♣ Relationships Between Measurements of Fat Deterioration During Heating and Frying in RBD Olein

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The relationships between measurements of fat deterioration during static heating and heating with intermittent frying of potato crisps in RBD olein in the presence and absence of TBHQ were evaluated. Significant linear relationships were found between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant. Nonlinear relationships were found between smoke point, acid value and polar components. The relationships between polymer content and polar components, $E_{1\,cm}^{1\%}$ at 232 nm and wavelength (λ) for which $E_{1\,cm}^{10\%} = 1$ also were found to be nonlinear.

During frying, various chemical processes such as oxidation, hydrolysis, polymerization and fission take place. These processes lead to the production of numerous decomposition products. Typical routes of deterioration of frying fats and oils and a list of methods for evaluation of oil deterioration have been described by Fritsch (1).

Assessment of frying fat deterioration has been a subject of much current concern because of the high volume of fried food products being produced. It is important for the industry to have simple, objective methods for assessing frying fat quality, as premature discarding of frying fat is an economic disadvantage while abuse and over use of frying fat can affect product quality (2,3).

One of the first attempts to define a deteriorated frying fat was proposed by the German Society for Fat Research in 1973 (4). It stated: "A frying fat is deteriorated if, without any doubt, odor and taste are not acceptable; if, in case of a doubtful sensory measurement the concentration of petroleum ether insoluble oxidized fatty acids is 0.7% or higher and if the smoke point is lower than 170 C, the concentration of petroleum insoluble oxidized fatty acids is 1.0% or higher." It was later suggested that 27% polar components, as determined by column chromatography, corresponded to 1.0% oxidized fatty acids (5). More recently, a Food Oil-Sensor which indicates the change in dielectric constant was evaluated as a quick alternative method for measuring frying fat deterioration (1,6). Besides these methods, other methods which have been used for determination of fat deterioration include methods for assessment of peroxide value, iodine value, dienes, refractive index, viscosity, odor, carbonyls, nonurea adduct forming esters and polymers. Since many factors affect the rate of deterioration of fat used for deep-fat frying, no single procedure will be reliable under all conditions (1).

This paper reports the relationships between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant. Relationships between smoke point, acid value and polar components and those between polymer content and polar components, $E_{1\,cm}^{1\%}$ at 232 nm and wavelength (λ) for which $E_{1\,cm}^{10\%} = 1$ are also discussed.

EXPERIMENTAL PROCEDURES

Materials. RBD olein was obtained directly from the supplier, Lam Soon Oil and Soap Mfg. Bhd. Potatoes were obtained from a local supermarket. TBHQ (97%) was obtained from Aldrich Chemical Co. Inc., Milwaukee, Wisconsin.

Heating and frying experiments. An evaluation of RBD olein during heating and frying in four different systems for five hr/day for eight consecutive days was carried out. The systems included (a) static heating at 180 C (system 1), and (b) heating at 180 C with intermittent frying of 100-g batches of potato chips at one-half-hr intervals in RBD olein without antioxidant (system 2); in RBD with 200 ppm TBHQ prior to frying on the first day (system 3), and in RBD olein which had TBHQ added up to a level of 200 ppm at the start of each day (system 4). For these experiments, 4 kg of RBD olein was initially put into a Valentine Industrial Fryer. The details of the frying experiments are as given previously (7).

Oil samples were removed from the fryer at the end of alternate days and kept for analysis. In the static heating experiments, an extra 150 g oil was removed at the end of each day. This is equivalent to the amount of oil that would have been lost if fryings were carried out.

Analysis of oils. AOCS official methods (8) were used for the determination of peroxide value and smoke point. IUPAC methods (9) were adopted for the determinations of *p*-anisidine, acid and iodine values and UV absorbance at 232 nm. Oil color was also measured spectrophotometrically for determination of the wavelength for which $E_{1\,cm}^{10\%} = 1$ (10). The dielectric constant was measured with a Food Oil-Sensor (Model NI-20). The instrument was calibrated with a standard zero which was provided with it. The percentages of polar components and polymer content were determined

TABLE 1

Characteristics of the Fresh RBD Olein Used in Experiments

Characteristics of the Oil	
Peroxide value	0.8 meq/kg
p-Anisidine value	1.0
Iodine value	57.3
Acid value	0.12 mg KOH/g
Total polar components	5.5%
Dielectric constant	1.4
Polymers	0%
Smoke point	218 C
Fatty acid composition	
C16:0	40.2%
C18:0	4.1%
C18:1	43.3%
C18:2	10.6%
Others	1.8%

using column chromatography (5) and the method of Peled et al., respectively (11). The C18:2/C16:0 ratio was calculated from the fatty acid composition of the oil which was determined by gas chromatography (12,13).

