of water in fat extended the induction period. Later Greenbank and Holm (53) expressed the same belief when they made a study of the factors concerned in the autoxidation of butterfat. They found that the presence of water or water vapor seems to retard the autoxidation of fats. Ritter and Nussbaumer (123) explained these results on the basis that butter serum must contain some substances which retard the oxidation of the butterfat. They found that the rate of oxidation of pure butterfat was scarcely affected by the addition of a quantity of water equal to that contained in butter. It appears that in butter the moisture itself does not play as important a role as does the material which it carries. They explained this effect on the basis of the cephalin and lecithin content of the serum. Thome (196) also believed that since the moisture content of butter is always high, changes in it will have little effect on the oxidative deterioration of butter.

Radema (114) examined samples of spray-dried whole milk from five factories. Portions of each sample were adjusted to moisture contents of 1.7, 2.4 and 4.2%, each portion being further subdivided

and stored in the dark at temperatures of 9, 20, 30 and 37°C for about one year. Samples were examined at intervals for flavour, moisture content, sulfhydryl reaction, peroxide numbers, reducing properties, TBA test and color in ultraviolet light. The results showed that the keeping quality of spray-dried whole milk decreased with increasing storage temperature and that high moisture content encouraged the development of tallowy flavour while a low moisture content encouraged a "glue-like" flavour.

Titov (151) reported that Meleshin butter contains moisture in a more highly dispersed state than ordinary churn butter and he believed that this particular property was responsible for the better keeping quality of the butter. Bogdanov and Titov (10) also studied the effect of moisture dispersion on the keeping quality of the butter. The role of protective substances said to be contained in the butter plasma was investigated by comparing butters made from two lots of "cream" prepared from butter by the addition of (1) salted water or (2) milk. When examined after 1 year's storage at -10°C the butterfat extracted from the latter butter had a better flavour and received a higher score than that from the former. In further experiments normal unwashed butter with finely dispersed moisture was awarded more points after 1 year's storage at -10°C than that containing moisture in large droplets. Csizar (25) attempted to show a relationship between water, fat and protein content of butter and its keeping quality. There was no correlation between acidity or air-content of butter and its keeping quality but the evenness of moisture distribution affected the keeping quality.

The first of these is the fact that the
 
to carry out its policy.

Salt - Washburn and Dahlberg (156) showed that salt, aside from its antiseptic property, hastened the deterioration of butter. Oily, metallic and fishy flavours showed up to a greater extent in salted than in unsalted butter. Guthrie et al. (60) showed that salt in butter greatly retards bacterial growth. Butters containing no salt were prone to become old or stale, but seldom oily. They concluded that this may be attributed to inhibited bacterial growth since they were stored at 10°C.

Jacobsen (79) reported that the destructive action of salt apparently was of greater importance than freezing in reducing the number of bacteria in salted butter. Thurston and Brown (150) concluded that since the concentration of salt is associated with the development of fishy flavour, and since fishy flavour apparently is the result of hydrolysis and oxidation of lecithin, salt tends to favor oxidative changes. Washburn and Dahlberg (155) have found that salted butter is more likely to turn fishy in storage than unsalted butter. Sommer and Smit (137) also reported that salt caused fishiness in butter.

Pandit et al. (104) compared butter samples with no or up to 3 washings, with 0 - 2.5% sodium chloride and from churned cream with acidity adjusted to 0.22 - 0.75% lactic acid. Acid values and peroxide values were measured and flavour was assessed at 7-day intervals during storage at 40°F. It was found that unwashed unripened butter containing 2% sodium chloride had the best keeping quality. Its flavour was improved at 0.45% acidity and it could still be stored

for 5 weeks. Kratochvil et al. (81) studied the keeping quality of unsalted and salted butter (1.5% salt) made in a wooden butter churn from cream ripened to 11.9° SH. The butter was wrapped in parchment paper or lined aluminum foil and was stored at 4 or 18°C for 48 days and tested organoleptically and chemically. The results showed that the salting had an adverse effect on organoleptic quality of butter during storage, particularly at the higher temperature and when the butter in parchment paper was exposed to light and sunshine. The use of aluminum foil improved substantially the keeping quality of salted butter.

Malm (90) found that high salt content (about 2%) retarded bacterial development but tended to promote oxidative deterioration. Grishchenko et al. (58) obtained evidence that the tendency of butter to become oily increased with increasing salt content and this became more pronounced the longer the butter was held in storage. Barnicoat (4) pointed out that deterioration of butter during storage at 14°C made from good quality cream was increased by high acidity, high copper and iron content and high salt content. Anderson and Olson (2) noted a slight deterioration of butter samples which they stored for 7 days at 80°F especially those with salt concentrations of 12 to 14% in the non-fat portion. Loftus-Hills and Conochie (87) found that a combination of pure magnesium chloride and sodium chloride in butter-fat promoted oxidative deterioration.

Acid - Many research workers (8, 61, 88, 103) have noted the detrimental effect of ripening cream on the keeping quality of the butter. Mortenson

(96) found that the percent acid in the cream was inversely proportional to the keeping quality. Sommer and Smit (137) found that the rate of oxidation is proportional to acidity.

Ritter (122) found that acidity was an important factor in the development of fishy flavour. Holm (69) correlated the change of butter flavour in storage with chemical changes which were brought about by oxidation. Greenbank (51) showed the importance of the use of high quality sweet cream for churning butter. He reported that cream having an acidity of 0.13 to 0.19% results in a butter with better keeping quality than with higher acidity. He found that butter made from cream of less than 0.2% acidity never became fishy. Storgards and Hietaranta (138) however, argued that the trimethylamine arising from lecithin and suspected to be responsible for off-flavour quality of butter is not considered an oxidation product since it is formed as a result of the reduction of lecithin. They argued that by increasing the pH decomposition of lecithin is prevented.

Masek et al. (92) confirmed the adverse effect of high acidity on butter stability. Rahmn (116) recommended that the pH of print butter intended for frozen storage should be between 6.4 and 7.1 in order to obtain the best keeping quality.

Dixon (31) reported that the pH of dairy products is temperature dependent. He recommended that for critical work temperature control to within plus or minus 1°C is required to equal the accuracy of pH measurement. Pont (110) observed a better keeping quality of

butter made from cream of lower acidity. Thurston and Brown (151) concluded that acidity appears to play an important role in the deterioration of butter which, under some conditions, appears to be the result of oxidation.

Antioxidant - Greenbank and Holms (56) found hydroquinone, phthalic acid and maleic acid to be good antioxidants. Of these three, maleic acid was the best. Olcott and Mathill (101) found pyrogallol, hydroquinone, pyrocatechol and hydroxyhydroquinone to be excellent antioxidants. Coe and LeClerc (21) found that maleic and phthalic acid, hydroquinone and pyrocatechol act as antioxidants.

Olcott and Emerson (100) found tocopherols to have antioxidant properties in lard. Takashi and Yoschiichi (142) found the phenols in incompletely burned oak smoke to have antioxygenic properties. Ritter and Nussbaumer (124) reported antioxidative properties of hydroquinone.

Koenig (78) reported that parchment paper used as butter wrapper treated with oat flour hexane extract, which they termed Avenol, had protective action against the development of rancidity. Dahle and Josephson (27) found that by treating parchment paper with finely ground oat flour which they called Avenex, flavour defects were retarded at 45°F but had little benefit as long as butter remained in storage at -15°F. They found that a water extract of Avenex improved the keeping quality of butter without affecting the flavour or incorporating sediment into the butter. Dahle (26) found that oat flour in

butter delayed stale and cheesy flavours. Several workers (24, 26, 27 78) found a similar retarding effect on the development of oxidized flavours in butter. They also found that the use of avarized parchment paper retarded surface flavours and improved keeping quality.

El-Negoumy and Hammond (34) studied the effect of different antioxidants in butter stored at temperatures from -18 to 38°F. They found that development of oxidized flavour was not significantly retarded by antioxidants at either temperature. Kotova (80) studied the effectiveness of several antioxidants in delaying fat oxidation as well as their effect on organoleptic properties of butter. The antioxidants were propyl gallate, ascorbyl stearate, nordihydroguaiaretic acid and carotene. The antioxidants were added to high fat cream and the keeping quality of the resultant butter presumably made by the Melechin process was assessed from the increase in peroxide value of butterfat at 10°C during 48 hours. The results show that propyl gallate, propyl gallate plus carotene and nordihydroguaiaretic acid plus carotene very effectively prevented the increase in peroxide value, ascorbyl stearate was less effective and carotene was ineffective. The taste of the butter was found to be affected to a varying extent by most of the antioxidants tested.

Lea(84) observed that the relative efficiencies of a series of antioxidants can be altered considerably by comparatively small changes in the composition of the substrate or even the temperature of oxidation and that the change in activity from one complex food to another can be very large.

Techniques in Autoxidation Studies.

A variety of techniques are employed in autoxidation studies, some of these are highly specialized, such as for example countercurrent extraction, low temperature crystallization, molecular distillation, chromatography and urea complex formation.

Molecular distillation (141), chromatography (37) and low temperature fractional crystallization (1, 141) were used in earlier attempts to isolate methyl oleate peroxides. Urea complex formation (22, 128) was used later to isolate the peroxides by precipitating the nonperoxide portions of the autoxidation mixtures. Solvent extraction (112), countercurrent extraction (42, 77), and reversed phase partition chromatography (128, 139) were made use of in obtaining peroxide concentrates.

Secondary autoxidation products have been steam-distilled from milk fat (66) and from autoxidized methyl isolinolenate (62) and collected in a dry ice trap during the autoxidation of methyl linolenate (74). These volatile fractions have further been characterized by chromatographing the carbonyl components as the respective 2, 4 dinitrophenylhydrazones derivatives (16, 62, 74). Isolation of secondary oxidation products was also done by Lundberg and Chipault (89) in their study of oxidation of methyl linoleate at various temperatures.

It is realized that many common analytical methods may yield false values when applied to highly oxidized oils because of

the interference of large amounts of peroxides.

Review of Methods for Determination of Autoxidation Products.

Peroxides.

Iodimetry - There are several modifications of this method. They are all based on the assumption that potassium iodide and hydroiodic acid, when brought in contact with fatty peroxides, liberate iodine quantitatively in some simple stoichiometric manner, with two atoms of liberated iodine equivalent to 1 atom of active oxygen.

The peroxide method of Wheeler (156) is most widely used. Improvements on this method were discussed in a recent study where exclusion of oxygen and light from the reagents and reaction flasks were suggested (119).

Polarography - Lewis et al. (85, 86) found a linear relationship between wave height and peroxide value in the early stages of the oxidation of fats. Ricciuti et al. (117) made a study of the polarographic behaviour in a more detailed investigation. They showed that peroxides, hydroperoxides, aldehydes, ketones conjugated with a double bond and alpha diketones could be measured polarographically. They demonstrated that hydroperoxides could be determined quantitatively in the presence of other peroxide types. Later Kuta and Quackenbush (82) published similar results.

Ferric thiocyanate method - This is a colorimetric method. The main criticism of this procedure is that it is subject to considerable

error. Several workers (17, 18) have described such a method but the peroxide value as determined by this means is higher than that usually found with the iodometric method.

Dichlorophenol-indophenol method - This method was introduced by Hartman and Glavind (63). It also yields high values in the presence of air (64). The values, however, are reproducible and are useful in comparative studies.

