

RETARDATION OF AUTOXIDATION IN RAMYON,  
DEEP-FRIED INSTANT NOODLE

by

KWANG LAE RHO

B.S., Seoul National University, Korea, 1970

---

A MASTER'S THESIS

submitted in partial fulfillment of the  
requirements for the degree

MASTER OF SCIENCE


Department of Grain Science and Industry

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1982

Approved by:

  
Major Professor

SPEC  
COLL  
LD  
2668  
J4  
1982  
R46  
C.2

A11203 570005

"Wisdom is the principal thing;  
therefore get wisdom;  
and with all thy getting  
get understanding." (Proverbs 4:7)

## TABLE OF CONTENTS

	Page
LIST OF TABLES. . . . .	v
LIST OF FIGURES . . . . .	vi
ACKNOWLEDGEMENTS. . . . .	vii
INTRODUCTION. . . . .	1
LITERATURE REVIEW . . . . .	4
Nature of Rancidity. . . . .	4
Mechanism of Autoxidation. . . . .	4
Factors Affecting the Development of Oxidative Rancidity . . . .	6
Measurement of Oxidative Rancidity . . . . .	12
Measurement of Stability of Lipid toward Autoxidation. . . . .	15
MATERIALS AND METHODS . . . . .	17
General. . . . .	17
Preparation of Ramyon. . . . .	17
Trace Metals in Ingredients and Ramyon . . . . .	19
Accelerated Aging Tests on Ramyon. . . . .	19
Effect of Antioxidants in Frying Oil. . . . .	19
Antioxidant Effect of TBHQ Applied to Inner Surface of Package . . . . .	20
Effect of Chelating Agent Na <sub>2</sub> EDTA . . . . .	21
Hexanal Determination. . . . .	21
Determination of the Residue of TBHQ by TLC. . . . .	23
RESULTS AND DISCUSSION. . . . .	24
Trace Metals in Ramyon . . . . .	24
Effect of Antioxidant in Frying Oil. . . . .	25
Effect of TBHQ on the Inner Surface of Package . . . . .	28
Effect of the Chelating Agent Disodium EDTA. . . . .	30

Hexanal as a Measure of Rancidity in Ramyon. . . . .	31
CONCLUSIONS . . . . .	34
BIBLIOGRAPHY. . . . .	74



## LIST OF TABLES

TABLE		Page
I	Korean Standards for the Composition of All-Purpose Wheat Flour. . . . .	35
II	Minima and Maxima in the Composition of Ramyon . . . . .	36
III	Fatty Acid Composition of Some Common Lipids . . . . .	37
IV	Factors Affecting Oxidation. . . . .	38
V	Tocopherol Content of Various Lipids . . . . .	39
VI	Flavoring Substances in Water, Milk and Oil. . . . .	40
VII	Formula of Ramyon Dough and Composition of Ramyon Noodle .	41
VIII	Trace Metal Concentration. . . . .	42
IX	Analysis of Fresh Palm Oil . . . . .	43
X	Average Storage Time at 63 <sup>0</sup> C (145 <sup>0</sup> F) Until Organoleptic Detection of Rancidity in Ramyon . . . . .	44
XI	Time Period to Rancidity Detection in Ramyon Made with TBHQ in the Frying Oil or When Ramyon was Stored with TBHQ Applied to the Inner Surface of Package . . . . .	45
XII	Effect of Disodium Ethylenediaminetetraacetate on Development of Rancidity in Ramyon Using the Schaal Oven Test . . . . .	46
XIII	Hexanal Concentration <u>vs</u> Peak Area Ratio of Hexanal/4-Heptanone. . . . .	47
XIV	Hexanal Concentration in Ramyon <u>vs</u> Storage Days at 63 <sup>0</sup> C (145 <sup>0</sup> F). . . . .	48

## LIST OF FIGURES

FIGURE		Page
1	General Steps to Produce Ramyon. . . . .	49
2	Mixing Ingredients for Ramyon in the Laboratory. . . . .	50
3	Sheeting of Ramyon Dough Using the Ohtake Noodle Machine .	50
4	Cutting of Ramyon Dough Sheet on the Ohtake Noodle Machine. . . . .	52
5	Forming Four Ramyon Servings, Each Containing 140 g ("as is") Noodle . . . . .	52
6	Ramyon Steamer . . . . .	54
7	Ramyon Fryer . . . . .	54
8	Schematic Diagram for Overall Mechanism for Lipid Oxidation. . . . .	56
9	Autoxidation of Linoleic Acid to Give Hexanal. . . . .	57
10	Stability of Lipid-Containing Foods as a Function of Water Activity . . . . .	58
11	Chromatogram of Head Space When an Aliquot (10 mL) of a Standard Solution of 2.78 ppm Hexanal (HEX) and 2.74 ppm of Heptanone (HEP) was added to Sucrose (15 g) Followed by Boiling Water . . . . .	60
12	Molecular Structures of Antioxidants . . . . .	62
13	Effect of Antioxidants on Development of Rancidity in Ramyon, Fried in Oil Containing 0.02% Antioxidants . . . .	64
14	Thin Layer Chromatogram (TLC) of Various Acetone Solutions of TBHQ. . . . .	66
15	Hexanal Concentration based on Solid <u>vs</u> Peak Area Ratio of Hexanal/4-Heptanone . . . . .	68
16	Chromatogram of a Fresh Ramyon (dotted peaks) and Ramyon Stored Two Weeks at 63°C (145°F) (solid peaks) . . . . .	70
17	Hexanal Concentration <u>vs</u> Storage Days at 63°C (145°F). . .	72

## ACKNOWLEDGEMENTS

The author expresses his very grateful appreciation to his major professor, Dr. Paul A. Seib, for his valuable time, advice, encouragement, and guidance throughout his research and preparation of this thesis.

Sincere appreciation is extended to Dr. Okkyung Kim Chung and Dr. Do Sup Chung, members of the advisory committee, for their advice, precious help and warm encouragement.

Grateful acknowledgement is expressed to Dr. Charles W. Deyoe, head of the Department of Grain Science and Industry, for use of research facilities and materials.

The author is also indebted to the very nice people of the department who have helped, and willingly spared their time for the panel test. Sincere thanks is extended to Dr. David L. Wetzel, Mr. Randy Wheling, and Mr. Mao-Jung Lee for their help in use of the gas-liquid chromatograph.

Heartfelt thanks is also due to Dr. Robert Fry of the Chemistry Department, Dr. David Whitney and Mr. Larry Unruh of the Agronomy Department for their kindness in doing the mineral analyses by atomic absorption spectrophotometer.

He takes this opportunity to acknowledge the financial support of Nhong Shim Co., Seoul, Korea, and the moral support of his parents, Mr. and Mrs. Sung Ok Rho. He is grateful to his sister, Song Gil, and to his cousin, Dr. Kung Lae Rho, for their encouragement and motivation to continue his education.

Finally, special thanks are due to his wife, Teresa Jung Ja, for her sacrifices, taking good care of the family, and typing this thesis.

## INTRODUCTION

Ramyon is a unique deep-fried noodle having special characteristics. It is inexpensive, nutritious, convenient, and relatively easy to store. The increasing consumption of ramyon products in Asian countries and in major cities of developed countries has caught the attention of food scientists in the last two decades.

Ramyon is made from so-called all-purpose wheat flour, which in Korea is a blend of hard and soft wheat flour in the proportion of 1:1 to 4:6. Table I shows the Korean standards for all-purpose wheat flour.<sup>1</sup> The general steps to produce ramyon are shown in Figures 1-7.

The minima and maxima in the composition of ramyon by the Korean Standards are given in Table II. The fat content of ramyon noodle reaches up to 20% after frying at 140-190°C for 1-2 minutes. The fat content varies somewhat depending on the thickness and width of the noodle strands.

A variety of fats and oils, either alone or in combinations, are used in frying ramyon. Examples of frying oils are beef tallow, lard, palm oil, corn oil, coconut oil, rice bran oil, soybean oil, rapeseed oil, cottonseed oil, and sesame oil. The recent trend in the choice of frying oil has changed from animal fats to vegetable oils, which are sometimes partially hydrogenated.

The shelf-life of ramyon noodle is limited by oxidative rancidity. Some noodles would become rancid in a few days if there were no antioxidants. The average shelf-life of commercial noodles is several months. The growth of the deep-fried noodle industry intensifies the need to solve the oxidation problem. It is generally recognized that the factors influencing the shelf-life of ramyon are the fatty acid composition of the frying oil, the concen-

---

<sup>1</sup>All Tables and Figures are located at the end of the manuscript.

tration of heavy metals and antioxidants, packaging methods, and storage conditions. In storing ramyon, many factors affect its shelf-life such as light, temperature, humidity, and the type of packaging materials (Okada 1971, Nishijima et al 1976, Yamashita 1965, Cheigh and Kwon 1972, Hu and Kim 1974).

Although much effort has been made to retard the development of rancidity in ramyon since the late 1950's, there is still no clear-cut method to eliminate the problem in rancidity in ramyon, except by removing oxygen completely. The complete removal of oxygen is not only too costly but also too difficult to be practical (Koch 1962). The reasons why oxidative rancidity is difficult to control in the fried ramyon noodle are as follow:

1. The oils used to fry ramyon usually contain unsaturated fatty acids which, of course, react with oxygen and cause rancidity in ramyon. The fatty acids composition of some lipids commonly used in ramyon are listed in Table III.
2. The frying process causes complicated changes; the fat is partially hydrolyzed and thermally degraded and antioxidants are volatilized (Yuki et al 1971).
3. It is difficult to obtain adequate coverage of the large surface area of noodle strands by spraying antioxidant solution onto the noodle after frying as proposed by Sherwin (1972).
4. Heavy metals that promote rancidity are present in ingredients and processing equipment.
5. The period of time from production to consumption of ramyon sometimes extends past shelf-life of the product.

The broad objective of this study was to find an effective and useful method to retard rancidity in ramyon. There are four specified objectives:

1. To determine the concentration of trace metals in ramyon;
2. To fry ramyon in oil containing butylated hydroxyanisole (BHA),

tetiary butylhydroquinone (TBHQ), or a polymeric antioxidant (Poly-A, with the brand name of ANOXOMER), and determine the relative storage times to the organoleptic detection of oxidative rancidity;

3. To coat the inner surface of the ramyon package with TBHQ and compare the relative effectiveness of package surface application of TBHQ to its presence in the frying oil;

4. To test the effect of a chelating agent, disodium ethylenediamine-tetraacetate ( $\text{Na}_2\text{EDTA}$ ), in retarding the autoxidation of ramyon; and

5. To determine whether hexanal can be used as an index of oxidative rancidity in ramyon.

## LITERATURE REVIEW

### Nature of Rancidity

The term "rancidity" is commonly applied to off-flavors and off-odors that involve the fatty phase of foods (Lundberg 1961). Lea (1938) listed the possible causes of rancidity in fats, including undesirable changes caused by absorption of odors, action of enzymes, action of microorganisms, and atmospheric oxidation. Atmospheric oxidation occurs spontaneously when any material containing fat is exposed to the air, though the rate of change varies enormously with the type of fat and with the condition of storage.

Rancidity causes the development of off-flavors which make food products lose acceptability with consumers. The principal reason for rancidity development in most foods is oxidative rancidity (Scott 1965) which is referred to as "autoxidation" of lipid components. Autoxidation is defined as the spontaneous oxidation of a substance in contact with molecular oxygen (Berk 1976).

Even though a considerable volume of theoretical information is available on lipid oxidation (Lea 1938, Lundberg 1962, Schultz 1962, Labuza 1971, Simic and Karel 1980), all the factors controlling the oxidative deterioration of fried noodles are not completely known yet.

### Mechanism of Autoxidation

Autoxidation processes in food and biological systems are based on free radical reactions which involve a variety of organic radicals. Oxygen attacks the energetically preferred allylic bound hydrogen, i.e. the oxidation process starts at a carbon atom in the  $\alpha$ -position with respect to a double bond. The relative oxidation speeds for stearic, oleic, linoleic and linolenic acids are 1 to 100, to 1200, to 2400, respectively, and these figures represent the increasing activation of a methylene group for hydrogen abstraction

(Kläui and Pongracz 1982).

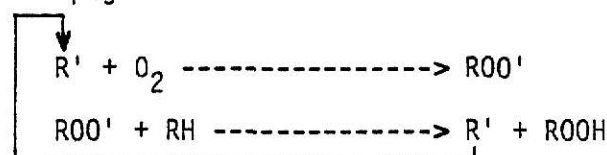
Free radicals are highly reactive chemical species with unpaired electrons in their outer orbitals; they play key roles in the transformation of energy and in cellular deterioration in biological systems (Schaich 1980).

Lipid autoxidation proceeds through a free radical mechanism consisting of the following steps (Farmer et al. 1972):

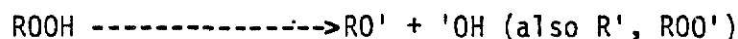
Step 1. Initiation



Step 2. Propagation



Step 3. Decomposition

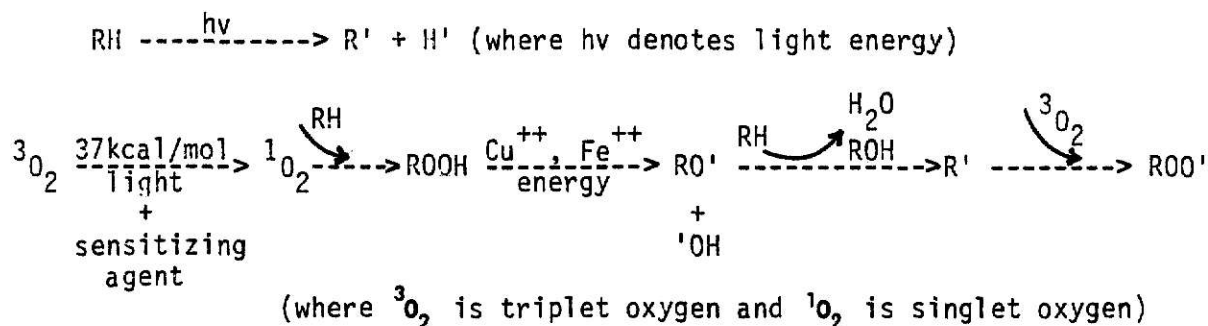


Step 4. Termination



(RH represents a lipid molecule, and X denotes a free radical inactivator.)

The initiation reactions of fat oxidation leading to radicals have been summarized by Kläui and Pongracz (1982) as follow:



The initiation reactions shown above are seen to be accelerated by sunlight, ultraviolet light, trace minerals, and temperature (Martell and Calvin 1953).

The hydroperoxides (ROOH) are important as the primary products of lipid



autoxidation; they are in themselves non-volatile, odorless, and tasteless (Berk 1976).

The peroxides formed can be fragmented into aldehydes, ketones, acids, and other degraded products (Fig. 8), which are responsible for the off-flavors of rancid products (Dugan 1976, Labuza 1971, Berk 1976). Polymerization and condensation reactions may also occur, and this type of spoilage is dominant in fats heated to high temperatures for long periods of time. Thus, the amount of peroxide in a rancid fat may be low because it has all decomposed (Labuza 1971), or because oxygen is limiting in a closed system (Klăui and Pongracz 1982).

The products found in autoxidation confirm the general free radical mechanism. However, the final distribution of the products depends on the relative rates of the secondary reactions, such as rearrangement of intermediate allylic radicals, further oxidation of intermediates, and disproportionation reactions (Logani and Davies 1980). As secondary oxidation reactions, scission and dismutation reactions yield compounds that are responsible for off-flavors and off-odors. The dominant aldehydes isolated from oxidized fats apparently arise from oleate or linoleate hydroperoxides by these reactions (Dugan 1976).

Franke<sup>l</sup> et al (1982) analyzed the volatile carbonyl compounds in the autoxidation of linoleic acid. Those workers found 66 mole % hexanal, 18 mole % 2-octenal, and 2-heptenal and 2,4-decadienal as minor components. Badings (1970) and Fritsch and Gale (1977) had previously identified hexanal as a major off-flavor compound in rancid foods. The mechanism of formation of hexanal from linoleic acid is shown in Figure 9.

#### Factors Affecting the Development of Oxidative Rancidity

The storage stability of dry foods is mostly limited by autoxidation of

lipids (Lingnert 1980). Since autoxidation occurs by reaction of unsaturated fatty acids with atmospheric oxygen, oxygen and unsaturated fatty acids are of major concerns. The unsaturation of lipids, or more specifically, its content of polyunsaturated fatty acids, is one of the most important factors (Lundberg 1962).

