# Effect of Ascorbyl Palmitate on the Quality of Frying Fats for Deep Frying Operations

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## ABSTRACT

The addition of 0.02% ascorbyl palmitate (AP) reduced color development of frying fat (animal fat/vegetable oil [A-V] shortening) and vegetable oil (partially hydrogenated soybean [V-S] oil) in simulation studies. It also reduced peroxide values, development of conjugated diene hydroperoxides (CDHP) and their subsequent degradation to volatile compounds, such as decanal and 2,-4 decadienal, indicating that AP has the ability to inhibit thermal oxidation/degradation of frying fats and oils. A commercial french fry fat had lower CDHP values compared to A-V fat in simulated studies, and fried chicken oil had lower CDHP values than the V-S oil. Peanut oil had higher thermal stability than the other fats and oils.

## INTRODUCTION

It has been estimated that of the 10 billion pounds of edible fats and oils consumed each year in the U.S., the major portion is used for frying foods (1). Deep fat frying is one of the most common methods world-wide for preparation and production of foods. In commercial deep fat frying operations, a fat is exposed continuously to heat, air and light for as long as ten hr per day at temperatures of 365-375 F (183-188 C), and it may be used to cook a variety of foods. Several studies have indicated that a relatively small amount of the fat is altered chemically by this severe treatment (2-5). Nevertheless, these changes have a significant effect on both the performance of the fat as a heat transfer medium and as an ingredient to enhance the organoleptic properties of fried foods. Thus, a more detailed knowledge of the deterioration of frying fats is important for the production of high quality, nutritious fried foods (6-9).

Antioxidants may be used at very low concentrations (0.01-0.05%) to lengthen the oxidation induction period. They are usually phenolic compounds such as BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), propyl gallate and tocopherols, and are used to inhibit free radical chain reactions. Citric acid also has been shown to prolong the induction of free radicals by chelating with metals present in fats and oils. Ascorbic acid lengthened the induction period by its oxygen scavenging ability (17). The diffusion of essential oils from herbs and spices associated with fried foods also may have a beneficial effect on frying oil stability (10). In some food plants, small carrot cubes were added to the frying pan to prolong the useful life of the oil. Janicek et al. (11) found that oxidation of frying oil was inhibited by such addition. Carotenoid pigments were suspected as the active component that protects frying fats against oxidation under specific processing conditions (12,13). Potatos and oat flakes also were found to contain natural antioxidants (14,15). The antioxidative activity of potatoes was found in the tuber juice (14).

AP is a fat soluble ester of palmitic acid and ascorbic acid. It protected deep fried potato chips from lipid peroxidation better than did BHT and provided better protection to the oils (16). It also was found to be more effective than either BHT or BHA in preventing vegetable oil oxidation (17). AP also was found to protect stored peanut butter from oxidation (18). It acts synergistically with other antioxidants such as d,1-$\alpha$ tocopherols. More important, however, is the fact that AP is listed in the 1982 Title 21 of the Code of Federal Regulations:182.3149 as a substance Generally Recognized as Safe (GRAS) for use as a chemical preservative, with no specific limitations or restrictions. It has never been tested as an antioxidant in deep frying oils for fast food services under the extreme conditions of high temperature (180-185 C) and long cooking times (10-11 hr/day). The melting point of AP is 119 C. Ingestion of this antioxidant by consumers would pose no health hazard because metabolic breakdown yields ascorbic acid and palmitic acid – both normal metabolites.

The purpose of this research was to test the effects of AP on retardation or inhibition of frying fats deterioration in laboratory studies and compare the quality of these fats to frying fats from a commercial deep frying operation.

## EXPERIMENTAL PROCEDURES

### Materials

V-S was obtained from Durkee, CM Corp. (Cleveland, Ohio). A-V (85% steam-distilled beef tallow fraction and 15% partially hydrogenated vegetable soy oil) blended shortening (3:1,v/v) was obtained from Biggers Brothers Inc. (Charlotte, North Carolina). AP was supplied by Hoffman-LaRoche Inc. (Nutley, New Jersey). Samples of commercial deep frying shortening were provided by a fast food outlet in New Orleans, Louisiana. Peanut oil for frying chicken parts was purchased from Louana Corp. (New Orleans, Louisiana), and A-V blend (9:1,v/v) for frying french fries was purchased from a commercial source. A pressure cooker from Henny Penny Inc. (Eaton, Ohio), was used to fry chicken parts, while an open vessel-type fryer was used for the french fries.

