TABLE IV

Unsaturation Sites in the Wax Esters Produced from *n*-Eicosane (C_{20})

Chain length of TMS-derivatives	Characteristic MS peaks (m/z)				Approximate proportions				
	Ion a	Ion b	Ion c	Ion d	Δ7	Δ8	Δ9	Δ10	Δ11
16 EE[a]	187,215	245,273	–	–	65	–	35	–	–
18 EE	201,215	273,284	–	–	–	–	90	10	–
20 EE	215,229,243	273,287,301	–	–	–	–	25	15	60
20 A	–	–	331	215	–	–	–	–	100

[a]EE = bis-TMS ether of fatty acid ethyl ester; A = tris-TMS ether of fatty alcohol.

11. Aasen, A.J., H.H. Hofsteller, B.T.R. Iyengar and R.T. Holman, Lipids 6:502 (1971).
12. Hankin, L., and P.E. Kolattukudy, J. Gen. Microbiol. 51:457 (1968).
13. Knapp, D.R., "Handbook of Analytical Derivatization Reactions," Part II, Chapt. 4, 1979.
14. Spencer, G.F., and W.H. Tallent, JAOCS 50:202 (1973).
15. Spencer, G.F., R.D. Plattner and T. Miwa, Ibid. 54:187 (1977).
16. Gisser, H., J. Messina and D. Chasan, Wear 34:53 (1975).

[Received July 17, 1981]

Kinetics of Bleaching of Vegetable Oils[1]

U.I. BRIMBERG, Food Division, Process Laboratory, Alfa-Laval AB, Tumba, Sweden

ABSTRACT

It was shown in a recent paper that the concentration c of remaining chlorophyll or carotene in rapeseed oil during the bleaching process follows a rate formula, $\log c/c_0 = -k \sqrt{t}$, characteristic of flocculation of colloids. Thus, the pigments are particulate and colloidally dispersed in the oil. The rate constant k was proportional to the added amount of clay. This paper reports experiments with palm oil. The same kinetics as those with rapeseed are valid. The effects of various parameters on the rate have been studied. The mechanism of the process is discussed.

INTRODUCTION

The bleaching of vegetable oils with bleaching clays in industry has been reviewed by Norris (1) and Kaufmann and Mukherjee (2). Extensive references to the literature are also given. There are a few papers (3-8) on the kinetics of the process that show an initial period of rapid bleaching, a later period of slow bleaching and a final period of constant color which is reached in 10-20 min. Unfortunately, the rate data are too few for quantitative treatment and deduction of rate formulae. We have, therefore, undertaken experiments to this purpose.

Results with rapeseed oil have already been published (9). Rate formulae were derived from the data and applied to the study of various parameters, such as amount of bleaching clay and water content. The formulae were discussed in terms of principles developed at Alfa-Laval by Berg (10).

The experiments with rapeseed oil showed that the bleaching process follows the rate formula:

$$\ln c/c_0 = -k\sqrt{t}, \qquad [I]$$

where t is the time from addition of the clay, c is the concentration of pigment at time t, c_0 the concentration at t = o and k is the rate constant. The rate formula and the rate constant were the same whether the bleaching was followed by measuring the concentration of chlorophyll or that of carotene (Fig. 1).

Equation I pertains to the destabilization of a colloid by removal of the stabilizer, in this case by adsorption onto the bleaching clay. Thus, chlorophyll and carotene are particulate substances in stable dispersion in the oil. The stabilizer is a surface-active lipid among the components of the oil. When enough stabilizer with attached pigments has been removed, the pigment particles aggregate among themselves and settle out until an equilibrium is reached.

This communication reports experiments with neutralized palm oil. The effects of the water content, the method of adding the clay, and the stirring rate were studied. Palm oil differs from rapeseed oil essentially by its lack of chlorophyll, by its much higher content of carotene and, perhaps, by containing a different set of surface-active lipids or different concentrations of them.

EXPERIMENTAL PROCEDURES

Materials

Palm oil. The oil was a neutralized oil of Malaysian origin containing 0.02% water and about 400 ppm of carotene, calculated as β-carotene.