Kajimoto (1979) summarized the five factors that control the autoxidation of fats. These factors, which were also studied by other investigators in various foods including ramyon, are as follow:

1. Characteristics of lipids; degree of unsaturation, and degree of conjugation of double bonds (Chan et al 1976, Triebold and Bailey 1932).
2. Packaging; materials and methods of packaging (Okada 1972, Chiang et al 1981).
3. Ambient conditions; temperature, aeration, humidity, and light (Cheigh and Kwon 1972).
4. Characteristics of product; concentration of fat, moisture (Labuza and Chou 1974, Chou et al 1973), antioxidants (Sherwin and Thompson 1967, Furia and Bellanca 1977, Weinshenker 1980), copper, iron, salt, and chelating agents (Choe et al 1977).
5. Process conditions; time and temperature of frying (Jacobson 1967), moisture content of the steamed noodle to be fried, local overheating, and contact with metals.

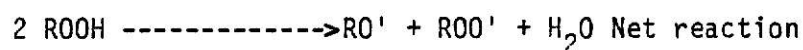
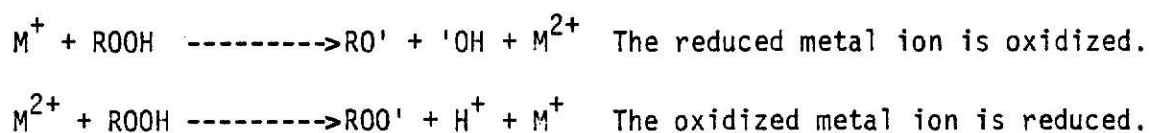
Schaich (1980) also listed the factors affecting the rate and course of autoxidation in foods (Table IV).

In 1971 Labuza studied the relationship between water activity and lipid oxidation. He reported that for most dry foods the optimum moisture content corresponding to the lowest rate of lipid autoxidation occurred when the food had an equilibrium relative humidity (ERH) of 25 to 35% (Fig. 10). It is thought that layering of water molecules over the dispersed fat molecules

provides a barrier to oxygen diffusion. Decreasing the water content removes the barrier, while increasing the water content provides mobility to pro-oxidants, such as metal ions. Pokorny (1979) also concluded that the stability against rancidity depends on moisture content, and the optimum moisture content to prevent autoxidation was 6% in crackers.

As expected, oxygen, temperature, sunlight, ultraviolet light, and trace metals (especially copper and iron) greatly accelerate the development of rancidity in the fried noodle (Choe et al 1977, Okada 1971). Acceleration of rancidity by trace metals was found to be in the following order:  $\text{Cu} > \text{Fe} > \text{Cr} > \text{Zn} > \text{Ni} > \text{Sn} > \text{Al}$  (Nishijima et al 1976). The two most important trace metals, copper and iron, were found to be present in commercial fats and oils up to 0.2 and 1.0 ppm, respectively (Pokorny 1979).

It is well recognized that heavy metals, particularly those possessing two or more valency states with a suitable oxidation-reduction potential between them, such as Co, Cu, and Fe, generally increase the rate of oxidative deterioration of lipids (Lea 1938, Schultz 1962). Metallic pro-oxidants contribute to the formation of additional radicals by acting as hydroperoxide decomposers. A metal, capable of existing in two valence states, functions typically as follows:



In a system containing multivalent metal ions, such as  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  or  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , the hydroperoxides decompose readily with formation of both  $\text{RO}'$  and  $\text{ROO}'$  radicals as the metal ions undergo oxidation-reduction (Dugan 1976).

In the presence of trace metals, particularly of copper, peroxides will

yield further radicals and theoretically, the chain reaction will continue until the substrate is oxidized, or as long as oxygen is available. Under practical conditions trace metals acting as catalysts for oxidation play a very important role since they are present in most substrates in sufficient amounts.

The oxidative stability of ramyon depends in large measure on its content of antioxidants (Okada 1971, Porter et al 1977). Antioxidants are more reactive than fat molecules (RH) towards free radicals. The newly formed free radical on an antioxidant disproportionates to give stable oxidized products; in this manner they stop the chain reaction (Johnson 1979).

The antioxidants, so-called primary antioxidants, interfere directly with the free radical propagation process and block the chain reaction. There exist synergists which have little effect on the autoxidation of lipids but are able to enhance considerably the action of primary antioxidants (Berk 1976). It is known that synergists by themselves in the absence of primary antioxidants have very little effect on the oxidation of foods. However, they enhance or greatly promote the effectiveness of primary antioxidants by binding pro-oxidant metals and forming inactive complexes that inhibit the decomposition of peroxides. There are several metal deactivators such as citric and ascorbic acids, their salts, and a number of various condensed phosphates; including sodium salts of pyrophosphate, tripolyphosphate, trimetaphosphate, tetrametaphosphate, and other combined polyphosphate (Martell and Calvin 1953, Lundberg 1961, Berk 1976). These metal deactivators chelate trace metals and minimize the problems related to their interaction with antioxidants.

The possible synergistic effect of acids with antioxidants has been well studied. With a given level of tocopherol (0.15%) in autoxidizing fat, both ascorbic and citric acids showed their greatest stabilizing effect at the

low level of 0.025% (Privett and Quackenbush 1954). Cort (1974) reported that ascorbyl palmitate alone was better than BHA and BHT in preventing vegetable oils. In combination with other known antioxidants, ascorbyl palmitate improves the shelf-life of vegetable oils, as well as potato chips (crisps). However, there is some difficulty in solubility of ascorbyl palmitate.

In 1961 Lundberg reported that the pro-oxidants did not alter, fundamentally, the mechanism of the oxidation or the qualitative nature of the products. The copper ion did not directly catalyze the oxidation of linoleate by oxygen, but rather, it catalyzed the decomposition of the peroxides. Citric acid can counteract the pro-oxidant effect of iron added to purified methyl esters of peanut oil and it acts as a synergist in the presence of phenolic antioxidants.

Kusaka et al (1969) found that no matter how high the surrounding temperature, if visible light of 450-550 nm and ultraviolet light near 385 nm were eliminated, then ramyon was not autoxidized over a period of a month. In their work, the noodles were packaged under vacuum.

The presence of NaCl in fried noodles appears to promote rancidity development (Hu and Kim 1974, Chiang et al 1981, Kim and Heo 1975). Metal impurities are invariably present in salt, and they are assumed to be primarily responsible for development of rancidity.

The antioxidant activity of tocopherol (Reinton and Rogstad 1981) was confirmed in ramyon by Kuwahara et al (1971), Yuki et al (1971), Terao et al (1980), and Okada (1971). In 1971 Okada reported that the induction period of lard was extended almost linearly by the addition of 5-20% sesame oil. When stored at 60°C, ramyon fried with lard containing 5% sesame oil had a longer induction period than those fried with lard alone. Sesame oil contains considerable amounts of tocopherol (Table V).

In general vegetable oils contain a mixture of tocopherols (Dugan and Kraybill 1956); Table V lists the total tocopherol content of lipids commonly used for frying ramyon. Even though soybean oil has the highest content of tocopherol, it also has one of the highest ratios of unsaturated fatty acids to saturated acids (Table III). Therefore, from the aspect of autoxidation stability, soybean oil might not be generally recommended.

Yuki et al (1971) reported that tocopherol survived frying conditions better than BHA. When the fat surface was protected from air during frying for up to 30 hours, tocopherol declined to 80% of its initial level, whereas BHA fell to below 50%. The difference in loss was due to the nature of volatility, decomposition, and steam distillation during frying.

Many foods, especially those of vegetable origin, contain tocopherols and ascorbic acid as natural antioxidants. Citric acid at 0.005% to 0.025% also shows synergistic activity with 0.03% of natural tocopherol; the citric acid extended the shelf-life of lard up to five times longer than the control containing tocopherol only (Privett and Quackenbush 1954).

In 1972 Sherwin evaluated the effect of antioxidants and chelating agents in crude palm oil, and found that 110 ppm TBHQ plus 365 ppm citric acid was the optimum level necessary to achieve the best overall protective effect in crude palm oil. The treatment resulted in a Totox value ( $2 \times$  peroxide value + anisidine value) that was one-third the value of the control.

The phenolic antioxidants give very good protection in fats and oils, and the addition of chelating agents such as citric acid, ascorbyl palmitate, sodium tripolyphosphate, and disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{EDTA}$ ), in combination with antioxidants insures reasonably long shelf-life (Labuza 1971). Lee (1978) also concluded that  $\text{Na}_2\text{EDTA}$  forms a highly stable iron chelate. It has been observed that a combination of ascorbic acid, citric acid, and antioxidants is synergistic in preventing autoxidation in ramyon

(Okada 1972, Choe et al 1977, Johnson 1979).

Okada and Koyama (1969) reported that the oxidative stability of lard and instant ramyon depended largely on the content of antioxidant. They presented two equations describing the relationship between the level of antioxidant (BHA) in lard and its induction period, and the relationship between the level of residual antioxidant with the period of frying time. The equations are as follow:  $\log (y - c) = a + bx$ , and  $\log y = \log a + (b) \cdot (\log t)$ , where a, b, and c are coefficients obtained as the results of experiments, y is the level of antioxidant, x is induction period, and t is the period of frying time.

Fritsch et al (1975) described that the stability improvement of a snack product fried in palm oil stabilized with TBHQ depended greatly on the frying condition used. They also observed that under bulk storage temperature, significant reductions in the formation of peroxides in palm oil were obtained with TBHQ but not with BHA and BHT. The reduction in peroxide formation in bulk storage of palm oil with TBHQ was reported to be much greater than anticipated as measured by the active oxygen method.

In frying ramyon, the loss of antioxidants mainly depends on their steam distillation and thermal decomposition. In general, those two properties are important to the use of an antioxidant in frying oil.

#### Measurement of Oxidative Rancidity

The techniques used to measure oxidative rancidity in foods have been reviewed by Gray (1978) and Logani and Davies (1980). Under normal conditions, the rate of rancidity development in most foods is related to the rate of formation of peroxides, which are referred to as the primary products of autoxidation. During the induction period, peroxides accumulate until their concentration causes them to interact and give a cascade of more radicals (Kläui



and Pongracz 1982). The cascade of new radicals ends the induction period suddenly, and off-flavors and odors are formed quickly.

In 1962 Lundberg found that with most of the common lipids and lipid-containing foods, rancidity is detectable organoleptically when between 0.1% and 1.5% of the fat has formed hydroperoxides. At the time rancidity becomes organoleptically detectable, the hydroperoxides decomposition reactions are taking place rapidly and undesirable flavors and odors are increasing quite sharply. The actual substances, on which the organoleptic evaluations rely, depend qualitatively and quantitatively not only on the extent of oxidation but also on various other factors.

There are numerous products that are responsible, either directly or indirectly, for rancid flavors and odors (Forss 1975). Volatile aldehydes and ketones are probably the most objectionable substances. The olfactory perception threshold values of the carbonyls and some other compounds formed is often extremely low. Therefore, the organoleptic evaluation is and always will be the best and the most significant criterion for judging the quality of lipids and lipid-containing foods (Kläui and Pongracz 1982).

Many chemical tests for rancidity have been developed based on the quantitative measurement of a single product or classes of products resulting from the oxidation reaction. However, there is no ideal chemical method which correlates well with the changes in organoleptic properties of oxidized lipids throughout the entire course of autoxidation (Ito et al 1970). It seems reasonable to determine the concentration of peroxides as a measure of the extent of oxidation, but this method is limited by the transitory nature of the hydroperoxides and possibly by limited amounts of oxygen. The peroxide value (POV) method is commonly used, but it is highly empirical (Gray (1978). During secondary processes, the content of active peroxide oxygen is reduced, so that the peroxide value is no longer a reliable measure of the



oxidation. On the other hand, the carbonyls formed can be easily determined analytically and may serve as parameters for the extent of oxidation (Oota 1979).

An alternative approach to the determination of the extent of lipid oxidation is to measure the carbonyl compounds, formed by degradation of the hydroperoxides, which contribute directly to the rancid flavor. Although the volatile carbonyl compounds are only minor side-products during the entire autoxidation of fatty acids, they are of great significance for the aroma of foods because their threshold concentrations for odor and taste are very low (Forss 1975, Kläui and Pongracz 1982). Table VI gives the threshold values for flavor perception of various substances formed during autoxidation.

In recent years, using gas chromatography-mass spectroscopy, Frankel et al (1982) studied the composition of autoxidation products of methyl oleate, linoleate, and linolate. They reported that the major volatile product from autoxidation of common unsaturated fatty acids was hexanal. Fritsch and Gale (1977) determined the hexanal concentration in low-fat foods (dehydrated) in 10 minutes by GLC analysis of the vapors in the head space above a 15-g sample suspended in boiling water. They concluded that the onset of rancid flavor occurred when the hexanal concentration increased to between 5 to 10 ppm in the sample. They also obtained a good correlation between sensory evaluation and hexanal concentration at 0.3 to 5 ppm. The level of hexanal where rancid off-flavor was found in oat cereal by Frankel et al (1982) is  $10^5$  larger than the threshold value in milk reported by Kläui and Pongracz (1982). Apparently the disagreeable taste of rancidity occurs at a much higher concentration of hexanal than the threshold level of detection in milk.

There are numerous tests and methods for the measurement of oxidative rancidity. They can be classified based on the type of reaction product used

as the index of rancidity:

1. The primary products of lipid autoxidation
  - \*Peroxide Value (POV) to measure hydroperoxides (Chang and Sung 1972)
2. The secondary products
  - \*Organoleptic test to detect volatile compounds (Cheigh and Kwon 1972)
  - \*Kries test for epihydrin aldehyde derivatives (Ito et al 1970)
  - \*Thiobarbituric acid (TBA) test for its reaction with malonic dialdehyde (Kim and Heo 1975)
  - \*Carbonyl Value for carbonyl compounds (Forss 1975)
  - \*Hexanal test (Frankel et al 1982, Fritsch and Gale 1977)
3. The changes in composition of lipids
  - \*Iodine Value (IV) for unsaturated fatty acids (Ito et al 1970)
  - \*Saturation Value for the ratio of the saturated fatty acids to total fatty acids (Kajimoto 1971)
  - \*Acid Value (AV) for free fatty acids (Chang and Sung 1972)
  - \*Fatty acid concentration upon autoxidation (Berger 1975)
4. A combination of measurement of primary and secondary products
  - \*POV and Carbonyl Value (Okada 1971)
  - \*POV and organoleptic test (Chang and Sung 1972)
  - \*Other combination

#### Measurement of Stability of Lipid toward Autoxidation

Accelerated tests are usually conducted to measure the stability of lipid-containing foods against oxidative deterioration (Ragnarsson et al 1977). Obviously, only the tests under actual storage conditions can truly evaluate the stability of a product. But, in practice, such testing is difficult to pursue. Accelerated tests have been reported to be generally

useful to predict the shelf-life of a product as determined by the initial stage of autoxidation (Berger 1971).

The most widely used accelerated autoxidation tests are the oven test (Dugan et al 1950), the active oxygen method (Kuwahara et al 1971), and the oxygen absorption test (Lundberg 1962). Of these three methods, the oven test requires the simplest equipment and still provides reliable and practical data. In addition to this, the test can be conducted with a reasonable degree of success by persons having a little or no technical knowledge (Joyner and McIntyre 1938).

## MATERIALS AND METHODS

### General

Two wheat flours which had no additives were used. The soft wheat flour was obtained from King Milling Co., Lowell, MI, and the hard wheat flour from Ross Industries-Cargill Inc., Wichita, KS. For ramyon production, a 1:1 blend of hard and soft wheat flours was used. Analyses of the blend showed 13.2% moisture, and 10.2% protein and 0.46% ash on a 14% moisture basis.

Palm oil with no-additives was obtained from Palmco Inc., Portland, OR. Sodium chloride and acetone were reagent grade from Fisher Scientific Co., Fair Lawn, NJ. Disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{EDTA}$ ) was a product of Fisher Scientific Co., Fair Lawn, NJ. Hexanal (99%), 4-heptanone (98%), and *t*-butylhydroquinone (97% TBHQ) were obtained from Aldrich Chemical Co., Milwaukee, WI. Butylated hydroxyanisole (BHA) was purchased from Sigma Chemical Co., St. Louis, MO. Polymeric antioxidant (Poly-A) was 10% POLY-AO<sup>TM</sup>-79 in corn oil with the commercial name ANOXOMER, and was obtained from Dynapol Co., Palo Alto, CA. Unfortunately the Dynapol Co. terminated business in April of 1982 after the present work was underway.

