Effects of Selected Chemical Treatments on Quality of Fats Used for Deep Frying¹

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Maintaining quality of fats and oils used for deep frying is important in food preparation. In this study, commercially used shortenings were treated with various adsorbents and/or additives with a view to extending their useful life. Quality parameters monitored were increases in dielectric constant, free fatty acids, color (absorbance at 420 nm) and total polar materials. Bleaching clay, charcoal, magnesium oxide and Celite, and their mixtures, effectively reduced one or more of these parameters in used vegetable and animal-vegetable shortenings. However, when the treated fats were used to fry more french fried potatoes in the laboratory, they often deteriorated more rapidly than the untreated control fats. The daily addition of 200 ppm ascorbyl palmitate to fresh, partially hydrogenated soybean oil shortening used to fry french fries retarded free fatty acid development but increased color development and dielectric constant. Treatments employed to extend the useful life of frying fats improved quality parameters, but continued frying after treatment led to greater deterioration than occurred in the untreated control samples.

Deep-fat frying is popular throughout the world for cooking many foods (1-3). The quality and stability of frying fats are therefore of concern to food technologists, nutritionists and consumers. During commercial deep-fat frying, changes eventually occur in the frying fat that may adversely affect the flavor and nutritional value of foods (4). These changes include a variety of deteriorative reactions, including thermal oxidation, hydrolysis and polymerization, which result in off-flavors, darkening and foaming (5,6). Economic considerations and the need to produce fried foods of uniformly desirable quality have stimulated interest in extending the useful life of frying fats used by fast service restaurants and other institutions (7). However, only limited information dealing with extension of useful life is available in the scientific literature. Furthermore, foods were not fried with the fat, and common commercial practices such as intermittent heating and periodic additions of fresh fat usually were not followed (8).

The current study was conducted to evaluate the efficacy of selected chemicals in extending the quality and stability of frying shortenings. Two aspects were investigated. In Series A, samples of a commercially used shortening were treated and analyzed for improve-

ment in dielectric constant change, free fatty acids, total polar materials and color development as measured by absorbance at 420 nm. In Series B, both fresh and used shortenings were treated and then subsequently used for frying french fries in the laboratory to observe the extent of added service life.

EXPERIMENTAL PROCEDURES

Materials. Fresh shortening was Fancy Fry (Wilsey Foods, Inc., Los Angeles, California), a partially hydrogenated soybean oil (PHSO). Used shortening was obtained from a local fast-service restaurant and was an animal-vegetable (AV) type that had been employed to fry french fries and batter-coated fish pieces. Frozen partially fried french fries, 3/8" regular cut, (Vita-Bite Foods, Portland, Oregon) were used for both the commercial cooking and the laboratory frying experiments.

Adsorbents employed to treat the used fats were: Tonsil Optimum, activated powdered bleaching clay (gift from L.A. Salomon and Bro. Inc., Port Washington, New York); Norit F, activated charcoal powder (American Norit Company, Inc., Jacksonville, Florida); Celite 503, diatomaceous earth (J.T. Baker Chemical Co., Phillipsburg, New Jersey); and magnesium oxide powder U.S.P. (Mallinckrodt Chemical Works, St. Louis, Missouri). Additives used were: SAG100 dimethylpolysiloxane (DMPS) silicone antifoam (Union Carbide, San Francisco, California); butylated hydroxytoluene (BHT) antioxidant (Sigma Chemical Co., St. Louis, Missouri); and ascorbyl palmitate (AP) antioxidant (Hoffmann-La Roche Inc., Nutley, New Jersey).

Methods. Two series of experiments were carried out. In series A, samples of the commercially used AV shortening were treated with different mixtures and concentrations of adsorbents. In series B, both commercially used AV shortening and laboratory used PHSO shortening were treated with adsorbents and/or additives, then the treated fats were used to fry french fries in the laboratory.

