STABILIZATION OF FOOD PRODUCTS

AGAINST OXIDATIVE CHANGES BY USE OF

OAT FLOUR AND AN HEXANE EXTRACT OF OAT FLOUR

.dülü.

STABILIZATION OF FOOD PRODUCTS AGAINST OXIDATIVE CHANGES BY USE OF OAT FLOUR AND AN HEXANE EXTRACT OF OAT FLOUR

By

Virgil LeRoy Koenig

Bachelor of Arts University of Kansas City Kansas City, Missouri 1936

Submitted to the Department of Chemistry Oklahoma Agricultural & Mechanical College in partial fulfillment of the requirements for the degree of

> MASTER OF SCIENCE 1938

APPROVED:

In Charge of Thesis.

Otto m Smith Head of Department.

Dean of Graduate School.

ACKNOWLEDGMENT

To the Musher Foundation, Incorporated, the writer desires to express his gratitude for their making this study possible. He also thanks Mr. Sidney Musher for his advice and cooperation.

To Dr. V. G. Heller whose self-sacrificing cooperation and kind supervision has made this study a most pleasant one, the writer wishes to express his thanks and appreciation.

The writer thanks Mr. W. C. Loy who helped materially in scoring the butter samples.

PREFACE

The problem of autoxidative deterioration of foods has always been more or less a difficult one to solve. Numerous methods, including the use of many antioxidants, have been suggested for solving this problem. It has seemed that all methods of control have presented serious difficulties which have made their use impossible for many of the food products. Since the discovery of the antioxidant properties of cereal flours, and of these flours chiefly oat flour, the possibility of its use in inhibiting autoxidation has become a field whose horizon is growing brighter as research progresses. This thesis is a report of some observations as to the value of oat flour and oat flour products as antioxidants for butter, lard, bacon, pears, and apples.

TABLE OF CONTENTS

Α.	Acknowledgment	lii
В.	Preface	iv
C.	Introduction	1
	Causes of Rancidity	
	Methods of Detecting Rancidity 4	
	Methods of Preventing Rancidity 5	
	Theory of Action of Antioxidants 7	
D.	Butter Studies	9
	Methods 9	
	Results 12	
	Conclusions 12	
Ε.	Work With Apples and Pears	13
	Methods 13	
	Results 14	
	Conclusions 20	
F.	Work With Lard and Bacon	21
	Methods 21	
	Results 28	
	Conclusions 30	
G.	Ribliography	32

INTRODUCTION

That the development of rancidity and oxidized flavors in fats and fatty foods is a very important economical problem cannot be gainsaid. It has been estimated that many tons of fat are wasted annually because of spoilage due to the development of rancidity. It can be easily seen that the development of rancidity affects noticeably the market value of fatty foods. Not only from an economic standpoint is the development of rancidity important, but also from a nutritional standpoint. Lowen, Anderson, and Harrison (25), referring to several investigators, state that there is evidence of the formation of toxic compounds and loss of nutritional value in rancid oils. They also state that vitamin A is destroyed by the development of rancidity. It can be concluded, then, that rancidity can be destructive not only economically, but also nutritionally.

Causes of Rancidity

Rancidity, in the broad sense of the word, includes the development of offensive and disagreable flavors in fats and fatty foods. The main causes of rancidity can be ascribed, it is thought (18), to two chief divisions; namely, enzymatic and atmospheric oxidation or autoxidation. Atmospheric oxidation or autoxidation, according to Hilditch and Armstrong (18), is perhaps the primary cause of the onset of rancidity. In fats made up of glycerides of unsaturated fatty acids, the oxidation takes place at the ethnoid linkages (21)(43)(18). The glyceryl radicle of the fat or the free carboxylic acid residue of the fatty acid are not directly concerned with the oxidation. The oxidation products are oxidic or peroxidic in structure, and on further decomposition break up into simpler compounds (39) (43)(18); namely, aldehydes, lactones, ketones, oxy and hydroxy acids, and other lower molecular weight acids. The formation of peroxides is illustrated by the following equation:

By further oxidation, the peroxides being relatively unstable, are oxidized to simpler compounds. The entire chain of reactions occurring in the process of rancidity (and rancidity must be looked upon as the result of a chain reaction) is little understood. Light (18)(24) catalyzes atmospheric oxidation, and Coe (4)(5)(6) has shown that certain wave lengths of light are much more efficient than other wave lengths. Heat and certain metals (21), such as copper, zinc,

etc., also catalyze the reaction.