RESULTS AND DISCUSSION

The characteristics of the fresh RBD olein used in these experiments are given in Table 1. The relationships between indicators of frying oil quality given in Table 2 and Figures 1-6 have been based on the results of studies on the effect of TBHQ on the quality characteristics of RBD olein during frying (7) and experiments on static heating of RBD olein.

Relationships between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant. The relationships between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant are given in Table 2. The correlation between each of these parameters is highly significant ($p < 0.001$) both when data in individual systems 1 through 4 are assessed separately and when the combined data for all the systems are considered together. There were no significant differences ($p < 0.05$) between the slopes of regression lines in different systems for relationships between iodine value and C18:2/C16:0 ratio and between polar components and dielectric constant. Tests for differences in the intercepts of regression lines of equal slopes showed there were no significant differences ($p < 0.05$) for the relationship between iodine value and C18:2/C16:0 ratio but there were significant differences in intercepts ($p < 0.05$) for the relationship between polar components and dielectric constant. Tests for parallelism of lines of regression in different systems showed there were significant differences ($p < 0.05$) for relationships between polar components and iodine value, polar components and C18:2/C16:0 ratio, dielectric constant and C18:2/C16:0 ratio and between dielectric constant and iodine value.

The highly significant correlation coefficients obtained for relationships between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant are noteworthy. The highly significant correlation between iodine value and C18:2/C16:0 ratio and the absence of significant differences between the slopes and intercepts of regression lines in all systems suggest that the iodine value, which is an indication of the overall change in the degree of unsaturation, is closely related to the C18:2/C16:0 ratio regardless of frying and heating conditions used in these experiments. The highly significant correlation between polar components and dielectric constant found in this study is in line with the good correlation found between these two parameters by other workers (14). It was found that the correlation coefficient between polar components and dielectric constant was 0.991 ($n = 24$) when the combined data for three shortenings with different stabilities deteriorated both by frying potatoes and by heating without frying were evaluated (14). RBD olein used in these experiments had initial polar components of 5.5%. This represents the initial concentration of mono- and diglyceride components in the oil. The presence of these components in palm oil and its fractions has also been reported (15). A study on corn oil

TABLE 2

Relationships Between Indicators of Frying Fat Deterioration in Heating and Frying Experiments With the Same Batch of Palm Olein With and Without TBHQ[a]

System	No. of values	Equation	Correlation coefficient[b]
		Iodine value versus C18:2/C16:0 ratio	
1	5	y = 60.943x + 41.136	0.99*
2	10	y = 58.332x + 41.652	0.99*
3	10	y = 60.401x + 41.427	0.99*
4	10	y = 60.109x + 41.739	0.99*
Overall	35	y = 60.034x + 41.500	0.99*
		% Polar components versus dielectric constant	
1	5	y = 6.435x - 3.848	0.99*
2	10	y = 6.500x - 2.723	0.99*
3	10	y = 6.526x - 2.616	0.99*
4	10	y = 6.372x - 2.914	0.99*
Overall	35	y = 6.476x - 2.969	0.99*
		% Polar components versus iodine value	
1	5	y = -3.614x + 212.977	-0.99*
2	10	y = -4.097x + 239.767	-0.99*
3	10	y = -4.033x + 236.923	-0.99*
4	10	y = -4.208x + 247.659	-0.99*
Overall	35	y = -3.984x + 234.349	-0.99*
		% Polar components versus C18:2/C16:0 ratio	
1	5	y = -221.191 + 64.487	-0.99*
2	10	y = -241.424 + 69.522	-0.99*
3	10	y = -244.173 + 69.937	-0.99*
4	10	y = -255.786 + 72.525	-0.99*
Overall	35	y = -241.863 + 69.462	-0.99*
		Dielectric constant versus iodine value	
1	5	y = -0.562x + 33.731	-0.99*
2	10	y = -0.630x + 37.278	-0.99*
3	10	y = -0.618x + 36.704	-0.99*
4	10	y = -0.658x + 39.190	-0.99*
Overall	35	y = -0.614x + 36.570	-0.99*
		Dielectric constant versus C18:2/C16:0 ratio	
1	5	y = -34.410x + 10.625	-0.99*
2	10	y = -37.076x + 11.103	-0.99*
3	10	y = -37.402x + 11.115	-0.99*
4	10	y = -39.955x + 11.805	-0.99*
Overall	35	y = -37.246x + 11.166	-0.99*

[a]The range of values used for calculation of the overall linear regression equations is: dielectric constant (1.28-7.80); iodine value (46.6-57.3); percent polar components (5.4-47.4), and C18:2/C16:0 ratio (0.094-0.271). The C18:2/C16:0 ratio refers to the ratio of glyceride bound fatty acids.