Bleaching clay A. Tonsil Optimum from Süd-Chemie, Germany. It was sieved to remove particles larger than 50 μm to facilitate observations in the microscope, especially to avoid confusing large structures formed during the bleaching with large particles of the bleaching clay. The clay contained 7.7% water as determined according to Karl Fischer. In one experiment, the clay was dried for 5 hr at 130 C, after which it contained 1.97% of water according to Karl Fischer.

Bleaching clay B. Tonsil Standard FF with 7.3% water.

Bleaching clay C. Tonsil L 80 (moisture content not determined).

Methods

Two series of bleaching experiments were done: series I–1 kg of oil was treated with 1% of clay A at 90 C for periods up to 3 hr. The experimental technique was the

---

[1] Presented at the AOCS meeting, New Orleans, May 1981.

same as before (9). The bleaching vessel was a 2-L Pyrex glass flask equipped with an anchor stirrer of stainless steel. The stirring rate was 275 rpm. The vessel was immersed in a thermostated glycerol bath of 90 C. We found that the evaporating water condensed on the cool lid of the flask and flowed back into the oil. Therefore, we heated the lid with an electrical heating band to prevent condensation. During the heating of the oil and throughout the experiment, a stream of N_2 was maintained above the oil surface.

Samples were taken at regular intervals and immediately filtered through a layer of Celite 545 to obtain rapid filtration. At the same time, other samples were taken without filtration and kept in closed bottles for determination of the total water content. In each experiment, a sample was taken at the operating temperature immediately before addition of the clay.

Series II—A sample of 300 g of oil was heated to 100 C and transferred to the heated vessel of a high-speed Turmix blender. The temperature was held at ca. 100 C by means of an electric heating band wrapped around the vessel. The Turmix vessel was filled with N_2 and a stream of N_2 was maintained in the vessel throughout the experiment. Samples were taken every second min and were immediately filtered.

Analysis

The amount of carotene was determined in a Beckman DB spectrophotometer. The absorbance was recorded for each sample in the range 380-500 nm. The peak at 445 nm was taken as a measure of the carotene content. The sample was diluted to a concentration of 1 or 2% (w/v) by addition of spectrograde iso-octane. All data in the figures are given for a 2% solution.

The water content was determined by the Karl Fischer method. A mixture of chloroform and methanol (4:1) was used as solvent.

RESULTS

Influence of Water

The results obtained at 4 different initial contents of water in the system are shown in Figure 2. The lowest water content was obtained by drying the clay (experiment I:2), the higher concentrations, 0.27 and 0.52%, by mixing water into the oil in a high-speed blender just before the bleaching (experiments I:3,4).

The best bleaching effect was obtained by using the water contents of oil and clay as received, 0.02 and 7.7%, respectively (experiment I:1).

The rate constants of the 2 first linear periods are given in Table I. The data show that k_1 decreases with increasing initial water content.

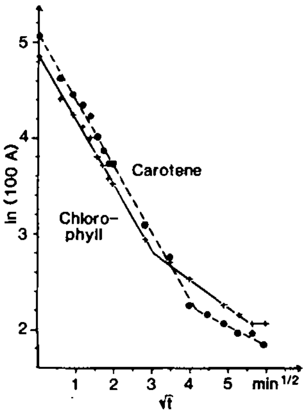

FIG. 1. Bleaching of rapeseed oil at 80 C with 1% of clay B. Remaining amounts of carotene and chlorophyll measured by light absorbance at 445 and 660 nm, time in min (9).

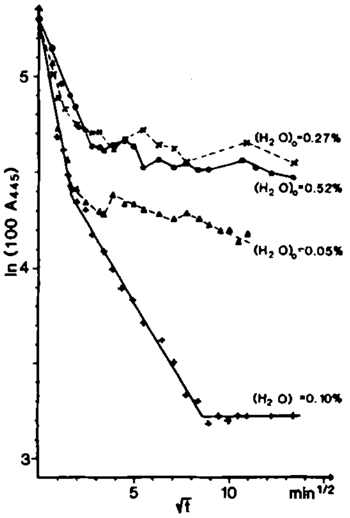

FIG. 2. Bleaching of palm oil at 90 C with 1% of clay A at different initial total amounts of water in the system. Time in min.