### Preparation of Ramyon

1. Mixing. The formula used for ramyon in this work is given in Table VII. Wheat flour (1 kg) was placed in a Hobalt-A 200 mixer (Fig. 2, Hobart Corp., Troy, OH), and 330 mL of a 5.7% brine solution was added slowly over a period of one minute while mixing at low speed. Mixing was continued four minutes at medium speed. The optimum water absorption in noodle making was determined by observing the mass after mixing. At the proper level of absorption, spheres of dough up to the size of walnuts were formed, along with other less water-rich crumbs.

2. Resting. A 10 minute lay-time or rest period at room temperature was provided to distribute the moisture in the dough well.

3. Sheeting. A laboratory model noodle machine (Fig. 3, Ohtake Noodle Machine Co., Tokyo, Japan) was used to sheet and cut the noodles. The initial dough sheet was formed by passing through the smooth rolls (150 mm width, 180 mm diameter) with a gap setting of 4 mm. The first sheet was folded in half lengthwise and was passed again through the smooth rolls in the same direction with a 4 mm gap to complete sheet formation. The sheet was then passed through the rolls seven more times, gradually reducing the thickness of the sheet (4.0>3.5>3.0>2.7>2.4>2.1>1.8 mm), until the final thickness of the sheet reached 1.5 mm. The sheet was wound on a spool between sheeting steps.

4. Cutting. The noodle cutters consist of two pairs of slotted rolls which are made of brass. They are aligned so as to form a square shaped hole with a cross-section of 1.5 x 1.5 mm. The final dough sheet was cut by hand transversely into 30 cm long sheets that were then fed into the cutter (Fig. 4). The noodle strands from the cutter were directed onto a slow-moving belt such that the noodle strands formed a "wavy" appearance.

5. Forming. The wavy noodle strands (140 g, "as is") were put into a wire-net basket to form the noodle serving in the desired shape (Fig. 5).

6. Steaming. The noodles were subsequently steamed in an aluminum steamer (Fig. 6) for 5 minutes on each side. Four servings were steamed per batch and the noodles were covered with a thick cloth to prevent water from dripping on them.

7. Frying. Four servings of steamed noodles (140 g each) were immersed in 4 kg palm oil at 180°C in a Belshaw 611 fryer (Fig. 7, Belshaw Bros. Inc., Seattle, WA). The temperature of the oil dropped to 160°C and was kept there for 70 seconds. The fried noodles were removed from the

fryer and allowed to drain 20 seconds to remove excess oil.

8. Cooling and packaging. After cooling to room temperature, the ramyon serving (~110 g each) was crushed into pieces approximately 2-5 mm long by mortar and pestle, and then put into two oz (~59 mL) glass jars for the Schaal oven test. Each jar contained 10 g of noodles and ~40 mL of head space.

#### Trace Metals in Ingredients and Ramyon

Samples (0.5 g) of palm oil, wheat flour, salt, and crushed ramyon were placed in micro-Kjeldahl flasks for wet combustion. A mixture of concentrated sulfuric acid (3 mL) and concentrated nitric acid (8 mL) was added to the flask. The content of the flask was boiled gently 3 hours, cooled, and diluted to volume (100 mL) with water. Trace metals in the digests were determined using a Perkin Elmer atomic absorption spectrophotometer (model 603) and standard solutions of copper and iron purchased from J. T. Baker Chemical Co., Phillipsburg, NJ. Copper and iron were determined at 324.7 and 248.3 nm, respectively.

#### Accelerated Aging Tests on Ramyon

Three separate storage experiments were conducted. The oil, freshly prepared with a given antioxidant, was used in a frying experiment. Each batch of oil was discarded after a single frying of ramyon.

First Storage Experiment - Effect of Antioxidants in Frying Oil Ramyon was fried in palm oil containing 200 ppm of either BHA, TBHQ, Poly-A or no antioxidant (control).

Prior to frying, each antioxidant of 800 mg was dissolved completely in 4000 g of fresh palm oil. After frying, 500 g of each type ramyon was crushed into approximately 2-5 mm lengths using a mortar and pestle. Each

sample was then divided into 50 jars (2 oz) containing 10 g of noodle each. The four kinds of samples were labeled control, BHA, TBHQ, and Poly-A. There was a total of 200 jars used in the experiment. The 200 sample jars were placed in an incubator at 145°F (63°C) to conduct the Schaal oven test. The samples were examined periodically using an organoleptic panel test (Joyner and McIntyre 1938).

For comparison, a portion (total 300 g) of the freshly fried ramyon was frozen immediately after frying and kept in frozen storage until use as a control in the organoleptic tests.

The stored ramyon samples were evaluated organoleptically by the threshold method described by the American Society for Testing and Materials (1977). This method follows the procedure of (i) an orientation session prior to formal panel testing, (ii) formal panel sessions, and (iii) analysis and interpretation. The panel members consisted of five people trained to make qualitative distinction between fresh ramyon and ramyon just beginning to develop rancidity. A sample from each test regiment was taken from the incubator daily, cooled to room temperature, coded with a three digit number, and delivered to the panel members. The onset of rancidity of the samples was detected by taste and smell. The results were expressed as days to develop rancid flavor at 63°C (145°F), and the mean and standard deviation for the five panel members were calculated.

Second Storage Experiment - Antioxidant Effect of TBHQ Applied to Inner Surface of Package There were four treatments and one control in this experiment. The four treatments involved the application of TBHQ (0, 200, 500, and 1000 ppm) on the inner surface of the package but no antioxidant in the frying oil. Another noodle was prepared with 200 ppm TBHQ in the frying oil.

TBHQ (100 mg) was dissolved in 100 mL of acetone. This solution (0.4 mL, 1 mL, or 2 mL) was applied evenly over the inner surface of a ziploc bag (5 x 8 cm) to give TBHQ on the surface equal to ~200, 500, or 1000 ppm, respectively, based on the oil (~20%) in the fried noodle. The amount of TBHQ per unit of the package area was calculated to be ~0.4, 1 or 2 mg/40 cm<sup>2</sup>.

We used thin layer chromatography to determine whether TBHQ oxidized during surface application on the package. Those experiments are described in another part of the experimental section.

Samples (10 g) of ramyon were put into the bags, and the bags were then enclosed inside capped 2 oz glass jars. The jars were then placed in an incubator at 63°C (145°F), and the onset of rancidity was determined by the Schaal oven test as described in the first storage experiment.

Third Storage Experiment - Effect of Chelating Agent Na<sub>2</sub>EDTA There were three treatments and one control to evaluate the effect of Na<sub>2</sub>EDTA added to the frying oil. The control noodles were fried in oil containing no antioxidants or Na<sub>2</sub>EDTA. The three treatment samples of ramyon were fried in oil containing either (1) 200 ppm TBHQ, (2) a mixture of 200 ppm TBHQ and 200 ppm Na<sub>2</sub>EDTA, or (3) a mixture of 200 ppm TBHQ and 500 ppm Na<sub>2</sub>EDTA. The ramyon samples were prepared and evaluated by the Schaal oven test.

#### Hexanal Determination

Hexanal was determined in the head space above noodles using a slight modification of the chromatographic method of Fritsch and Gale (1977). The gas chromatograph was a Hewlett Packard model 5750 equipped with a flame ionization detector. 4-Heptanone was used as an internal reference standard, and separations were done on an aluminum column (10 ft long x ¼ inch i.d.) packed with 10% silicone OV-101 on acid washed 60-80 mesh chromosorb W



(Supelco Inc., Bellefonte, PA). The GLC conditions were as follow: column temperature, 100°C; injection port temperature, 200°C; detector temperature, 150°C; nitrogen flow rate, 25 cc/min; detector air flow, 280 cc/min; detector hydrogen flow, 30 cc/min; and chart speed, 0.5 inch/min. Hexanal concentration was determined in duplicate for each sample, and was reported as the mean value of ppm hexanal in a sample.

A standard curve of hexanal concentration vs peak area ratio of hexanal/4-heptanone was made. Five standard solutions of a mixture of hexanal and 4-heptanone were prepared in 1000 mL of water containing 2.5, 5.0, 7.5, 10.0, and 12.5  $\mu$ L of hexanal and 5  $\mu$ L of the internal standard 4-heptanone. An aliquot (10 mL) of each standard solution was then added to 15 g of sucrose in a 250 mL centrifuge bottle, and boiling water was added until the total volume was 150 mL. The bottle was immediately capped with a septum cap and swirled for 60 seconds. Then 5.0 mL of the head-space gas was taken with a gas-tight syringe and injected into a gas chromatograph at a rate of about 1 mL per second.

Peak areas were calculated as the product of the width at half-height times the height. For example, the mean peak area ratio of hexanal/4-heptanone was found to be 0.508 when the standard solution containing 5  $\mu$ L/1000 mL of both hexanal and 4-heptanone was used (Fig. 11). The concentration of hexanal used in constructing the standard curve was calculated in ppm based on sucrose. In our example, 10.0 mL of a standard solution containing 0.05  $\mu$ L (41.7 ng) of hexanal and 0.05  $\mu$ L (41.1 ng) of 4-heptanone was added to 15 g of sucrose. The corresponding concentrations of hexanal and 4-heptanone were 2.78 and 2.74 ppm, respectively, based on sucrose.

The concentration of hexanal in a ramyon sample was determined from the standard curve or simply by multiplying its peak area ratio by 5.47. The factor 5.47 was derived from the expression  $2.78/2.74:X/2.74 = 0.508:R$ ,

where X is the concentration of hexanal in ppm in an unknown sample and R is its peak area ratio. Simplifying this expression gives  $X = 5.47R$ .

#### Determination of the Residue of TBHQ by TLC

Silica gel plates GHLF #21521 "UNIPLATE" (Analtech Co., Newark, NJ) were used for thin layer chromatography (TLC). A mixture of methanol and chloroform (1:9, v/v) was selected as developing solvent. The components on a plate were located by spraying with aqueous sulfuric acid (50%) followed by ashing on a hot plate. The procedure consisted of spotting a solution (5 $\mu$ L), developing in the solvent chamber for three minutes, removing the plate and evaporating the solvent, spraying with 50% sulfuric acid, and ashing on a hot plate.

In the second storage experiment on noodles, 0.4 mL of a TBHQ solution (1.0 mg/mL) was applied to the inner surface of a plastic package and dried. Thus, 0.4 mg of TBHQ was spread on the inner surface of the bag after evaporation of the acetone. The bag was rinsed with 1.0 mL acetone, and that acetone solution was examined by TLC along with four other solutions. Thus, five different acetone solutions were spotted:

(1) an acetone extract of a polyethylene bag without TBHQ applied to its inner surface;

(2) an acetone extract of a polyethylene bag with TBHQ (0.4 mg) applied to its inner surface;

(3) an acetone solution of reference TBHQ solution (0.4 mg/mL);

(4) an acetone extract of a polyethylene bag containing TBHQ (0.4 mg) on its inner surface and in which ramyon was stored for three weeks at 63°C; and

(5) an acetone extract of a polyethylene bag containing TBHQ (0.4 mg) on its inner surface and in which ramyon was stored for one week at 63°C.

## RESULTS AND DISCUSSION

### Trace Metals in Ramyon

Table VIII shows the concentration of the trace metals in the ingredients and in ramyon ranged from 0.15 to 0.32 ppm for copper, and 0.92 to 1.97 ppm for iron. From the formula given in Table VII and the trace metal concentrations in Table VIII, the concentration of trace metal in the noodle was calculated on a dry weight basis. The calculated amounts of copper and iron were 0.16 and 1.53 ppm, respectively, which were slightly below the experimental values of 0.19 and 1.71, respectively. Therefore, the ramyon-making process increased the levels of copper and iron by 19 and 12%, respectively. The suspicious steps in ramyonmaking that may have increased iron and copper levels in this work would be mixing, cutting, and forming in the wirenet containers.

In common fats, rancidity development is hastened markedly by the presence of 0.1 ppm of copper, or 1.0 ppm of iron in the form of dissolved ions (Lundberg 1962). These trace metals frequently are introduced into commercial fats and oils from processing equipment and also from raw materials. Flour is the main source of copper and iron in ramyon, and the amounts of minerals in the flour alone are high enough to catalyze the reaction of unsaturated fatty acids and atmospheric oxygen. However, 2% salt in the formula accounts for 2.9% and 0.9% of the copper and iron in the noodle, respectively. Thus, the heavy mineral content of salt probably contributes significantly to the rancidity development in ramyon.

It has long been thought that sodium chloride (NaCl) accelerates the development of rancidity in foods. Because commercial grades of NaCl used for food purposes invariably contain small amounts of copper, iron, and other metallic contamination, it may well be that the trace metals are

primarily responsible for the supposed catalytic effect of NaCl (Choe et al 1977). It has also been reported by other investigators that trace metals appeared to promote or accelerate the rancidity development in ramyon (Hu and Kim 1974, Kim and Heo 1975). Therefore, the inactivation of trace metals by addition of a chelating agent is one practical means of delaying the initiation of autoxidation.

#### Effect of Antioxidant in Frying Oil

The objective of this phase of the study was to compare the effectiveness of three antioxidants BHA, TBHQ, and Poly-A in the frying oil to prolong the onset of rancidity in ramyon. Figure 12 shows the chemical structures of these antioxidants. Approximately half of the total fatty acids in palm oil are unsaturated fatty acids (Table III). The fatty acid composition of the palm oil (Table IX) used in this work was in good agreement with that reported in Table III.

BHA, TBHQ, and Poly-A were added to the oil before frying at a level of 0.02%, which is the maximum allowance by law (U.S. Code of Federal Regulation 1977). An accelerated rancidity test, the Schaal oven test, was used to determine the relative effectiveness of the antioxidants in delaying the onset of rancid odor and flavor. Test samples and a fresh sample (stored in freezer until tested) were tasted and compared by a taste panel consisting of five members. The results were expressed as days to develop rancid flavor at 63°C (145°F).

Table X shows the average storage time until detection of rancidity compared to the frozen control. The data are plotted in Figure 13. In the accelerated aging test, the addition of 200 ppm of the antioxidant Poly-A, BHA, or TBHQ extended the shelf-life of ramyon at 145°F by 5, 6, and 9 days, respectively, beyond the 5-day shelf-life of the control. Thus, Poly-A and

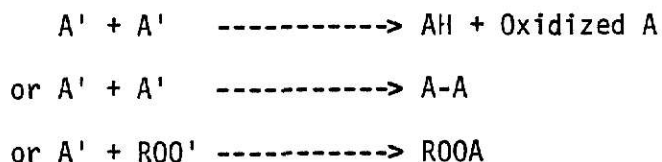
BHA doubled and TBHQ tripled the shelf-life of the ramyon noodle compared to the antioxidant-free sample. The Schaal oven test ranked the antioxidants in the relative order Poly-A<BHA<TBHQ.

Prior investigators (Sherwin 1972, Fritsch et al 1975, Sherwin and Thomson 1967) reported that TBHQ was much more effective than BHA in vegetable oils. Our results agree quite well with that generalization. Although there are exceptions, the order of relative effectiveness of antioxidants in pure oils usually correlates with their effectiveness in foods containing the oil (Smouse et al 1974).

In theory, a substance may retard oxidative rancidity in a variety of ways, such as competitive reaction with oxygen, retardation of the initiation step, blocking of propagation by destroying or binding free radicals, inhibition of catalysts, and stabilization of hydroperoxides (Berk 1976). The three antioxidants used in this study (Fig. 12) are likely to act as hydrogen donors and thereby block propagation of radicals, which retards the initiation reaction. The most effective action in retarding rancidity, besides eliminating oxygen, is blockage of propagation. In this process, the antioxidant (AH) acts as a hydrogen donor to a free radical such as  $ROO'$  or  $R'$  by reacting as follows:



The antioxidant free radical  $A'$  is relatively inert and enters some termination reaction (Berk 1976) such as:



The cost effectiveness of an antioxidant in a food system involves not only its purchase price and relative efficacy, but also the expense of labor,

equipment, and time necessary for its incorporation into the product. The cost effectiveness of antioxidants varies widely from one substrate to another; however, one can compare the cost per day of shelf-life extension. For example, BHA was priced at \$18.56/lb and TBHQ \$24.25/lb in April of 1982. When 0.8 g of antioxidant was used in 4 kg of oil, the cost of antioxidant was 4.09¢ for BHA and 5.35¢ for TBHQ. The extension of shelf-life of ramyon by BHA was 6 days, and that of TBHQ was 9 days; therefore, it cost 0.602¢ and 0.594¢ per day of extension for BHA and TBHQ, respectively. We can conclude that TBHQ was the more cost-effective than BHA to retard rancidity in ramyon. In addition, the longer shelf-life, afforded to the noodle containing TBHQ, is more likely to result in purchase of the product and no stale loss.

