Soil Removal as a Rate Process

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Abstract

The rate of soil removal during multiple cycle washing has been studied for three artificially soiled cotton test cloths. Results are considered in relation to a soil removal rate concept proposed some years ago by Vaughn, Vittone, and Smith. It is shown that the rate of removal for these soils, when washed in the Terg-O-Tometer with a built, anionic, synthetic detergent, does not correspond to a simple first order rate process as proposed by Vaughn et al. Rather, it was found that under a variety of washing situations the percentage soil removal increased linearly with the log of cumulative wash time. Further, it was shown that for those experiments involving detergent concentration or level of mechanical action, the slopes of these log time relationships, which reflect the rate of soil removal, vary in the expected manner.

Introduction

Some 20 years ago, Vaughn and his co-workers (1) presented an interesting concept on the detergency of soiled fabrics in relation to time of washing. According to this concept, soil removal, in the absence of redeposition, was considered to be a rate process. They proposed that for a given type of soil the rate of removal was directly proportional to the concentration of removable soil in the fabric, expressed as follows:

$$\frac{-d(R_\infty - R_t)}{dt} = f(R_\infty - R_t) \qquad [1]$$

Where:

R_∞ = % Removal at time (t) = ∞
R_t = % Removal at time (t) = t

Integration of Equation 1 gives:

$$\ln \frac{(R_\infty - R_t)}{R_\infty} = -kt \qquad [2]$$

Or in exponential form:

$$R_t = R_\infty - R_\infty e^{-kt} \qquad [3]$$

The equations above are equivalent to the kinetic equations for a simple, first order, chemical reaction, i.e., the rate is directly proportional to the concentration of reacting substance. In this case, the reacting substance is the removable soil. The constant, k, in this case has the physical significance of a specific soil removal rate, and represents the fraction of removable soil which would come off in the next time interval under a steady state of removal.

The concept of an irremovable soil level is implicit in this analysis of the removal process. Provided that this concept is tenable, a value of removal at infinite time, R_∞, can be obtained from plots of R_t vs. e^{-kt}. Extrapolation to the point where $e^{-kt} = 0$ gives the predicted soil removal for infinite wash time. With this value of R_∞ at hand, the residual soil at any time, t, can be obtained simply by subtraction.

By rearranging Equation 2 as shown below, it can be seen that a plot of $\ln(R_\infty - R_t)$ against t should give a straight line of slope = k. Thus, according to this treatment, the specific soil removal rate for a given detergent system should be simply determinable.

$$\ln(R_\infty - R_t) = -kt + \ln R_\infty \qquad [4]$$

The possibility of obtaining the rate constant of a soil removal process seemed of great value in our work on characterizing detergency systems for home laundry usage.

In the subsequent years, the work cited above has received considerable attention in the literature of detergency. Utermohlen and Wallace (2) applied the Vaughn equations in their soil removal studies on iron oxide pigments. Bacon and Smith (3), Schwartz and Perry (4), and Niven (5) have all given some attention to this concept. Since this work was carried out a number of years ago, it possessed certain limitations in regard to the characterization of current home laundry wash systems. For example, Vaughn, et al. worked with a specialized test fabric soiled with Norit C (activated carbon), lubricating oil, and Crisco. They used this test fabric with soap as the detergent, and used the Launder-O-Meter as their test device.

It was the object of the present study to re-evaluate this concept using a more modern test fixture, the Terg-O-Tometer; using a built, anionic synthetic detergent instead of soap; using a variety of commercial artificial soil cloths; and applying some of the more recent refinements in the handling of reflectance data for the calculation of soil removal.