These results with palm oil are different from those previously obtained with rapeseed oil (9). In the rapeseed oil experiments, the bleaching effect increased with increasing initial water content and the rate constant k increased linearly with the initial water content up to 0.48%, the highest content then used (Fig. 3). It is notable that at very low initial contents of water the rate constant was the

TABLE I

Rate Constant k in the Formula $1n\ c/c_0 = -k \circ \sqrt{t}$ for Periods 1 and 2 in the Bleaching of Palm Oil at 90 C with 1% of Clay A

Experiment	Experimental conditions	H_2O (%)	k_1	k_2
I:1	Clay as powder, oil dried	0.10	0.51	0.17
2	Clay (dried) as powder oil dried	0.05	0.54	uncertain
3	Clay as powder, water added to oil	0.52	0.21	–
4	Clay as powder, water added to oil	0.27	0.35	0.13
5	Clay as slurry in bleached oil, oil dried	0.09	0.51	0.14
6	Clay as slurry in unbleached oil, oil dried	0.09	0.50	0.06

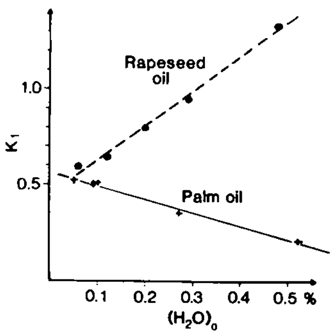

FIG. 3. The rate constant, k, in $\ln c/c_0 = -k\sqrt{t}$ for the first period of bleaching plotted against the initial total content of water of the system $(H_2O)_0$ for palm oil and rapeseed oil (9).

same, although the oils were different. The kind of clay and the temperature also were different, i.e., Tonsil Standard and 80 C for the rapeseed oil and Tonsil Optimum and 90 C for the palm oil. The amount of clay, however, was 1% for both oils.

Another difference from the previous results is the oscillation of the carotene concentration shown by 3 of the curves in Figure 2. This phenomenon is discussed later. It was not observed in the curve for dried oil and normal water content of the clay (experiment I:1), nor in the bleaching experiments with rapeseed oil (9).

Apart from these differences, the results with respect to the kinetics are the same as those with rapeseed oil. Equation I applies and there are 2 branches of the curve at 2 different slopes. The event terminates abruptly at the final level and does not approach the final level asymptotically. In experiment I:1, 70% of the carotene was removed in the first period, which lasted 4 min. The final level was reached after 45 min and 88% of the carotene had then been removed.

Mode of Adding Bleaching Clay

In practice, bleaching clay is added either as a powder or as a concentrated slurry prepared separately by mixing the clay with a portion of oil, usually bleached oil. In order to test whether the mode of adding clay influences the kinetics of bleaching, we did 2 experiments with a slurry of 1 part clay A to 2 parts oil. In experiment I:5, the oil was bleached, and in experiment I:6 it was not bleached. The slurry was added at the bleaching temperature.

The results are shown in Figure 4 together with experiment I:1 as a reference, in which the clay was added as a powder. The 3 curves seem to coincide in the first period, but those for the slurries enter the second period sooner and then show a smaller rate than the reference. Also, there are oscillations in the color of the oil for the slurry experiments in the final period. However, after some delay, the clay of the slurries became effective again and the oil color rapidly reached the final level of the reference, apparently at the same rate constant as in the initial period. The further course of the event was not studied. This rapid bleaching started about 2 hr after initiation of the process.

The results were deemed not practical, and therefore they were not pursued. However, these results may apply to palm oil only and are not necessarily applicable to other oils. Also, the concentration of the slurry was very high and perhaps not well chosen.

Disappearance of Water

The total water content of the system was followed during the bleaching. The results obtained in experiments 2 and 3 are given in Figure 5. In the experiments with added water and a high initial water content of the system, there was a rapid decrease of the water content in the first minutes. Later, a slower disappearance followed and finally a constant level was reached. In the case of very little initial water (experiment 2), there was also a decrease of the water content during the first 25 min and then a level of 0.02% water was reached and maintained.

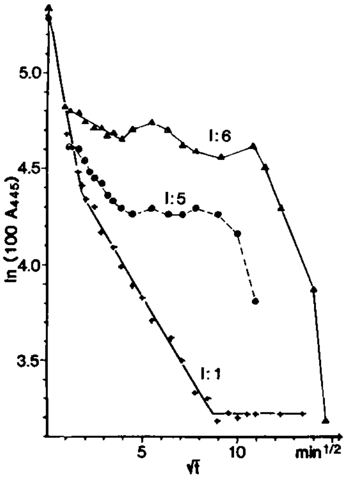

FIG. 4. Bleaching of palm oil at 90 C with 1% of clay A added in various ways: I:1 as a powder, I:5 as a slurry of clay and bleached oil 1:2, I:6 as a slurry of clay and the unbleached oil 1:2. Time in min.