In series A, used fats were mixed with selected adsorbent(s) at 90 C for 15 min and then filtered at 90 C through a Buchner funnel with Whatman #1 paper under vacuum. In series B, used fats were mixed with various levels of a standard adsorbent mixture of 45% clay, 5% charcoal, 25% magnesium oxide and 25% Celite; and filtered as above. The additives DMPS and BHT were added to filtered fat as 1 and 5% solutions in petroleum ether to give final concentrations of 10 and 50 ppm, respectively. AP (200 ppm) was added as a 15% solution in ethanol. Solvents were removed by heating treated fats to 150 C with agitation.

Laboratory frying. A commercial two-unit fryer, capacity 5 l per unit (Wells Manufacturing Corp., South San Francisco, California), was used for laboratory frying of french fries. The fryer thermostat was set at 190 C and the fat temperature averaged 182 C during a

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3- to 4-min fry period. Ten lots of frozen french fries, each lot corresponding to 5% w/v of the fat, were processed daily. Make-up shortening (10% by weight) was added after each daily adsorbent treatment. Fat samples for analysis were taken after each frying period.

ANALYTICAL PROCEDURES

Dielectric constant changes (DCC). Changes in the dielectric property of the samples were determined (9) with a Foodoil Sensor model NI-20 (Northern Instruments Corp., Lino Lakes, Minnesota). Calibration with fresh fat and analysis were the same as in the manufacturer's operating manual.

Free fatty acids (FFA). Percentages of free fatty acids were determined by AOCA method 28.029 (10) and were expressed as oleic acid.

Total polar materials (TPM). Percentages of total polar materials were estimated by the method of Billek et al. (11).

Absorbance. As an index of color development (6), the absorbance at 420 nm of a 50% v/v solution of fat in isooctane was measured at 40 C in a Beckman DU Spectrophotometer with a Gilford source and detector.

All the above analytical procedures were performed at least in duplicate, and the values reported are means. Each of the procedures was tested for reproducibility with the commercially used fat and was found to vary less than 4%.

RESULTS

Series A. Physical and chemical changes in the AV shortening used commercially for frying french fries and batter-coated fish pieces over a 4-day period (40 hr) are shown in Figure 1. These results illustrate progressive deterioration of the shortening up to time of discard and are consistent with the trends reported earlier for several restaurants using PHSO shortenings for frying chicken and french fries (4). There were good correlations between DCC and the other indices of deterioration (TPM, R = 0.96; Abs. 420 nm, R = 0.95; FFA, R = 0.88).

Samples of used AV shortening from the same source as above were treated as follows: T1, 5% activated bleaching clay; T2, 5% activated charcoal; T3, 5% MgO; T4, 5% Celite; T5, 4.5% clay, 0.5% charcoal; T6, 2.5% clay, 2.5% MgO; T7, 2.5% clay, 2.5% MgO, 2.5% Celite; T8, 4.5% clay, 0.5% charcoal, 2.5% MgO, 2.5% Celite; T9, 4.5% clay, 0.5% charcoal, 5% MgO, 2.5% Celite; T10, 9% clay, 1% charcoal, 10% MgO, 2.5% Celite.

The treatments varied in the degree of improvement of the parameters used to measure deterioration (Fig. 2). Improvement (%) was calculated for each parameter as being equal to:

 $\frac{\text{Untreated Used Fat} - \text{Treated Used Fat}}{\text{Untreated Used Fat} - \text{Unused Fresh Fat}} \times 100$

Improvements were greatest when treatment was done after the first day of frying (10 hr) and were generally least effective after the 4th day (40 hr). The treatments improved DCC, FFA and Abs. 420 nm (color) relatively more than TPM. DCC were improved by



FIG. 1. Effects of commercial deep-fat frying on selected quality parameters of an AV (animal-vegetable) shortening. Note progressive increases with time of frying in DCC (dielectric constant change), absorbance at 420 nm (color), FFA (free fatty acids), and TPM (total polar materials).

bleaching clay (T1), charcoal (T2) and mixtures containing these two adsorbents (T5, T8-T10). FFA were improved especially by MgO (T3) and mixtures containing MgO (T6-T10). Color was reduced effectively by all treatments. These results confirm and extend those reported by Hoover (12) for MgO and by Pan et al. (13) for activated clay and charcoal.

The proportion of adsorbents in treatment T8 was selected for the standard mixture used in all subsequent adsorbent treatments.