[b]*Denotes significance at 0.001 level.

showed that oil with 27% polar components gave a dielectric constant reading of 3.7 on the Food Oil-Sensor (2). In these experiments, RBD olein with 27% polar components had a dielectric constant reading of 4.63. The observation of a significant relationship between iodine value and dielectric constant found in this study was also exemplified for three shortenings with different stabilities (14). A linear correlation coefficient of 0.947 was obtained when 18 pairs of readings obtained during deterioration of soybean, animal and vegetable
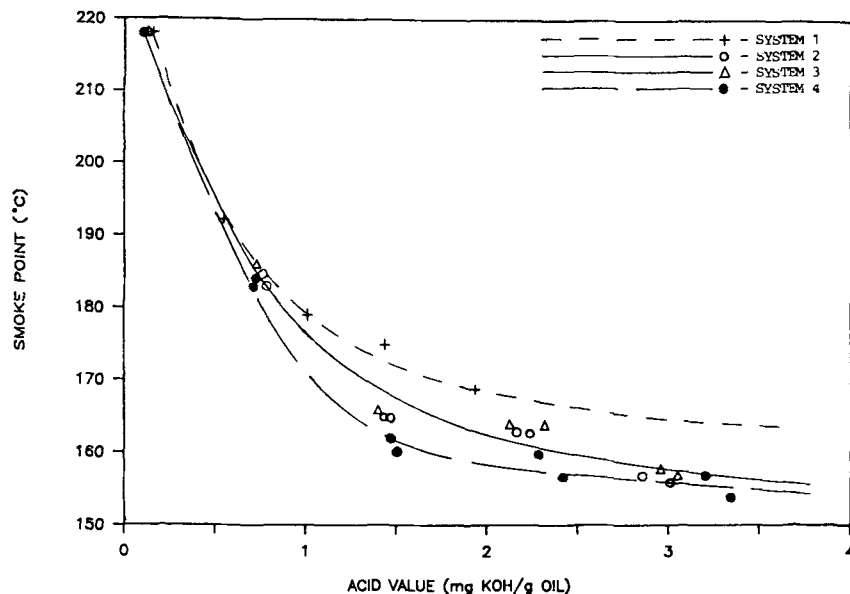
M.A. AUGUSTIN, T. ASAP AND L.K. HENG

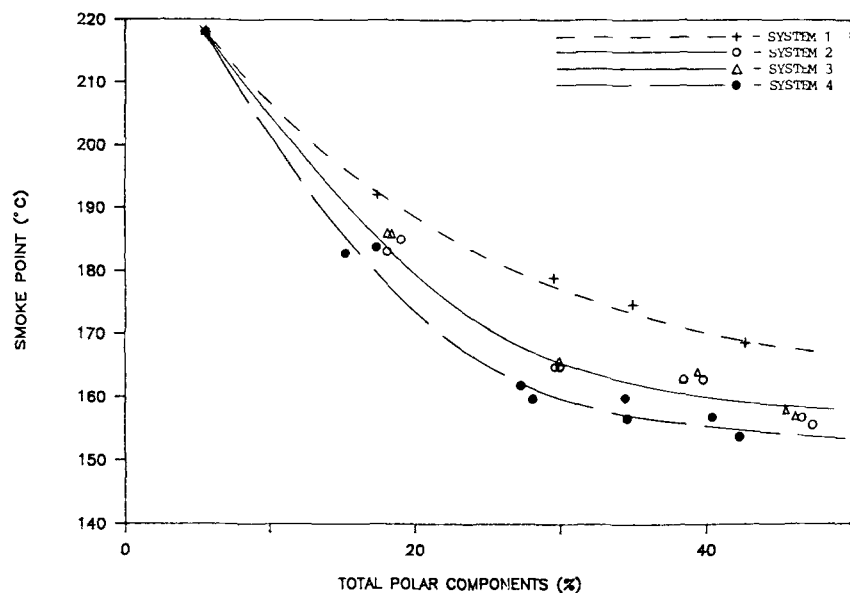FIG. 1. Smoke point vs acid value.