Figure 6 shows the disappearance of the carotene and water in experiment 6. There is no obvious relationship between the 2 events.

Influence of Stirring Rate

The mixing of clay into oil at 80-100 C usually is easy and rapid because the oil readily wets the clay. Conceivably, however, the bleaching process could be accelerated by rapid stirring, beyond that required for maintaining the clay particles in suspension. In order to check this point, a few exploratory experiments were conducted at 100 C with the neutralized palm oil and 0.75% of clay C.

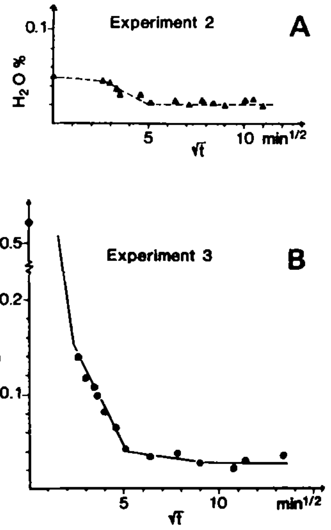

FIG. 5. (A) The disappearance of total water with time in exp. 2 with dried palm oil and dried clay A. Time in min. (B) Disappearance of total water with time in exp. 3 with added water to the palm oil and clay A as received. Time in min.

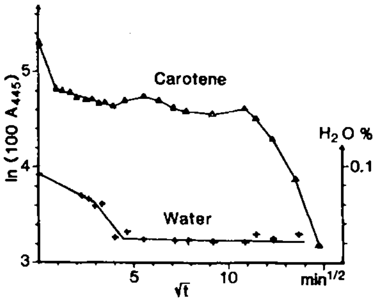

FIG. 6. Disappearance of carotene and water in exp. 6 with clay A added as a slurry in unbleached oil. Time in min.

The stirring was either very rapid (Turmix blender at about 7,000 rpm), intermediate (Turmix at about 2,500 rpm) or very slow (manual stirring with a glass rod, just enough to keep the clay dispersed). After 2 min, the clay was filtered off and the absorbance was measured. The results, given in Table II, show that the effect of the stirring rate is little. It appears that bleaching is most effective at the slowest stirring.

Corresponding experiments were done with a neutralized rapeseed oil and 1% of clay B. The results in Table II show the same results as with the palm oil. Only the chlorophyll was removed to a lesser extent with the very slow stirring.

Experiments were then conducted with the Turmix blender at the 2 speeds and a temperature of 100 C (experiments II:1 and 2). The results are shown in Figures 7-9. Figure 7 shows that the kinetics follow Equation I. The best bleaching was obtained with the lower speed as in the preceding experiments. The corresponding absorbance curves in the range 360-540 nm are shown in Figures 8 and 9. They reveal different patterns of color reduction. At the higher speed, 7,000 rpm, the color reduced less in the range 430-480 nm but more in the range 360-430 nm. Conceivably, substances absorbing light in the range 360-430 nm are more easily oxidized to colorless substances. In the other range, 430-480 nm, the substances are, to some extent, redispersed by the intense mixing.

The results obtained are in agreement with experience for soybean oil as given in the review by Brekke (11).

Observations Using the Microscope

Without added bleaching clay, the oil contains no visible pigment particles. The rapeseed oil is red in dark-field illumination. It therefore contains particles that scatter light, which must be chlorophyll particles. The palm oil, lacking chlorophyll, is black in dark-field illumination. Thus, the carotene particles are too small to scatter visible light.

It has been known for a long time that colloid particles of a size much smaller than the wavelength scatter light of a wavelength related to the particle size. Many colloids, such as the gold sol (12), as usually prepared, scatter blue light and appear red in transmitted light. When such a colloid is precipitated, its particle size increases and the color shifts toward violet.