Enzymatic action on fats is traced chiefly to mold spores that may infect the fat. Molds possess numerous enzymes. Lipolytic enzymes, which, if the medium is suitable, tend to produce free fatty acid. According to Hilditch and Armstrong (18), there is some evidence that enzymes of the peroxidase type also are responsible for oxidation changes, not only of the same nature as atmospheric oxidation, but even in the case of saturated fatty acids which are assumed to be converted by oxidation at the B-carbon atom from the carboxyl group into ketonic acids and ultimately into methyl ketones:

 $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH} \longrightarrow -\text{CO} \cdot \text{CH}_2 \cdot \text{COOH} \longrightarrow -\text{COCH}_3$.

While exidation of saturated acids in this way does not occur as frequently as exidation of unsaturated fatty acids, and is of entirely different nature, the statement that only unsaturated fats undergo exidation during the development of rancidity is incorrect.

In thinking of the development of rancidity, it must not be concluded that only one of these causes is responsible for rancidity in a fat at a time. While rancidity may be caused by atmospheric exidation or enzymatic activity independent of each other, usually both factors are at work simultaneously, thus making the process quite complicated.

Some think that the acidity of fats is connected with the rancidity of fats, but according to Jamieson (21), "It should be emphasized that the presence of free fatty acids either in small or large quantities is no indication whatsoever of rancidity, or that such a product may become necessarily rancid."

Some Methods of Detecting Rancidity

It is observed (21) that when fats become rancid, the iodine number decreases, while the specific gravity, Reichert-Meissl, Polenske and acid values as well as the unsaponifiable matter, more or less increase; however, the measurement of these changes cannot be taken as a measure or detection of rancidity. Various chemical tests for rancidity have been proposed, but in reality, to date, none have surpassed the organoleptic test.

The Kreis test, which is quite prominent, notwithstanding the fact that it has been rejected by the Fat
Analysis Commission of Germany, consists chiefly of
shaking a dilute ethereal solution of phloroglucinol
with the fat in the presence of hydrochloric acid.

A pink coloration develops if the fat is rancid.

Jamieson (21), referring to W. C. Powick, states that
epihydrin aldehyde is thought to be the compound that
reacts with phloroglucinol in the Kreis test to give
the characteristic color. It is also stated that the

aldehyde is probably formed from oleic acid. The chief objection to the Kreis test is that various substances interfere with the test.

The Perexide test as used by Wheeler (44) will be taken up under the section dealing with lard and bacon.

Royce (41) has developed a test for rancidity which is based upon the oxidation-reduction properties of methylene blue. The method no doubt gives a fairly sensitive determination. It cannot be applied to fats that contain moisture above traces, hence it would not be feasable for many naturally occurring fats and a great many food products. The apparatus is fairly complicated. For pure oils, it is reported to be a very good method.

Methods of Preventing Rancidity

Having presented the problem of rancidity--something of its causes and results, it now remains to
find means of preventing and inhibiting the development of rancidity. Modern means of refrigeration,
sterilization, and transportation have greatly reduced
the development of rancidity in that it has reduced
the growth of molds and fungi to a minimum; however, the problem of autoxidation is not entirely
solved and remains with us. Coe (4)(5)(6) and
Morgan (26)(27) have employed opaque and colored
wrappers to inhibit the development of rancidity.

Oxygen can be removed by vacuum packing; however, this would not seem practical for all types of food.

Antioxidants have recently been suggested as offering possibilities in inhibiting the development of rancidity.

Since the first report of an antioxidant, the number of antioxidants has grown to a large list. Phenolic compounds such as hydroquinone, pyrogallol, and resorcinol have been known to inhibit exidation changes in fats for the last ten or twelve years (15)(19)(20)(28). Maleic acid has also been proposed (14)(15). In recent years, carotinoid pigments (36)(37) (42) and lecithin (12)(19)(22)(38) have been found to inhibit rancidity. Most recently, however, the discovery of crushed oil-bearing seeds, cereal flours (16)(17)(30)(31)(32)(33)(34)(35), and the extracts from these flours (13)(34) as antioxidants have proved very valuable. Due to odors, colors, or possible toxic properties of some of the better antioxidants, together with the hesitation on the part of the public to buy and the lack of approval by food administration officials for foods containing any foreign substance has made the use of antioxidants difficult. The cereal flours have a mild flavor and can produce no harmful effects upon the body; therefore their use is more practical in every way. The use of oat flour has

proved itself valuable because of its mild flavor and bland odor as well as its low cost. Its value as an antiexidant has been demonstrated in a general way by Peters (40) and Musher (40)(35). Lowen (25) and his coworkers have demonstrated its use in Halibut liver and Salmon oils. Dahle and Josephson (9), and Mueller and Mack (29) demonstrated its use in ice cream. The following have demonstrated its use in butter: Dahle and Josephson (10)(11), Corbett and Tracey (8), and the writer (23). The following employed it in lard: Musher (32), Conn and Asnis (7), and Bull (3). Bull (2) employed it as an antioxidant in bacon, and Ziegler and Miller (45) in hams and bacon. Bedford and Joslyn (1) studied its use in shelled walnuts and walnut oils. Research is still in progress on various food products.