Carbonyl Compounds

It is a well-established fact that the major constituents of oxidized flavour of dairy products are carbonyl compounds (39, 40, 75, 76). For this reason several methods for the estimation of these compounds have resulted from many studies. Prill (111) devised a method for estimation of the alpha diketo compound. It is based on oximation of the diketo compounds present in the fat. The dioximes which are formed by the reaction are converted to derivatives of iron, nickel or copper, which are soluble in benzene with the formation of characteristically colored solutions.

O'Daniel and Parsons (99) suggested that the color developed during fat saponification may serve to indicate the presence of carbonyl compounds. They believed that the color developed during such treatment is due to the presence of quinoid compounds which results from aldol condensation of alpha diketones.

Lappin and Clark (83) developed a sensitive method for the estimation of carbonyl compounds using 2, 4-dinitrophenylhydrazine.

This was used by Neumer and Dugan (98) for estimating the stability of dry dog food and showed that the break in the rate curve of development of carbonyl compounds occurred simultaneously with the change in the rate of development of peroxides. The method of Lappin and Clark was modified by Berry and McKerrigan (6). They made use of two different wavelengths in the estimation of the presence of saturated and unsaturated carbonyl compounds. Henick et al. (67) further modified this procedure by using carbonyl-free benzene to minimize error. Trichloroacetic acid was used as a catalyst.

Bryant and Smith (13) developed a method in which the sample is added to a solution of hydroxylamine-hydrochloride in pyridine-bromphenol blue. After completion of the reaction the pyridine hydrochloride which is formed is titrated.

Thiobarbituric Acid Test - This test is concerned with the estimation of the oxidation of lipids through its formation of red color in a suitable solvent. The pigment is obtained as a result of a reaction between 2-TBA and malonic dialdehyde besides other aliphatic aldehydes.

Patton and Kurtz (108) have studied the reaction involved in the test and applied the test to detection of oxidation in milk fat. They found that malonic dialdehyde gave a strong test and that the TBA test is much more sensitive than the Kreis test. The latter did not begin to yield measurable colors until after very oxidized flavour appeared, whereas the TBA test gave good responses during the development

of perceptible rancidity. Methyl oleate hydroperoxides were also found to give the color reaction. Bernheim et al. (5) found that the color formed in the test is the result of a reaction between 2-TBA and oxidized unsaturated fatty acids or their degradation products. Briggs and Bryant (7) investigated various experimental factors of the TBA reaction with certain oxidized fatty acids and fatty esters. The procedure consists of heating the sample and the reagent together and then measuring the resulting red color in a spectrophotometer.

There are many variations of the TBA test; most of them being concerned with the adjustment to the particular fats or lipids under investigation. A method for fishery products was suggested by Yu and Sinnhuber (159) and later modified by the same authors (132). Others such as modifications for cereal and baked products (14), milk (33), butterfat (108), unsaturated fatty acids (157) frozen pork (130, 153), soybean oil, cottonseed oil and lard (129) were also developed.

Photochemical Methods - Oxidation-reduction indicators such as methylene blue have been utilized in different ways to estimate fat stability.

Greenbank and Holmes (54) used methylene blue. They found that the initial change in fats and oils could be detected through their action on the indicators in the presence of light. For this photochemical method the dye is mixed with the fat and the rate of reduction of the color of the dye indicates the rate of oxidation of the fat. Royce (125), however, found that the end point of the test was not satisfactory due to the formation of secondary color changes.

Coe (19) introduced a chemical procedure which he called chlorophyll value. It is based on the extent to which the natural fluorescence of chlorophyll was quenched when oxidized fat was added to it. The natural fluorescence of oils decreased as oxidation proceeded. French and Lundberg (41), however, did not find any stoichiometric relations between the quenching of the fluorescence and oxidation.

In 1943 Gudheim (59) constructed an accelerated light testing machine having approximately the same spectral distribution properties as sunlight to make a study on the effect of light on the odor and flavour of fat.

EXPERIMENTAL METHODS

The butter and butterfat were exposed to fluorescent light of the cool white variety which is the most commonly used type.

The state of oxidation of butter and butterfat was determined through the application of the peroxide test of Wheeler (158), the carbonyl test of Lappin and Clarke, as modified by Berry and McKerrigan (6), and determination of organoleptic properties by a small taste panel. The bleaching of the butter exposed to the light was recorded by photographs taken during the progress of bleaching.

Three sets of butter samples were tested. The first set was taken from different grocery stores at random. These samples were divided into two groups. The second group consisted of samples about which information as to distance from the light source and length of time of exposure were known. No such information was available about the first group.

The second set of samples was obtained unexposed from a local dairy. These samples were subjected to exposure to fluorescent lamps in the laboratory for various periods of time and at various distances from the light. They were exposed with parchment cover on and were tested periodically.

Before analysis, each sample of butter was divided into two parts. The first part consisted of layers of 1/4 inch thickness taken from the surface of the butter and designated (I) and the other

part consisted of the remainder after removal of the surfaces, and it is designated (II). This procedure was followed to determine the extent of penetration of the oxidation reaction to the interior of the samples.

The third set of samples was exposed to the lamp without wrappers. This set was divided into two groups. The first group, which is designated as (III), consisted of 1/4 inch of layers of butter and exposed to the light uncovered. The second group designated as (IV) was subjected to purification and dehydration and was poured into the petri dishes at approximately the same thickness as (III) and exposed to the light.

Chemical tests were done in triplicate and the average is presented in the tables.

The temperature used for exposure in the laboratory was 5°C. This is the usual keeping temperature used in grocery stores.

Preparation of butterfat (29) - Butterfat was prepared from butter by removal of the non-lipid material. The butter was melted, and washed repeatedly with warm water until the wash water became clear. The washed fat was then dried at the vacuum pump at about 50°C and subsequently filtered on a Buchner funnel.

Organoleptic Evaluation - All samples were tested by a small panel of tasters before chemical tests were run. A ranking method (36) was used and the following symbols were used to indicate the state of oxidation as judged by the panel:

- not oxidized

+ oxidized

++ highly oxidized

 

Bleaching of the butter was recorded photographically. The pictures were taken with the use of a green filter to obtain better contrast.

Peroxide Value (156) - Five grams of the fat were dissolved in 30 ml of acetic acid - chloroform (3:1). Saturated potassium iodide (1/2 ml) was added and the mixture was flushed with nitrogen for one minute. Thirty ml of distilled water and a few drops of starch indicator were added and the mixture titrated with 0.01 N sodium thiosulfate to a colorless end point.

Carbonyl Values - The Lappin and Clarke method as modified by Berry and McKerrigan (6) was used. This involved the formation of 2, 4 dinitrophenylhydrazones in benzene solution with trichloroacetic acid as a catalyst. The absorbances at 430 and 460 m μ were used to determine total saturated and unsaturated carbonyl compounds.

150 mg of the fat were weighed in 25 ml volumetric flask and filled up to mark with carbonyl free benzene. Five ml of the solution was pipetted into a 50 ml volumetric flask and 3 ml of trichloroacetic acid (6.5 g of trichloroacetic dissolved in 150 ml of carbonyl-free benzene) and 5 ml of saturated solution of 2, 4 dinitrophenylhydrazine in benzene were added. The sample was incubated for 30 minutes at 60°C in a water bath. After cooling to room temperature, 10 ml of 4% potassium hydroxide in methyl alcohol were added and diluted to 50 ml with methyl alcohol. After 10 minutes, measurements of the carbonyls are taken at 430 and 460 m μ . A blank was determined.

RESULTS

Butter samples exposed to fluorescent light (cool white) showed marked deterioration as indicated by the results of chemical and organoleptic tests.

Table 1 outlines the results of the tests done on butter samples obtained at random from grocery stores. Organoleptic tests indicated that 10 out of the 12 samples of series (I) were highly oxidized, 1 slightly oxidized, and 1 not oxidized. The poor flavour exhibited by a majority of the samples seems to indicate that the butter samples had been exposed for some length of time before they were removed from the display cases. It is known that butter may oxidize during prolonged storage (15, 70, 122, 146), and it could be suggested that the butter may have been oxidized before it was put in the display cases. However, this possibility can be discounted as butter is carefully graded by official inspectors.

The results of the peroxide tests seem to indicate that there is little relationship between flavour and peroxide value. This agrees with the findings of Keeney and Doan (75) who found in their study of fat oxidation that there is little relationship between flavour and peroxide value. This is because peroxides are in themselves flavourless substances although they are the precursors of off-flavour compounds.

The samples of series (I) and (II) with the maximum total carbonyl values tasted only slightly oxidized while the samples of

series (I) and (II) with relatively low total carbonyl values tasted highly oxidized. Reports in the literature on flavour resulting from the autoxidation of milk and milk products agree that the main components of these flavours are carbonyl compounds (3, 40, 75, 76). However, the component or components directly responsible have not been identified with certainty. It appears that in this investigation, the presence of high carbonyl levels do not necessarily indicate that the compounds responsible for oxidized taste are present. The results confirm the findings of Day and Lillard (3) who concluded from their investigation of autoxidation of milk lipids that a complete spectrum of saturated and unsaturated carbonyl compounds was necessary to produce the flavours resulting from oxidation. The different flavours were believed to arise from the various ratios and levels of these compounds in the fats at certain times and under certain conditions.

Table 2 outlines the results of the measurement of the state of oxidation of butter samples exposed on supermarket display shelves. The samples were exposed for different lengths of time before testing. The flavour score indicated that the majority of the samples of series (I) were highly oxidized irrespective of the length of time of exposure. This finding is in agreement with the results of a study made by El-Negoumy et al. (34). They found in their study of the volatile components of autoxidized milk fat using gas chromatography, that a single fraction could reproduce the oxidized flavour in dairy products during the early stages of oxidation. That these samples are in the

CONTENTS
ORIGINAL ARTICLES
The Medical Profession and the Public
The Medical Profession and the Public
The Medical Profession and the Public
The Medical Profession and the Public

DEPARTMENTS
The Medical Profession and the Public
The Medical Profession and the Public
The Medical Profession and the Public
The Medical Profession and the Public

THE JOURNAL OF THE AMERICAN MEDICAL ASSOCIATION
PUBLISHED WEEKLY
CHICAGO, ILL., MAY 1, 1913
Subscription price, \$5.00 per annum in advance.
Single copies, 15 cents.

Entered as Second-Class Matter, May 2, 1912, under Post Office No. 384, at Chicago, Ill., under special agreement of Post Office and General Delivery.
Acceptance for mailing at special rate of postage provided for in Act of October 3, 1917, authorized on May 1, 1913.
Postage paid at Chicago, Ill.

Published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.
Editor, J. C. Raper, M.D., 535 North Dearborn Street, Chicago, Ill.
Business Manager, J. C. Raper, M.D., 535 North Dearborn Street, Chicago, Ill.

Copyright, 1913, by American Medical Association
Printed by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.
The Journal of the American Medical Association is published weekly, except on Sundays and holidays, when it is published bi-weekly. It is published by the American Medical Association, 535 North Dearborn Street, Chicago, Ill.

initial stage of oxidation seems to be indicated by the results of the peroxide tests. There was relatively little variation in peroxide values of the samples of series (I) irrespective of the length of time of exposure, indicating that the samples were in their induction period. This is also true of the samples of series (II) although lower peroxide values were obtained.