Experimental Methods and Materials

Detergent. All wash runs were carried out in the Terg-O-Tometer using a laboratory formulated detergent free of optical brightener. This detergent included all of the major constituents of a typical high sudsing, anionic home laundry formulation except for the fluorescent dyes. Following Frishman's recommendations, the detergent had the following formulation (6):

22%	Alkylaryl Sulfonate from Nacconol NR
33%	Sodium Sulfate from Nacconol NR
44%	Anhydrous Sodium Tripoly Phosphate (Monsanto)
1%	Carboxymethyl Cellulose (Hercules Low Viscosity)

The detergent was prepared as a 0.4% solution in distilled water and diluted as necessary for the various

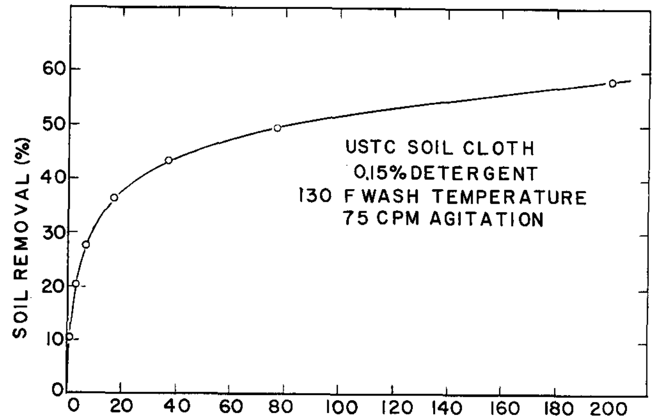

FIG. 1. Soil removal as a function of cumulative wash time for USTC soil cloth.

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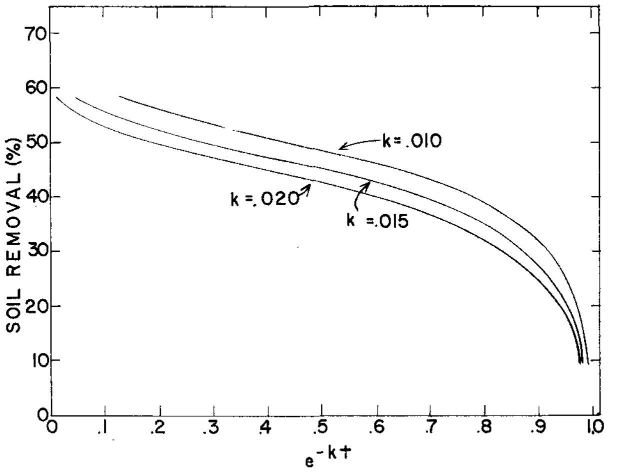

Fig. 2. Plots of soil removal as a function of e^{-kt} for various values of k.

runs. Fresh solutions of the detergent, not more than three days old, were used for all runs.

Water. Water employed in both wash and rinse was a synthetic hard water of 100 ppm hardness as $CaCO_3$. For work with the synthetic hard water, a stock solution of 2000 ppm hardness was prepared according to Harris (7). Fifty ml of this stock solution were added to 950 ml distilled water to give a 1000 ml bath of 100 ppm hardness.

Soil Cloths. Three different standard soiled cotton fabrics were used in the experiments: USTC Soil Cloth; F. D. Snell Soil Cloth; EMPA Soil Cloth. The EMPA, which is somewhat less familiar in this country, has been described by Weder (8).

Reflectance Measurements and Soil Removal Calculations. All reflectance measurements, before and after washing, were made with a Hunter Multi-Purpose Reflectometer (Gardner Labs. Inc.) using the green tristimulus filter. Observed reflectance readings were converted to (K/S) values via the Kubelka-Munk relationship (9). The percentage soil removal was then calculated from the (K/S) values via the relationship of Bacon and Smith (3). An excellent summary of this calculation procedure is given by Harris, Sullivan, and Weeks (10).

The calculation outlined above is based on the assumption that the (K/S) values are a linear function of the mass of soiling pigment in the test fabric. While this assumption has not been proven for the three carbon black-based soil cloths used in this study, the validity of the assumption has been proven during soil removal for a number of similar soils including graphite, carbon black, and lamp black (3,10,11). It seemed reasonable to assume that the Kubelka-Munk theory should apply for the commercial soil cloths used in these experiments.

Typical Wash Schedule. Throughout this work numerous variables were examined as to their effect on rate of soil removal. To clarify the experimental procedure, the wash schedule for one typical experiment with the USTC test cloth is detailed below.