Theory of the Action of Antioxidants

Greenbank and Holm (15), quoting from the work of Moureau and Dufraisse, explains the mechanism of antioxidants by employing the theory of antagonistic peroxides. This is illustrated by the following steps:

A
$$\neq$$
 $O_2 \longrightarrow A(O_2)$; $A(O_2) \neq B \longrightarrow AO \neq BO$
AO \neq BO $\longrightarrow A \neq B \neq O_2$

$$A \neq O_2 \rightarrow A(O_2); B \neq O_2 \rightarrow B(O_2)$$

 $A(O_2) \neq B(O_2) \rightarrow A \neq B \neq 2O_2$

where A = the activated molecule

B = the antioxidant.

While the above mechanism will illustrate the process, it is only a theory and should be considered as such.

With these words of introduction, a discussion of the work carried out at this institution with the use of oat flour as an antioxidant for food products will be presented. Work with butter, fruit, bacon, and lard is reported herein.

BUTTER STUDIES

An oat flour-treated parchment paper, called by its trade name, Avenized parchment, and a hexane extract of oat flour whose trade name is Avenol were used for the work with butter. This Avenized parchment paper together with a quantity of unavenized parchment paper and the Avenol were supplied through the facilities of the Musher Foundation Incorporated.

This work on butter has been published (23), and for a description of the work done, a portion of the publication will be quoted here:

Methods

"A chemical method for studying the development of tallowiness and rancidity in butter as well as other dairy products has been intensively studied, but still not perfected. There seem to be substances in butter that interfere with the chemical tests. Difference in taste and odor of butter can be detected long before chemical methods show any change—in fact, the butter has to reach an advanced stage of rancidity before chemical tests seem to indicate oxidation. The method which seems to be most widely used is that of Wheeler and consists in measuring the peroxides formed. Suitable correlations between the peroxide numbers and the organoleptic tests were, however, not obtained; therefore the organoleptic butter score was resorted to entirely.

"Twenty-five pounds of creamery butter were obtained from an Oklahoma Commercial Creamery. Comparable samples of one-quarter of a pound each were wrapped in Avenized parchment and in control parchment. A third sample was mixed with 0.06% Avenol and wrapped in control parchment. Part of the samples were stored at 50°F. and part at 0°F. The butter stored at 50°F. was scored every two weeks and that 0°F. was scored every four weeks for a seventeen-week period. The usual method of scoring based on a perfect score of 100, was used.

TABLE I Score of Butter Held at 50° F.

	Surface of the Butters			Inside of the Butters		
Time	Control	Avenized Parchaent	0.06% Avenol	Control		0.06% Avenol
2 weeks	89 slightly rancid	90 slightly old	88 off- flavor*	90 very slightly	90 slightly old	88 off- flavor*
4 weeks	89 slightly rancid	89.5 slightly old	88.5 slightly off- flavor*	89.5 slightly old	89.5 slightly old	88.5 slightly off- flavor*
7 weeks	88.5 slightly rancid old	89 slightly stale	90	89 stale	89.5 old cream	90
9 weeks	87.5 stale slightly rancid	87.5 stale	89.5 very slightly stale	87.5 stale	87.5 stale	89.5 very slightly stale
ll weeks	87 rancid	88.5 stale	90	88 stale slightly rancid	89.5 slightly old	90
13 weeks	86 rancid stale cheesy	87.5 stale rancid cheesy	90 slightly stale	89	89 stale	90 slightly stale
15 weeks	86 rancid	87 slightly rencid stale	89.5 slightly off- flavor	88.5 stale	89.5 slightly stale	89.5 slightly off- flavor
17 weeks	87 cheesy stale	88 stale tallowy	88.5 tallowy	88 cheesy stale	88.5 stale slightly	89 slightly stale

*This off-flavor was probably due to the Avenol (Hexane extract of oat flour). This off-flavor disappeared and the quality of the butter improved.

TABLE II Score of Butter Held at 0° F.

	Surface	of the But			of the But	
Time	Control	Avenized Parchment	0.06% Avenol	Control	Avenized Parchment	0.06% Avenol
		102			~~	
4 weeks	89.5 very slightly old	90	88	90	90	88 oily off- flavor*
9 weeks	88.5 old slightly stale card- board flavor	89.5 slightly old	90 slightly greasy body	88.5 old slightly stale	89.5 slightly old	90 slightly greasy body
13 weeks	salt crust prevented scoring	salt crust prevented scoring	89.5 slightly greasy body	89 stale	89 slightly old and slightly stale	90 slightly greasy body
17 weeks	87 cheesy stale tallowy	88 stale slightly cheesy slightly rancid	89 oily flavor	86.5 tallowy cheesy rancid old	88 stale slightly cheesy slightly rancid	89 oily flavor

^{*}This off-flavor probably due to the Avenol.