We can generally describe the requirements for an ideal antioxidant for frying ramyon as follow: (1) lack of toxicity at the concentration needed in ramyon; (2) ease of application, which often means good oil solubility; (3) effectiveness at low concentration, which means sufficient potency at a concentration of 0.02% or less; (4) no objectionable factors such as undesirable flavor and color change; (5) stability at high temperatures up to 200°C; (6) sufficient "carry-through" to the ramyon product during frying; and finally (7) reasonable cost. Among these factors, stability and carry-through are major concerns from the technical point of view.

The timing of adding an antioxidant to the oil in ramyon is also very important for its effectiveness. As oxidation proceeds by a radical chain reaction, any deleterious substances, once produced, always remains in the oil. Thus, antioxidants are most effective when they are added as soon as possible to the refined oil. In general, low dosages of antioxidants are effective in preventing the onset of autoxidation, but even high dosages will be ineffective once the oxidation has started (Kläui and Pongracz 1982).

The loss of antioxidant during the frying operation is of considerable importance in ramyon processing. A ramyon maker must continually replenish the antioxidant leaving the fryer in the water vapor. Ideally, the oil absorbed by ramyon during the frying step should contain the same antioxidant concentration as in the frying oil; but this is not always the case with monomeric antioxidants such as BHA, BHT, and TBHQ. The water vapor generated at the surface of frying oil steam-distills a significant portion of antioxidant out of the oil (Yuki et al 1971). The prevention of steam-distillation of antioxidants is an area that should be explored in the future to overcome rancidity problems in ramyon.

Though much progress has been made in food antioxidant technology, there is still an urgent need to determine the proper usage of currently available antioxidants to retard rancidity.

#### Effect of TBHQ on the Inner Surface of Package

Applying TBHQ to the inner surface of the package was compared to adding TBHQ in the frying oil on the shelf-life of ramyon. A 0.1% acetone solution of TBHQ was applied to the inner surface ( $40 \text{ cm}^2$ ) of zip-loc polyethylene bags and after the acetone evaporated at room temperature, the bags contained one of three levels of TBHQ (0.4, 1.0, or 2.0 mg) as a thin film. The ramyon sample (10 g) was put into each bag, and the bags were then placed in lidded glass jars to prevent the loss of rancid off-flavors and off-odors during accelerated rancidity development at  $63^\circ\text{C}$ . It is likely that the jars also prevented loss of TBHQ from the system.

Thin layer chromatography (TLC) was used to determine whether the TBHQ on the inner surface of the bag was oxidized by air during drying of the film. When the inner surface of an uncoated polyethylene zip-loc bag was rinsed with acetone, TLC of the rinse (Lane 1, Fig. 14) showed the presence of two



components with  $R_f$  values 0.87, and 0.65. It is likely that those components are plasticizers that make the film flexible. When a bag previously coated with TBHQ was rinsed with acetone, TLC of the rinse (Lane 2, Fig. 14) showed the presence of three components with  $R_f$  values 0.87, 0.65, and 0.56. The slowest moving component ( $R_f$  0.56) traveled the same distance on the plate as reference TBHQ (Lane 3, Fig. 4). Based on the single spot of TBHQ in Lanes 2 and 3 of Fig 14, an oxidized form of TBHQ was not detected; it is assumed that TBHQ remained totally in its reduced form when it was applied to the surface of a bag.

When TBHQ was applied to the surface of a bag, the quantity of TBHQ on the inner surface decreased during storage of the noodles. The inner surface of bags initially coated with 0.4 mg TBHQ (equivalent to 200 ppm TBHQ based on the oil in 10 g of ramyon) was rinsed with acetone (1.0 mL) after storage of the noodles at 145<sup>0</sup>F for one and three weeks. An aliquot (5.0  $\mu$ L) of each extract (Lanes 4 and 5, Fig. 14) was compared to the initial level of TBHQ (Lane 3). By visual inspection, the intensity of the residual amount of TBHQ on the inner surface of the package decreased approximately 50% in one week (Lane 5), and about 80% in three week storage at 145<sup>0</sup>F (Lane 4, Fig. 14). Apparently, the fat in the ramyon absorbed the TBHQ as it vaporized from the surface of the package. The intense and fast-moving spots ( $R_f$  0.83) in Lanes 4 and 5 (Fig. 14) were probably due to triglycerides that adhered to the inner surface of the package.

The data in Table XI shows that when compared to a no antioxidant control, the presence of 200 ppm in the frying oil extended the shelf-life 9 days at 63<sup>0</sup>C (145<sup>0</sup>F), while the same quantity of TBHQ on the inner surface of the bag extended shelf-life 19 days. Thus, TBHQ on the package surface was twice as effective in prolonging shelf-life of ramyon than an equal amount of TBHQ in the frying oil. It seems likely that rancidity first



develops on the surface of ramyon due to more light, oxygen and perhaps iron and copper on the noodle surface. When TBHQ evaporates from the surface of a package, the antioxidant condenses on the surface of the noodle. The high concentration of TBHQ on the noodle surface increases its effectiveness in delaying rancidity.

It should be noted that the control sample in a 2 oz glass jar alone gave a shelf-life of 5.2 days (Table X) at 63°C, while the control packaged in bags inside of glass jars had a shelf-life of 18.4 days (Table XI). That difference was undoubtedly due to the packaging method. The latter had a double protection of bag and jar, so oxygen might be limited in the samples inside bags.

Table XI also shows that the higher the concentration of TBHQ on the surface, the longer the shelf-life of ramyon noodles. At 200, 500, and 1000 ppm TBHQ on the surface, the shelf-life extension was 19, 22, and 27 days, respectively. These results agree with the general findings of Bruck et al (1981) who studied the interaction of fat-containing food with plastic packaging. They reported that the migration behavior of antioxidants from polyolefins and polyvinylchloride (PVC) to products was quite precise. The rate of the migration was a function of temperature and the concentration of antioxidant in the polymer. Recently, liners for some cereals and cracker products are coated with wax containing antioxidants (Bruck et al 1981, Lundberg 1962).

#### Effect of the Chelating Agent Disodium EDTA

A study was conducted to show the effect of a chelating agent disodium EDTA on the stability of ramyon during storage. Table XII shows that the addition of Na<sub>2</sub>EDTA prolonged the shelf-life of ramyon. When compared to ramyon fried in oil containing 200 ppm of TBHQ, which extended shelf-life

by 11 days past the control, frying in oil containing a mixture of 200 ppm of TBHQ and 200 ppm or 500 ppm of  $\text{Na}_2\text{EDTA}$  extended shelf-life by 14 or 16 days, respectively. The addition of  $\text{Na}_2\text{EDTA}$  to the antioxidant TBHQ prolonged the shelf-life of ramyon past the TBHQ alone.

#### Hexanal as a Measure of Rancidity in Ramyon

Gas-liquid chromatography was used to measure hexanal (Fritsch and Gale 1977) as an index of rancidity development in ramyon.

In this method an internal reference standard 4-heptanone was added to the sample contained in a centrifuge bottle (250 mL). The bottle was partially filled with boiling water, capped, and an aliquot of the head space was injected into the chromatograph to measure hexanal.

A standard curve of hexanal was first constructed using several known concentrations of hexanal mixed with a constant concentration of internal standard 4-heptanone. The known amounts of hexanal/heptanone were added to sucrose in the centrifuge bottle, and after addition of boiling water, the head space was assayed for hexanal. The integrated peak area ratios of hexanal/4-heptanone at the different concentrations of hexanal are given in Table XIII and the data are plotted in Figure 15. These data show the linear relationship between hexanal concentration and peak area ratio of hexanal/4-heptanone.

To determine the hexanal in ramyon, a known quantity of 4-heptanone was added and the noodles were suspended in boiling water and once again, the head-space vapors were injected into the chromatograph. Figure 16 shows that hexanal and heptanone were resolved completely from the mixture of the other compounds in the head space of a freshly made noodle, and a ramyon stored for two weeks at  $145^{\circ}\text{F}$ . Table XIV and Fig. 17 summarize the hexanal concentration in ramyon vs storage days at  $63^{\circ}\text{C}$  ( $145^{\circ}\text{F}$ ). The results con-

firm the relative effectiveness of TBHQ>BHA>Poly-A determined organoleptically.

From the taste panel data given in Table X and the curves in Figure 17, it can be concluded that the onset of rancidity as determined organoleptically by the Schaal oven test occurred when the concentration of hexanal in ramyon exceeded 3.5 ppm. At 3.5 ppm hexanal, the curves in Fig. 17 predict a shelf-life at 63°C of 6, 9, 11, and 14 days for the control, Poly-A, BHA, and TBHQ, respectively, whereas the experimental values in Table X were 5.2, 10.4, 11.4, and 13.8 days, respectively. In general our results agree with the detection of rancid flavor in dry oat cereal (low fat) at 5 to 10 ppm hexanal by Fritsch and Gale (1977).

The oxidative deterioration of lipids involves primarily autoxidation reactions which are accompanied by a variety of secondary reactions. Recently, Gray (1978) has reviewed the detection and measurement of lipid oxidation in foods. There are many chemical and physical methods developed to quantify oxidative deterioration with the objective of correlating the data with off-flavor development. Traditional chemical methods to measure rancidity include peroxide value, thiobarbituric acid number, and carbonyl value. We prefer the determination of hexanal as a simple, effective, and reproducible method in measuring the oxidative deterioration of ramyon. Furthermore, sample preparation of ramyon for hexanal determination involves no grinding or extracting, thereby eliminating the chance of losing volatile off-flavors and off-odors.

There are many mechanisms and pathways that give volatile secondary products in the autoxidation of fats. One of the pathways from linoleic acid to hexanal is shown in Fig. 9. In the mechanism, the initial free radical on linoleic acid is present as one of three resonance hybrids. After formation of the hydroperoxides on C-9, C-11, and C-13, the hydroperoxide

on C-13 undergoes chain scission and rearrangement between C-12 and C-13 to give hexanal.

The main source of linoleic acid in ramyon is the frying oil, but wheat flour also contains 1.5 to 2.0% of oil, in which approximately one-half of the fatty acids are linoleic acid. Thus, approximately 25% of the linoleic acid in ramyon noodles arises from wheat flour.

The rate of lipid oxidation in ramyon is affected not only by its fatty acids' composition but also by the other factors such as antioxidants, chelating agents, processing conditions, and other factors not yet elucidated. Ramyon product is a complex mixture of many organic and inorganic compounds. Any attempt to define the quality of a food from the measurement of a single compound such as hexanal would be presumptuous. However, the measurement of a single compound can provide valuable information when properly applied and interpreted (Fritsch and Gale 1977). In ramyon products whose fat contains substantial quantity of linoleic acid, an increase in hexanal concentration to 3.5 ppm or more was found to indicate a significant deterioration in quality due to lipid oxidation.

In commercial practice, the shelf-life of ramyon might extend beyond the time when hexanal concentration reaches to 5~10 ppm, because the seasoning used in ramyon soup and the wheat flavor of the cooked noodles are strong enough that they mask the rancid flavors to some extent.

The results of the present work extend the usefulness of hexanal determination in comparison to the organoleptic detection of autoxidation. Furthermore, hexanal determination can quantify the degree of autoxidation that has taken place in the stored ramyon.

## CONCLUSIONS

The following conclusions were arrived at under laboratory conditions:

1. The copper and iron concentration in ramyon, which were found to be 0.19 and 1.71 ppm, respectively, increased by 19% and 11%, respectively from those calculated values using the mineral contents of the ingredients. Oxidative rancidity is known to be significantly accelerated when copper and iron levels reach 0.1 ppm and 1.0 ppm in oil, respectively.

2. A polymeric antioxidant (Poly-A) and BHA approximately doubled and TBHQ tripled the shelf-life of ramyon compared to a control sample, when each antioxidant was added to the frying oil at 200 ppm, BHA gave slightly longer shelf-life than Poly-A.

3. When a mixture of TBHQ (200 ppm) and disodium ethylenediaminetetraacetate was added to the frying oil, the shelf-life of ramyon was prolonged approximately four times beyond that of a control sample.

4. TBHQ applied to the inner surface of the package extended the shelf-life of ramyon twice as long as an equal quantity (200 ppm) of TBHQ present in the frying oil.

5. Hexanal was found to be a good indicator of the development of oxidative rancidity in ramyon. The organoleptic evaluation showed that the flavor of ramyon was objectionable at a hexanal concentration above approximately 3.5 ppm. The relative effectiveness of the antioxidants Poly-A, BHA, and TBHQ determined by the rate of release of hexanal in the stored ramyon was the same order as determined by an organoleptic test.

TABLE I  
Korean Standards for the Composition  
of All-Purpose Wheat Flour

Composition	First Grade Standard
Moisture	Less than 14.5%
Ash	Less than 0.5%
Protein	More than 9.0%
Particle size	Less than 5.0 $\mu\text{m}$
Sand	Less than 0.03%

TABLE II  
Minima and Maxima in the Composition of Ramyon<sup>a</sup>

Items	General Composition
Moisture <sup>b</sup>	Less than 10%
Fat <sup>c</sup>	More than 15%
Protein <sup>c</sup>	More than 8.5%
Ash <sup>c</sup>	Less than 3%
Peroxide value	Less than 60 meq/kg of fat

<sup>a</sup>Korean standards

<sup>b</sup>Wet basis

<sup>c</sup>Dry basis

TABLE III  
Fatty Acid (F.A.) Composition of Some Common Lipids<sup>a</sup>

Lipid	Total Saturated F.A.	Unsaturated F.A.					P/S <sup>b</sup>
		16-1	18-1	18-2	18-3	Total	
Palm Oil	47.9	0.5	37.9	9.0	0.3	47.7	0.2
Coconut Oil	86.3	0.4	5.7	1.8	--	7.9	0.02
Corn Oil	12.7	0.1	24.6	57.3	0.8	82.8	4.6
Soybean Oil	15.1	0.3	22.8	50.8	6.8	80.7	3.8
Beef Tallow	43.5	--	36.0	3.7	0.6	40.3	0.1

<sup>a</sup>Weihrauch et al. 1977.

<sup>b</sup>P/S = polyunsaturated fatty acid/saturated fatty acid.



TABLE IV  
Factors Affecting Oxidation<sup>a</sup>

Accelerating Factors	Inhibitory Factors
High temperature	Refrigeration
Light	Exclusion of oxygen
Ionizing radiation	Blanching
Peroxides	Antioxidants
Organic metal catalysts	Metal deactivators
Trace metals	(chelating agent)
Free fatty acids	Saturation
Polyunsaturated and Conjugated fatty acids	

<sup>a</sup>Schaich 1980

TABLE V  
Tocopherol Content of Various Lipids<sup>a</sup>

Refined Lipid	Total Tocopherol (mg/100 g. lipid)
Corn	95
Cottonseed	92
Palm	56
Rapeseed	55
Rice Bran	91
Sesame	65
Soybean	125
Beef Tallow	1.0
Lard	2.7

<sup>a</sup>Lange 1954

TABLE VI  
 Flavoring Substances in Water, Milk and Oil<sup>a</sup> Threshold  
 Values for Flavor Perception (ppb)

Substance	Threshold Values		
	Water	Milk	Oil
Acids			
Butyric Acid	6.8	25.0	0.6
Capric Acid	3.5	7.5	200.0
Alcohols			
Butanol	--	0.5	--
Hexanol	--	0.5	--
Esters			
Methyl Butyrate	--	0.025	--
Ethyl Capronate	--	0.075	--
Ketones			
2-Hexanone	--	0.4	--
2-Heptanone	--	0.7	--
Aldehydes			
Hexanal	--	0.05	0.15
Octanal	--	0.07	--
n-Deca-2,4-dienal	0.05	--	0.28

<sup>a</sup>Kläui and Pongracz 1982.

TABLE VII  
Formula of Ramyon Dough and Composition of Ramyon Noodle

Ingredients	Dough Formula (parts)	Finished Ramyon (%)
Wheat Flour	100 <sup>a</sup>	72.1
Water	33	6.5
Salt	2	1.7
Frying Oil Absorbed	-	19.7

<sup>a</sup>Water content - 13.2%

TABLE VIII  
Trace Metal Concentration<sup>a</sup>

Material	Trace Metal Concentration <sup>b</sup> (ppm)	
	Copper	Iron
Blended Wheat Flour <sup>c</sup>	0.18	1.97
Salt	0.32	0.92
Palm Oil	0.15	1.23
Fried Noodle <sup>c</sup>	0.19	1.71

<sup>a</sup>Determined after wet combustion using atomic absorption spectrophotometer at 324.7 nm for copper and 248.3 nm for iron.

<sup>b</sup>Reported on dry basis

<sup>c</sup>Moisture content 13.2% for flour and 6.5% for fried noodle.