The results of the tests done to follow the progress of oxidation of butter exposed in the laboratory at a distance of 10 inches from the light source are presented in Table 3. Exposure of 4 to 26 hours resulted in slightly oxidized flavour and after 2 days the samples tasted highly oxidized. The samples of series (II) did not have oxidized flavour after exposure from 2 to 10 hours and after 12 hours to 2 days' exposure they tasted slightly oxidized. Highly oxidized flavour was detected after 3 days to 4 weeks' exposure. The result of the peroxide tests demonstrated that the samples of series (I) were at the end of the induction period after two weeks' exposure when the value jumped to 29.74. The end of the induction period is indicated when a sudden increase in peroxide value occurs. This condition was also observed in the samples of series (II) although the peroxide values were not quite as high. It appears that the oxidation of the samples started at the surface and then gradually spread to the interior of the samples. This seems to support the findings of Dahle and Josephson (27) who found in his study of surface oxidation of butter that deterioration

of the samples starts at the surface before the interior of butter samples was affected. The results of the carbonyl tests seem to agree with the results of our previous experiments as shown in Tables 1 and 2. High levels of carbonyl compounds were not always accompanied by a highly oxidized flavour. The difficulty in detecting the carbonyl compounds responsible for oxidized flavour by chemical tests show that these compounds are probably highly specific. This was shown by Day and Lillard (28) who reported that oxidized flavour in milk fat is the result of combination of specific carbonyl compounds, namely, n-alkanals and alk-2-enals. They made this conclusion after finding that the qualitative composition of the mixture was the same regardless of the stage of oxidation of the fat.

Table 4 gives the results of the state of oxidation of butter samples exposed to fluorescent light at a distance of 20 inches. Samples of series (I) tasted highly oxidized after exposure for 18 hours. Samples of series (II) did not taste oxidized until after 10 hours exposure. Highly oxidized flavour was detected after exposure for 3 days. The peroxide values indicated that the induction period of the samples of series (I) ended after 2 weeks' exposure. The samples of series (II) showed that peroxides were still accumulating up to four weeks' exposure. Since the progress of a photochemical reaction depends on the amount

 

of energy absorbed by the substrate molecules, this observation appears to be in keeping with the distance between sample and light source. The results of the carbonyl tests closely parallels those of the flavour scores.

Table 5 gives the results of the tests done with butter samples exposed to fluorescent light at a distance of 30 inches. Organoleptic tests indicated that the samples of series (I) were slightly oxidized after 2 and up to 18 hours' exposure. They became highly oxidized thereafter. The results of peroxide tests indicated that the samples of series (I) were still in their induction period even after 4 weeks' exposure. Here again the role of the distance from the light is evident from the amount of the peroxides formed. The samples of series (II), giving lower peroxide values also indicated that they are in their induction period even after 4 weeks' exposure. The total carbonyl values showed the same trend as the development of oxidized flavour.

Table 6 gives the results of the tests done on butter and butterfat samples exposed at a distance of 10 inches from the light. The butterfat was prepared by melting of butter and repeated washing with warm water until the fat was clear and free from protein and phospholipids. It appears that more rapid oxidation occurred in the butterfat than in the butter because in two weeks the maximum amount of peroxides was formed in the butterfat whereas the

butter samples were still accumulating peroxides. According to Patton (106), triglycerides are relatively more stable when phospholipids are present in the aqueous phase of milk, and the phospholipids are preferentially oxidized. When water is absent the triglycerides are relatively more susceptible to oxidation, whereas the phospholipids are more stable. Since the butterfat was free of phospholipids the shorter induction period observed in the samples could be explained by this fact. The result of the carbonyl tests appears to indicate that high amount of carbonyls did not necessarily show off-flavour. This pattern of behaviour was also observed on the first set of butter samples. It is interesting to note that samples of almost the same amount of carbonyls gave off-flavour tastes of varying degrees. The specificity of the compounds responsible for oxidized flavour was the subject of several investigations (1, 3, 6, 10, 15, 36, 39, 40). Butter developed an oxidized flavour before the butterfat. This seems to agree with the findings of Tarassuk et al. (144) who observed that the origin of trainy flavour is in the phosphatide portion of the fat globule membrane material and that the flavour was produced by oxidation of the unsaturated fatty acids

of the phosphatides. The latter observation seems to hold true also for carbonyl formation in the samples. It was observed that higher amounts of carbonyls were present in the butter than in the butterfat. Since no phospholipids were present in the butterfat, butter could be expected to accumulate more carbonyls.

Table 8 gives the results of the tests done with butter and butterfat at a distance of 30 inches from the light. The induction period of the butter ended after exposure of 4 weeks. However, there was no appreciable change in the peroxide values of the samples of butterfat even after 4 weeks' exposure. This does not mean, however, that the samples did not reach the end of the induction period. More carbonyls seem to accumulate in the butter than in the butterfat. This is a pattern observed also in our previous experiment as shown by the results presented in Table 7. It is observed, however, that the butter developed oxidized flavour before the butterfat.

It has been reported that the development of rancidity in butter is accompanied by bleaching of carotene (69). The bleaching

of the butter in our experiment is presented photographically.

Figure 1 shows butter as it is exposed to light in the display shelves of a typical supermarket. Figure 2 shows the butter samples wrapped as they were exposed to light in the laboratory. Figures 3 to 8 show the butter samples after they were exposed to light for one week, the bleaching of the butter is indicated by the colour contrast between the control and the exposed sample.

Figures 9 to 14 show the butter samples after they were exposed for 2 weeks. The bleaching of the butter is more intense. The part of the butter covered by the dark-coloured trademark on the parchment seemed to have been protected somewhat. The protection of the parchment where it overlaps can also be seen.

Figures 15 to 20 show the butter samples after they were exposed to light for 3 weeks. Colour contrast between the exposed and the protected parts is more pronounced and bleaching is more distinct. The distance from the light seems to play a role since the contrast in the intensity of bleaching can be observed at different distances. There is more distinct and intense bleaching of the butter exposed at shorter distance for the same amount of time.

The first thing I noticed when I stepped out of the car was the cold. It was a sharp contrast to the warm blanket I had been sitting under. I looked up at the sky, which was a pale, hazy blue. The air smelled like wet earth and distant rain. I took a deep breath, feeling the coolness of the air fill my lungs. The ground beneath my feet was soft and spongy, like a bed of moss. I walked slowly, my boots crunching on the leaves and twigs. The trees around me were tall and thin, their branches reaching up towards the sky. The leaves were a mix of green and yellow, some still clinging to the branches and others already on the ground. The sun was low in the sky, casting a warm glow over the scene. The overall feeling was one of peace and tranquility, a moment of quiet reflection in a beautiful, natural setting.

As I walked further into the forest, the path became more defined. The trees were closer together, their branches forming a canopy overhead. The light filtering through the leaves was dappled and soft. I noticed a small stream flowing through the forest, its water clear and cold. The sound of the water was a gentle murmur, a constant presence in the background. The air was thick with the scent of pine and earth. I stopped for a moment, looking down at the water. The reflection of the trees and the sky was perfect, creating a mirror image of the world above. I felt a sense of awe and wonder, a reminder of the beauty and mystery of the natural world. The path led me deeper into the forest, where the trees were even taller and the light even softer. The feeling of being in a secret, hidden place was overwhelming. I knew that this was a special moment, one that I would never forget.

The path continued to wind through the forest, leading me to a clearing. The trees here were shorter and more spread out, allowing more light to reach the ground. The grass was a vibrant green, and there were many small flowers and plants growing. A small stream flowed through the clearing, its water sparkling in the sunlight. I walked to the edge of the stream and sat down on a large, flat rock. The water was so clear that I could see the bottom, where small stones and pebbles lay. The sound of the water was a soothing melody, a reminder of the flow of life. I closed my eyes and listened to the sounds of the forest. The rustle of leaves, the chirping of birds, the hum of insects. It was a symphony of nature, a beautiful and harmonious sound. I felt a sense of peace and contentment, a feeling of being exactly where I needed to be. The sun was now higher in the sky, and the light was warm and golden. The overall feeling was one of joy and happiness, a moment of pure bliss in the heart of the forest.

Figures 21 to 26 show the intensity of bleaching after four weeks' exposure. In this case even the darker part of the parchment affords little protection as indicated by Figure 21, which represents the shortest distance. At a greater distance, however, the protection of the dark-coloured part of the parchment paper is still evident, indicating that distance plays a role in butter bleaching.

THE UNIVERSITY OF CHICAGO
LIBRARY
1207 EAST 58TH STREET
CHICAGO, ILL. 60637
TEL. 773-936-5000
FAX 773-936-5001
WWW.CHICAGO.EDU

TABLE 1. Measurement of state of oxidation of butter samples obtained from supermarket display shelves.

Sample No.	Flavour Score		Peroxide Value Meq/kg		Carbonyls (Mmoles/kg)				Total Carbonyls	
	I	II	I	II	Saturated	I	II	I	II	
1	++	++	4.00	2.00	5.78	1.80	5.28	6.84	11.06	8.64
2	++	+	1.30	0.76	4.25	5.19	2.97	2.96	7.32	8.15
3	++	-	1.20	0.92	2.37	3.30	1.37	2.23	3.74	5.53
4	-	-	0.56	0.39	3.06	2.25	3.05	0.85	6.11	3.10
5	+	+	1.19	0.64	14.80	17.94	5.80	6.11	20.60	24.05
6	++	+	0.79	0.46	1.62	1.90	3.94	3.72	5.56	5.62
7	++	+	1.49	0.83	5.18	4.46	3.82	2.58	9.00	7.04
8	++	++	3.64	1.42	3.59	3.72	2.46	2.48	6.05	6.20
9	++	++	2.51	1.62	3.59	1.60	2.94	3.98	6.53	5.58
10	++	+	2.15	3.68	3.14	6.51	2.61	1.55	5.75	8.06
11	++	+	2.00	0.84	1.30	1.53	2.82	5.04	4.12	6.57
12	++	++	4.64	0.80	2.69	1.11	2.41	1.02	5.10	2.13

(I) surface layers 1/4 inch thick
 (II) the butter remaining after removal of the surface layers
 (- denotes not oxidized, + slightly oxidized and ++ highly oxidized)

Date	Particulars	Debit	Credit
1890			
Jan 1	Balance		100.00
Jan 10	By Cash	50.00	
Jan 20	To Cash		25.00
Jan 30	By Cash	75.00	
Feb 10	To Cash		100.00
Feb 20	By Cash	125.00	
Feb 30	To Cash		50.00
Mar 10	By Cash	150.00	
Mar 20	To Cash		75.00
Mar 30	By Cash	175.00	
Apr 10	To Cash		100.00
Apr 20	By Cash	200.00	
Apr 30	To Cash		125.00
May 10	By Cash	225.00	
May 20	To Cash		150.00
May 30	By Cash	250.00	
Jun 10	To Cash		175.00
Jun 20	By Cash	275.00	
Jun 30	To Cash		200.00
Jul 10	By Cash	300.00	
Jul 20	To Cash		225.00
Jul 30	By Cash	325.00	
Aug 10	To Cash		250.00
Aug 20	By Cash	350.00	
Aug 30	To Cash		275.00
Sep 10	By Cash	375.00	
Sep 20	To Cash		300.00
Sep 30	By Cash	400.00	
Oct 10	To Cash		325.00
Oct 20	By Cash	425.00	
Oct 30	To Cash		350.00
Nov 10	By Cash	450.00	
Nov 20	To Cash		375.00
Nov 30	By Cash	475.00	
Dec 10	To Cash		400.00
Dec 20	By Cash	500.00	
Dec 30	To Cash		425.00
Total		5000.00	5000.00

TABLE 2. Measurement of state of oxidation of butter samples exposed on supermarket display shelves.