Detergent: Frishman lab. formulated.
Concentration: 0.15% by wt.
Bath Volume: 1000 ml 100 ppm synthetic hard water.
Temperature: 130 ± 1F.
Agitation: 75 cycles/min.
Load Make-Up: 8 USTC (3½ x 4½ in) soil swatches plus white stuffer swatches to give 26–27 g load.

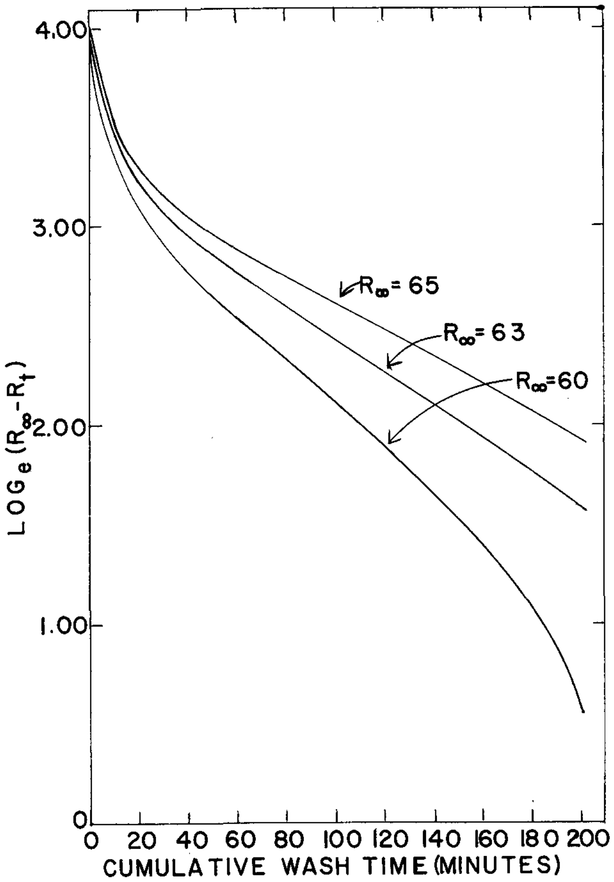

Fig. 3. Plots of the log of residual soil content as a function of cumulative wash time for various values of R_∞.

Rinse: Each load rinsed in 1000 ml 100 ppm water for 1 min under same conditions as for wash.

After rinsing, soil swatches were dried overnight on a glass plate at room temp and then read on the reflectometer. The same load was subjected to several short duration wash cycles with the wash times selected to give negligible self-redeposition. Measurements made on white cotton stuffer swatches added in each wash cycle indicated that redeposition was indeed negligible; the average decrease in reflectance was only 1.5 percentage units.

In the particular run selected for description, the load was washed seven times with the selected wash times:

1,2,4,10,20,40, and 123 min.

These times were chosen to obtain small and approximately equal increments of soil removal.

Experimental Results

Experiment 1. This was run to check the Vaughn theory; it was run exactly as for the typical run described in the previous section, i.e., USTC Soil Cloth, 130F, 75 cpm, .15% detergent. A plot of soil removal, R_t, as a function of the cumulative wash time, t, is given in Figure 1.

To test the Vaughn theory, it was next necessary to obtain a value of soil removal at infinite wash time, R_∞, from plots of R_t against e^{-kt}. Such plots were made with k set at:

.005, .010, .015, .020, .050, .060, .070

Plots for several different values of k show in Figure 2. It was immediately apparent that extrapolation to a unique value of R_∞ at $e^{-kt} = 0$ was dif-