TABLE IX  
Analysis of Fresh Palm Oil<sup>a</sup>

Items		Results
Color, Lovibond		23Y-2.3R
Acid value (as Oleic)		0.06%
Peroxide value		nil.
Iodine value		52.9
Saponification value		195.1
Wiley's melting point		104.6 <sup>0</sup> F
Fatty acid composition by GLC		
C 12	Lauric	0.11
C 14	Myristic	0.96
C 16	Palmitic	43.05
C 16:1	Palmitoleic	0.1
C 18	Stearic	5.29
C 18:1	Oleic	40.23
C 18:2	Linoleic	10.08
C 20	Arachidic	0.18

<sup>a</sup>Supplier's analysis

TABLE X  
Average Storage Time at 63°C (145°F) until Organoleptic  
Detection of Rancidity in Ramyona<sup>a</sup>

Treatment <sup>b</sup>	Days	
	Mean	Standard Deviation
Control	5.2	0.45
Poly-A	10.4	0.89
BHA	11.4	1.52
TBHQ	13.8	1.64

<sup>a</sup>Samples stored in glass jars and their smell and taste were compared to those of a sample held in frozen storage until tested.

<sup>b</sup>Poly-A, BHA, and TBHQ tested at 200 ppm in frying oil.

TABLE XI

Time Period to Rancidity Detection in Ramyon Made with TBHQ  
in Frying Oil or When Ramyon was Stored with TBHQ  
Applied to the Inner Surface of Package

Treatment <sup>a</sup>	Days at 63°C (145°F)	
	Mean	Standard Deviation
Control <sup>b</sup>	18.4	0.89
200 ppm TBHQ in Frying Oil	27.2	1.79
200 ppm TBHQ on package <sup>c</sup>	37.0	3.08
500 ppm TBHQ on package <sup>c</sup>	39.8	2.05
1000 ppm TBHQ on package <sup>c</sup>	44.6	3.13

<sup>a</sup>All samples were put into ziploc bags and stored in glass jars.

<sup>b</sup>No TBHQ in oil or on package surface.

<sup>c</sup>Concentration of TBHQ based on oil (~2 g) in 10 g of noodles.



TABLE XII  
Effect of Disodium Ethylenediaminetetraacetate on  
Development of Rancidity in Ramyon  
Using the Schaal Oven Test

Treatment	Days at 63°C (145°F)	
	Mean	Standard Deviation
Control	4.8	0.45
200 ppm TBHQ in Oil	15.4	1.14
200 ppm TBHQ and 200 ppm EDTA in Oil	18.6	1.89
200 ppm TBHQ and 500 ppm EDTA in Oil	20.6	2.30

TABLE XIII

Hexanal Concentration vs Peak Area Ratio  
of Hexanal/4-Heptanone

Mixture (ppm <sup>a</sup> )		Peak Area Ratio of Hexanal/Heptanone
Heptanone	Hexanal	
2.74	1.39	0.261
2.74	2.78	0.508
2.74	4.17	0.661
2.74	5.56	1.012
2.74	6.69	1.284

<sup>a</sup>Concentration of hexanal and 4-heptanone based on sucrose.

TABLE XIV

Hexanal Concentration (ppm) in Ramyon vs Storage Days at 63°C (145°F)

Treatment <sup>a</sup>	Days				
	0	6	13	16	20
Control <sup>b</sup>	1.90	3.52 <sup>c</sup>	9.93 <sup>c</sup>	14.64 <sup>c</sup>	--
Poly-A	0.84	2.18	5.82 <sup>c</sup>	11.33 <sup>c</sup>	--
BHA	0.53	1.31	5.20 <sup>c</sup>	8.00 <sup>c</sup>	13.33 <sup>c</sup>
TBHQ	0.59	1.40	2.90	4.79 <sup>c</sup>	6.63 <sup>c</sup>

<sup>a</sup>All antioxidants were 200 ppm based on oil.<sup>b</sup>Without antioxidant in frying oil.<sup>c</sup>Has rancid flavor.

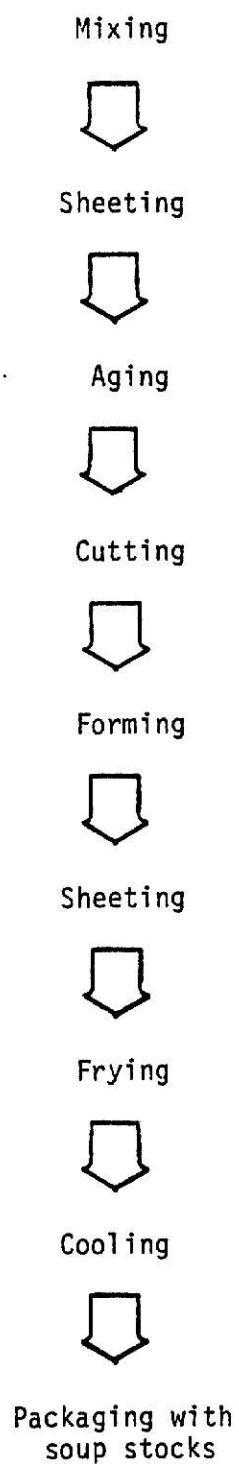


Fig. 1. General Steps to Produce Ramyon



Fig. 2. Mixing Ingredients for Ramyon in the Laboratory

Fig. 3. Sheeting of Ramyon Dough using Ohtake Noodle Machine

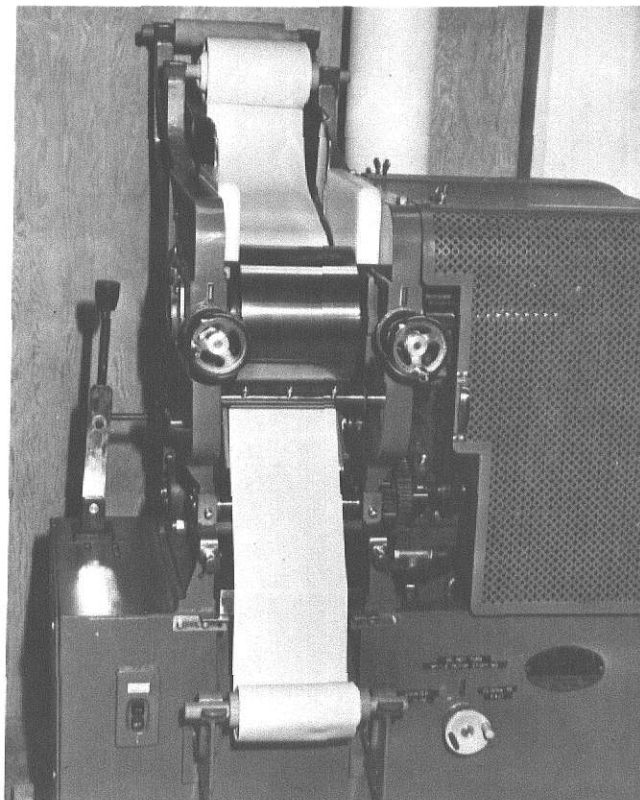






Fig. 4. Cutting of Ramyon Dough Sheet on the Ohtake Noodle Machine

Fig. 5. Forming Four Ramyon Servings, Each Containing 140 g  
("as is") Steamed Noodle

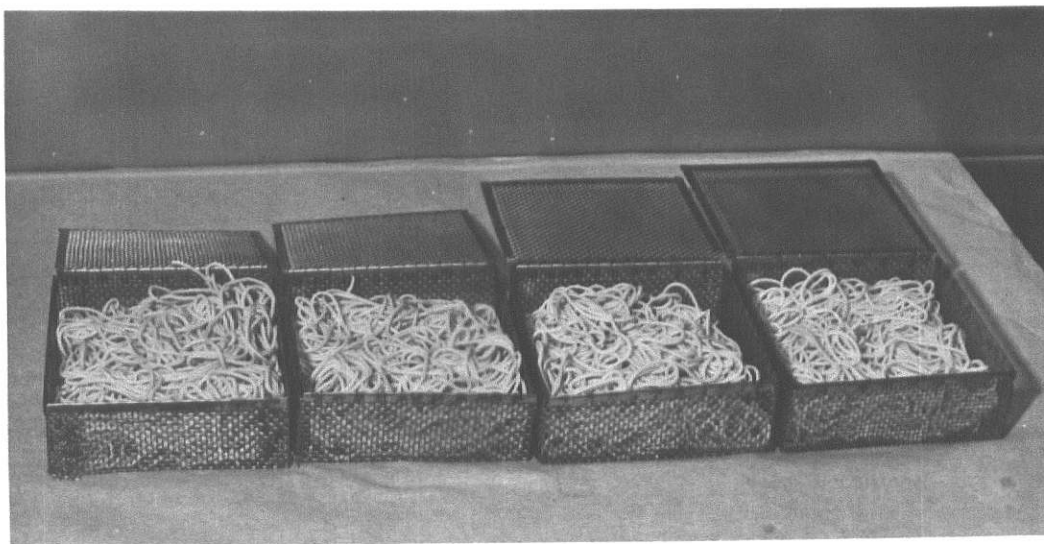
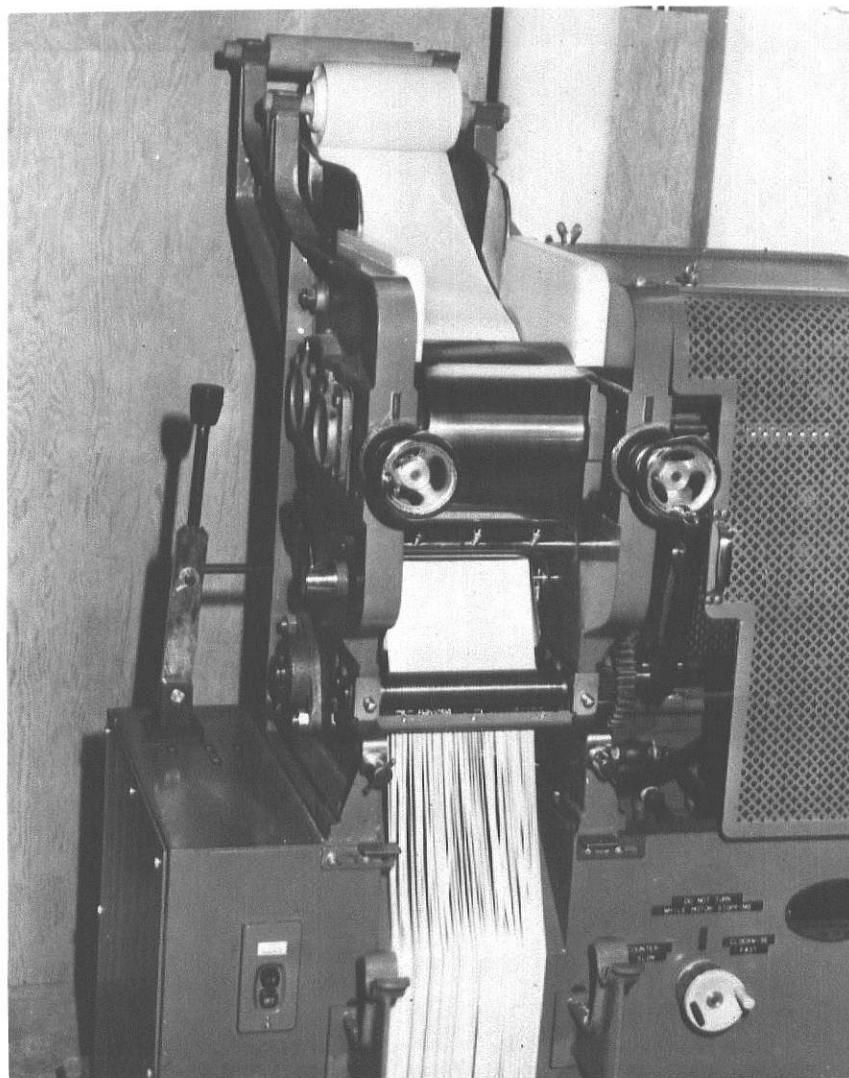
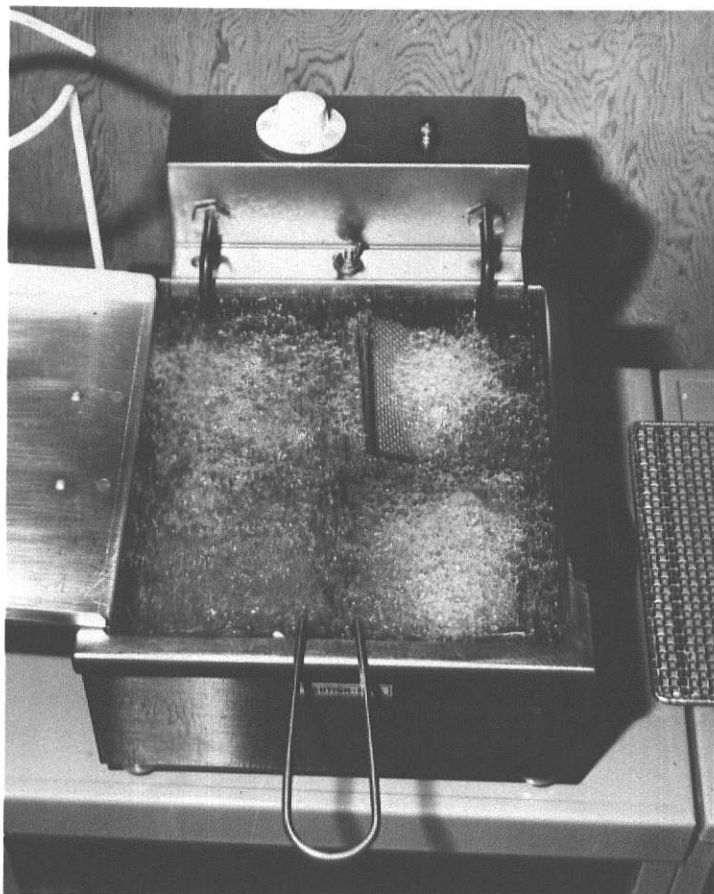




Fig. 6. Ramyon Steamer

Fig. 7. Ramyon Fryer



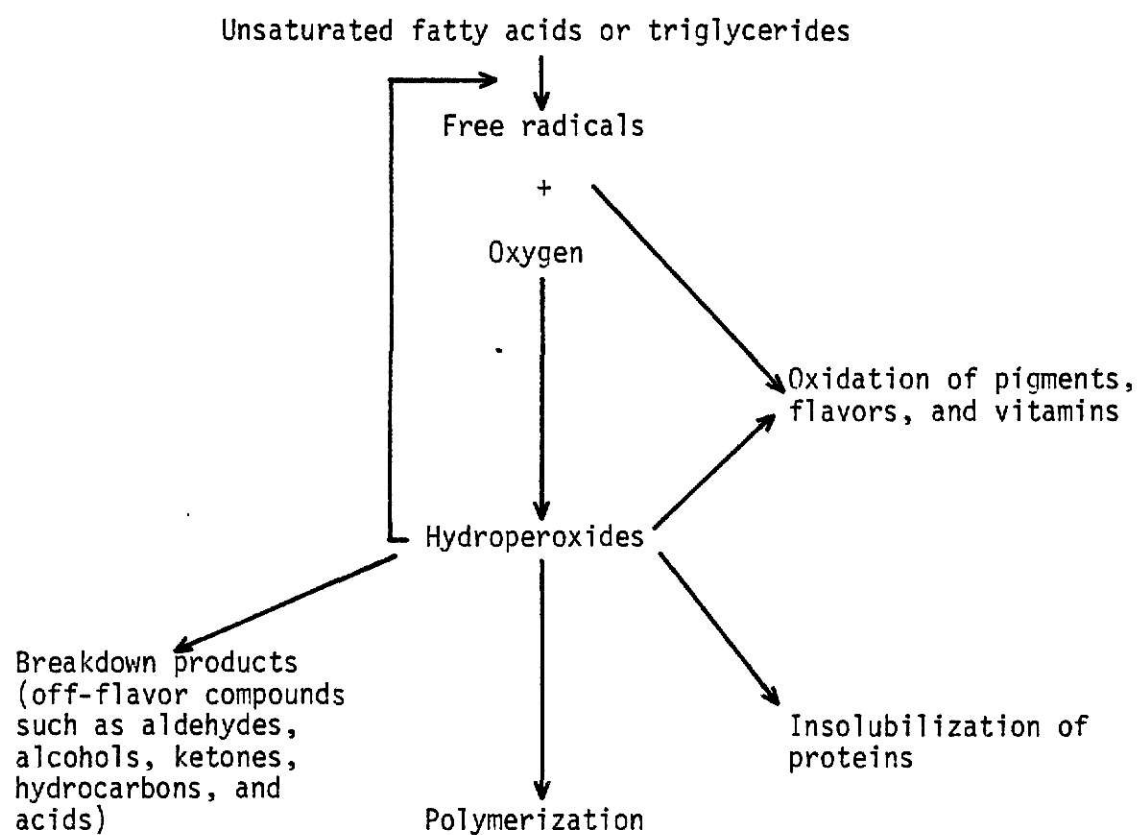


Fig. 8. Schematic Diagram for Overall Mechanism of Lipid Oxidation (Labuza 1971).