The rating was based upon the general nature and texture of the butter. In addition to the score, certain definite criticism was given the butter as is shown in the tables. Both the inside and surface of the butter were sampled.

Results

"Tables I and II give the results of the butter stored at 50°F. and 0°F., respectively. The butter wrapped in Avenized parchment was better than the control all through the test period. For the first four weeks, the butter mixed with Avenol and stored at 50°F. had a distinct off flavor and accounted for the low score. This off flavor was attributed to the presence of hexane. The disappearance of this foreign flavor after four weeks was probably due to the evaporation of the hexane. After the first four weeks, the butter mixed with Avenol proved to be the best sample and the most resistant to the development of rancidity. Before the butter stored at O'F. could be scored, it had to be kept at 50°F. for half a day in order to soften. The butter mixed with Avenal had the same off-flavor for the first four weeks as that stored at 50°F., but after that time, proved to be the best sample and the most resistant to the development of rancidity.

Conclusions

"The value of Avenized parchment and Avenol as inhibitors to the development of rancidity in butter has been studied.

"The Avenized parchment and Avenol show a definite protective action toward butter in the development of rancidity. Avenol shows a greater inhibiting action to the development of tallowiness and rancidity than does Avenized parchment; however, the Avenized parchment inhibits sufficiently to warrant its use beyond a doubt."

WORK WITH APPLES AND PEARS

Ground whole oats, known by the trade name, Avenex #3, and Avenol were used in the studies on apples and pears. The Avenex and Avenol were furnished by the Quaker Oat Company through the facilities of the Musher Foundation Incorporated.

Methods

A quantity of Jonathan apples, Rome Beauty apples, and Bartlett pears were obtained from local markets. Care was taken in selecting the apples and pears so that only sound specimens of uniform size were obtained. Quantities of each variety of apples together with the pears were stored in separate cardboard boxes containing partitions so that each specimen was isolated. They were kept under the following conditions: Some were packed in Avenex #3, others were coated with a light layer of Avenol, and a third group was left untreated to serve as controls. The boxes were kept in the laboratory at room temperature where there was ample ventilation.

Photographs of the fruit were taken at various intervals. At these intervals, the observations of the general appearance and texture of the fruit were recorded along with the photographs: This served as

the only means of judging the effectiveness of oat flour as a protector for fresh fruit. The pears required a shorter test period than the apples, because they spoil more rapidly.

Results

On plates 1, 2, and 3 are the photographs and brief descriptions of the fruit at various stages during the test period. The test period for the apples consisted of seventy days, while the test period for pears was forty-two days.

All through the test period, the fruit packed in Avenex seemed to be superior to the other fruit. The fruit coated with Avenol wrinkled and dried up before the controls. The pears packed in Avenex had more of a rich golden color after being kept for a week or two than did the other pears. Likewise, the apples packed in Avenex had a better texture and appearance than the other apples. Jonathan and Rome Beauty apples' keeping qualities are almost identical—that is to say, no appreciable differences were noticed between the two varieties of apples.

Just what plant physiological processes are altered when Avenex protects the fruit from spoilage the writer cannot say. Since Avenex possesses antioxidant properties, it is quite natural to

Plate 1. JONATHAN APPLES



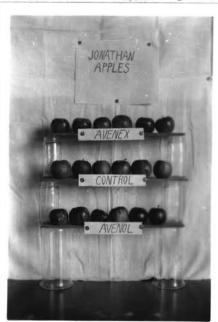
7 days All about the same.



26 days
Avenex -- best.
Control -- good.
Avenol -- wrinkled.



Avenex -- good.
Control -- slightly puffy.
Avenol -- slightly wrinkled.

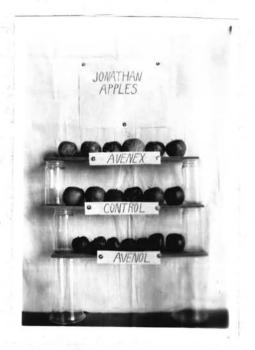


35 days
Avenex -- best.
Control -- good.
Avenol -- very wrinkled.

JONATHAN APPLES (continued)

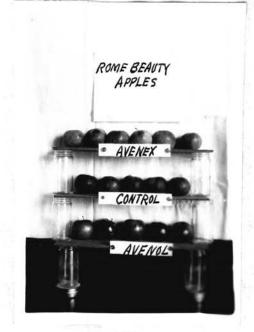


49 days
Avenex -- best.
Control -- wrinkled, soft.
Avenol -- very badly
wrinkled.