Sample No.	Days Exposed	Flavour Score		Peroxide Value Meq/kg		Carbonyls Saturated		Carbonyls Unsaturated		Total Carbonyls	
		I	II	I	II	I	II	I	II	I	II
1	1	++	++	1.53	0.47	0.13	0.09	0.12	0.08	0.25	0.17
2	1	++	+	1.33	1.66	0.11	0.07	0.10	0.09	0.21	0.16
3	1	++	-	2.41	1.46	0.09	0	0.04	0	0.13	0
4	1	+	-	2.92	1.12	0.86	0.03	0.29	0.06	1.15	0.90
5	1	+	-	1.95	0.61	0.63	0	0.22	0	0.85	0
6	1	++	+	1.81	0.37	0.98	0.31	0.44	0.15	1.42	0.46
7	1	++	+	1.88	0.78	0.59	0.53	0.49	0.74	1.08	1.27
8	2	+	-	0.95	0.44	2.37	2.03	1.08	0.91	3.45	2.94
9	2	+	+	1.87	0.38	0.18	0.30	0.20	0.32	0.38	0.62
10	2	++	+	1.57	0.47	0.80	0.70	0.07	0.74	0.87	1.44
11	2	++	+	2.67	0.98	0.48	0.82	0.99	0.51	1.47	1.33
12	2	+	+	2.66	1.18	0.23	0.16	0.17	0.15	0.40	0.31
13	2	++	-	2.11	0.78	1.32	0.16	1.34	0.58	1.66	0.74
14	3	++	+	1.23	0.32	0.19	0.44	0.48	0.22	0.67	0.66
15	3	++	+	2.14	0.39	0.28	0.24	0.24	0.45	0.52	0.69
16	3	+	+	2.66	1.07	0.30	0.30	0.29	0.25	0.59	0.55

(I) surface layers 1/4 inch thick

(II) the butter remaining after removal of the surface layer

(- denotes oxidized, + slightly oxidized and ++ highly oxidized)

Before exposure the butter samples were first grade with no oxidized flavour.

TABLE 3. Progress of oxidation of butter exposed to fluorescent light at a distance of 10 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Carbonyls Saturated		Carbonyls Unsaturated		Total Carbonyls	
		I	II	I	II	I	II	I	II	I	II
1	2 hrs	-	-	0.75	0.53	2.41	0.78	2.40	1.01	4.81	1.79
2	4 hrs	+	-	1.70	0.69	0.73	0.45	1.15	0.60	1.88	1.05
3	6 hrs	+	-	0.95	0.75	6.74	4.25	7.64	4.93	14.38	9.18
4	8 hrs	+	-	1.45	0.65	1.87	1.84	1.62	2.99	3.49	4.83
5	10 hrs	+	-	1.17	0.55	1.34	3.70	1.81	1.77	3.15	5.47
6	12 hrs	+	+	0.87	0.46	0.68	2.69	2.38	6.98	3.06	9.67
7	16 hrs	+	+	0.55	1.30	2.56	4.88	5.88	3.91	8.44	8.79
8	18 hrs	+	+	0.57	0.60	17.28	6.25	4.30	3.03	21.58	9.28
9	24 hrs	+	+	1.93	0.53	16.34	8.64	2.88	3.21	19.22	11.85
10	26 hrs	+	+	1.90	0.76	1.90	0.76	4.39	3.23	6.29	3.99
11	2 days	++	+	2.67	1.29	0.81	0.17	0.33	0.53	1.14	0.70
12	3 days	++	++	3.76	1.74	0.76	0.78	0.95	0.95	1.71	1.73
13	4 days	++	++	2.26	1.32	0.24	0.06	0.63	0.40	0.87	0.46
14	5 days	++	++	2.23	0.83	0.70	15.85	9.98	1.66	10.68	17.51
15	1 week	++	++	1.76	0.57	3.42	5.35	5.32	8.38	8.74	13.73
16	2 weeks	++	++	5.66	1.05	1.00	0.54	4.50	12.19	5.50	12.73
17	3 weeks	++	++	29.74	4.80	0.53	0.69	0.97	0.23	1.50	0.92
18	4 weeks	++	++	12.75	3.25	7.07	9.42	13.18	7.78	20.25	17.20

(I) surface layers 1/4 inch thick

(II) the butter remaining after removal of the surface layer

(- denotes not oxidized, + slightly oxidized and ++ highly oxidized)

Before exposure, the butter samples were first grade with no oxidized flavour.

TABLE 4. Progress of oxidation of butter exposed to fluorescent light at a distance of 20 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Saturated		Unsaturated		Total Carbonyls	
		I	II	I	II	I	II	I	II	I	II
1	2 hrs	+	-	0.82	0.42	0.81	0.63	0.81	0.88	1.62	1.51
2	4 hrs	+	-	0.89	0.86	0.70	0.55	0.98	1.66	1.68	2.21
3	6 hrs	+	-	0.77	0.57	0.71	0.31	0.92	0.42	1.63	0.73
4	8 hrs	+	-	0.76	0.34	0.27	0.43	0.49	0.15	0.76	0.58
5	10 hrs	+	+	0.49	1.32	0.76	0.37	0.16	0.10	0.92	0.47
6	12 hrs	+	+	1.00	0.53	0.72	0.03	4.01	5.19	4.73	5.22
7	16 hrs	+	+	0.49	0.45	0.26	0.27	0.08	0.39	0.34	0.66
8	18 hrs	++	+	0.77	0.66	0.85	0.90	0.39	0.70	1.24	1.60
9	24 hrs	++	+	0.35	0.22	0.11	0.97	0.26	0.15	0.37	1.12
10	26 hrs	++	+	2.18	0.66	2.35	2.28	0.82	0.94	3.17	3.22
11	2 days	++	+	1.85	0.69	2.31	1.62	0.85	0.79	3.16	2.41
12	3 days	++	++	2.65	1.29	0.05	0.16	3.08	3.69	3.13	3.85
13	4 days	++	++	2.72	1.02	0.72	0.03	4.01	5.19	4.73	5.22
14	5 days	++	++	7.12	3.52	1.05	2.82	4.82	2.82	5.87	5.64
15	1 week	++	++	3.19	2.78	3.42	5.35	5.35	8.38	8.77	13.73
16	2 weeks	++	++	19.58	2.24	0.22	0.10	1.35	0.57	1.57	0.67
17	3 weeks	++	++	7.76	3.34	3.20	1.97	7.32	6.16	10.52	8.13
18	4 weeks	++	++	9.85	2.12	0.22	2.12	0.40	0.23	0.62	2.35

(I) surface layers 1/4 inch thick

(II) the butter remaining after removal of the surface layer

(- denotes not oxidized, + slightly oxidized and ++ highly oxidized)

Before exposure, the butter samples were first grade with no oxidized flavour.

TABLE 5. Progress of oxidation of butter exposed to fluorescent light at a distance of 30 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Saturated		Unsaturated		Total Carbonyls	
		I	II	I	II	I	II	I	II	I	II
1	2 hrs	+	-	0.36	0.19	2.19	3.28	1.78	3.61	3.79	6.89
2	4 hrs	+	-	0.25	0.19	3.29	2.68	5.53	0.38	8.82	3.06
3	6 hrs	+	-	1.17	0.30	0.46	0.05	0.38	3.40	9.84	3.45
4	8 hrs	+	+	0.97	0.96	0.33	0.48	3.72	4.07	4.05	4.55
5	10 hrs	+	+	0.97	1.50	0.74	0.70	0.13	0.26	0.87	0.96
6	12 hrs	+	+	0.98	0.55	1.78	0.70	6.02	3.98	7.80	4.68
7	16 hrs	+	+	0.24	0.32	0.05	0.47	0.05	0.77	0.10	1.24
8	18 hrs	+	+	0.42	0.66	0.18	0.08	0.21	0.76	0.39	0.84
9	24 hrs	++	+	0.24	0.32	0.22	0.10	0.10	0.08	0.32	0.81
10	26 hrs	++	+	1.78	1.34	2.45	0.05	0.89	0.98	3.34	1.03
11	2 days	++	+	2.20	1.34	2.09	0.08	0.82	0.82	2.91	0.90
12	3 days	++	++	2.37	0.89	1.49	0.75	5.05	4.28	6.54	5.03
13	4 days	++	++	2.22	0.77	0.42	2.30	3.62	3.27	4.04	5.57
14	5 days	++	++	3.52	2.13	1.05	1.32	3.33	2.13	4.38	3.45
15	1 week	++	++	3.81	0.11	2.96	2.97	4.25	5.19	7.31	8.16
16	2 weeks	++	++	2.39	1.23	3.46	0.40	11.80	28.93	15.26	29.33
17	3 weeks	++	++	2.13	1.78	17.32	2.51	27.17	1.29	44.49	3.80
18	4 weeks	++	++	3.77	1.41	0.22	0.08	0.40	0.23	0.62	1.03

(I) surface layers 1/4 inch thick

(II) the butter remaining after removal of the surface layer

(- denotes not oxidized, + slightly oxidized and ++ highly oxidized)

Before exposure, the butter samples were first grade with no oxidized flavour.

TABLE 6. Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 10 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Carbonyls (Mmoles/kg)		Total Carbonyls	
		III	IV	III	IV	Saturated	Unsaturated	III	IV
1	2 hrs	+	-	0.69	0.62	0.93	0.85	5.09	5.79
2	4 hrs	+	+	0.93	0.93	2.05	3.34	2.37	1.59
3	6 hrs	+	+	1.26	1.28	0.30	0.11	6.71	8.51
4	8 hrs	+	+	1.01	0.71	0.27	0.24	4.73	5.09
5	10 hrs	++	+	0.56	0.53	0.05	2.31	4.19	1.76
6	12 hrs	++	++	1.52	0.95	2.02	0.05	2.26	4.18
7	16 hrs	++	++	1.13	1.32	0.74	3.64	4.22	1.43
8	18 hrs	++	++	2.19	1.00	0.64	1.06	7.66	4.25
9	24 hrs	++	++	3.36	1.93	1.86	1.44	2.81	5.52
10	26 hrs	++	++	2.04	2.09	0.43	1.53	9.28	5.65
11	2 days	++	++	4.65	2.74	1.01	0.82	6.80	4.67
12	3 days	++	++	3.20	2.32	0.59	0.67	7.05	6.13
13	4 days	++	++	7.55	6.71	1.13	1.66	5.20	5.28
14	5 days	++	++	4.09	3.48	2.11	1.98	5.84	6.19
15	1 week	++	++	8.44	6.63	2.80	1.66	7.14	5.00
16	2 weeks	++	++	12.47	12.45	2.11	1.98	5.84	6.19
17	3 weeks	++	++	13.39	9.87	6.76	6.87	18.78	30.65
18	4 weeks	++	++	8.15	6.75	9.17	13.41	13.23	13.41
								25.54	37.52
								22.40	26.82

(III) surface layers 1/4 inch thick

(IV) purified sample of butterfat and exposed uncovered in petri dish

Before exposure, the butter samples were first grade with no oxidized flavour.