The effects of concentration of the above standard adsorbent mixture in improving the quality of a PHSO shortening previously used to fry french fries in the laboratory over six days (36 hr) are shown in Table 1. Improvement increased with increased levels of adsorbent up to 10%. Fat losses also increased progressively. At the 10% adsorbent level, DCC, color and FFA were reduced 18, 37 and 74% respectively.

Series B. The effects of a single adsorbent treatment of a commercially used AV shortening subsequently used to fry french fries in the laboratory are given in Table 2. The additives, 1,000 ppm AP, 50 ppm BHA and 10 ppm DMPS, were added after adsorbent treatment and prior to the 45-hr cumulative frying period. The above treatment initially reduced DCC, color and FFA by 8, 8 and 72%, respectively. However, color and FFA increased markedly after three subsequent 5-hr frying periods while DCC increased slightly.

The effects of daily adsorbent treatment of fresh



FIG. 2. Efficacy of various adsorbent treatments on quality of commercially used AV (animal-vegetable) shortening. Same quality parameters as in Fig. 1. Fat samples were taken for treatment after daily 10-hr frying periods. Treatments are described in text. Missing treatment numbers indicate that these treatments were not performed. For each parameter, improvement (%) = $100 \times (\text{Untreated Used Fat} - \text{Treated Used Fat})/(\text{Untreated Used Fat} - \text{Unused Fresh Fat}).$

PHSO shortening used to fry french fries in the laboratory are shown in Table 3. Compared to the untreated control, treated fats showed significant improvement in DCC, color and FFA through 18 hr. However, after 24 hr of frying, the treatment actually accelerated deterioration and 5 ppm DMPS was added to control excess foaming. After 30 and 36 hr, the treated fat had deteriorated far more than the untreated control fat.

The effects of daily adsorbent plus additive treatment of commercially used AV shortening subsequently used to fry french fries in the laboratory are given in Table 4. Compared to the untreated control, in the first treatment after 30 hr frying, DCC, color and FFA were reduced by 6, 14 and 58%, respectively. After 35 and 40 hr of frying, compared to the control, treated fats showed slight improvement in DCC and FFA but deteriorated in color. At 45 hr, DCC remained

TABLE 1

Effects of Adsorbent	Concentration in	Treatment of	Used Fat ^a
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Adsorbent ^b %	DCCc	Absorbance 420 nm	FFA %	Fat Loss %	
Untreated ^a	1.1	0.79	0.93	_	
2	1.1	0.59	0.82	8.5	
4	1.0	0.59	0.61	10.5	
6	1.0	0.57	0.47	11.5	
8	1.0	0.53	0.33	15.2	
10	0.9	0.50	0.24	16.0	

^aPHSO vegetable shortening used to fry french fries for 6 days (36 hr).

bAdsorbent was mixture of 5% bleaching clay:charcoal (10:1), 2.5% magnesium oxide and 2.5% Celite.

 $^c\mathrm{Dielectric}$ constant change (increase) as measured by Foodoil Sensor.

unchanged but color and FFA increased compared to the control. These increases were consistent with but not as pronounced as those given in Table 3.

The effects of adding 200 ppm AP after each day's frying of french fries during a 6-day period (6 hr/day) are shown in Figure 3. The fresh starting fat was a PHSO shortening. Development of FFA was retarded, but both color and DCC were increased over the untreated control.

DISCUSSION

The results of Series A of this study indicated that treatments with selected adsorbents could improve fat quality as measured by changes in DCC, FFA, TPM and color. Bleaching clay and powdered charcoal were most effective when used in the early stages of deterioration. MgO was useful primarily to reduce FFA. Celite acted principally as a filter aid for treatment by the mixtures of adsorbents.