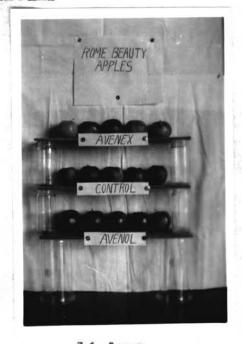


70 days
Avenex -- wrinkled, spotted,
but best.
Control -- wrinkled and soft.
Avenol -- very wrinkled and
dried up.

Plate 2. ROME BEAUTY APPLES



7 days Avenex -- all about same. Control -- " 11 11 Avenol --



14 days Avenex -- good. Control -- good. Avenol -- slightly wrinkled.



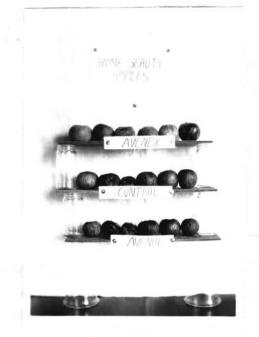
26 days Avenex -- definitely best. Control - soft.



35 days Avenex --- definitely best. Control -- soft. Avenol -- soft and wrinkled. Avenol --- soft and wrinkled.

ROME BEAUTY APPLES (Continued)





49 days
Avenex -- best.
Control -- soft and wrinkled.
Avenol -- very wrinkled.

70 days

Avenex -- best, beginning
d. to get soft and wrinkled.

Control -- soft and wrinkled.

Avenol -- very wrinkled.

Plate 3. BARTLETT PEARS

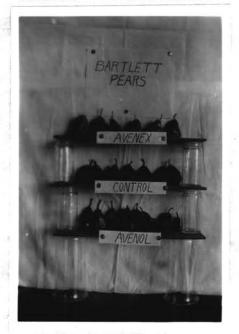


7 days All about the same.



19 days Avenex --- definitely best. Control -- soft and spotted. Avenol --- wrinkled.





42 days Avenex -- best. Avenex -- best but wrinkled. Control -- spotted, wrinkled. Control -- wrinkled, dried up. Avenol -- soft, spotted. Avenol -- soft, wrinkled, dried up.

believe that surface oxidizing enzymes may be retarded, or temporarily or partially inactivated. Peroxidase may be retarded in its catalytic action. Perhaps, peroxides themselves are adsorbed or reduced.

As a subject for further investigation, studies of the value of water extracts of Avenex #3 for the prevention of coloration of apples during the process of drying should be interesting. Commercial evaporators are faced with the problem of the coloration of apples as well as other fruit during evaporation. Sulfur dioxide has been used to discolor dried fruit, but with some degree of hesitation, because of its possible toxicity. If the anti-oxidants in oat flour are sufficiently effective to prevent or inhibit coloration, an important application of it could be made in the fruit industry.

Conclusions

Avenex does seem to protect apples and pears to some degree. Whether it protects sufficiently to warrant its use commercially remains yet to be decided.

Avenol, as was used, did not protect the fruit, but rather seemed to be detrimental.

WORK WITH LARD AND BACON

The use of a suitable antioxidant would be most helpful in inhibiting the development of rancidity in lard, bacon, and other fat meat. Musher (32) and Bull (3) have reported work in which a mixing of certain percentages of Avenex (oat flour) in lard has retarded the development of rancidity. Conn, Asnis (7), and Bull (3) have reported that Avenized parchment wrappers retard the development of rancidity in lard. Musher (35), Bull (2), and Ziegler and Miller (45) have reported that dusting of Avenex on bacon and other cured meat retards the development of rancidity. Ziegler and Miller, in the paper referred to, state that spraying Avenol on bacon retards the development of rancidity. From the results of the above investigators, it is evident that Avenex, Avenol, and Avenized parchments do show possibilities in the meat industry.

The work carried on in this laboratory consisted of studying the value of Avenized parchment and Avenol in the keeping of lard and bacon in the dark at ordinary room temperature.

Methods

Quantities of lard and sliced bacon were obtained at a local market. Comparable samples

of lard and bacon were wrapped in Avenized parchment and control parchment and stored in the dark at room temperature. Samples of bacon coated lightly with Avenol and wrapped in control parchment were stored with the other samples. Two kinds of parchment were used. Lard samples were wrapped in Avenized and regular 40# "Rhinelander Lard Pak" and Avenized and control 40# "Patapar". Bacon was wrapped in Avenized and regular 40# "Rhinelander Lard Pak" and Avenized and control 30# "Patapar". Samples of bacon sprayed with Avenol were wrapped in Control 30# "Patapar". The Avenized parchment in both cases was treated with oat flour on both sides. The Regular "Lard Pak" is a greaseproof paper. The samples of lard and bacon were examined at various periods for peroxide numbers and for eder.

Peroxide value has been used quite extensively as a measure of the development of rancidity, assuming of course, that the development of peroxides is an indication of the development of rancidity.