### Methods

Deep frying oil quality is altered by high temperatures and long heating periods in the presence of air and light, with and without the addition of various foods. In this study, frying oils were collected from laboratory simulation studies (without added food) and from a commercial outlet (with added food).

### Simulated Studies

Simulation studies (series I and II) were designed to test effects of the antioxidant AP on inhibition or retardation of frying fat oxidation over a 10-day period. Series I consisted of 0.02% AP added only at the beginning of the experiment. In series II, 0.02% AP was added at the beginning and after every two days of the 10-day period. Both V-S oil and A-V fat were used in the simulated studies, with and without added AP.

Approximately 200 g of each fat or oil were weighed into duplicate 400 ml beakers. One served as a control, while the other contained the frying shortening plus 0.02% AP. The beakers were placed on a copper sheet fixed to the top of a Corning hotplate and heated continuously for 10-11 hr each day at 360 F (180-182 C) for a 10-day period. At the end of each day, the shortenings were set aside to cool and covered with aluminum foil. Samples of 5-10 ml were collected from each beaker initially and after 2, 4, 6, 8 and 10-day heating periods. The samples were stored in sealed vials in a refrigerator for subsequent analysis of color development, peroxide values (PV), CDHP and rapid gas chromatographic (GC) volatile profiles.

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### Commercial Deep Frying FAts/Oils

Frying shortenings were collected initially and after 2, 4, 6, 8 and 10 days of commercial use. The samples were kept in a refrigerator (4 C) for the same analyses as the simulation studies.

### Measurement of Color Development

A Gilford UV-VIS Microprocessor-Controlled Spectrophotometer System 2600 with programmed printer attachment was used to scan the spectrum from 300-500 nm for the frying fats and to determine the wavelength for maximum absorption of the darkest orange color from the 10-day A-V fat (the control of simulation studies) and the darkest brown color of the 10-day oil used to fry chicken. Color development for all samples then was determined by reading the absorbance at this wavelength (363 nm).

Aliquots of 0.5 fat were weighed into a 10 ml graduated centrifuge tube, with hexane added to bring the volume to 10.0 ml. The mixture was mixed gently until the fat or oil was dissolved completely. Absorbance of the solution was determined at 363 nm.

### PV and CDHP Measurements

Peroxide values were determined by AOAC method 28.022 (19). CDHP values were determined as described by St. Angelo et al. (20).

### GC Volatile Profiles

The direct GC method developed by Dupuy et al. (21) was used for the analysis of volatiles from the oxidized frying fats and oils. The column and operating conditions used were those described by Dupuy et al. (22,23). A Finnigan 4000 Gas Chromatograph/Mass Spectrometer/Incos Data System operated in the electron impact mode was used to identify volatile compounds. Conditions used were the same as those described for GC analysis except that helium was the carrier gas instead of nitrogen.

## RESULTS AND DISCUSSION

Deep frying fats and oils deteriorate when they are heated for long periods of time and are exposed to air and/or different varieties of foods. Physical changes include increased color development, changes in viscosity and density and foam formation; chemical changes are autoxidation, oxidation, polymerization, isomerization, hydrolysis and pyrrolysis.

### Physical Changes in Frying Fats and Oils

Physical change was estimated by measuring color development of the frying oils. In simulated studies, the single addition of 0.02% AP reduced color development in both A-V fat and V-S oil. The addition of 0.02% AP every second day for 10 days in series II reduced color development in both frying shortenings, but there was not much difference compared to results of series I (Fig. 1). The yellow color of fresh frying fat is believed to be due partly to carotenoid pigments and xanthophylls in the vegetable oil. As the oil is exposed to light and heat for longer periods, these pigments have more opportunity to absorb energy from the visible light spectrum and a darker color results. AP is known to act as an oxygen scavenger. It also can react synergistically with other antioxidants present in fats and oils to inhibit the oxidation of polyunsaturated fatty acids. It appears that the inhibition of AP oxidation suppresses color development and indicates that AP may have an unexpected beneficial effect by reducing color development.