The results of Series B demonstrated that while initial treatments improved fat quality, subsequent frying showed that the useful life of the fats was not markedly extended. Daily adsorbent treatments affected the potential stability of used fats and resulted in excess foaming. Daily additions of AP to fresh fat retarded FFA formation but increased both DCC and color. Some possible causes of these adverse effects could be increased pH, soap formation and Maillard reaction products. Blumenthal et al. (14) reported the formation of alkaline contaminant materials, such as soaps, that result from the interaction of food constituents with oil degradation products. Gwo et al. (15) found that AP has the ability to inhibit thermal oxidation/degradation of frying fats and oils; however, their results were based on simulation studies where the fats were heated without added food. They suggested that the inhibition of AP oxidation suppressed color development. Our results differ from those of Gwo et al. in that AP resulted in increased color when french fries were cooked. This darkening may be attributed to non-enzymatic browning resulting from the formation

TABLE 2

Effects of a Single Treatment^a of Used Shortening^b Subsequently Used to Fry French Fries

Frying Time ^c (hr)	DCC^d	FFA %	
40-untreated	2.40	1.16	2.21
40-treated ^a	2.20	1.07	0.62
45	2.30	1.17	1.02
50	2.40	1.74	1.26
55	2.50	1.86	1.63

^aTreated with 5% bleaching clay:charcoal (10:1), 2.5% magnesium oxide, 2.5% Celite. Then 1,000 ppm ascorbyl palmitate, 50 ppm BHA and 10 ppm dimethylpolysiloxane were added after filtration and prior to the 45-hr cumulative frying period.

^bAnimal-vegetable shortening from fast service restaurant used for 40 hr to deep fry french fries and batter-coated fish pieces.

^cCumulative time fat used in restaurant plus time used to fry french fries in laboratory.

^dDielectric constant change.



FIG. 3. Effects on quality (Fig. 1) of 200 ppm as corbyl palmitate added daily to PHSO shortening used to fry french fries over 6 days (6 hr/day).

TABLE 3
Effects of Daily Treatment a of Fresh Fat ^b Used to Fry French Fries

Frving	Control (Untreated)			$Treated^a$			
Time ^c (hr)	DCCd	Abs 420 nm	FFA %	DCC	Abs 420 nm	FFA %	
0	_	0.08	0.06	_	_		
6	0.20	0.17	0.08	0.20	0.20	0.08	
12	0.40	0.27	0.17	0.30	0.19	0.18	
18	0.50	0.38	0.30	0.30	0.33	0.34	
24	0.60	0.53	0.44	0.80	0.49	0.90^{e}	
30	0.80	0.62	0.59	1.30	1.57	2.22	
36	0.95	0.80	0.90	2.25	2.98	5.11	

aTreated with 5% bleaching clay:charcoal (10:1), 2.5% Celite and 2.5% magnesium oxide following each 6-hr frying period.

^bPHSO vegetable shortening.

^cTimes (cumulative) used to fry french fries in laboratory.

dDielectric constant change.

 e5 ppm dimethyl polysiloxane added after 24 hr frying to reduce foaming.

of Maillard reaction products from interaction of the ascorbyl moiety and amines from the potatoes (16).

The treatments used in the present study were designed with the objective of extending the useful life of frying fats. The results showed that the quality parameters varied in degree of improvement but continued frying after treatment caused greater deterioration than occurred in the untreated controls.

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TABLE 4

Effects of Daily Treatment ^a	\mathbf{of}	Used	Shortening ^b	Subsequently
Used to Fry French Fries				

Frying Time ^c (hr)	Cont	Control (Untreated)			$Treated^{a}$			
	DCCd	Abs 420 nm	FFA %	DCC	Abs 420 nm	FFA %		
30	1.70	0,66	1.46	1.60	0.57	0.61		
35	2.20	0.78	1.73	1.80	1.02	1.56		
40	2.60	0.94	1.88	2.40	1.18	1.77		
45	3.00	1.15	2.25	3.00	1.34	2.95		

^aTreated with 5% bleaching clay: charcoal (10:1), 2.5% Celite and 2.5% magnesium oxide. Then 1,000 ppm ascorbyl palmitate, 50 ppm BHA and 10 ppm dimethylpolysiloxane were added following each 5-hr frying period.

^bAnimal-vegetable shortening from fast service restaurant used for 30 hr to deep fry french fries and battered fish pieces.

 c Cumulative time fat used in restaurant plus time used to fry french fries in laboratory.

^dDielectric constant change.

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