TABLE 7. Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 20 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Carbonyls (Mmoles/kg)		Total Carbonyls	
		III	IV	III	IV	Saturated	Unsaturated	III	IV
1	2 hrs	+	-	0.46	0.48	1.20	7.24	8.16	8.98
2	4 hrs	+	-	0.46	0.45	0.58	5.38	6.78	5.40
3	6 hrs	+	-	0.57	0.57	0.30	7.71	8.97	7.06
4	8 hrs	+	+	0.91	0.73	0.70	6.67	6.97	4.71
5	10 hrs	+	+	0.44	0.45	1.13	2.69	3.27	3.54
6	12 hrs	+	+	0.46	0.47	0.99	2.36	3.44	4.97
7	16 hrs	++	+	2.05	2.13	2.70	3.91	6.66	6.87
8	18 hrs	++	++	0.97	1.03	0.73	8.05	8.93	8.62
9	24 hrs	++	++	1.51	1.01	0.30	7.22	7.84	4.08
10	26 hrs	++	++	1.11	1.52	0.76	6.52	6.81	10.50
11	2 days	++	++	2.17	2.62	0.03	28.64	47.43	6.44
12	3 days	++	++	1.68	1.58	4.42	6.84	7.14	36.38
13	4 days	++	++	4.71	3.34	0.11	9.01	10.08	4.51
14	5 days	++	++	1.67	1.87	0.24	5.58	6.02	4.83
15	1 week	++	++	4.14	3.55	0.03	2.60	2.64	5.73
16	2 weeks	++	++	8.43	8.43	0.84	9.70	10.20	7.04
17	3 weeks	++	++	10.17	12.06	5.00	0.78	14.39	15.32
18	4 weeks	++	++	11.74	11.11	3.19	11.41	15.52	14.80

(III) surface layers 1/4 inch thick

(IV) purified sample of butterfat and exposed uncovered in petri dish

Before exposure, the butter samples were first grade with no oxidized flavour.

TABLE 8. Progress of oxidation of uncovered butter and butterfat samples exposed to fluorescent light at a distance of 30 inches.

Sample No.	Time Exposed	Flavour Score		Peroxide Value Meq/kg		Carbonyls (Mmoles/kg)		Total Carbonyls	
		III	IV	III	IV	Saturated	Unsaturated	III	IV
1	2 hrs	-	-	0.37	0.38	2.18	2.24	5.03	9.50
2	4 hrs	-	-	0.50	0.45	1.23	0.88	1.76	4.51
3	6 hrs	+	-	0.45	0.48	0.58	1.01	6.01	7.09
4	8 hrs	+	-	2.16	1.09	2.41	0.73	0.73	1.18
5	10 hrs	+	+	1.28	1.06	0.60	0.93	1.18	4.28
6	12 hrs	+	+	0.64	0.57	0.27	0.64	4.06	2.55
7	16 hrs	++	+	1.10	1.09	1.04	0.04	4.70	6.67
8	18 hrs	++	+	1.02	0.97	0.30	0.32	6.80	7.30
9	24 hrs	++	++	1.10	1.33	4.20	1.48	8.85	5.00
10	26 hrs	++	++	1.07	1.19	0.33	0.05	7.59	6.00
11	2 days	++	++	2.18	2.17	0.42	2.30	3.62	3.27
12	3 days	++	++	1.62	1.82	3.93	3.22	7.12	4.57
13	4 days	++	++	3.59	3.14	0.47	0.46	4.00	3.98
14	5 days	++	++	1.03	1.87	1.00	0.26	4.59	5.72
15	1 week	++	++	2.23	3.17	1.11	0.73	5.17	4.20
16	2 weeks	++	++	2.55	2.79	2.11	1.98	5.84	6.19
17	3 weeks	++	++	3.20	4.09	6.76	6.87	18.78	30.65
18	4 weeks	++	++	6.26	3.89	6.73	3.41	9.55	7.84
								7.21	11.74
								2.99	5.39
								6.59	8.10
								3.14	1.91
								1.78	5.21
								4.33	3.19
								5.74	6.71
								7.10	7.62
								13.05	6.48
								7.92	6.05
								4.02	5.57
								11.04	4.79
								4.47	4.44
								5.59	5.98
								6.28	9.93
								7.95	8.17
								25.54	37.52
								16.28	11.25

(III) surface layers 1/4 inch thick

(IV) purified sample of butterfat and exposed uncovered in petri dish

Before exposure, the butter samples were first grade with no oxidized flavour.

59 • AON

Fig. 1. Typical butter display shelf in a supermarket.

Fig. 2. Butter in parchment wrap for exposure test.
Note side (a) and side (b).

Fig. 3. Butter exposed for one week at a distance of 10 inches from the light, side (a).

Fig. 4. Butter exposed for one week at a distance of 10 inches from the light, side (b).

Fig. 5. Butter exposed for one week at a distance of 20 inches from the light, side (a).

[Faint, illegible text or markings at the bottom of the page, possibly a signature or a line of text.]

Fig. 6. Butter exposed for one week at a distance of 20 inches from the light, side (b).

Fig. 7. Butter exposed for one week at a distance of 30 inches from the light, side (a).

Fig. 8. Butter exposed for one week at a distance of 30 inches from the light, side (b).

Fig. 9. Butter exposed for two weeks at a distance of 10 inches from the light, side (a).

Fig. 10. Butter exposed for two weeks at a distance of 10 inches from the light, side (b).

— *Hydrolysis* —

Fig. 11. Butter exposed for two weeks at a distance of 20 inches from the light, side (a).

Fig. 12. Butter exposed for two weeks at a distance of 20 inches from the light, side (b).

Fig. 13. Butter exposed for two weeks at a distance of 30 inches from the light, side (a).

Fig. 14. Butter exposed for two weeks at a distance of 30 inches from the light, side (b).

Fig. 15. Butter exposed for three weeks at a distance of 10 inches from the light, side (a).

Fig. 16. Butter exposed for three weeks at a distance of 10 inches from the light, side (b).

Fig. 17. Butter exposed for three weeks at a distance of 20 inches from the light, side (a).

Fig. 18. Butter exposed for three weeks at a distance of 20 inches from the light, side (b).

Fig. 19. Butter exposed for three weeks at a distance of 30 inches from the light, side (a).

Fig. 20. Butter exposed for three weeks at a distance of 30 inches from the light, side (b).

NOV • 65

Fig. 21. Butter exposed for four weeks at a distance of 10 inches from the light, side (a).

NOV • 65

Fig. 22. Butter exposed for four weeks at a distance of 10 inches from the light, side (b).

NOV • 65

Fig. 23. Butter exposed for four weeks at a distance of 20 inches from the light, side (a).

Fig. 24. Butter exposed for four weeks at a distance of 20 inches from the light, side (b).

NOV • 65

Fig. 25. Butter exposed for four weeks at a distance of 30 inches from the light, side (a).

NOV • 65

Fig. 2. Butter in parchment wrap for exposure test.
Note side (a) and side (b).

DISCUSSION

During oxidation changes occur in the chemical as well as the biological properties of fats. In our experiments, it was demonstrated that with increasing exposure of butter to fluorescent light, the peroxide and carbonyl values changed greatly and this seemed to be closely paralleled by organoleptic changes.

It appears that the artificial lighting that is used in display cases plays an important part in butter oxidation. In some instances, it was observed that where the carbonyl determination gave very low values, the butter samples did not taste oxidized even if the peroxide values were comparatively high. It has been established that the major components of oxidized flavour in dairy products are carbonyl compounds (39, 40, 76, 78, 143). However, our observations demonstrate that the carbonyls responsible for off-flavour are highly specific. This observation was made by other investigators of oxidized flavour (3, 6, 23, 25, 28, 36).

According to Thome and Mattson (147), butterfat has a relatively long induction period. The results of our tests seem to verify this statement since the butter samples had an average induction period of 2 weeks, at which time large increases in

Section

 
the hundredth is the fact that the

peroxide values occurred. The same authors stated that the length of the induction period and the rate of oxidation during the active period, that is, the period when peroxides are formed in large amounts, are affected by the contents of conjugated C18 fatty acids and linolenic acid. The variations in the rate of oxidation of the different fats during the active period are attributed to variations in the contents of dienoic and trienoic acids. Dugan (32) noted that longer incubation periods at lower temperatures tended to bring out odours and flavours which will make a fat unfit for many uses, even though it is not rancid either in terms of peroxide value or organoleptic evaluation. The results of our experiments seem in agreement with this finding. This is especially observed with the samples exposed in the laboratory.

The parchment covered samples that were exposed at a distance of 10 inches from the light seemed to have a well-defined induction period. The interior samples had the same well-defined induction period although they did not develop high peroxide values. According to Patton (106), dairy products follow the common hydroperoxide mechanism of lipid oxidation, that is, they have an induction period during which the amount of peroxides formed increases only slowly, the end of this period is indicated by a sudden increase in peroxide value.

The parchment covered samples exposed at a distance of 20 inches from the light also had a distinct induction period. The higher total carbonyl contents were accompanied by relatively low peroxide values. The interior samples also had high carbonyl values at the time of maximum carbonyl formation at the surface. The organoleptic tests indicated that the fat at this point was already highly oxidized. Henick et al. (67), in their study of corn and soybean oils autoxidized at 98.7°C, observed that the content of unsaturated carbonyls exceeded that of the saturated ones, which only increased markedly at a later stage of rancidity. Berry and McKerrigan (6) believed that this was due to the fact that initially carbonyl compounds formed from linolenic and linoleic acyl groups were unsaturated; breakdown of the primary carbonyl compounds by scission then led to unsaturated or saturated short chain carbonyls, and because these compounds have powerful off-flavours they will apparently result in the appearance of organoleptic rancidity.

It appears that butterfat does not develop oxidized flavours as fast as butter does. This seems to agree with the findings of Patton (106) who argued that with butter which represents an aqueous system of phospholipids dispersed in fat, both fat and phospholipids are susceptible to oxidation, the latter being more easily oxidized. It appears that there is a

difference in the susceptibility of phospholipids to oxidation depending upon whether they are present in fat or water. The butter samples had lower unsaturated carbonyl values than butterfat. This seems to indicate that the presence of phospholipids has an effect on the formation of unsaturated carbonyls, it may be that the phospholipids inhibit the formation of carbonyls or they may promote the rapid breakdown of carbonyls so that they are not detected in the test. The latter argument seems favored by various studies (120,140, 145, 147, 149, 150). A similar pattern seems to be followed by the results listed in tables 7 and 8. Swanson and Sommer (140) have shown that the development of oxidized flavour is primarily due to the partial oxidation of phospholipids. This was verified by the results of a study made by Riel and Sommer (120).

While the peroxide value is used as a measure of oxidation of fats, it is not usually a good criterion for flavour score of fat (32). Evans (36) observed in his experiments with soybean oil that the peroxide value is not consistent with the flavour score, especially when the oil was subjected to different conditions of oxidation. This seems to be the case also with the results of the experiments presented in Tables 1 to 8. Many of the butter samples with peroxide values of less than 1 tasted

highly oxidized and butter samples with higher peroxide values did not give any oxidized flavour. In some cases, samples having the same or nearly the same peroxide values had different flavour scores. Caution is needed therefore, in the interpretation of relationship of peroxide value and flavour score as was mentioned by Dugan (32).

Results of our experiments show there are cases when butter samples with very high carbonyl values tasted only slightly oxidized. This seems to support the findings of Badings (3), who suggested that an autoxidizing fat is in a dynamic state and therefore any chemical or organoleptic tests reflect only the situation of the oxidizing fat at the particular time of sampling. However, several samples with very low carbonyl values gave highly oxidized flavour. According to Keeney and Doan (76) oxidation products responsible for off-flavour are perceptible in far smaller concentration than can be detected chemically. This was also shown by Patton (107), who reported that deca-2,4-dienal can be detected organoleptically at a concentration of one part per billion. It appears that in this particular condition, organoleptic evaluation would be more sensitive than chemical tests since it would be difficult to measure the compounds responsible for off-flavour at this very low level.