Color development in a commercial fried chicken oil and a french fry fat over a 10-day period are illustrated in Figure 2. Peanut oil used for frying batter-coated chicken parts

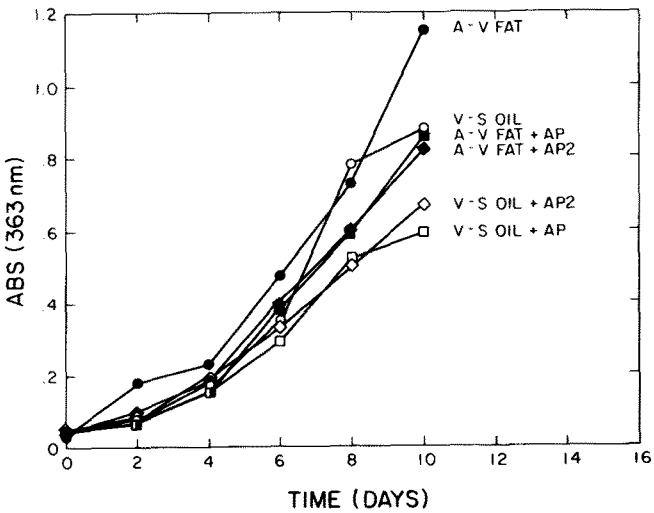


**FIG. 1. Color development in V-S oil and A-V fat with and without 0.02% AP in series I and II.**

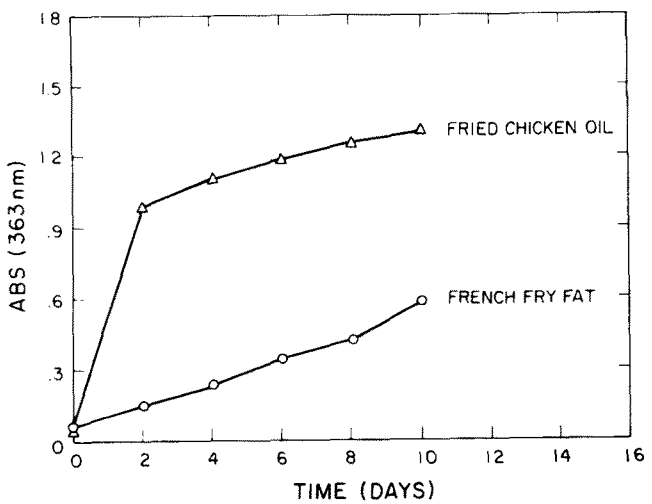


**FIG. 2. Color development in fried chicken oil and french fry fat over 10-day frying period.**

developed a darker color than the A-V shortening used for frying french fries. However, the color of both the fried chicken oil and the french fry fat were nearly the same at the beginning of the cooking period. They became darker as cooking times continued and larger quantities of food were being cooked. The dark brown color of fried chicken oil is derived in part from ingredients in the batter coating. Phospholipids can diffuse into the frying oil from a batter containing egg yolk and contribute to the darkening color of frying fats (24). In addition, carmelization and carbonization of starch from wheat flour in the coating can occur while frying chicken and cause the formation of Maillard reaction products. It is believed that antioxidants present in fats and oils, such as tocopherols, BHA and BHT, also may cause some color problems by two possible means. First, they may interact with certain food components to provide products having unacceptable color. Second, antioxidants themselves may change through oxidation to form end products with undesirable color (25). The specific components responsible for this color development still are not confirmed. According to results in Figure 2, french fries seem to be able to absorb some color pigments

TABLE I

**Peroxide Values of A-V Fat and V-S Oil of Simulation Studies Series I and II and Commercial Fats at 0, 2, 4, 6, 8 and 10 Days**