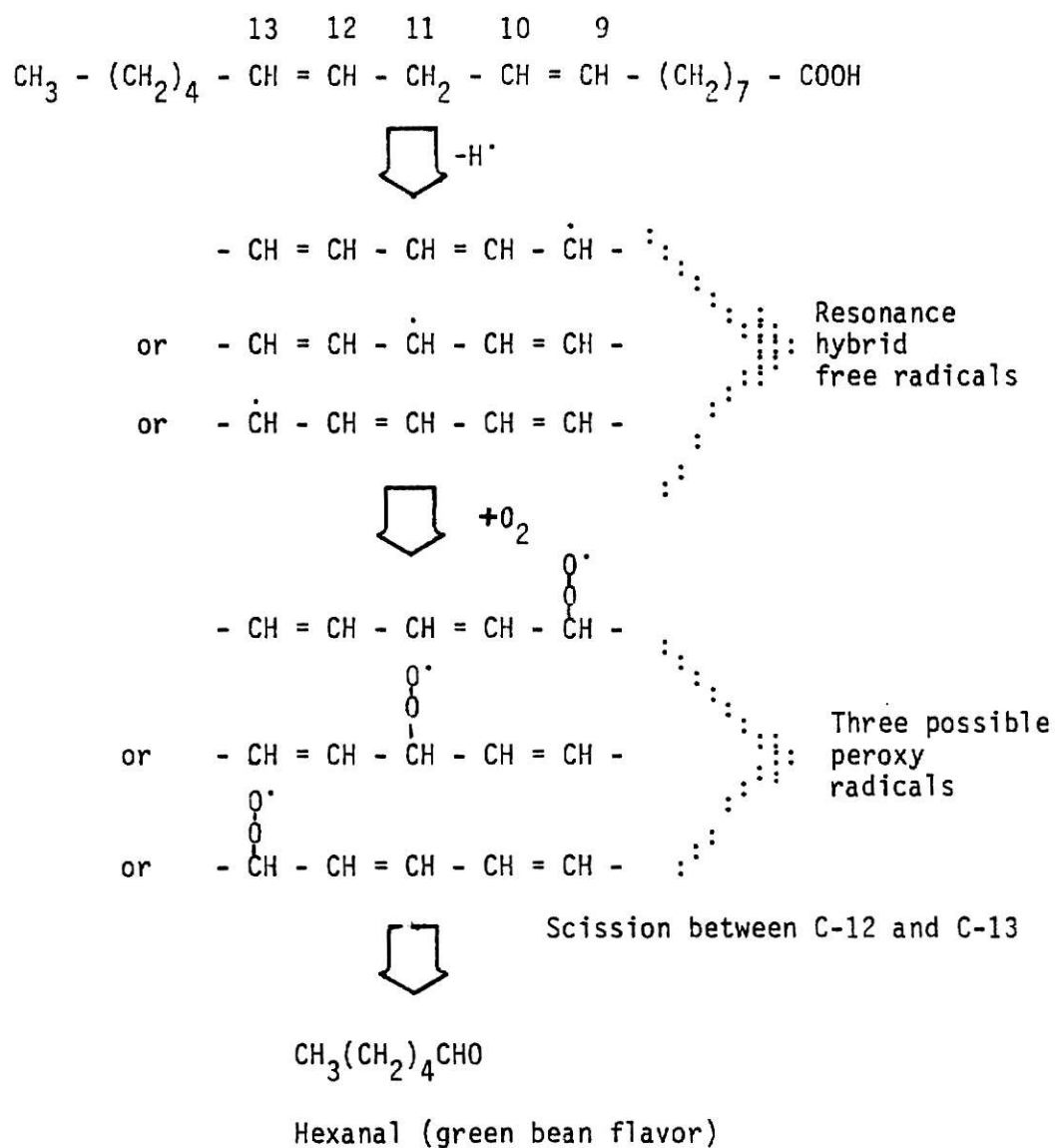


Fig. 9. Autoxidation of Linoleic Acid to Give Hexanal (Dugan 1976).





Fig. 10. Stability of Lipid-Containing Foods as a Function of Water Activity (Labuza 1971).

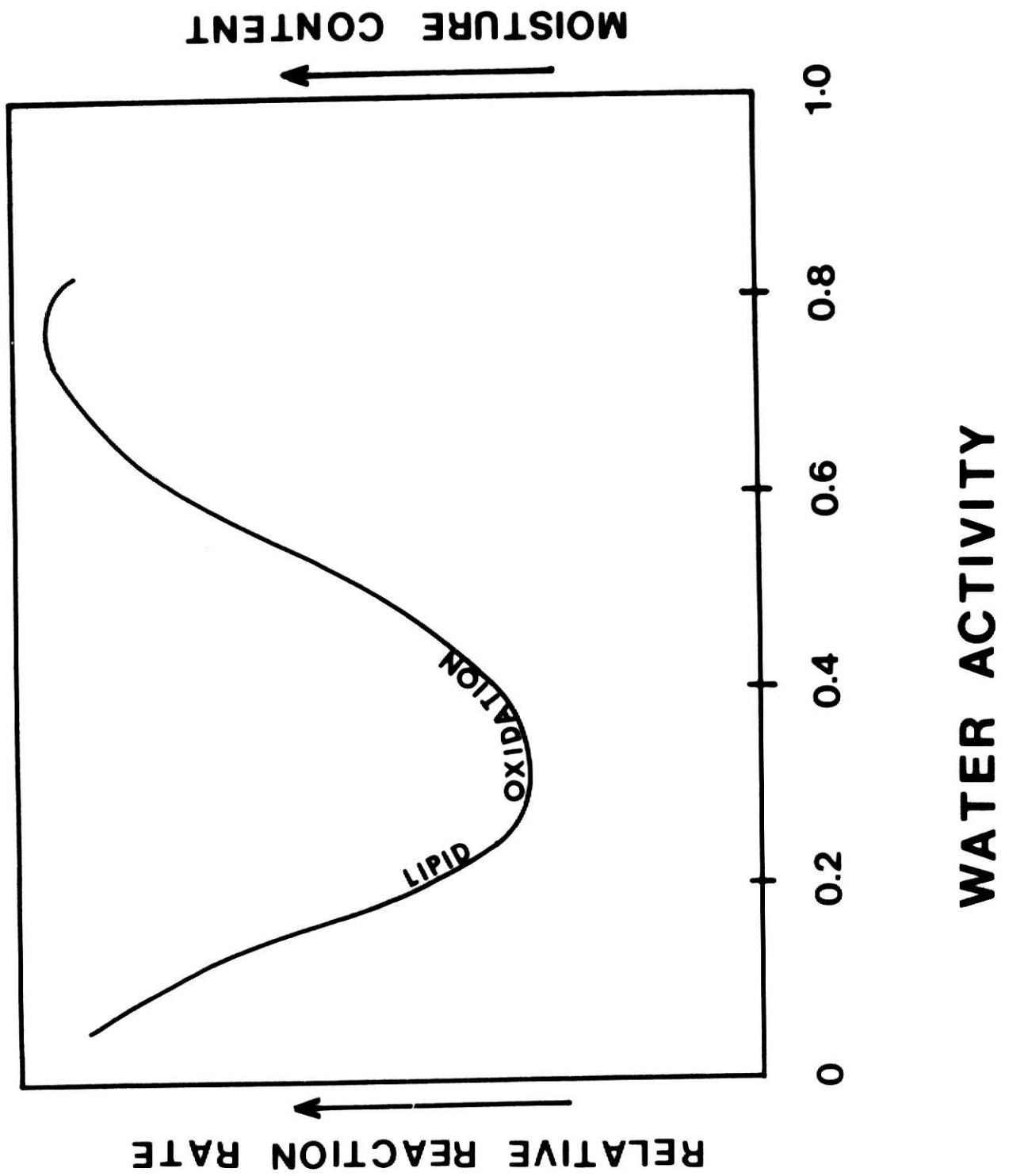




Fig. 11. Chromatogram of Head Space When an Aliquot (10 mL) of a Standard Solution of 2.78 ppm Hexanal (HEX) and 2.74 ppm 4-Heptanone (HEP) was Added to Sucrose (15 g) Followed by Boiling Water.

HEPTANONE

HEXANAL

PEAK AREA RATIO  
HEX/HEP : 0.508

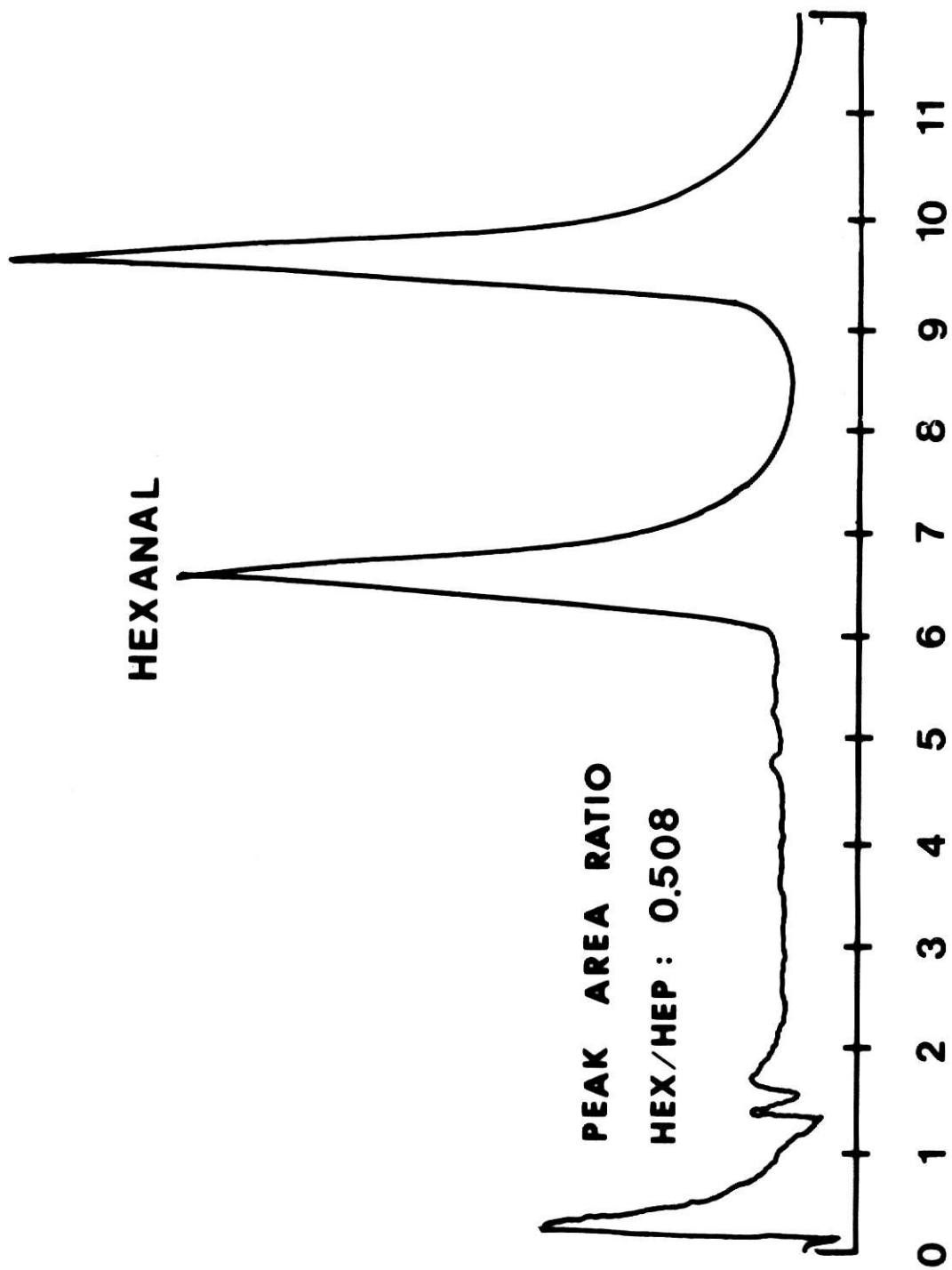
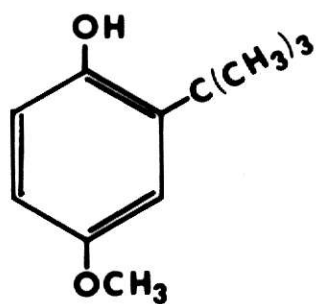
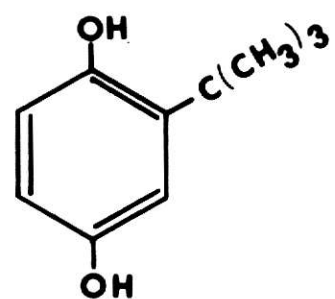
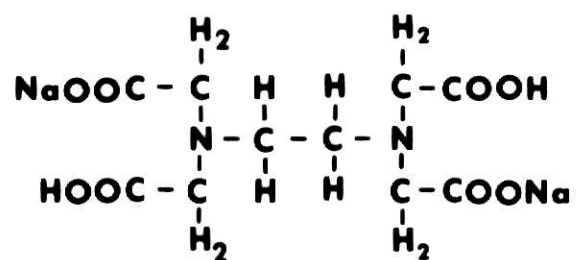
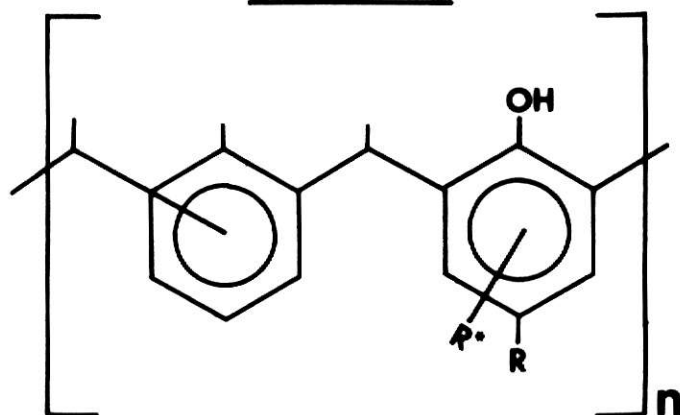




Fig. 12. Molecular Structures of Antioxidants (Poly-A was proposed by Furia and Bellanca 1977).

**BHA****TBHQ****Disodium EDTA****POLY-A**

**R : -OH, -OMe or ALKYL group**

**R\* : H, or ALKYL group**





Fig. 13. Effect of Antioxidants on Development of Rancidity in Ramyon,  
Fried in Oil Containing 0.02% Antioxidants.