The bleaching of the butter exposed with parchment cover is illustrated by a series of photographs. They were taken weekly for four weeks to show the changes in colour. It appears that both the distance from and the length of time to exposure to the light have an effect on the butter. A study of the photographs reveals a gradual bleaching of the samples from the first week to the fourth week, when the surface colour was almost completely bleached. There were, however, fine points that cannot readily be observed in the photographs such as for example, the darker blotches where the butter forms crevices which did not receive as much light as the rest of the surface, and the slightly darker colour where the parchment paper did not adhere evenly to the butter surface.

It can be concluded from the results presented in this thesis, that light induced oxidation of butter in retail stores is a serious problem. It is possible that the quality of butter available to the consumer is greatly affected by oxidative deterioration.

Several remedies can be suggested, one is the replacement of the commonly used cool white lamps with lamps having less of the harmful short wave length radiation. This is not likely to afford complete protection and does not seem to offer a practical solution to the problem. The second possibility is the shielding of the butter from the light by packaging in aluminum foil or cardboard containers. Although the cost of the packaging material will be somewhat higher, this will give full protection, and is already in practical use in some locations. It appears that this approach deserves careful consideration by the butter industry, as it will result in greatly improved butter quality and increased consumer satisfaction.

 

BIBLIOGRAPHY

1. Allen, R.R., and Kummerow, F.A.
Factors Affecting the Stability of Highly Unsaturated
Acids III. The Autoxidation of Methyl Eleostearate.
J. Am. Oil Chem. Soc. 28:101 (1951)
2. Andersen, R.E. and Olson, H.C.
The Effect of Added Salt on the Deterioration of High-
Fat Cream Stored Without Refrigeration.
Tech. Bull. Okla Agric. Exp. Sta. T-41 (1941)
3. Badings, H.T.
Principles of Autoxidation Processes in Lipids with
Special Regards to the Development of Autoxidation Off-
Flavours.
Neth. Milk Dairy J. 14:215 (1960)
4. Barnicoat, C.R.
Experiments on the Packing and Storage of Butter X.
Experiments on Predicting the Storage Life of Butter.
N.Z. Jl. Sci. Technol. 33:37 (1951)
Cited by Ingham, S.E.
In:Dairy Sci. Abstr. 14:478 (1952)
5. Bernheim, F., Bernheim, M.L. and Wilbur, K.M.
The Reaction Between TBA and the Oxidation Products
of Certain Lipides.
J. Biol. Chem. 174:257 (1948)
6. Berry, N.W. and McKerrigan, A.A.
Carbonyl Compounds as a Criterion of Flavour Deterioration
of Edible Fats.
J. Sci. Fd. Agric. 9:693 (1958)
7. Biggs, D.A. and Bryant, W.M.D.
The Thiobarbituric Acid Test for Butterfat Oxidation.
Can. J. Technol. 31:138 (1953)
8. Briggs, L.H.
The Autoxidation of Butterfat. I. Factors Influencing the
Reaction.
J. Dairy Res. 3:61 (1932)
9. Briggs, L.H.
The Autoxidation of Butterfat. II. Comparison of Tests
for Detecting Oxidation Changes.
J. Dairy Res. 3:70 (1932)

THE

OF THE

AND

OF THE

OF THE

OF THE

OF THE

OF THE

OF THE

10. Bogdanov, V. and Titov, V.
Povshenie Stoykosti Slivochnogo Masla.
Mol. Prom. 12:26 (1951)
Cited by Lang, F. Improving the Keeping Quality of Butter.
Dairy Sci. Abstr. 14:670 (1952)
11. Brown, C.W. and Dustman, R.B.
A study of the Relations of Titrable Acidity to Metal-Developed Oxidized Flavour in Milk.
J. Dairy Sci. 21:144 (1938)
12. Browne, C.A.
The Spontaneous Decomposition of Butterfat.
Ind. Engng. Chem. 17:44 (1925)
13. Bryant, W.M.D. and Smith, D.M.
Improved Hydroxylamine Method for the Determination of Aldehydes and Ketones. Displacement of Oxime Equilibria by Means of Pyridine.
J. Am. Chem. Soc. 57:57 (1935)
14. Caldwell, E.F. and Grogg, B.
Application of the TBA Test to Cereal and Baked Products.
Fd. Technol. 5:145 (1951)
15. Carson, B.W. and Thurston, L.M.
A Review of Oxidation in Milk and Milk Products as Related to Flavour.
J. Dairy Sc. 23:629 (1940)
16. Chang, S.S. and Kummerow, F.A.
The Relationship Between the Oxidative Polymers of Soybean Oil and Flavour Reversion.
J. Am. Oil Chem. Soc. 31:324 (1954)
17. Chapman, R.A. and Mackay, R.
The Estimation of Peroxides in Fats and Oils by the Ferric-Thiocyanate Method.
J. Am. Oil Chem. Soc. 26:360 (1949)
18. Chapman, R.A. and McFarlane, W.D.
A Colorimetric Method for the Determination of Fat-Peroxides and Its Application in the Study of the Keeping Quality of Milk Powders.
Can. J. Res. 21:133 (1943)
19. Coe, M.R.
Photochemical Studies of Rancidity: A Note on the Possibility of Using "Chlorophyll Values" as Means of Estimating the Stability of an Oil or Fat.
J. Am. Oil Chem. Soc. 16:146 (1939)

20. Coe, M.R. and LeClerc, J.A.
Photochemical Action, A Cause of Rancidity.
Cereal Chem. 9:519 (1932)
21. Coe, M.R. and LeClerc, J.A.
Photochemical Studies of Rancidity: Antioxidant
vs. Green Light Protection.
Oil Soap: 12:231 (1935)
22. Coleman, J.E., Knight, H.B. and Swern, D.
Reactions of Fatty Materials with Oxygen XVII. Some
Observations on the Secondary Products of Autoxidation
of Methyl Oleate.
J. Am. Oil Chem. Soc. 32:135 (1955)
23. Columbic, C.C., Martin J. and Daubert, B.F.
Flavour Reversion in Soybean Oil II. The Effect of
Atmosphere of Different Oxygen Concentration in Flavour
Reversion of Soybean Oil.
Oil Soap. 23:360 (1946)
24. Corbett, W.G. and Tracy, D.H.
Use of Antioxidant to Prevent Tallowiness in Butter
Natn. Butt. Cheese J. 29:8 (1938)
25. Csiszar, J.
Egy év Vajvizsgalati eredményei. IV. Befejezo
koslemenye. Osszefugges a vaj kemiai - fizikai tulaj-
donsagai es az erzeszervi minosef (iz es szag), valamint
az eltarthatosag kozott.
Tejgazdasag 5:9 (1947).
cited by Burton, J.M. The Results of One Year Butter-
Control Work. (Part IV) Correlation Between the Physico-
Chemical and Organoleptic Properties of Butter and its
Keeping Qualities.
Dairy Sci. Abstr. 12:195 (1950)
26. Dahle, C.D.
An Antioxidant for Dairy Products
Natn. Butt. Cheese J. 29:8 (1938)
27. Dahle, C.D. and Josephson, W.S.
Delaying Oxidative Changes in Butter.
Natn. Butt. Cheese J. 28:18 (1937)
28. Day, E.A. and Lillard, A.
Autoxidation of Milk Lipids. I. Identification of
Volatile Monocarbonyl Compounds from Autoxidized Milk Fat.
J. Dairy Sci. 43:585 (1960)
29. deMan, J.M.
Physical Properties of Milkfat I. Influence of Modification.
J. Dairy Res. 28:81 (1961)

30. deMan, J.M. and Engelhardt, J.
Polarographic Determination of Copper and Iron in Fats.
Lab. Pract. 1188 (1964)
31. Dixon, B.
The Effect of Temperature on the pH of Dairy Products.
Aust. J. Dairy Technol. 18:141 (1963)
32. Dugan, L.
Stability and Rancidity
J. Am. Oil Chem. Soc. 32:605 (1955)
33. Dunkley, W.L. and Jennings, W.G.
A Procedure for Application of the Thiobarbituric Acid
Test to Milk.
J. Dairy Sci. 34:1064 (1951)
34. El-Negoumy, A.M. and Hammond, C.G.
Effect of Antioxidant in the Development of Oxidized
Flavour in Cold Storage Butter.
J. Dairy Sci. 43:859 (1960)
35. Emery, J.A. and Henley, R.R.
Studies on Rancidity. I. Influence of Air, Light and
Metals on the Development of Rancidity.
Ind. Engng. Chem. 14:937 (1922)
36. Evans, C.D.
Flavour Evaluations of Fats and Oils.
J. Am. Oil Chem. Soc. 32:596 (1955)
37. Farmer, E.H., and Sutton, D.A.
The Course of Autoxidation Reactions in Polyisoprenes
and Allied Compounds. Part IV. The Isolation and
Constitution of Photochemically Prepared Methyl Oleate
Peroxide.
J. Chem. Soc. 119 (1943)
38. Fierz-David, H.E.
Rancidity of Fats.
Z. Angew Chem. 38:6 (1925)
cited by Scherubel, E. Chem. Abstr. 19:1503 (1925)
39. Forss, D.A., Pont, E.G. and Stark, W.
The Volatile Compounds Associated with Oxidized Flavour
in Skim Milk.
J. Dairy Res. 22:91 (1955)
40. Forss, D.A., Pont, E.G. and Stark, W.
Further Observations on the Volatile Compounds Associated
with Oxidized Flavour in Skim Milk.
J. Dairy Res. 22:345 (1955)

THE FIRST PART OF THE HISTORY OF THE
LIFE OF THE LATE KING OF GREAT BRITAIN

CHARLES THE SECOND

BY JOHN BURNET

IN TWO VOLUMES

LONDON

Printed by J. Sturges, at the Angel in St. Dunstons Church

1724

THE SECOND PART OF THE HISTORY OF THE
LIFE OF THE LATE KING OF GREAT BRITAIN

CHARLES THE SECOND

BY JOHN BURNET

IN TWO VOLUMES

LONDON

41. French, C.S. and Lundberg, W.O.
Fluorescence of Chlorophyll in Fats in Relation to Rancidity.
Oil Soap 21:23 (1944)
42. Fugger, J., Zilch, K.T., Cannon, J.A. and Dutton, H.J.
Analysis of Fat Oxidation Products by Countercurrent Distribution Methods. II. Methyl Oleate.
J. Am. Chem. Soc. 73:2861 (1951)
43. Futschik, J. and Aigner, M.
Über den Einfluss des Kunstlichen Lichtes auf die Qualität der Butter.
Milchwiss. Berichte, Wolfpassing 4:173 (1954)
cited by Mann, E.G. The Effect of Artificial Light on the Quality of Butter. Dairy Sci. Abstr. 17:430 (1955)
44. Futschik, J. and Aigner, M.
Massnahmen zur Verringerung bzw. Verhinderung des qualitätsvermindernden Einglusses von Leuchstoffrohrenlicht.
Dtsch. Molkereiztg. 81:703 (1960)
cited by Lang, F. Measures for the Reduction or Prevention of the Quality-Reducing Effect of Fluorescent Light.
Dairy Sci. Abstr. 43:2687 (1960)
45. Gaddis, A.M., Ellis, R. and Currie, G.T.
Carbonyls in Oxidizing Fat. V. The Composition of Neutral Volatile Monocarbonyl Compounds from Autoxidized Oleate, Linoleate, Linolenate Esters and Fats.
J. Am. Oil Chem. Soc. 38:371 (1961)
46. Gebhardt, H.T. and Sommer, H.H.
Residual Current Measurements in Control of Metal Solution in Milk.
Ind. Engng. Chem. Analyt. Ed. 3:414 (1931)
47. Gebhart, H.T. and Sommer, H.H.
The Solubility of Metals in Milk. I. The Solubility of Copper Under Various Conditions.
J. Dairy Sci. 14:416 (1931)
48. Gebhart, H.T. and Sommer, H.H.
The Solubility of Metals in Milk. II. Submerged Corrosion Tests of Various Metals in Milk.
J. Dairy Sci. 15:42 (1932)
49. Giermak, A.
Things Are Getting Rougher All the Time.
Milk Prod. J. 54:8 (1963)
50. Greenbank, G.R.
Variations in the Oxidation-Reduction Potential as a Cause for the Oxidized Flavour in Milk.
J. Dairy Sci. 23:274 (1940)