| Treatment | Peroxide values meg/kg sample)[a] at day | | | | | |
|---|---|---|---|---|---|---|
| | 0 | 2 | 4 | 6 | 8 | 10 |
| A-V Fat (control) | 1.2[c] | 3.6[b] | 4.2[a] | 3.2[b] | 3.5[b] | 3.1[b] |
| A-V fat + 0.02% AP[b] (series I) | 0.9[i] | 3.3[g] | 3.6[f] | 2.9[h] | 3.8[ef] | 4.0[e] |
| A-V fat + 0.02% AP | 0.9[tu] | 1.1[st] | 1.5[r] | 0.7[u] | 1.4[rs] | 1.2[st] |
| V-S Oil (control) | 1.2[e] | 3.0[c] | 3.2[b] | 2.7[d] | 3.6[a] | 3.5[a] |
| V-S Oil + 0.02% AP (series I) | 1.0[k] | 1.1[k] | 2.7[h] | 2.0[j] | 2.4[i] | 3.0[h] |
| V-S Oil + 0.02% AP (series II) | 1.0[x] | 1.0[x] | 1.3[vw] | 0.5[y] | 1.5[v] | 1.3[w] |
| French fry fat[b] | 0.8[d] | 1.6[c] | 3.0[a] | 2.4[b] | 2.2[b] | 3.3[a] |
| Fried chicken oil | 1.6 | * | * | * | * | * |

*The color of the fried chicken oil was too dark to measure peroxide values.

[a]Statistical analysis: Duncan's Multiple Range Test at 0.05 level by treatment. Values in the same row with different superscript letters are significantly different (P 0.05).

[b]AP-Ascorbyl palmitate; french fry fat was animal fat/vegetable oil shortening; fried chicken oil was peanut oil.

from the frying oil or may contain an antioxidant, and thereby decrease color development more than batter-coated foods.

### Chemical Changes in Frying Fats and Oils

Chemical changes in the frying fats and oils were determined by measuring the development of PV, CDHP and GC volatile profiles.

### Peroxide Values

PV is a measure of the amount of peroxides formed in fats and oils through autoxidation and oxidation processes. Indirectly, it is a measure of the degree of initial oxidation of fats and oils.

In simulation studies series I and II, the formation of lipid peroxides seemed to increase from day 0 to day 4 frying, then dropped on the sixth day, increasing significantly again by eight days of frying (Table I). Since high heat (360-370 F) was used on these oils, peroxides formed during autoxidation may have decomposed to secondary products. This may contribute to the drop in PV at day 6, as the PV was reduced by adding 0.02% AP to the fat. Adding 0.02% AP every second day for 10 days (series II) reduced PV more than the single addition (series I). The reduction of PV in series II is significant except for the day 0 A-V fat and the day 0 and day 2 V-S oil. Since AP is an oxygen scavenger, the extent of peroxide development may be controlled by adding AP to frying oils. As the only food grade antioxidant permitted in unlimited levels by the FDA, AP addition is a potential means of controlling PV development in frying fats.

PVs of frying oils from the commercial outlet also are shown in Table I. They increased significantly from day 0 to day 4 frying, decreased between day 6 and day 8, then increased to day 10. This phenomenon cannot be explained simply by the formation of peroxides through autoxidation. However, peroxides are sensitive to temperature changes and can break down to carbonyl and hydroxy compounds under conditions of high heat, air and light as are present in commercial deep fat frying operations. PV cannot be measured when the color of the fat is too dark, as was the case with used fried chicken oil.

### Conjugated Diene Hydroperoxide

The CDHP method of St. Angelo et al. (26) determines the degree of hydroperoxide formation in fat-containing foods