After reading the work of Coe and LeClerc (4) and Coe (6), one is led to believe that rancidity in oils and fats is not the result of the formation of peroxides since high peroxide values have been found in fats that were not rancid, and low peroxide values in fats that were rancid. Rather, there is strong

indication that rancidity in oils and fats is not the result of the formation of peroxides, but is the result of a photochemical reaction wherein the compound which is responsible for organoleptic rancidity is formed. The above authors make the statement that organoleptic tests are the only reliable tests for rancidity, regardless of whether or not an oil has been exposed to light. Light, then, seems necessary for the development of rancidity in oils and fats.

The development of rancidity in bacon and other cured meats is a somewhat different story. The writer is of the opinion that light is not necessary for the development of rancidity in cured meat because of the action of enzymes, which being inactivated in lard because of heat, are not entirely inactivated by the curing processes. Here the peroxide value has served better as an indication of the development of rancidity. In this laboratory, the peroxide values of lard and the fat extracted from the stored bacon were determined.

The usual method for determining the peroxide number is that of Wheeler (44) and is briefly given:

"Three to ten grams of oil are dissolved in 50 ml. of solvent mixture (60% glacial acetic acid, 40% chloroform) and 1 ml. of saturated potassium iodide solution added. The mixture is stirred by giving a rotary motion to the flask. After exactly one minute from the time of addition of potassium iodide, 100 ml. of water are added and the liberated iodine is titrated with 0.1 N or 0.01 N sodium thiosulfate, depending on amount of iodine liberated. Starch is added toward the last as an indicator. Vigorous shaking is necessary

at the very last to remove the last traces of iodine from the chloroform layer. The results may be conveniently expressed as moles of peroxide per 1000 grams of oil."

A modification of this method was used in this laboratory for determination of peroxide numbers. The method is: The lard or bacon wrapped in the parchment is weighed. It is then extracted in a Soxhlet extractor with petroleum ether, b.p. 30-80°C. until all the fat is removed. Bacon is usually extracted over night, and lard in much less time. When extraction is complete, the excess ether is allowed to collect in the extractor and is poured into a container. The extract, containing the fat is poured into a 200-milliliter volumetric flask and made up to volume with the ether collected in the extractor. The bacon minus the fat is dried with the paper (in the case of lard, just the paper) in an oven at 100°C. until all ether is removed (about 15 minutes). The residue and paper are weighed. This weight subtracted from the first weight gives the weight of the fat--about 15 to 20 grams for lard and about 7 to 15 grams for bacon.

A 50-ml. aliquot of the extract is transferred into a 300-ml. Erlenmeyer flask. Twenty-five ml. of glacial acetic acid are added with thorough mixing. One ml. of saturated potassium iodide is added. After thorough

mixing, the mixture is allowed to stand two minutes (counting time as soon as the potassium iodide is added). At the end of the two minutes, 100 ml. of water are added. The liberated iodine is titrated with 0.01 N sodium thiosulfate until a light yellow color. Five ml. of starch solution are then added and titration is continued until the blue color disappears. During titration, the mixture must be shaken vigorously so that the iodine in the ether layer will be reduced, The number of ml. of thiosulfate, used, are multiplied by 4, since a 50-ml. aliquot of a total volume of 200 ml. was used. The peroxide number, which is defined as the number of ml. of 1 N thiosulfate per 1000 grams of fat, is calculated by the following formula:

where

m = ml. of sodium thiosulfate used.

N = normality of sodium thiosulfate.

G = weight of fat in grams.

The chemical reaction for the liberation of iodine may be represented as follows:

TABLE III

LARD WRAPPED IN 40# RHINELANDER LARD PAK

Peroxide Numbers and Odor Observations

Note: Below, / indicates degree of odor development. The peroxide numbers are average values of duplicate and sometimes triplicate determinations.

1	Time	Regular Lard Pak	Avenized Lard Pak
8	days	0.62	1.26
 14	days	3.87	4.44
22	days	3.76	2.17
37	days	8.26	6.31
57	days	5.62	4.59
65	days	6.20	8.11
79	days	13.06	9.42 /-
86	days	24.37 ++	14.33 /-
92	days	24.97 <i>444</i>	14.13

TABLE IV

LARD WRAPPED IN 40# PATAPAR

Peroxide Numbers and Odor Observations

Note: Below, / indicates degree of odor development. The peroxide numbers are average values of duplicate and sometimes triplicate determinations.

T	ime	Control Patapar	Avenized Patapar
8	days	2.26	1.40
14	days	2.39	2.54
22	days	2.56	2.54
36	days	9.43 /-	10.52
58	days	5.48 #	6.80
66	days	11.66	7.88 /-
81	days	13.37	16.68 /-
87	days	20.52 +++	28.07 ++-
94	days	49.37 <i>4444</i>	24.00
101	days	40.45	32.50 +++-

28.