51. Greenbank, G.R.
The Oxidative Deterioration of Dairy Products.
XII Int. Dairy Congr. 2:284 (1949)
52. Greenbank, G.R.
The Oxidation of Fats in Storage.
Oil Soap 13:140 (1936)
53. Greenbank, G.R. and Holm, G.E.
Some Factors Concerned in the Autoxidation of Fats.
Ind. Engng. Chem. 16:598 (1924)
54. Greenbank, G.R. and Holm, G.E.
A Photochemical Method for Measuring Susceptibility
of Fats and Oils to Oxidation.
Ind. Engng. Chem. Analyt. Ed. 2:9 (1930)
55. Greenbank, G.R. and Holm, G.E.
Photochemical Oxidation of Cottonseed Oil.
Ind. Engng. Chem. Analyt. Ed. 25:167 (1933)
56. Greenbank, G.R. and Holm, G.E.
Promoting the Oxidation of Fats and Oils.
Ind. Engng. Chem. Analyt. Ed. 33:1058 (1941)
57. Greenbank, G.R. and Weihe, H.D.
The Oxidative Deterioration of Butter Oil at Various
Temperatures with Added Antioxidants.
J. Dairy Sci. 40:601 (1957)
58. Grishchenko, A., Lapshin, A. and Shuvalov, V.
Masloizgotovitel nepryvnogo deystviya tipa GLSh-1.
Mol. Prom. 12:16 (1951)
cited by Lang, F. Continuous Buttermaking Machine Type
G.L.sh-1. Dairy Sci. Abstr. 13:269 (1951)
59. Gudheim, A.R.
Some Factors Pertaining to the Packaging of Shortening
in Glass.
Oil Soap 20:197 (1943)
60. Guthrie, E.E., Shceib, B.J. and Stark, C.N.
The Effect of Certain Factors upon the Keeping Quality
of Butter.
J. Dairy Sci. 29:267 (1936)
61. Haglund, E., Platon, B., Waller, E. and Soderberg, E.
Medd. Centralanstalt. forsoksvasendet Indbruks No. 347
Mejeriavdel No. 37 (1929)
cited by Dahlen, M.A. The Effect of the Method of Prep-
aration on the Keeping Qualities of Butter. Chem. Abstr.
32:4509 (1929)

62. Harrison, J.B. and Daubert, B.F.
Flavour Reversion in Soybean Oil. VII. The Autoxidation
of Isolinoleic Acid.
J. Am. Oil Chem. Soc. 30:371 (1953)
63. Hartman, S. and Glavind, J.
A New Sensitive Method for the Determination of Peroxides
of Fats and Fatty Acids.
Acta Chem. Scand. 3:954 (1949)
64. Hartman, L. and White, M.D.L.
The Significance of Peroxide Determination in Fats by the
Dichloro-Indophenol Method.
J. Sci. Fd. Agric. 3:112 (1952)
65. Henderson, J.L. and Roadhouse, C.L.
Factors Influencing the Initial Induction Period in the
Oxidation of Milkfat.
J. Dairy Sci. 17:321 (1934)
66. Henick, A.S.
Detection of Deterioration Products of Autoxidizing Milkfat
by Infrared Spectrophotometry.
Fd. Technol. 5:145 (1951)
67. Henick, A.S., Benca, M.F. and Mitchell, J.H. Jr.
Estimating Carbonyl Compounds in Fats and Foods.
J. Am. Oil Chem. Soc. 31:88 (1954)
68. Herrington, B.L. and Brereton, J.G.
A Simple Method for the Detection of Copper in Alloys.
J. Dairy Sci. 20:197 (1937)
69. Holm, G.E.
The Oxidative Determination of Dairy Products.
XII Int. Dairy Congr. 2:284 (1949)
70. Holm, G.E. and Greenbank, G.R.
The Keeping Quality of Butterfat with Special Reference
to Milk Powder.
Proc. Wld. Dairy Congr. 2:1253 (1923)
71. Holm, G.E., Wright, P.A. and Greenbank, G.R.
Variations in the Susceptibility of the Fat in Dry Whole
Milks to Oxidation When Stored at Various Temperatures
and in Various Atmospheres.
J. Dairy Sci. 10:33 (1927)
72. Hunziker, O.F. and Hosman, D.F.
Tallowy Butter - Its Causes and Prevention.
J. Dairy Sci. 1:320 (1917)

73. Jacobsen, D.H.
Bacterial Content and Keeping Quality of Butter after
Removal from Storage.
J. Dairy Sci. 21:187 (1938)
74. Kawahara, F.K., Dutton, H.J. and Cowan, J.C.
Volatile Cleavage Products of Autoxidized Methyl Linolenate.
J. Am. Oil Chem. Soc. 29:633 (1952)
75. Keeney, M. and Doan, F.J.
Studies on Oxidized Milkfat. I. Observations on the
Chemical Properties of the Volatile Flavour Material
from Oxidized Milkfat.
J. Dairy Sci. 34:713 (1951)
76. Keeney, M. and Doan, M.J.
Studies on Oxidized Milkfat. II. Chemical and Organoleptic
Properties of Volatile Materials Obtained by Fractionation
with Various Solvents and Girard's Reagent.
J. Dairy Sci. 34:728 (1951)
77. Khan, N.A., Lundberg, W.O. and Holman, R.T.
Displacement Analysis of Lipids. IX. Products of Oxidation
of Methyl Linoleate.
J. Am. Chem. Soc. 76:1779 (1954)
78. Koenig, V.L.
Stabilization of Butter Against Oxidized Flavour.
Natn. Butt. Cheese J. 28:26 (1937)
79. Koops, J.
Antioxidant Activity of Ascorbyl Palmitate in Cold-Stored
Cultured Butter.
Neth. Milk Dairy J. 18:38 (1964)
80. Kotova, O.
Antiokisliteli dlya molochnogo zhira.
Mol. Prom. 20:37 (1959)
cited by Lang, F. Antioxidants for Butterfat. Dairy Sci.
Abstr. 22:538 (1960)
81. Kratochvil, L., Stoskova, I. and Loukotova, L.
Studium vlivu chloridu sodneho na trvanlivost masla
Prumysl Potravin: 11:182 (1960)
cited by Lang, F. Effect of Sodium Chloride on the Keeping
Quality of Butter. Dairy Sci. Abstr. 22:2756 (1960)
82. Kuta, E.J. and Quackenbush, F.W.
A Polarographic Study of Organic Peroxides.
Analyt. Chem. 32:1069 (1960)

83. Lappin, G.R. and Clark, L.C.
Colorimetric Method for Determination of Traces of
Carbonyl Compounds.
Analyt. Chem. 23:541 (1951)
84. Lea, C.H.
Antioxidants in Dry Fat System.
J. Sci. Fd. Agric. 9:693 (1960)
85. Lewis, W.R. and Quackenbush, F.W.
The Use of the Polarograph to Distinguish Between the
Peroxide Structures in Oxidized Fats.
J. Am. Oil Chem. Soc. 26:53 (1949)
86. Lewis, W.R., Quackenbush, F.W., and de Vries, T.
Polarographic Studies of Organic Peroxides in Non-Aqueous
Solutions.
Analyt. Chem. 21:762 (1949)
87. Loftus-Hills, G. and Conochie, J.
The Oxidant Effect of Commercial Salt in Fats and Oils.
J. Coun. Sci. Industr. Res. Aust. 18:355 (1945)
cited by Muers, M.M. Dairy Sci. Abstr. 9:244 (1947)
88. Loftus-Hills, G. and Sharp, L.R.
A Study of Factors Influencing the Keeping Quality of
Some Victoria Salted Butters in Cold Storage.
J. Dairy Res. 5:124 (1934)
89. Lundberg, W.O. and Chipault, J.R.
The Oxidation of Methyl Linoleate at Various Temperatures.
J. Am. Chem. Soc. 69:833 (1947)
90. Malm, B.
Forsok med olika pH i farsksmor.
Mejeritekn. Medd. 17:83 (1956)
cited by Arup, P.S. Experiments with Varying pH in Fresh
Butter. Dairy Sci. Abstr. 19:134 (1957)
91. Malm, B. and Hildingstons, B.
Kyldisbelysnings inverkan pa smorets kvalitet.
Svenska Mejeritidn. 47:469 (1955)
cited by: Hiscox, E.R. The Effect of the Lighting in Cold
Cabinets on Butter Quality. Dairy Sci. Abstr. 17:816 (1955)
92. Masek, J., Maxa, V. and Vedlich, M.
A Contribution to the Research Concerning a Suitable Manu-
facturing Process of Long Keeping Quality Cold Storage Butter.
XIV Int. Dairy Congr. 2:246 (1956)

 

93. McConnell, J.E. and Eoselen, W.B. Jr.
Effect of Storage Conditions and Antioxidants on the
Keeping Quality of Packaged Oils.
J. Am. Oil Chem. Soc. 24:6 (1947)
94. Miscall, J. and Cavanaugh, G.W.
Copper in Dairy Products and its Solution Under
Various Conditions II.
J. Dairy Sci. 22:379 (1929)
95. Moser, H.A., Evans, C.D., Cowan, J.C. and Kwolek, W.F.
A Light Test to Measure Stability of Edible Oils.
J. Am. Oil Chem. Soc. 47:30 (1965)
96. Mortensen, M.
The Improvement of Flavour and Keeping Quality of Hand-
Separator Cream-Butter.
J. Dairy Sci. 7:460 (1924)
97. Nestrelayev, A.
Effect of Light and Air on Butterfat.
Milchwirtsch 6:1
cited by Van Slyke, L.L. Chem. Abstr. 4:836 (1910)
98. Neumer, J.F. and Dugan, L.R.
The Use of Antioxidants in Dry Dog Food.
Ed. Technol. 7:189 (1953)
99. O'Daniel, L. and Parsons, L.B.
A Rapid Test for Alpha Dicarbonyls
Oil Soap 20:72 (1943)
100. Olcott, H.S. and Emerson, O.H.
Antioxidants and the Autoxidation of Fats. IX. The
Antioxidant Properties of the Tocopherols.
J. Am. Chem. Soc. 59:1008 (1937)
101. Olcott, H.S. and Mathill, N.C.
Antioxidants and the Autoxidation of Fats. VII. Prelim-
inary Classification of Inhibitors.
J. Am. Chem. Soc. 58:2204 (1936)
102. Osborne, T.B. and Leavenworth, C.S.
Protein Copper Compounds.
J. Biol. Chem. 28:109 (1948)
103. Overman, O.R.
Factors Relating to the Keeping Quality of Butter.
Natn. Butt. Cheese J. 27:16 (1936)