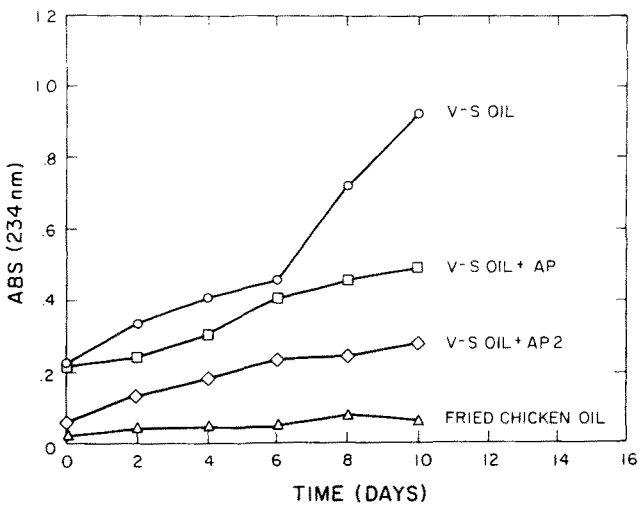


**FIG. 3. CDHP values of V-S oil with and without the addition of 0.02% AP (series I and II) and fried chicken oil.**

with a minimum of handling. Oxidation of unconjugated polyunsaturated fatty acids is accompanied by an increase in ultraviolet absorption at 234 nm due to formation of CDHP. Higher CDHP values show higher degrees of oxidation; lower CDHP values indicate that the fatty acids are more stable to oxidation. Figures 3 and 4 show the reduction in CDHP by the addition of 0.02% AP to both V-S oil and A-V fat. It is more appropriate to use this method to measure oxidation of V-S oil than of A-V fat, because V-S oil contains more polyunsaturated fatty acids than the saturated A-V fat. Multiple additions of 0.02% AP for the 10-day period in series II showed even lower CDHP values, a positive effect on possible oxidation of these fats and oils. The recovery of AP from the fats over a 10-day frying period was 96% for V-S oil and 90-96% for A-V fat (Cort, W.M., personal communication), which means that AP is potentially still active, even at these conditions of high heat, light and long frying times. It is interesting to note that A-V fat with multiple additions of 0.02% AP (series II) showed an actual drop in

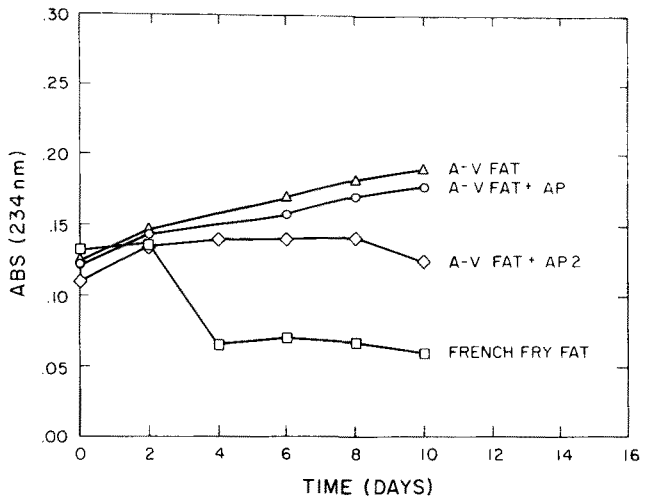


**FIG. 4. CDHP values of A-V fat with and without the addition of 0.02% AP (series I and II) french fry fat.**

CDHP value after 10 days of frying (Fig. 4). After 10 days of frying at this high temperature, it appears that the conjugated diene system may have been degraded to produce new undetected forms of peroxides.

CDHP values for the commercial deep frying fats also were compared to fats in the simulation tests. Generally, CDHP values of french fry fat seemed to decrease during the 10-day frying period. French fried potatoes seem to be able to reduce oxidation of the frying oil, consistent with Pokorny's observation (14) that potatoes contain natural antioxidants in the tuber juice. French fry fat (an A-V fat) contains fewer unconjugated polyunsaturated fatty acids that contribute to the decreased CDHP. Because the fried chicken oil (100% peanut oil) contains more polyunsaturated fatty acids, these CDHP values are more like the V-S oil (Fig. 3) than the french fry fat. In this comparison, the fried chicken oil had lower CDHP values than the simulated tests' V-S oil. Ingredients from the batter coating on the chicken, such as spices used to enhance flavor (25), may be responsible for the apparent oxidation reduction. In addition, the commercial pressure cooker used to fry the batter-coated chicken not only decreased the exposure of hot oil to light but also decreased the exposure to air during frying by creating a type of "water blanket" (steam) above the oil. The steam generated from frying foods can partially block the direct contact of frying oil with oxygen in the air. In the presence of light, pigments from either vegetable oil or animal fat can create activated or excited oxygen molecules not limited by an energy barrier in their reaction with saturated or unsaturated hydrocarbons (27). This is consistent with Alexander's and others' findings (28) that pressure deep frying of fats results in less deterioration than laboratory heating, as shown by chemical analysis, coefficient of digestibility and metabolizable energy studies.

Soybean oil contains linolenic acid (8.3%) and linoleic acid (54.5%), whereas peanut oil contains linoleic acid (30.9%) and no linolenic acid (29). Soybean oil must be partially hydrogenated in commercial practice to remove most of the linolenic acid, as this is most susceptible to oxidation. There still may be some residual linolenic acid, so that V-S oil appears more unstable than peanut oil under conditions of high temperature, light and air.