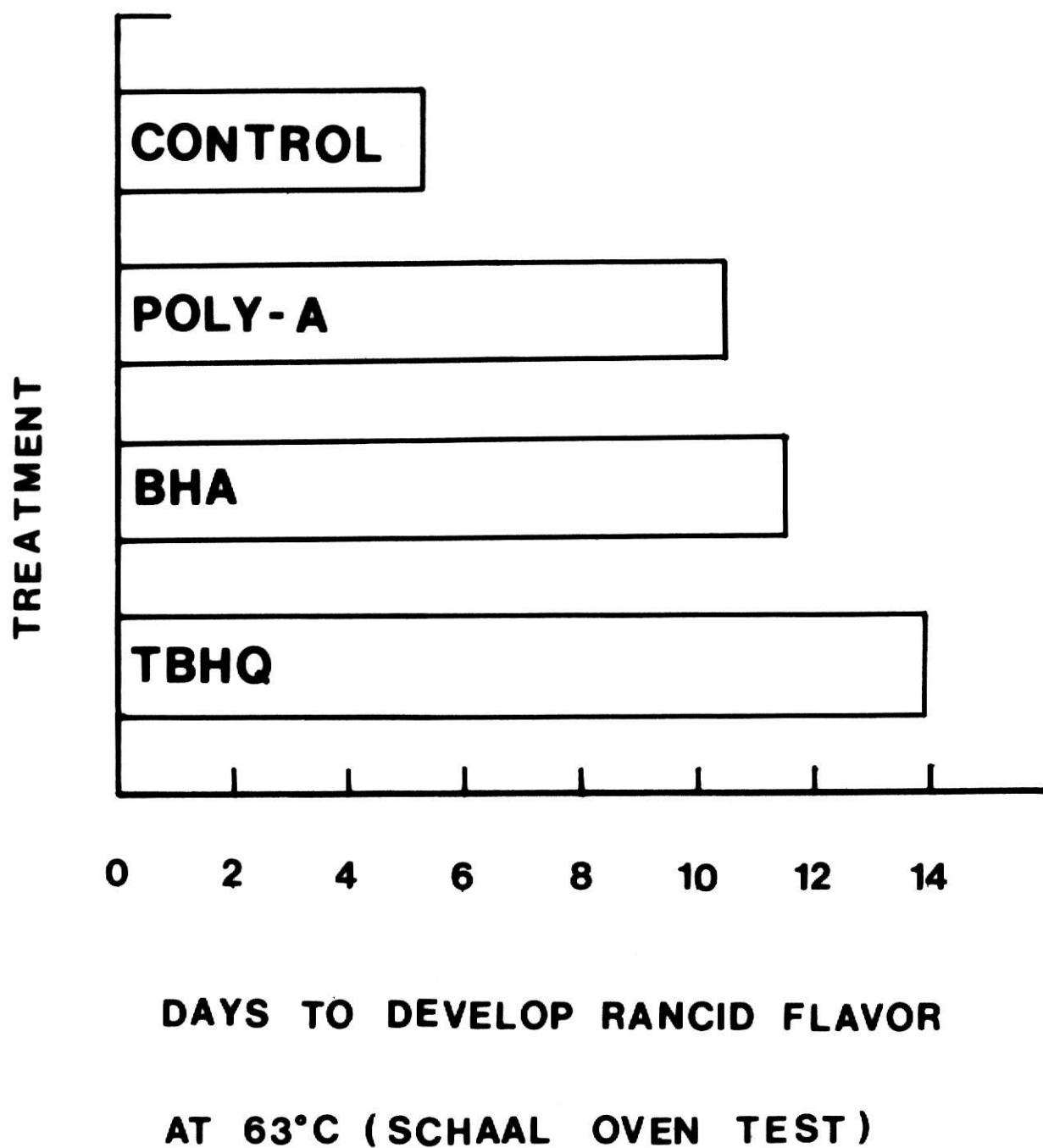




Fig. 14. TLC of Various Acetone Solutions of TBHQ.

1. Acetone solution (5  $\mu$ L applied to plate) obtained by rinsing polyethylene bag with acetone (1.0 mL).
2. Acetone solution (5  $\mu$ L) obtained by rinsing polyethylene bag previously coated with 0.4 mg TBHQ with 1.0 mL acetone.
3. Acetone solution (5  $\mu$ L) containing 0.4 mg TBHQ/mL.
4. Acetone solution (5  $\mu$ L) obtained by rinsing polyethylene bag with 1.0 mL acetone. The bag was initially coated on its inner surface with 0.4 mg TBHQ, loaded with 10 g ramyon, and stored 3 weeks at 63°C (145°F).
5. Acetone solution (5  $\mu$ L) obtained by rinsing polyethylene bag with 1.0 mL acetone. The bag was initially coated on its inner surface with 0.4 mg TBHQ, loaded with 10 g ramyon, and stored one week at 63°C (145°F).

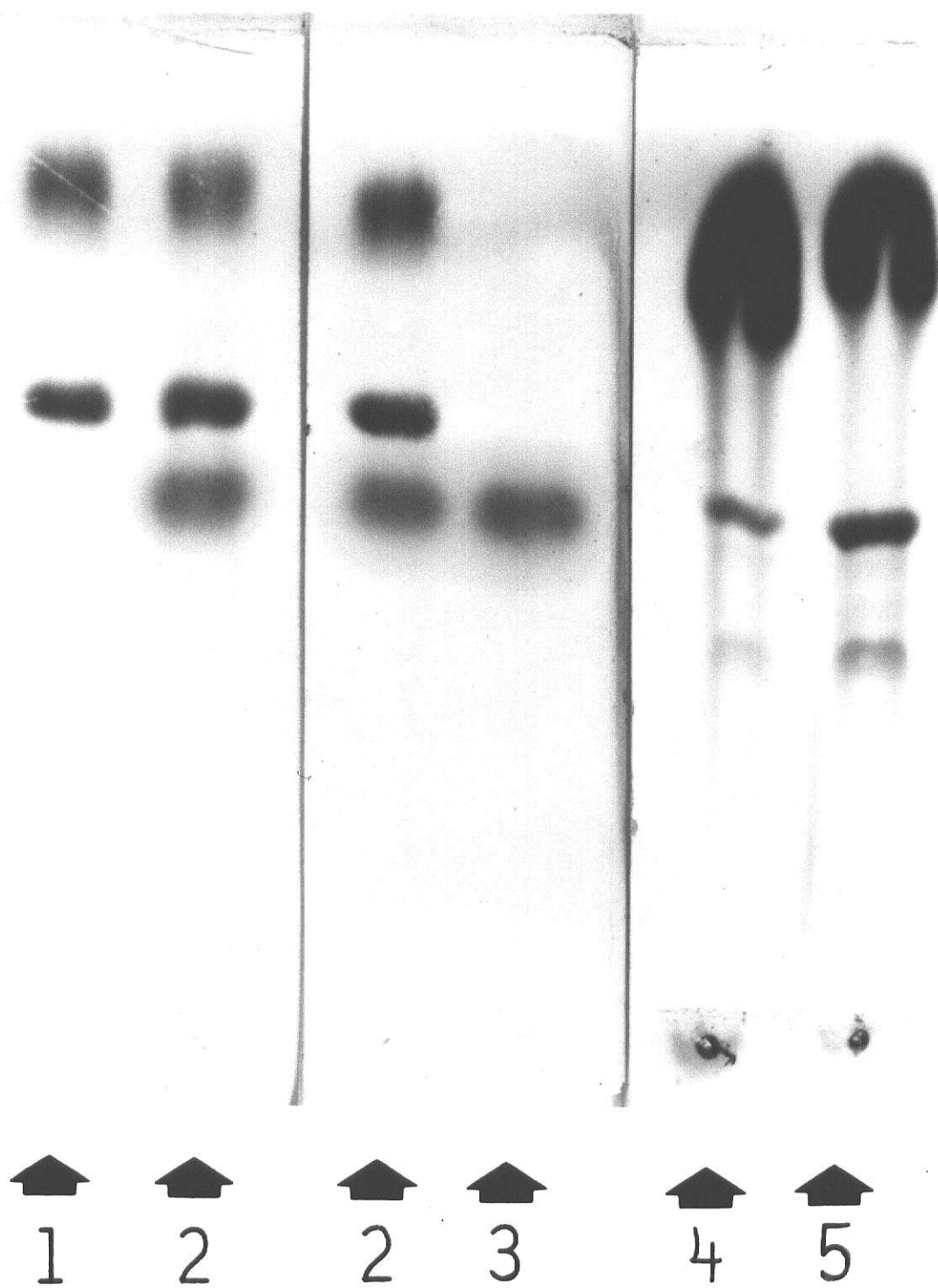




Fig. 15. Hexanal Concentration Based on Solid vs Peak Area Ratio of  
Hexanal/4-Heptanone.



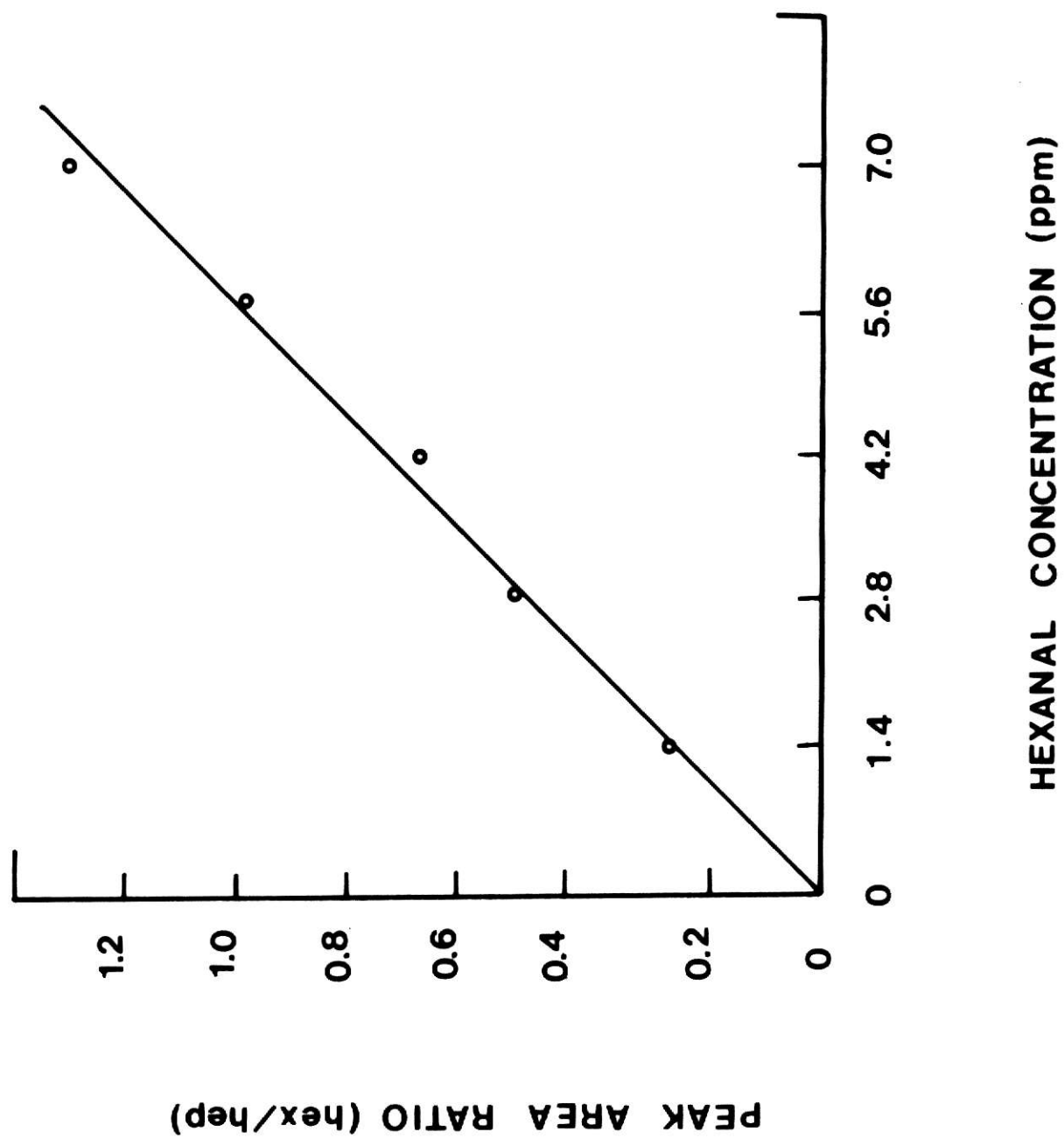




Fig. 16. Chromatogram of a Fresh Ramyon (dotted peaks) and Ramyon stored Two Weeks at 63<sup>0</sup>C (145<sup>0</sup>F) (solid peaks).

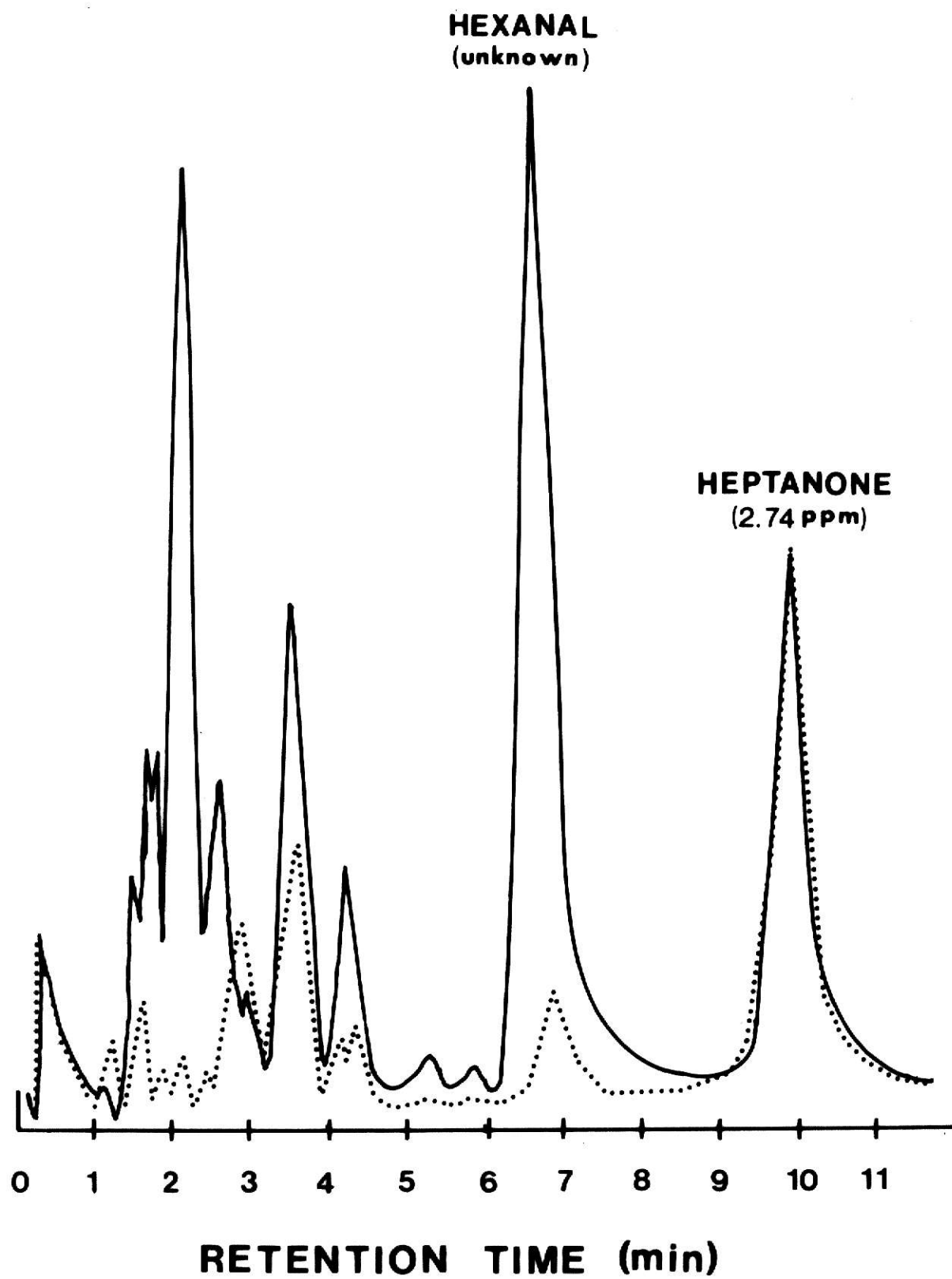
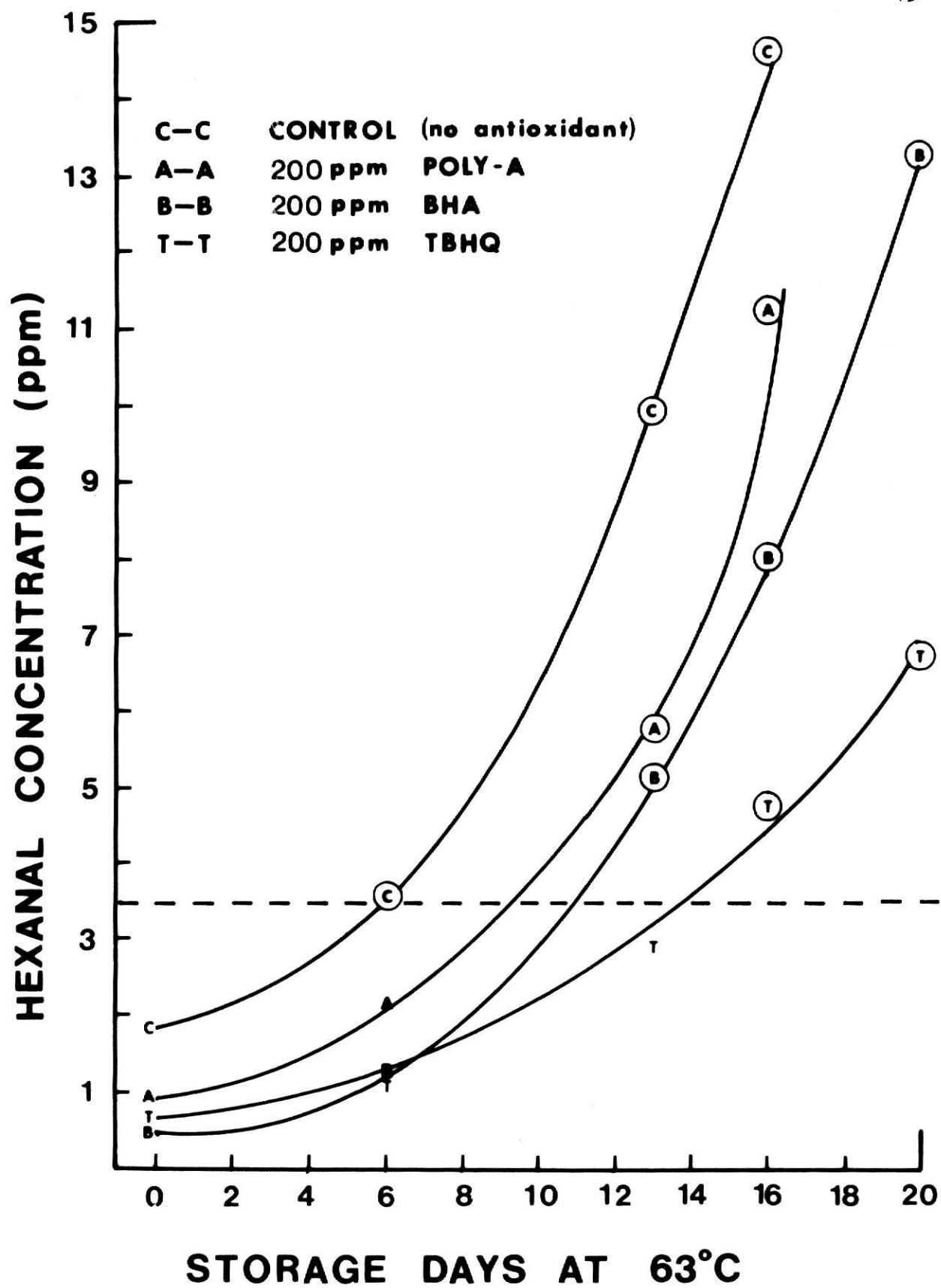




Fig. 17. Hexanal Concentration vs Storage Days at 63°C (145°F) (circles have rancid flavors). The dotted line indicates rancidity can be detected organoleptically when hexanal reaches approximately 3.5 ppm in ramyon.