104. Pandit, N.N., Rawat, R.S. and Singh, S.N.
Studies on the Keeping Quality of Cream During Storage
at 40°F.
Agra Univ. J. Res. (Sci.) 9:243 (1960)
cited by Davies, J.M. Dairy Sci. Abstr. 24:1256 (1962)
105. Parodi, P.W.
Surface Deterioration of Cold-Stored Butter.
Aust. J. Dairy Technol. 18:25 (1963)
106. Patton, Stuart
Dairy Products
In: Symposium of Foods: Lipids and Their Oxidation.
Schultz, H.W., Day, E.A. and Sinnhuber, R.O., eds.
The AVI Publishing Company, Inc. (1962)
107. Patton, S., Barnes, I.J. and Evans, L.E.
n-Deca-2, 4-dienal. Its Origin from Linoleate and Flavor
Significance in Fats.
J. Am. Oil Chem. Soc. 36:28 (1959)
108. Patton, S. and Kurtz, G.W.
2-Thiobarbituric Acid as a Reagent for Detecting Milk Fat
Oxidation.
J. Dairy Sci. 34:669 (1959)
109. Pedersen, A.H. and Andersen, K.P.
Nogle undersøgelser over ascorbinsyreindhold og lysinducerede
smagsfejl i konsummaelk.
Beretn. Forsogsm. Kbh. 118 (1959)
cited by Jansen, K. Examination of the Ascorbic Acid Content
and Light Induced Flavour of Market Milk. Dairy Sci. Abstr.
22:2685 (1962)
110. Pont, E.G.
The Acidity of Cream in Relation to Fat Losses in Churning
and Keeping Quality of Salted Butter.
Aust. J. Dairy Technol. 17:30 (1962)
111. Prill, E.D.
Color Tests for the Detection of Alpha-Dicarbonyl Compounds
Formed in the Autoxidation of Fats.
Oil Soap 19:107 (1942)
112. Privett, O.S., Lundberg, W.O. and Nickell, C.
Preparation of Peroxide Concentration from Autoxidized Fatty
Acid Esters.
J. Am. Oil Chem. Soc. 30:17 (1953)
113. Prucha, M.J., Brannon, J.M. and Ruehe, H.A.
Carbonation of Butter.
J. Dairy Sci. 8:318 (1925)

114. Radema, L.
The Effect of Storage Temperatures and Moisture Content
in the Keeping Quality of Whole Milk Powders.
Neth. Milk Dairy J. 8:125 (1954)
115. Radema, L.
De invloed van licht op de smaak van melk en enkele
melkprodukten.
Misset's Zuivel 66:197 (1960)
cited by Mann, E.K. Effect of Light on Flavour of Milk
and Some Dairy Products. Dairy Sci. Abstr. 22:2684 (1960)
116. Rahmn, E.
The Technique of Manufacturing and Storing Butter in
Retail Packages.
XIV Int. Dairy Congr. 2:99 (1956)
117. Ricciuti, C., Coleman, J.E. and Willits, C.O.
Statistical Comparison of Three Methods for Determining
Organic Peroxides.
Analytical Chem. 27:405 (1955)
118. Rice, E. and Miscall, J.
Copper in Dairy Products and its Solution in Milk Under
Various Conditions.
J. Dairy Sci. 6:261 (1923)
119. Riemenschneider, R.W., Turere, J. and Speck, R.M.
Modification of the Swift Stability Test.
Oil Soap 20:169 (1943)
120. Riel, R.R. and Sommer, H.H.
Isolation and Characterization of Some Oxidation Products
Associated with Oxidized Flavour.
J. Dairy Sci. 38:1215 (1955)
121. Ritter, W.
The Detection of Copper in Milk and Cream by the Peroxidase
Action.
Schweiz. Milchztg. 61:525 (1935)
cited by Sanders, G.P. Chem. Abstr. 30:2274 (1936)
122. Ritter, W.
The Influence of Certain Factors on the Development of
Oxidation Flavour in Milk and Dairy Produce.
XII Int. Dairy Congr. 2:292 (1949)
123. Ritter, W. and Nussbaumer, T.
The Oxidation of Butterfat. I. Peroxide Formation in
Butterfat.
Scheiz Milchztg. 64:59 (1938)
cited by Sanders, G.P. Chem. Abstr. 32:7148 (1938)

124. Ritter, W. and Nussbaumer, T.
Oxidation of Butterfat II. The Influence of Copper
in Peroxide Number of the Butterfat.
Schweiz. Milchzeitung. No. 38, 1938
cited by Riddel, W. J. Dairy Sci. 22:A98 (1939)
125. Royce, H.D.
Stability of Fats and Oils.
Ind. Eng. Chem. Analyt. Ed. 2:9 (1930)
126. Salkowski, E.
The Rancidity of Fats.
Z. Nahn. Genussm. 34:305 (1919)
cited by Zoller, H.F. Chem. Abstr. 14:784 (1920)
127. Scott, R.
Is Your Butter Safe Under Fluorescent Lamps?
Dairy Engng. 347 (1962)
128. Sephton, H.H. and Sutton, D.A.
The Chemistry of Polymerized Oils. V. The Autoxidation
of Methyl Linoleate.
J. Am. Oil Chem. Soc. 33:263 (1956)
129. Sidwell, C.G., Salwin, H., Benca, M. and Mitchell, J.H.
The Use of TBA as a Measure of Fat Oxidation.
J. Am. Oil Chem. Soc. 28:101 (1951)
130. Sidwell, C.G., Salwin, H. and Mitchell, J.H.
Measurement of Oxidation in Dried Milk Products with TBA.
J. Am. Oil Chem. Soc. 32:13 (1955)
131. Siegfried, M.
The Action of Light and Air in Butterfat.
Milchwirtschaftl. Zentr. 4:530
cited by Van Slyke, L.L. Chem. Abstr. 3:844 (1909)
132. Sinnhuber, R.O. and Yu, T.C.
2-TBA Method for the Measurement of Rancidity in Fishery
Products. II. The Quantitative Determination of
Malonaldehyde.
Fd. Technol. 12:9 (1958)
133. Smith, L.M., Frankel, E.N., Haab, E.N. and Jack, E.L.
Effect of Phospholipids and Unsaponifiable Matter on
Oxidative Stability of Milkfat.
J. Dairy Sci. 41:472 (1958)
134. Smith, A.C. and MacLeod, P.
The Effect of Artificial Light on Milk in Cold Storage.
J. Dairy Sci. 38:870 (1955)

 
of steepest descent.

135. Soldberg, P. and Reidar, B.
Recent Dairy Research in Scandinavia.
Dairy Sci. Abstr. 24:415 (1962)
136. Sommer, H.H.
Fishy Flavour in Butter.
Proc. Wld's. Dairy Cong. 2:974 (1923)
137. Sommer, H.H. and Smit, B.J.
The Fishy Flavour in Butter.
Agric. Expt. St. of U of Wiscon. Res. Bull. 57 (1923)
138. Storgards, F. and Hietaranta, M.
On the Formation of Oily and Fishy Flavour in Butters.
XII Int. Dairy Congr. 2:389 (1949)
139. Sutton, D.A.
Some Investigations with Long Chain Compounds.
J. Am. Oil Chem. Soc. 32:16 (1955)
140. Swanson, A.M. and Sommer, H.H.
Oxidized Flavour in Milk. I. The Effect of the Development of Oxidized Flavour on the Iodine Number of Phospholipid Fraction of Milk.
J. Dairy Sci. 38:1215 (1955)
141. Swift, C.E., Dollear, F.G. and O'Connor R.T.
The Oxidation of Methyl Oleate. I. The Preparation, Properties and Reactions of Methyl Hydroperoxide & Oleate.
Oil Soap 23:355 (1946)
142. Takahashi, E. and Yoschiichi, M.
Oils of Smoked Fishes. I. Antioxygenic Properties of Smoked Herring Meal.
J. Agric. Chem. Soc. Jap. 14:19 (1928)
cited by Kihara, Y. Chem. Abstr. 32:7148 (1938)
143. Tamsma, A.F.
A Study of the Volatile Fraction Isolated from Oxidized Milk Fat. II. Further Characterization of Compounds Responsible for the Oxidized Flavour.
J. Dairy Sci. 38:487 (1955)
144. Tarassuk, N.P., Koops, J. and Pette, J.W.
The Origin and Development of Trainy (Fishy) Flavour in Washed Cream.
Neth. Milk Dairy J. 13:275 (1959)
145. Tarassuk, N.P., Koops, J. and Pette, J.W.
Trainy (Fish) Flavour in Washed Cream. II. The Role of pH in the Oxidation of Fat Globule Membrane Phosphatides.
Neth. Milk Dairy J. 13:279 (1959)

146. Thome, K.E.
Changes in Quality of Butter During Storage.
XIII Int. Dairy Congr. 2:499 (1953)
147. Thome, K.E. and Mattson, S.
Investigations into the Oxidative Defects in Butter.
XIII Int. Dairy Congr. 3:1056 (1953)
148. Thome, K.E. and Olsson, T.
Influence of Equipment on the Keeping Quality of Butter.
XIII Int. Dairy Congr. 2:528 (1953)
149. Thurston, L.M. and Barnhart, J.L.
A Study of the Relation of Material Adsorbed on Fat
Globules to the Richness of Flavour of Milk and Certain
Milk Products.
J. Dairy Sci. 18:131 (1935)
150. Thurston, L.M., Brown, W.C. and Dustman, R.B.
Oxidized Flavour in Milk I. The Probable Relationship
of Lecithin to Oxidized Flavour of Materials Adsorbed.
J. Dairy Sci. 18:301 (1935)
151. Titov, A.
Structura i stoikost slivochnogo masla, vyabatyvanemogo
po sposobu meleshina.
Mol Prom. 15:15 (1954)
cited by Lang, F.
Structure and Keeping Quality of Meleshin Butter.
Dairy Sci. Abstr. 17:470 (1955)
152. Turgeon, J., Stebnitz, V.C. and Sommer, H.H.
The Application of Riiter's Test for the Detection of
Copper in Milk and Dairy Products.
J. Dairy Sci. 20:475 (1937)
153. Turner, E.W., Paynter, W.D., Montie, E.J., Bessert, M.W.,
Stuck, G.M. and Olson, F.C.
Use of the 2-Thiobarbituric Acid Reagent to Measure
Rancidity in Frozen Pork.
Fd. Technol. 8:326 (1954)
154. Vleeschauwer, A.de, Tijtgat, B. and Hendricks, H.
L' influence de la lumiere, de la riboflavine et des
ions metalliques sur l'oxygdation de l'acide ascorbique.
World Congr. Agric. Res. (1959)
cited by Evans, D.E. Influence of Light, Riboflavin
and Metal Ions on the Oxidation of Ascorbic Acid.
Dairy Sci. Abstr. 22:1140 (1960)

155. Washburn, R.M. and Dahlberg, A.C.
The Influence of Salt on the Changes Taking Place
in Storage Butter.
J. Dairy Sc. 1:114 (1917)
156. Wheeler, D.H.
Peroxide Formation as a Measure of Autoxidative
Determination.
Oil Soap 9:89 (1932)
157. Wilbur, K.M., Berheim, F. and Shapiro, O.W.
The TBA Reagent as a Test for the Oxidation of
Unsaturated Fatty Acids by Various Agents.
Arch. Biochem. 24:305 (1949)
158. Whitfield, B.H.
The Effect of Milk Upon Metals and Metals Upon Milk.
Milk Dlr. 24:34 (1934)
159. Yu, T.C. and Sinnhuber, R.O.
2-TBA Acid Method for the Measurement of Rancidity in
Fishery Products.
Fd. Technol. 11:104 (1957)

B29847