## GC Method

Oxidation of unsaturated fatty acids initially gives rise to the formation of hydroperoxides, which can be decomposed further to secondary products such as alcohols, acids, ketones and aldehydes. These secondary products contribute directly to off-flavors of fat-containing foods or act indirectly as precursors of flavor deterioration. Dupuy et al. (30) found that as quality of the oil decreased, the concentration and number of volatile products increased. Thus, the total volatiles (total peak area) measured by GC can be used to demonstrate the deterioration of frying fats and oils.

Commercial french fry fat was selected for GC-MS analysis of the components. The results are shown in Figure 5, the volatiles profile. In comparison to Figures 6 and 7, the amounts of volatiles increased over a 10-day frying period in both A-V fat and V-S oil. Using a mass spectrometer to identify the peaks, we found more volatiles in peaks 5, 7 and 12 (hexanal, 2-heptenal and *trans, cis*-2,4-decadienal, respectively), from V-S oil (Fig. 6) than in A-V fat, whereas

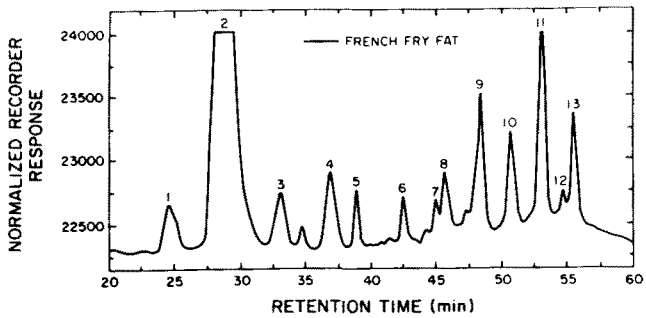


**FIG. 5. GC volatile profile of day 10 french fry fat. Identity of peaks are: (1) pentane, (2) hexane, (3) heptane, (4) octane, (5) hexanal, (6) heptanal, (7) 2-heptenal, (8) octanal, (9) nonanal, (10) 2-nonenal, (11) decanal, (12) *trans,cis*-2,4-decadienal and (13) *trans,trans*-2,4-decadienal.**

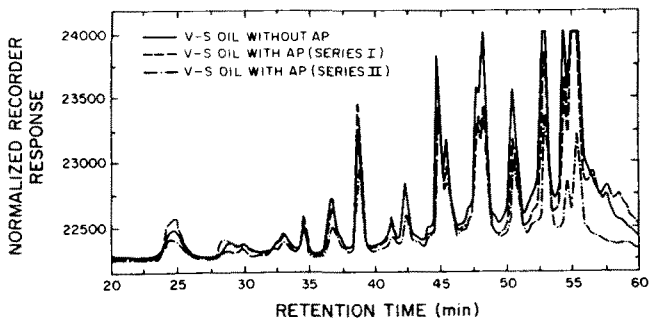


**FIG. 6. GC volatile profiles of V-S oil with and without 0.02% AP in series I and II simulation studies, after 10 days of frying. Same peak designations as in Fig. 5.**

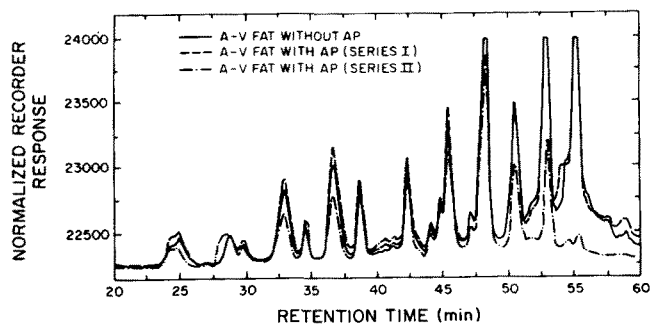


**FIG. 7. GC volatile profiles of A-V fat with and without 0.02% AP in series I and II simulation studies, after 10 days of frying. Same peak designations as in Fig. 5.**

A-V fat (Fig. 7) contained more heptane (peak 3) than did V-S oil. Heptane, octane, 2-nonenal, decanal and *trans, trans*-2,4-decadienal were reduced in A-V fat volatiles compared to the control without AP antioxidant. In the V-S oil (Fig. 6), octane, hexanal, nonanal, 2-nonenal, decanal and *trans, cis*- and *trans, trans*-2,4-decadienals decreased in the heated fat volatiles with added AP.