FIG. 2. Smoke point vs total polar components (%).

shortening deteriorated by frying as well as by heating without frying (14).

The significant linear correlations between these four parameters, iodine value, polar components, C18:2/C16:0 ratio and iodine value, further suggest that the values of these quality parameters are not grossly affected by changes in heating and frying conditions and the level of TBHQ added to the medium. In view of the acceptance that total polar material is the most reliable method for measuring fat deterioration during frying (1), it can be concluded that changes in iodine value and C18:2/C16:0 ratio would also provide reliable measures of deterioration. The simple method of using dielectric constant was reliable in this case because the

initial characteristics of RBD olein used for the different systems were the same; in addition, only one type of food was fried. In frying systems where there is dilution of the frying fat from fat in the food, the use of dielectric constant as a reliable measure of oil deterioration may be limited. Dielectric constants of different fresh fats have been found to be different (14).

It should be noted that the relationships given in Table 2 are based on data for one batch of RBD olein subject to different frying conditions. The initial characteristics of different batches of RBD olein may be different. The iodine values of palm olein have been found to be in the range 56.1–60.6, while the contents of C18:2 and C16:0 in palm olein samples were found to
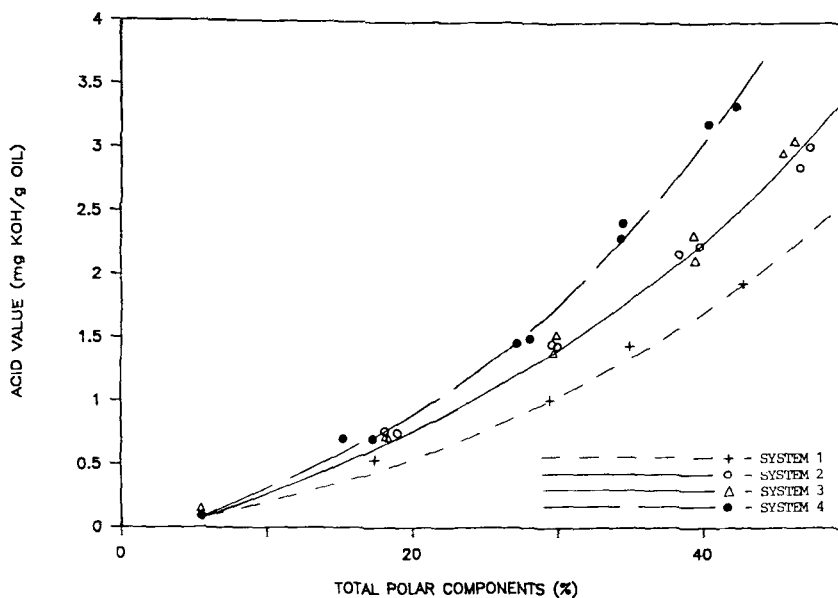
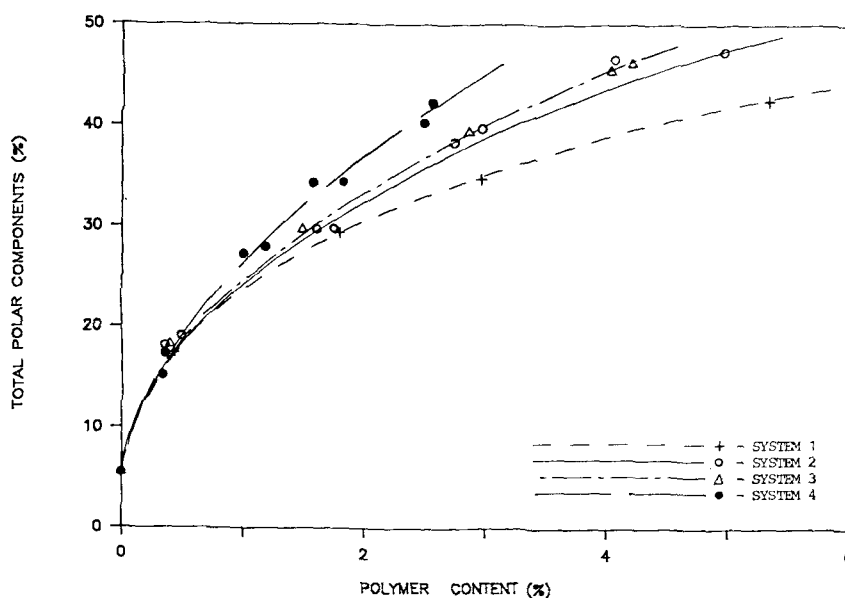FIG. 3. Acid value vs total polar components (%).