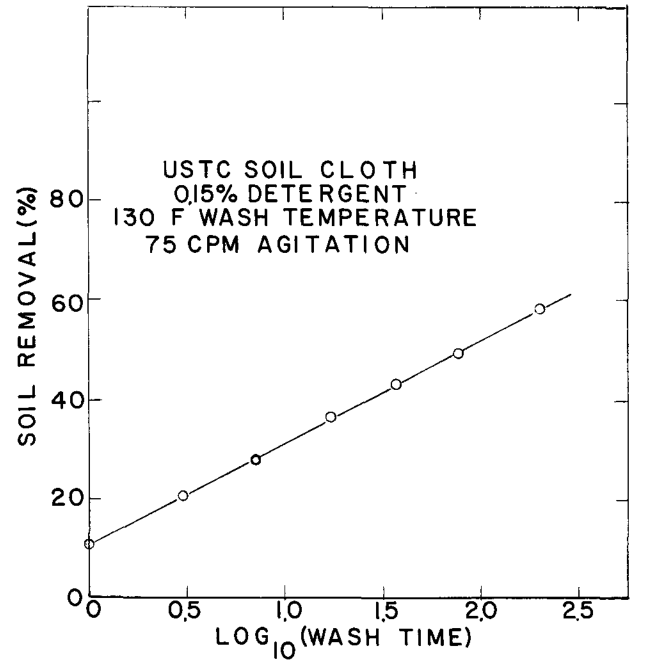

FIG. 4. Soil removal for the USTC soil cloth as a function of the log of cumulative wash time.

ficult because of the curvature at low values of the independent variable. However, it appeared that if a unique value of R_∞ actually existed, it must lie in the range between 60–65% soil removal.

Plots of $\ln(R_\infty - R_t)$ vs. time were made for various selected values of R_∞ in the range 60–65%. In no case were the plots linear, as would be required for confirmation of the Vaughn theory. See Figure 3 for typical plots.

Based upon the non-linearity of the log residual soil vs. time plots, our first tentative conclusion was: soil removal in the Terg-O-Tometer with a built synthetic detergent does not correspond to a simple first order rate process for this specific soil. The rate of removal during multiple washing seems to follow a decidedly different course. Empirically it was found that the soil removal varied linearly with the log of wash time. A plot of this relationship is given in Figure 4.

Experiment 2. Effect of Detergent Concentration on Log Time Relationship. The linear soil removal vs. log time relationship obtained in Experiment 1, while lacking the theoretical basis of the kinetic approach, appeared to be a useful simplification in the treatment of detergency data. We were particularly interested in knowing if this empirical relationship had general applicability to other soils, and also in knowing how the constants of the line would respond to the usual detergency variables of concentration, temperature, and agitation rate.

Based upon previous comparisons of commercial soils cloths, it was known that the soil removal of the USTC fabric was significantly dependent on the detergent concentration employed. It was therefore selected for the present study of concentration effects.

Two multiple wash tests were carried out using the USTC cloth. All conditions were the same in the two runs except the detergent concentration. The two runs of Experiment 2 were made at 140F with 100 cycle/min agitation, using the Frishman detergent in the synthetic hard water. Agitation during the 1 min rinse was reduced to 30 cycle/min to preclude the possibility of soil removal during the rinse process.

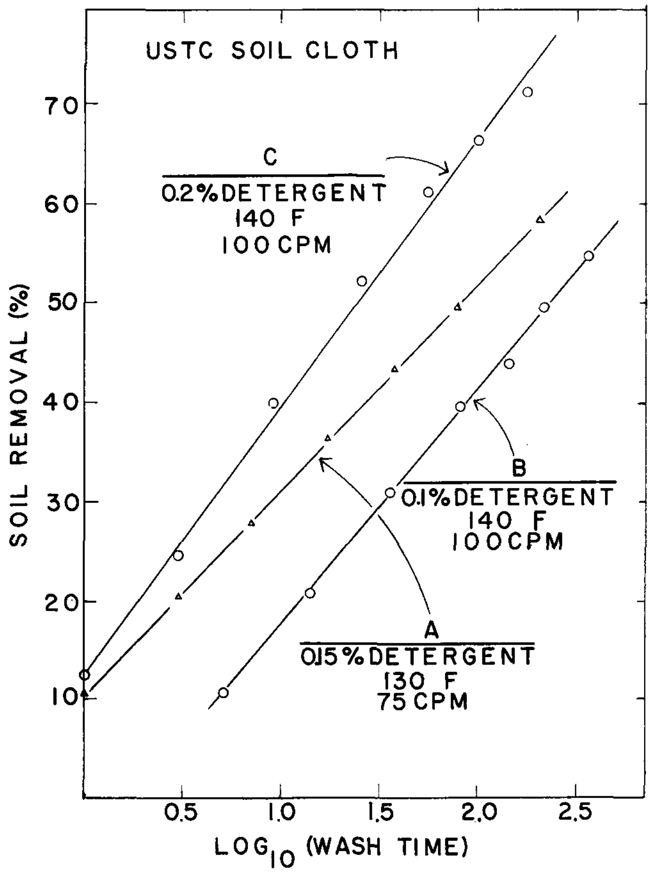

FIG. 5. Effects of detergent concentration on the log time relationship for the USTC soil cloth.