The reduction in decanal is a volatile product from thermal decomposition of linoleic acid. Its reduction signifies the ability of AP to inhibit thermal oxidation of frying fats and oils and provides an acceptable means of protecting frying fats from flavor deterioration and harmful effects of autoxidation-derived mutagenic compounds. In a comparison of samples of A-V fat and V-S oil with single additions of AP (series I), the volatiles from A-V fat contained more heptane, octane, heptanal and nonanal, whereas V-S oil had more hexanal, 2-heptaenal and *trans, cis*-2,4-decadienal. When samples of A-V fat and V-S oil with multiple additions of AP (series II) were compared, V-S oil contained more 2-heptenal and *trans, trans*-2,4-decadienals, whereas A-V fat contributed more heptane, octane, heptanal and nonanal to the GC volatile profiles. Beef tallow contains 44.0% oleic acid and 0.3% linoleic acid (29), which contributes to the observed increases in octane and heptane in A-V fat. Linoleic acid also decomposes to form pentane through the 13, 14-bond cleavage from the 13-hydroperoxy isomer (39,42), so that some pentane via oxidation of A-V fat is expected. The ability of french fries to reduce oxidation end products from A-V fat during deep frying may be consistent with Pokorny's observations (14) noted earlier.

Typical GC volatile profiles of A-V fat and V-S oil with and without the addition of 0.02% AP (series I and II) are illustrated in Figures 6 and 7. AP (series I) does not seem to have as great an effect on reduction of GC volatiles from thermal degradation of A-V fat (Fig. 7) as it does on V-S oil (Fig. 6). The amounts of nonanal, 2-nonenal and *trans, cis*-2,4-decadienal were decreased when 0.02% AP was added in series I. Both figures clearly show a reduction in total volatile compounds in both fats in series II.

GC total peak area of V-S oil and A-V fat with and without added AP in series I and II is shown in Figures 8 and 9. AP reduced the total volatiles by inhibiting the formation of hydroperoxides from the oxidized fats and oils. This effect was more pronounced in the V-S oil. In series II, the reduction of total volatiles by addition of 0.02% AP every other day was notable in both V-S oil and A-V fat. Obviously, the added AP reduced oxidation of frying fats. Decreases in total volatiles between day 8 and day 10 may be caused by decomposition of some volatile compounds to nonvolatiles not detectable by GC or to polymerization of secondary products and peroxides.

In commercial deep frying fats, fried chicken oil contained less volatile material than did french fry fat (Figs. 8 and 9). Spices in batter coating and the use of a pressure cooker may contribute to this decrease in GC total volatiles, as mentioned previously for CDHP. These results correlate well with the earlier CDHP values. During frying, many chemical reactions, such as isomerization, polymerization, hydrolysis, cyclization, fragmentation and pyrolysis take place under severe conditions. In addition, monohydroperoxides can undergo further oxidation and condensation to form a complex mixture of monomeric and polymeric polar and nonpolar products. These reactions may contribute to the drop in fried chicken oil volatiles after nine days. Figure 9 shows some irregularities in GC total volatiles of heated A-V shortening. With multiple additions of AP (series II), A-V fat seemed to have the least total volatiles after six days of frying, whereas french fry fat showed the least at days 2, 4 and 6. The reasons for these results are unknown.

The deterioration of frying fats and oils at high temperatures is complicated, because oxidative and thermolytic reactions are occurring simultaneously, and both saturated and unsaturated fatty acids undergo chemical decomposition when exposed to high heat in the presence of oxygen (15). The volatile compounds observed in GC analysis depend on the composition of the frying fats. Thus, the amount, type and location of unsaturation in fatty acids of frying oils affects the volatile products derived from thermal decomposition of hydroperoxides. The assumption is made that volatile products are derived primarily from the breakdown of hydroperoxides. Most studies on thermal degradation of fatty acids reported mainly oleate, linoleate and linolenate hydroperoxides. Major volatile carbonyls included 2-undecanal, octanal, nonanal and decanal (31). As the major unsaturated fatty acid in vegetable oils, linoleic acid has been studied extensively. *Cis,trans*- and *trans,trans*-conjugated diene 9- and 13-hydroperoxides are produced from free radical autoxidation (32-35), which can give rise to hexanal, 2,4-decadienal, and methyl-9-oxon-