FIG. 4. Total polar components (%) vs polymer content (%).

be between 10.34-13.4% and 37.9-41.7%, respectively (16). Analyses of oils in our laboratory showed that different samples of RBD olein had polar components in the 4.5-9.5% range and dielectric constants of 1.17-1.48. These differences in the initial characteristics among different samples of palm olein would give rise to differences in the equations of regression lines for relationships between iodine value, C18:2/C16:0 ratio, polar components and dielectric constant. In separate frying experiments, the relationships between polar components and dielectric constant for two other batches of RBD olein used for intermittent frying of potato slices were y = 6.466x + 0.179 (r = 0.9951,

n = 5) and y = 6.798x - 0.098 (r = 0.9982, n = 5). The initial percentage of polar components and dielectric constant for these two batches of oil were 9.5% and 8.2% and 1.48 and 1.17, respectively. Regression equations obtained for relationships between polar components and the C18:2/C16:0 ratio for those two batches of oil were y = -248.499x + 75.328 (r = -0.9923, n = 5) and y = -222.565x + 67.088 (r = -0.9950, n = 5). The initial percentage of polar components and C18:2/C16:0 ratio of oils used were 9.5% and 8.2% and 0.268 and 0.267, respectively. Although different equations of regression lines for relationships between indicators of frying oil deterioration were obtained, it was neverthe-
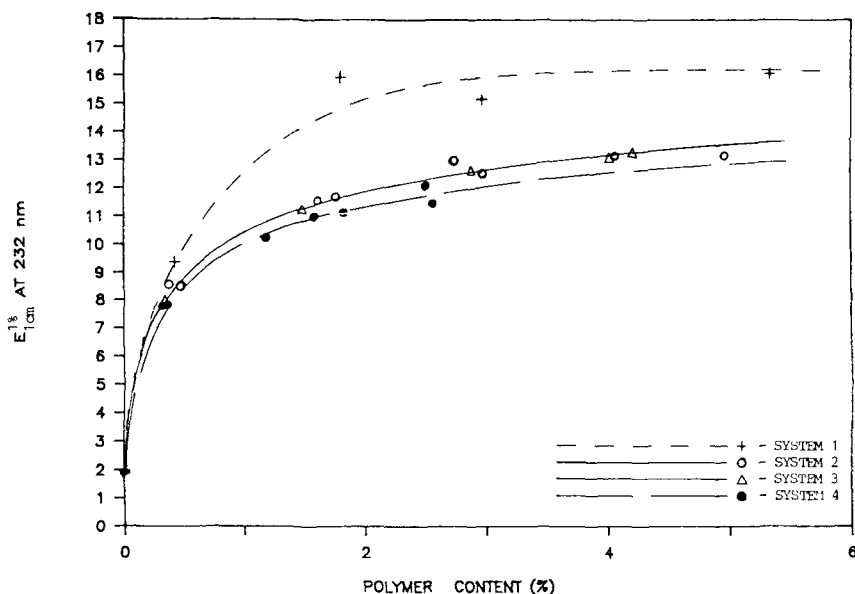
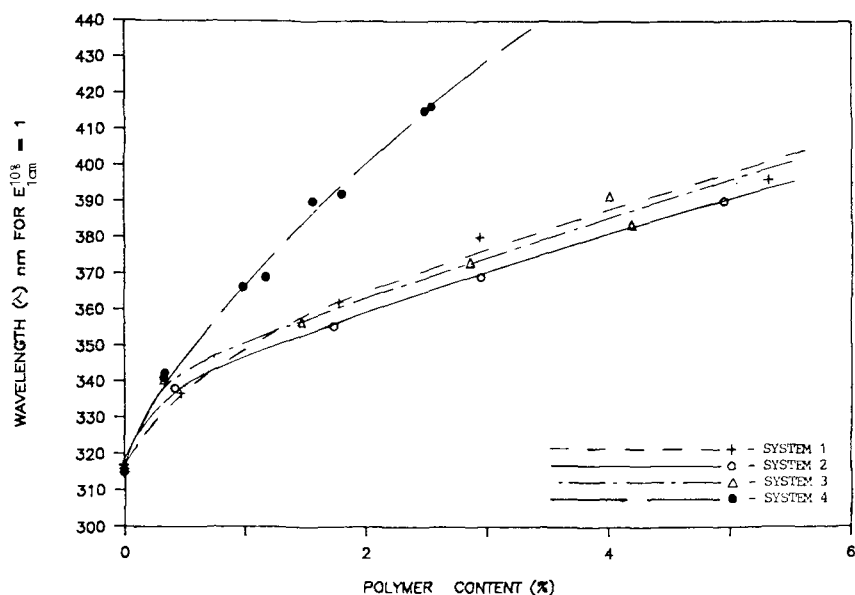FIG. 5. E $^{1\%}_{1\,cm}$ at 232 nm vs polymer content (%).