Plots for the data at the two concentrations are given in Figure 5; also given as the middle curve, is the original run on the USTC cloth at 0.15% detergent concentration (Exp. 1). In both runs of Experiment 2 the log time relationship is satisfactorily linear.

It is of interest to compare the slopes of the log time lines for the three runs on USTC cloth.

	A	B	C
	130F .15% Deterg. 75 cycle/min	140F .10% Deterg. 100 cycle/min	140F .20% Deterg. 100 cycle/min
Slope	20.7	24.0	26.7

For the two runs at 140F (B and C) it is seen that doubling the detergent concentration has produced a small increase in rate of removal. The third run at the intermediate detergent level cannot be directly compared since both wash temp and agitation rate are different. However, in comparing A and B it can be seen that increasing the temp and agitation rate as in Run B more than compensates for the deficiency of detergent in this run, at least as regards the slope of the log time relationship.

Experiment 3. Effect of Agitation Level on Log Time Relationship. Based again on the previous comparisons of commercial artificial soil cloths, the Snell soil cloth was known to have high sensitivity to the level of mechanical action employed in washing and was thus selected for the present study of the effect of agitation rate on soil removal. Two comparative multiple wash runs were made at 50 and 100 cycle/min, respectively. These two runs of Exp. 3 were made at 140F with the concn of the Frishman detergent maintained at 0.2% in the 100 ppm synthetic

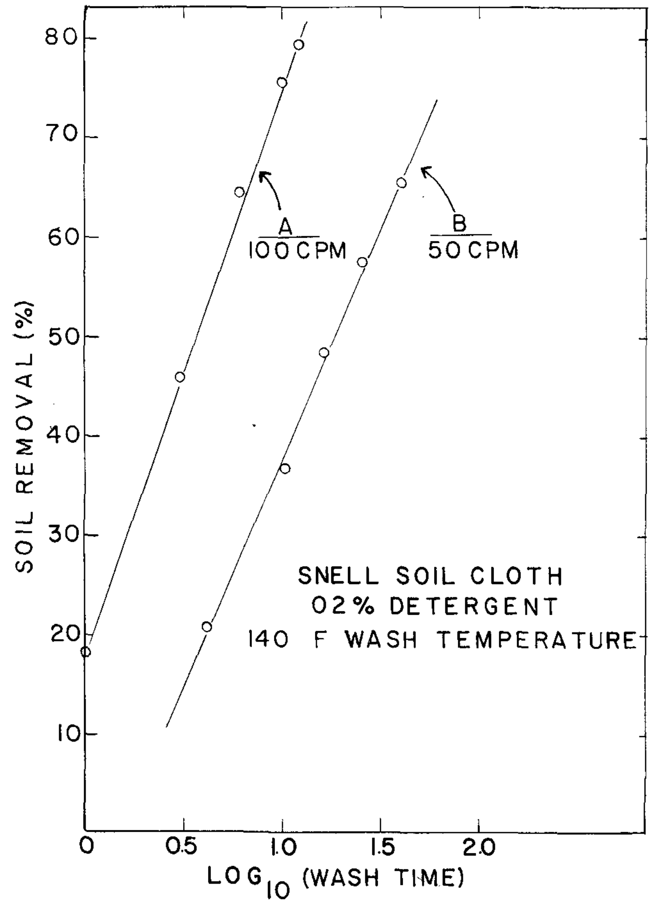

Fig. 6. Effects of agitation rate on the log time relationship for Snell soil cloth.

hard water. As in Exp. 2, the rinses after each wash were of 1 min duration at 30 cycle/min agitation.