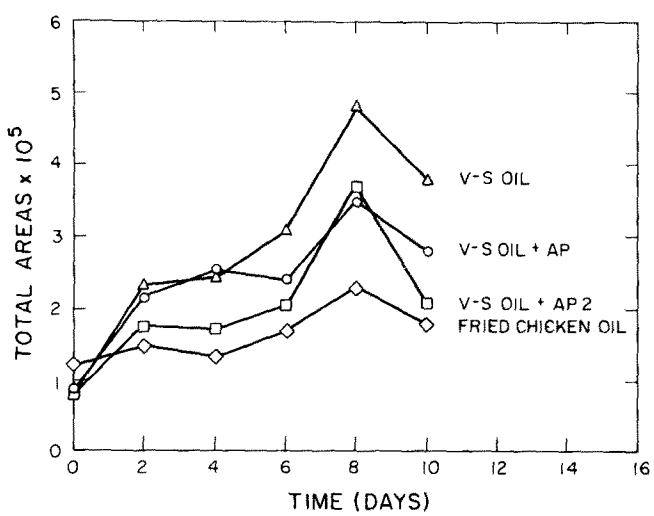


**FIG. 8. GC total volatiles (area) of V-S oil with and without the addition of 0.02% AP (series I and II) and fried chicken oil. Same peak designation as in Fig. 5.**

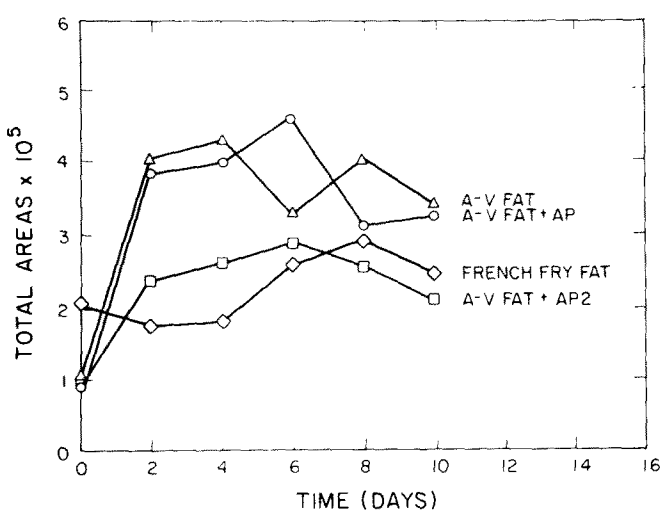


**FIG. 9. GC total volatiles (area) of A-V fat with and without the addition of 0.02% AP (series I and II) and french fry fat. Same peak designation as in Fig. 5.**

onanoate (31), but 2-heptenal also was found from autoxidation of linoleate esters (36-39). Decomposition of linolenic acid can yield a mixture of isomers of *cis,trans,trans-* conjugated diene-triene 9-, 12-, 13- and 16-hydroperoxides from free radical autoxidation (32-34, 40). Major volatile carbonyls from thermally decomposed linolenic acid include acrolein, propanal, 3-hexenal, 2,4-heptadienal and 3,4,7-decatrienal (31). Kimato and Gaddis (41) and Swoboda and Lea (38) reported that hexanal was the major volatile compound formed during low temperature autoxidation, whereas 2,4-decadienal predominated upon thermal decomposition.

In general, the volatiles present in day 10 fried chicken oil were very different from those found in day 0 samples. Possible causes are antioxidants in batter-coated chicken pieces, less light on the hot fat because of the pressure cooker and the higher flash point of peanut oil. It is hard to believe that peanut oil quality in day 10 samples could be better than at day 0, since 1620 lb. chicken meat were fried in this oil over the 10-day period. During frying, steam from the frying chicken pieces may have carried volatiles out of the hot oil, decreasing the amount of volatiles measured in day 10 samples as proposed by Weiss (29). It was not possible to investigate this AP effect under commercial conditions. However, these results suggest that AP could be an effective antioxidant for enhancing the stability of deep frying fats.

With both animal and vegetable frying fats, AP was able to control and/or decrease the thermal-oxidative changes over a 10-day period.

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