Results

Tables III and IV give the peroxide numbers and odor observations of the lard wrapped in the two wrapping papers. The odor development in both cases is greater in the control than in the Avenized papers. The peroxide numbers show fluctuations which may be due partly to sampling. For about the first fifty days, there is no noticeable differences in peroxide numbers. After the first fifty days, the peroxide numbers show more differences. The final determinations show the control to have a much higher peroxide number in both cases. The lard samples never developed a real offensive rancid odor. The odor became strong, however. Since rancidity in oils and fats is believed to be a photochemical reaction, the delay in the final stages of rancidity can be accounted for since the lard was stored in the dark. and was not subject to the catalyzing effect of light.

The peroxide numbers and odor observations for the bacon are given in Tables V and VI. In Table V, the results for the "Rhinelander Lard Pak" show at the thirty-ninth day test period the peroxide value to be lower for the regular than for the Avenized wrappers. The odor was, however, much worse. During the development of rancidity, the peroxides can be further oxidized into shorter chain compounds, and in this case, the

TABLE V

BACON PACKED IN 40# RHINELANDER LARD PAK

Peroxide Numbers and Odor Observations

Note: Below, / indicates degree of rancidity by odor The peroxide numbers are average values of duplicate and sometimes triplicate determinations.

Time	Regular Lard Pak	Avenized Lard Pak
16 days	5.58	8.72
24 days	39.35 +++	11.69
39 days	18.72 ////	77.75 ##
59 days	141.25 ////	113.70

TABLE VI BACON WRAPPED IN PATAPAR 30#

Peroxide Numbers and Odor Observations

Time		Sprayed with Avenol	Control	Avenized P	atapar
15	days	9	2.83 #	0	
23	days	1.05	5.27 +/+	2.14	
38	days	3.17 //-	34.02 ////	14.57 //	
60	days	85.20 //-	84.67 <i>++++</i>	38.08 +++	
71	days	138.97 <i>4/4/4</i>	94.80	36.39 ++++	

The final samples in any case were very offensive-that is, they had reached the final stages of rancidity.

peroxide number would decrease. The final results show a much larger peroxide value for the control.

The results of Table VI are most interesting, because Avenol was also used. The Avenol sample had very low peroxide numbers until the sixtieth day. The peroxide number on the sixtieth day took a sudden increase and was higher than the control. The last determination was much the highest. To account for the high peroxide number, one must assume that peroxides developed in the oat oil (Avenol), thus increasing the total peroxide number. As a whole, the bacon in the Avenized parchment was much the best both organoleptically and as judged by peroxide numbers.

Conclusions

Avenized parchment paper exhibits its antioxidant properties by retarding peroxide development to a certain degree in lard and in a greater degree in bacon—the lard and bacon being stored in the dark.

Organoleptic observations indicate lard and bacon in Avenized wrappers superior to control wrappers.

Peroxide numbers and organoleptic findings are favorable for Avenol in early stages of the test period, but are not so favorable in the final stages; however, all of the bacon samples were rancid in the final test.

Bacon acquired a strong rancid odor in the dark, while the lard never reached the final stage of rancidity.

BIBLIOGRAPHY

- (1) Bedford, C. L. and Joslyn, M. A. 1937. Oat flour and hexane extract of oat flour as antioxidants for shelled walnuts and walnut oil. Food Research, 2:455.
- (2) Bull, Sleeter. 1937. Rancidity and mold in cured bacon retarded. The National Provisioner, September 25, 1937.
- (3) Bull, Sleeter. 1938. Retarding rancidity in lard and pork fats. The National Provisioner, January 22, 1938.
- (4) Coe, M. R. and LeClerc, J. A. 1934. Photochemical studies of rancidity. Ind. Eng. Chem., 26:245.
- (5) Coe, M. R. and LeClerc, J. A. 1935. Photochemical studies of rancidity: Antioxidants vs green light protection. Oil and Soap, 12:231.
- (6) Coe, M. R. 1937. Photochemical studies of rancidity: Rate of peroxide development under constant intensity of light. Oil and Soap, 14:171.
- (7) Conn, R. C. and Asnis, R. E. 1937. Oat flour as an antioxidant. Ind. Eng. Chem., 29:951.
- (8) Corbett, W. J. and Tracy, P. H. 1937. Use of antioxidants to prevent tallowiness in butter. National Butter and Cheese Journal, December, 1937.
- (9) Dahle, C. D. and Josephson, D. V. 1937. An antioxidant for ice cream. Ice Cream Field, May, 1937.
- (10) Dahle, C. D. and Josephson, D. V. 1937. Improving the keeping quality of butter with treated parchment. National Butter and Cheese Journal, July 25, 1937.
- (11) Dahle, C. D. and Josephson, D. V. 1937. Delaying oxidative changes in butter. National Butter and Cheese Journal, September 25, 1937.
- (12) Evans, E. I. 1935. Antioxidant properties of vegetable lecithin. Ind. Eng. Chem., 27:329.