Plots of these data as a function of log time are given in Figure 6. Again relationships are linear. The soil removal rates given by the slopes of these two lines are considerably higher than for the USTC cloth. Also we see a rather strong dependence of the soil removal rate on agitation.

	A	B
Cycle/min	100	50
Slope	57.4	44.5

Experiment 4. Effect of Wash Temperature on Log Time Relationship. The last important variable investigated was wash temp. The Swiss EMPA soil cloth, which had previously been shown to have excellent sensitivity to washing temp, was selected for this purpose. Comparative wash temp were 80F and 110F. All runs were at 50 cycle/min with 0.2% Frishman detergent in the synthetic hard water. Mild wash conditions were selected for this test since soil is very easily removed from the EMPA test cloth.

Soil removal data for the two runs with EMPA soil cloth fall along straight lines when plotted as a function of log time; see Figure 7. For any given wash time, higher removal was obtained at the higher wash temp. However, the rate of soil removal, as indicated by the respective slopes, is lower at 110F than at 80F.

	A	B
Temp	80	110F
Cycle/min	50	50
Slope	14.5	10.3

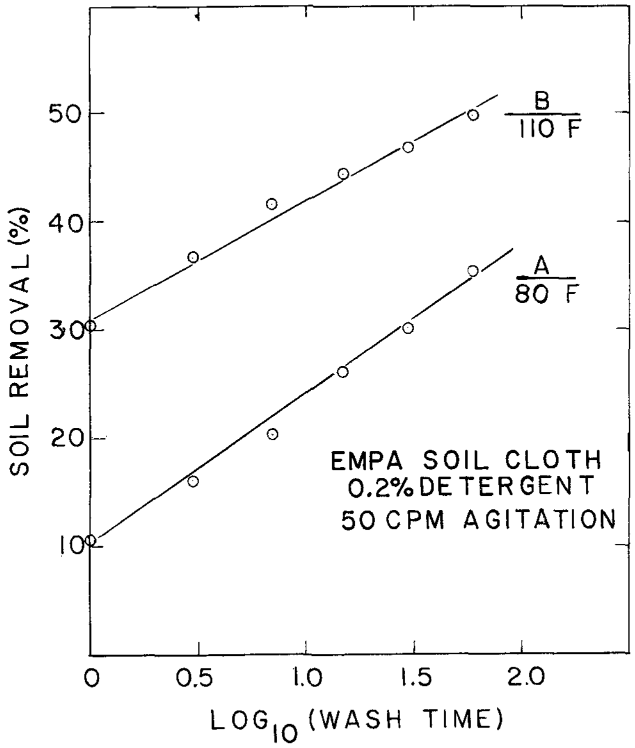

Fig. 7. Effects of wash temp on the log time relationship for EMPA soil cloth.

A confirmatory test was run with EMPA soil cloth again comparing the effects of temp. In this test temp were 110 and 140F, and agitation rate was 100 cycles/min. The slopes for the linear log time relationships are:

Temp	110F	140F
Cycle/min	100	100
Slope	17.4	10.6

Again the greater slope was observed for the multiple wash test at the lower temp.

Discussion

The linear log time relationship has been shown to be generally applicable to three different artificial test soils under a variety of washing conditions. For those experiments involving detergent concentration or level of mechanical action, the slopes of these relationships, which reflect the rate of soil removal, vary in the expected manner. However, for the experiment on temp effects, using the EMPA soil cloth, the larger slope values were obtained at the lower wash temp. Soil removal is extremely rapid for the EMPA cloths; a soil removal value of 30.2% was obtained in the first min of washing at 110F. It thus appears that events occurring within the first min of washing may contribute to the anomalous effect of temp on the apparent slopes of the log time relationships.

In all cases studied, the soil removal points remain on the linear log time line, even for the longest wash times. In one case this was carried out to a cumulative wash time of 350 min with no perceptible leveling off on the log time plot. Thus the concept of an irremovable soil level is not compatible with our experimental data.