FIG. 6. Wavelength (λ) nm for E $^{10\%}_{1\,cm}$ = 1 vs polymer content (%).

less evident that the relationship between each of the indicators of frying oil deterioration was highly significant in individual systems (p < 0.001).

Smoke point and acid value. A frying oil is considered to have reached the end of its frying life when the smoke point is less than 170 C (5). The acceptable limit for acid value is considered to be between 1 and 2 mg KOH/g oil (17), while the upper limit is 2.5 mg KOH/g oil (18). Figure 1 shows the relationship between acid value and smoke point. A smoke point of 170 C was found to correspond to an acid value of 1.8 mg KOH/g oil for static heating, while in frying experiments acid values of 1-1.4 mg KOH/g oil were obtained. This shows that differences between the relationship of smoke point and acid value may be expected when one batch of oil is subject to different frying conditions. Relationships between acid value and smoke point have been found in other frying systems (17), and the decrease in smoke point is regarded to be primarily a consequence of the increase in acidity, although other factors may be involved (18).

The relationships between smoke point and polar components and those between acid value and polar components are shown in Figures 2 and 3, respectively. The results show that the relationships between these parameters are influenced both by the type of frying conditions and the level of TBHQ in the frying medium. In view of the linear correlations between polar com-

ponents, iodine value, C18:2/C16:0 ratio and dielectric constant, it follows that relationships between each of the parameters, smoke point and acid value, with iodine value, C18:2/C16:0 ratio and dielectric constant are also nonlinear and affected by frying conditions and the presence of TBHQ.

Polymer content, color and UV absorbance. The relationship between polar components and polymers is given in Figure 4. Since there are significant linear relationships between polar components, dielectric constant, iodine value and C18:2/C16:0 ratio, it follows that polymer content also has a nonlinear relationship between the other mentioned parameters in individual systems. The limit of 27% polar components corresponds to 1.0-1.5% polymers in different systems. Billek et al. found that 15% polymeric triglycerides determined by gel permeation chromatography corresponded to 1.0% oxidized fatty acids or 27% polar components (5). It should be noted that polymer content in this work refers to the weight of that portion of oil which, after methanolysis, remained insoluble in methanol at room temperature (11) and thus differs from polymeric triglycerides, which consist of compounds with a molecular weight higher than that of monomeric triglycerides (5).

Figure 5 shows there is a nonlinear relationship between $E_{1\,cm}^{1\%}$ at 232 nm and polymer content in frying systems. The relationship differs when RBD olein is deteriorated by static heating alone. The reason for this difference is not understood. UV absorbance at 232 nm has been used in some measure for evaluation of oil deterioration where it has been found that the absorbance tends to increase initially and then plateau off during later stages of frying fat deterioration (11). This has been related to the establishment of an equilibrium between the rate of formation of conjugated dienes and the rate of formation of polymers formed by a Diels Alder reaction involving conjugated dienes.

There is also a clear relationship between color measured by the bathochromic shift and polymer content in each of the frying systems. Differences exist in the relationships for systems 1, 2 and 3, but these are small compared to the shift in the relationship to system 4 (Fig. 6). The darkening of oils has been related to the formation of polymeric products; thus, the relationship between color and polymer content could have been anticipated. The shift in the relationship in system 4 may be attributed to the effect of high concen-

trations of TBHQ and its breakdown products to oil darkening. Phenolic antioxidants have been known to cause undesirable darkening of oil- and fat-containing foods (19).

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