- (13) Freytag, F. D. and Smith, H. G. 1933. The 1938 unsaponifiable lipides of beef liver II. Vitamins A and E antioxygens. J. Biol. Chem., 100:319.
- (14) Greenbank, G. R. 1933. Inhibiting exidation and rancidity of oils and fats. U. S. 1,898,363, February 21, 1933.
- (15) Greenbank, G. R. and Holm, G. E. 1934. Antioxidants for fats and oils. Ind. Eng. Chem., 26:243.
- (16) Grettie, D. P. 1936. Preventing rancidity. Brit. 446,792, May 6, 1936.
- (17) Grettie, D. P. 1936. Stabilizing fats such as lard against rancidity. U.S. 2,052, 289, August 25, 1936.
- (18) Hilditch and Armstrong, "The industrial chemistry of the fats and waxes", pp. 276-280. (1927) D. Van Nostrand Company, New York.
- (19) Holmes, H. N., Corbett, R. E., and Hartzler, E. R. 1936. Lecithin and hydroquinone as antioxidants for vitamin A. Ind. Eng. Chem., 28:133.
- (20) Husa, W. J. and Husa, Lydia, M. 1928. The effect of various compounds on the rate of development of rancidity in fats and oils. Journal of American Pharmaceutical Association, 17:243.
- (21) Jamieson, George S., "Vegetable Fats and Oils", pp. 26-28. 1932. The Chemical Catalog Company, Inc., New York.
- (22) Kochenderfer, E. W. and Smith, H. G. 1932. Vegetable lecithin as an antioxidant. Proc. Iowa Acad. Sci., 39;169.
- (23) Koenig, V. L. 1937. Stabilization of butter against oxidized flavors. National Butter and Cheese Journal, August 10, 1937.

(24) Lea, C. H. 1931. Effect of light on the exidation of fats, Proc. Roy. Soc. (London) B 108:175.

- (25) Lowen, L., Anderson, L., and Harrison, R. W. 1937. Cereal flours as antioxidants for fishery products. Ind. Eng. Chem., 29:151.
- (26) Morgan, W. L. 1935. Retarding rancidity. Colored transparent cellulose wrappers. Ind. Eng. Chem., 27:1287.
- (27) Morgan. W. L. 1935. Light filtering sheets for protecting oils, fats and waxes, etc. from light of wave lengths producing decomposition. U.S. 2,043,860, June 9, 1935.
- (28) Moureau, C. and Dufraisse, C. 1922. Inhibiting exidation. Brit. 181,365, June 7, 1922.
- (29) Mueller, W. S. and Mack, M. J. 1937. Oat flour as an antioxidant in ice cream. Ice Cream Trade Journal, October, 1937.
- (30) Musher, S. 1931. Inhibiting rancidity in peanut butter. U.S. 1,816,338, July, 1931.
- (31) Musher, S. 1932. U.S. 1,841,842, January 19, 1932.
- (32) Musher, S. 1935. Cereals and seeds inhibit rancidity in lard. Food Ind. 7:167.
- (33) Musher, S. 1936. Stabilizing fats and oils. (to Musher Foundation, Inc.) U.S. 2,049,017, July 28, 1936.
- (34) Musher, S. 1936. Prevention of the exidation (the development of rancidity) especially in animal fats and oils. F.P. 785,927.
- (35) Musher, S. 1935. Inhibiting rancidity. Food Ind., July, 1935.
- (36) Newton, R. C. and Richardson, W. D. (to Swift and Co.) 1933. Stabilizing fats and oils against rancidity. U.S. 1,890,585, December, 1933.
- (37) Newton, R. C. 1932. Carotene as a natural antioxidant. Oil and Soap, 9:247.
- (38) Olcott, H. S. and Mattill, H. A. 1936.
 Antioxidation and the autoxidation of fats.IV
 Lecithin as antioxidant. Oil and Soap, 13:98.

- (39) Price, C. C. 1935. Can. Chem. Met. 19:134.
- (40) Peters, F. N. and Musher, S. 1937. Oat flour as an antioxidant. Ind. Eng. Chem., 29:146.
- (41) Royce, H. D. 1933. Stability of fats and oils. Application of the methylene blue test. Ind. Eng. Chem., Anal. Ed., 5:244.
- (42) Swift and Co., 1931. Fats and Oils. Fr. 713,967, March 27, 1931.
- (43) Triebold, H. O. 1931. Rancidity. Cereal Chemistry, 8:518.
- (44) Wheeler, D. H. 1932. Peroxide Formation as a measure of autoxidative deterioration. Oil and Soap, 9:89.
- (45) Ziegler, P. T. and Miller, R. C. 1937. Retarding rancidity in hams and bacon. Meat, December, 1937.