In the original concept of soil removal as a rate process, as proposed by Vaughn et al., the soil removal rate, k, was taken as an index for rating a given wash system. While these experiments have shown that the Vaughn concept is not valid for the detergent systems here studied, this testing approach involving multiple washes appears to have considerable merit as an evaluation tool. The procedure used here provides for a measure of soil removal which is free from the confounding effects of soil redeposition. The early washing periods, during which soils removal is rapid, must be brief so that negligible redeposition can occur. Results obtained from the multiple wash runs are then solely a measure of soil removal. The linear log time plot is useful in reducing the required number of data points.

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A Study of the Applicability of a Modified Thiobarbituric Acid Test to Flavor Evaluation of Fats and Oils[1]

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Abstract

A modified thiobarbituric acid test has been devised for the determination of certain components of oxidized fat. The reaction was carried out in a single phase solvent designed to eliminate the color extraction or fat removal steps of other TBA tests. A moderate temperature of 60C, with no added acid, was used to minimize breakdown of hydroperoxides and TBA. Under certain reaction conditions, temperature, sunlight, ferric ion, and oxygen can influence results. Of the aldehydes examined, the TBA reaction products of dienals showed an absorption peak at 532 mμ only, while the TBA reaction products of the saturated aldehydes showed a peak at 452 mμ only. The spectral behavior of TBA reaction products of monoenals was found to vary with the location of the double bond. Fat samples, aged at either 60C or 37.8C, were examined organoleptically and by the modified TBA test. The 452 mμ peak was of value in assessing the flavor of beef fat, cottonseed oil, and used frying fat, whereas the 532 mμ wavelength was of value in assessing the flavor of soybean oil, used frying fat, and pork fat.

Introduction

A number of different chemical methods have been used as aids in evaluating the flavor of fats and fat oxidation products. Among these are the benzidine test for aldehyde value, the carbonyl index of Chang and Kummerow, the carbonyl test of Henick et al., and gas chromatography (1–4). Perhaps the most widely used test in recent times for measuring unfractionated lipid off-flavors, however, has been the thiobarbituric acid (TBA) test. The TBA reaction has been of value in measuring off-flavor components of various fat-bearing foods such as pork, milk, cereals and baked goods, and oysters, as well as fats and oils (5–9). The basis of these tests has been the reaction of TBA with a fat oxidation product or products to form a red pigment absorbing at 532 mμ. Most of the TBA tests mentioned involve strongly acid conditions with some exposure to air. However, Tarladgis et al. have shown that acidity, heat, and the presence of peroxides in the fat sometimes can strongly influence the test results because of decomposition of the TBA reagent (10). Therefore, it appeared important to minimize these factors in any attempt to measure accurately the more subtle changes in carbonyls that occur in fats and fat-bearing products when held at moderate temperatures.

Most workers who have correlated TBA values with organoleptic scores have used the pink color developed at 532 mμ. However, several have noted the appearance of a peak in the 452 mμ region, denoting yellow color (11,12). Recently, it has been shown that the absorption peak at ca. 452 mμ can be attributed to the reaction product of TBA with aldehydes (10,13). Taufel and Zimmerman reported that the presence of ferric ion greatly increased the intensity of yellow formed by the reaction of TBA with aldehydes at 70C instead of the customary 100C (13). These workers also reported that the reaction products of dienals with TBA absorb at 532 mμ (13).

In this study a single-phase solvent of iso-octane, n-propanol, and water was developed to evaluate the usefulness of absorption peaks at 452 and 532 mμ to measure undesirable aldehyde flavors. No acid was added, and a moderate 60C temp was used to minimize changes in fat or reagent from excess acidity or heat. It was found that at 60C the yellow or 452 mμ peak became prominent. The pink color, representing absorption at 532 mμ, is less intense at this temp. Of considerable importance was the effect of oxygen, sunlight, temp, and ferric ion on results obtained. Of further importance was the spectral behavior of TBA reaction products of various aldehydes known to be flavor constituents of oxidized fats.

Procedures

The following fats were examined: hydrogenated vegetable oil used for frying chicken, beef fat, soybean oil, cottonseed oil, and rendered pork fat. The various fats and oils, except the cottonseed oil, were aged at 60C in glass beakers to accelerate off-flavor development from oxidation and to break down any

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[1] Presented at the AOCS meeting, Chicago, 1961.