## BIBLIOGRAPHY

- American Society for Testing and Materials. 1977. Manual on sensory testing methods. ASTM Special Technical Publication. 434: Philadelphia, PA.
- Badings, H.T. 1970. Cold-storage defects in butter and their relation to the autoxidation of unsaturated fatty acids. *Nederlands Milk and Dairy Journal* 24:3/4.
- Berger, K.G. 1971. Practical application of an accelerated stability test to rancidity problems in food processing. *British J. of Food Tech.* 6:253.
- Berger, K.G. 1975. Catalysis and inhibition of oxidation processes: part II. The use of antioxidants in foods. *Chemistry and Industry* 3:194.
- Berk, Z. 1976. The biochemistry of foods. Elsevier Scientific Publishing Co.: Amsterdam, Netherlands. p. 220.
- Bruck, C.G., Figg, K., and Rudolph, F. 1981. Interaction of fat-containing food with plastics packaging. *J. Am. Oil Chem. Soc.* 58:811.
- Chan, H., Prescott, F. and Swoboda, P. 1976. Thermal decomposition of individual positional isomers of methyl linoleate hydroperoxide. *J. Am. Oil Chem. Soc.* 53(10):572.
- Chang, H.K., and Sung, N. E. 1972. Studies on the storage of fat-containing foods. I. Effect of storage factors on the rancidity of fried instant noodles. *Korean J. of Food Sci. and Tech.* 4(1):18.
- Cheigh, H.S., and Kwon, T.W. 1972. Stability of lipids in ramyon. *Korean J. of Food Sci. and Tech.* 4(4):259.
- Chiang, B.H., Norton, H.W., and Anderson, D.B. 1981. The effect of hot-processing, seasoning, and vacuum packaging on the storage stability of frozen pork patties. *J. of Food Proc. and Pres.* 5:161.
- Choe, M., Kim, T.W., and Lee, Y.H. 1977. Effect of metal ions on the oxidation of soybean oil and its fried noodle. *Korean J. of Food Sci. and Tech.* 9(2):157.
- Chou, H.E., Acott, K.M., and Labuza, T.P. 1973. Sorption hysteresis and chemical reactivity: lipid oxidation. *J. of Food Sci.* 38:316.
- Cort, W.M. 1974. Antioxidant activity of tocopherols, ascorbyl palmitate, and ascorbic acid and their mode of action. *J. Am. Oil Chem. Soc.* 51:321.
- Dugan, L.R. Jr., Kraybill, H.R., Ireland, L., and Vibrans, F.C. 1950. BHA as an antioxidant for fats and foods made with fats. *Food Tech.* 11: 457.



- Dugan, L.R. Jr., and Kraybill, H.R. 1956. Tocopherols as carry-through antioxidants. *J. Am. Oil Chem. Soc.* 33:527.
- Dugan, L.R. Jr. 1976. Lipids, p. 169. In: Fennema, O. R. (ed.) *Principles of food science: Part I. Food Chemistry.* Marcel Dekker Inc.: New York, NY.
- Farmer, E.H., Bloomfield, G.F., Sundralingham, A., and Stutton, D.A. 1972. *Trans. Faraday Soc.* 38:348.
- Forss, D.A. 1975. Odor and flavor compounds from lipids. *Progress in the Chemistry of Fats and Other Lipids.* 13(4):177.
- Frankel, E.N., Neff, W.E., Selke, E., and Weisleder, D. 1982. Photosensitized oxidation of methyl linoleate: secondary and volatile thermal decomposition products. *Lipids* 17(1):11.
- Fritsch, C.W., and Gale, J.A. 1977. Hexanal as a measure of rancidity in low fat foods. *J. Am. Oil Chem. Soc.* 54:225.
- Fritsch, C.W., Weiss, V.E., and Anderson, R.H. 1975. Effect of antioxidants on refined palm oil. *J. Am. Oil Chem. Soc.* 52:517.
- Furia, T.E., and Bellanca, N. 1977. The properties and performance of poly AO<sup>TM</sup>-79: A nonabsorbable, polymeric antioxidant intended for use in foods. *J. Am. Oil Chem. Soc.* 54:239.
- Gray, G.I. 1978. Measurement of lipid oxidation. *J. Am. Oil Chem. Soc.* 55:539.
- Hu, T.R., and Kim, D.H. 1974. Stability of fat ingredients of deep fat fried instant noodle, biscuit, and cookies. *Korean J. of Food Sci. and Tech.* 6(1):24.
- Ito, Y., Isobe, K., Sekita, H., Osawa, M., Takeda, M., Tanabe, H., and Nagao, S. 1970. Rancidity of fats in foods. *J. of the Hygienic Soc. of Japan* 11(4):268.
- Jacobson, G.A. 1967. Quality control of commercial deep fat frying. *Food Tech.* 21:147.
- Johnson, F.C. 1979. The antioxidant vitamins. *CRC Critical Review in Food Sci. and Nutr.* 3:219.
- Joyner, N.T., and McIntyre, J.E. 1938. The oven test as an index of keeping quality. *Oil & Soap* 7:184.
- Kajimoto, G. 1979. Preservation stability of edible fats and oils. *Oil Chem. Japan* 28(10):738.
- Kajimoto, G. 1971. Deterioration of oils contained in fried foods during the storage. *J. of Home Economics Japan* 22(2):87.

- Kim, T.W., and Heo, T.R. 1975. Effect of NaCl concentration on the rancidity development in ramyon, deep fried instant noodle. Korean J. of Food Sci. and Tech. 7(1):51.
- Kläui, K., and Pongracz, G. 1982. Ascorbic acid and derivatives as antioxidant in oils and fats. p. 139. In: Counsell, J.N., and Hornig, D.H. (ed.) Vitamin C; ascorbic acid. Applied Science Publishers: Englewood, NJ.
- Koch, R.B. 1962. Dehydrated foods and model system. p. 230. In: Schultz, H.W. Lipid and Their Oxidation. AVI Publishing Co., West Port, CN.
- Kusaka, H., Fukazawa, A., and Matsuo, W. 1969. Studies of oxidizing denaturation of fat contained in the food: Effect of light and temperature on the instant ramen. Nutrition and Food, Japan 22(8):582.
- Kuwahara, M., Uno, H., Fujiwara, A., Yoshikawa, T., and Uda, I. 1971. Antioxidative effect of natural vitamin E on lard used for fry instant ramen. J. of Food Sci. and Tech., Japan 18(2):64.
- Labuza, T.P. 1971. Kinetics of lipid oxidation in foods. CRC Critical Reviews in Food Tech. 10:355.
- Labuza, T.P., and Choe, H.E. 1974. Decrease of linoleate oxidation rate due to water at intermediate water activity. J. of Food Sci. 39:112.
- Lange, W. 1954. Cholesterol, phytosterol, and tocopherol content of food products and animal tissues. J. Am. Oil Chem. Soc. 31:414.
- Lea, C.H. 1938. Rancidity in edible fats. Food Investigation Special Report #46. Dept. of Sci. and Industry Research, London, England. p. 37.
- Lee, K. 1978. Iron sources used in food fortification and their changes due to food processing. CRC Critical Review in Food Sci. and Nutr. 11(2):135.
- Lingnert, H. 1980. Antioxidative Maillard reaction products. III. Application in cookies. J. of Food Proc. and Pres. 4:219.
- Logani, M.K., and Davies, R.E. 1980. Lipid oxidation: Biologic effects and antioxidants. Lipids 15(6):485.
- Lundberg, W.O. 1961. Autoxidation and antioxidants. Vol. I. Interscience Publishers, London, England p. 508.
- Lundberg, W.O. 1962. Autoxidation and antioxidants. Vol. II. Interscience Publishers, London, England p. 453.
- Martell, A.E., and Calvin, M. 1953. Chemistry of the metal chelate compounds. Prentice-Hall, Inc., New York, NY p. 491.

- Nishijima, M., Kanmuri, M., Takahashi, S., Kamimura, H., Nakazato, M., Watari, Y., and Mimura, Y. 1976. Deterioration of oils and fats. Annual Report of Tokyo Metropolitan Research Laboratory of Public Health, Tokyo, Japan p. 27.
- Okada, Y., and Koyama, Y. 1969. Studies on the storage of instant ramen. III. Oxidative stability of lard used in instant ramen. J. of Food Sci. and Tech. Japan 16(8):359.
- Okada, Y. 1971. Studies on the storage of instant ramen. V. Antioxidative stability of commercial ramen. J. of Food Sci. and Tech. Japan 18(9):411.
- Okada, Y. 1972. Studies on the storage of instant ramen. IX. Utilization of natural tocopherol mixture in instant ramen. J. of Food Sci. and Tech. Japan 19(6):255.
- Oota, S.U. 1979. Deterioration of lipid-foods and its retardation. Saiwai Syo Bang, Tokyo, Japan p. 222.
- Pokorny, J. 1979. Stability of premixes of bakery products containing hydrogenated sunflower seed oil against autoxidation on storage. Scientific Papers of the Institute of Chemical Technology E50, Prague, Czechoslovakia.
- Porter, W.L., Levasseur, L.A., and Henick, A.S. 1977. Evaluation of some natural and synthetic phenolic antioxidants in linoleic and monolayers in silica. J. of Food Sci. 42:1533.
- Privett, O.S., and Quakenbush, F.W. 1954. The relation of synergist to antioxidant in fats. J. Am. Oil Chem. Soc. 31:321.
- Ragnarsson, J.O., Leick, D., and Labuza, T.P. 1977. Accelerated temperature study of antioxidants. J. of Food Sci. 42(6):1536.
- Reinton, R., and Rogstad, A. 1981. Antioxidant activity of tocopherols and ascorbic acid. J. of Food Sci. 46:970.
- Schaich, K.M. 1980. Free radical initiation in proteins and amino acids by ionizing and ultra violet radiation and lipid oxidation. Part III. Free radical transfer from oxidizing lipids. CRC Critical Reviews in Food Sci. and Nutr. 11:207.
- Schultz, H.W. 1962. Lipids and their oxidation. AVI Publishing Co., West Port, CN. p. 93.
- Scott, G. 1965. Atmospheric oxidation and antioxidation. Elsevier Publishing Co., Amsterdam, Netherlands p. 115.
- Sherwin, E.R. 1972. Antioxidants for food fats and oils. J. Am. Oil Chem. Soc. 49:468.

- Sherwin, E.R., and Thomson, J.W. 1967. TBHQ, an antioxidant for fats and oils and fat-containing foods. *Food Tech.* 21(6):109.
- Simic, M.G., and Karel, M. 1980. *Autoxidation in food and biological system.* Plenum Press, New York, NY
- Smouse, T.H., Lin, S.S., Maines, J.K., and King, P.R. 1974. The frying properties of a series of vegetable oils and the effectiveness of selected tests in predicting their frying stability. *Am. Oil Chem. Soc. meeting, Mexico City, Mexico.*
- Terao, J., Yamauchi, R., Murauchi, H., and Matsushita, S. 1980. Inhibitory effects of tocopherols and beta-carotene on singlet oxygen-initiated photooxidation of methyl linoleate and soybean oil. *J. of Food Proc. and Pres.* 4(1/2):79.
- Triebold, H.O., and Bailey, C.H. 1932. A chemical study of rancidity. *Cereal Chem.* 9:91.
- U.S. Code of Federal Regulation. 1977. Title 21. Food and Drug. Apr. Government Printing Office, Washington, D.C.
- Weinshenker, N.M. 1980. Anoxomer. *Food Tech.* 34(11):40.
- Weihsrauch, J.L., Brignoli, C.A., Reeves III, J.B., and Iverson, J.L. 1977. Fatty acid composition of margarines, processed fats and oils. *Food Tech.* 2:80.
- Yamashita, T. 1965. Problems in fat oxidation in fried noodle. *Oil Chem. Japan* 14(12):754.
- Yuki, E., Kawaguchi, M., and Okada, Y. 1971. Studies on the utilization on natural tocopherol mixture on fats and fatty foods. II. Practical frying test on the fried noodle. *Oil Chem. Japan* 20(9):559.

RETARDATION OF AUTOXIDATION IN RAMYON,  
DEEP-FRIED INSTANT NOODLE

by

KWANG LAE RHO

B.S., Seoul National University, Korea, 1970

---

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the  
requirements for the degree

MASTER OF SCIENCE

Department of Grain Science and Industry

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1982

## ABSTRACT

Three methods of extending the shelf-life of ramyon noodles were examined; (1) addition of 200 ppm antioxidant (butylatedhydroxyanisole=BHA, tertiarybutylhydroquinone=TBHQ, and a polymeric antioxidant=Poly-A with the commercial name ANOXOMER) to the frying oil, (2) coating the inner surface of the polyethylene package with TBHQ equivalent to 200, 500, and 1000 ppm in oil, and (3) addition of a mixture of TBHQ (200 ppm) and disodium ethylenediaminetetraacetate ( $\text{Na}_2\text{EDTA}$  200 and 500 ppm) to the frying oil.

The ramyon samples were produced in the laboratory from wheat flour, salt, water, and palm oil for frying oil. The determination of storage stability was conducted by the Schaal oven test, which is an aging test wherein a food product is subjected to a constant temperature (145°F, 63°C) and examined periodically by a taste panel. The odor and taste of the stored ramyon samples were tested against a fresh sample by five panel members to detect the onset of rancidity.

When an antioxidant was added to the frying oil, it was found that Poly-A and BHA approximately doubled and TBHQ tripled the shelf-life of ramyon compared to the control. BHA gave a slightly longer shelf-life than Poly-A.

The second approach to prolong the shelf-life of ramyon noodle involved coating the inner surface of the package with the amount of TBHQ equivalent to 200, 500, and 1000 ppm in the frying oil. It was found that the surface application of TBHQ (200 ppm) extended the shelf-life twice as long compared to an equal amount of TBHQ (200 ppm) in frying oil.

The effect of a chelating agent  $\text{Na}_2\text{EDTA}$  on the shelf-life of ramyon was also examined. The combination of  $\text{Na}_2\text{EDTA}$  (500 ppm) and TBHQ (200 ppm) elongated the shelf-life of ramyon four times that of a control sample

containing no additives.

Hexanal in ramyon was found to be a good indicator of the development of oxidative rancidity. The organoleptic evaluation showed the flavor of ramyon was objectionable at a hexanal concentration of greater than 3.5 ppm. The relative effectiveness of the antioxidants BHA, TBHQ, and Poly-A could be determined by the rate of release of hexanal in the stored ramyon noodle.