When bleaching clay was added to a drop of unbleached palm oil on a microscope slide, the clay particles instantly turned green. At the same time, the natural color of the oil, yellow, disappeared within a zone around the clay particles. In a short time, green, gel-like lumps were formed, in which the very small clay particles seemed to be included.

The green color cannot be produced by blocking any one part of the visible light; it is obtained by mixing yellow and blue. The carotene, then, supplies the yellow and carotene particles provide the blue. These particles are large enough, say 100 nm, to scatter red light.

The color change was also observed by Khoo et al. (13). Bleaching clay was added to a solution of β-carotene in acetone and the supernatant solution turned greenish over a period of time.

Samples from the sediment after the bleaching were observed in the microscope. The green, gel-like lumps just mentioned dominated the field of view. In addition, there were yellow patches, occasionally red formations and, rarely, bright blue, slimy films.

It is inconceivable that these various colors could be produced by molecular light absorption by various reaction products of carotene. The colors must have been produced by carotene particles, or rather, aggregates of the original carotene particles scattering light according to size in the size range 25-150 nm.

The aggregation of colloid particles follows the rate formula (10):

$$dc/dt = -k/\sqrt{t} \qquad [II]$$

The aggregation is therefore readily distinguishable from the gel formation according to Equation I. Equation II has not been found in our data on bleaching, in which aggregation is thus not rate-determining. Aggregation thus is faster than flocculation in the presence of bleaching clay. Under other circumstances, it may well be rate-determining, however.

DISCUSSION

The kinetics of bleaching have been found to be essentially the same for palm and rapeseed oils. This is to be

TABLE II

Removal of Color (%) of Initial Color after Bleaching for 2 min at Different Mixing Speeds[a]

Oil	Mixing	Removal of color (%) at:					
		400 nm	420 nm	445 nm	470 nm	475 nm	660 nm
Palm oil	Intense[b]	25	36	41	44	–	–
	Intermediate[c]	27	40	45	48	–	–
	Very slow[d]	29	40	44	47	–	–
Rapeseed oil	Intense[b]	61	68	71	–	74	73
	Intermediate[c]	63	72	76	–	80	75
	Very slow[d]	60	70	78	–	81	63

[a] The palm oil was bleached with 0.75% of clay C at 100 C and the rapeseed oil with 1% of clay B at 80 C. The color was measured at different wavelengths.

[b] Turmix blender at 7,000 rpm.

[c] Turmix blender at 2,500 rpm.

[d] Stirring by hand with a glass rod.

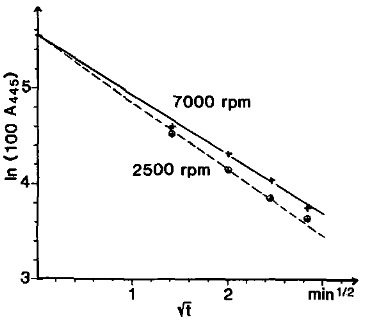

FIG. 7. Bleaching of palm oil at 100 C with 1.5% of clay B in a Turmix blender at 2 different speeds. Time in min.

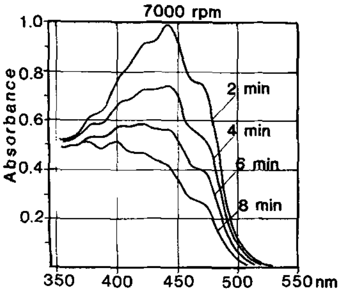

FIG. 8. Bleaching of palm oil at 100 C with 1.5% of clay B in a Turmix blender at 7,000 rpm. Absorbance at different wavelengths in the range of 350-550 nm.

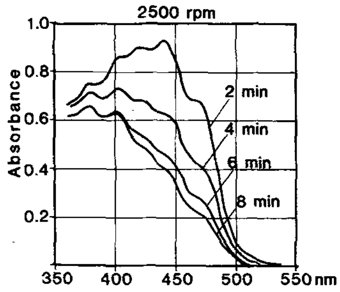

FIG. 9. Bleaching of palm oil at 100 C with 1.5% of clay B in a Turmix blender at 2,500 rpm. Absorbance at different wavelengths in the range 350-550 nm.

expected, since with rapeseed oil carotene and chlorophyll were removed according to the same formula. Even the rate constant was the same, except for a small difference that may be attributed to heat bleaching of the carotene. But the results with palm oil differ from those with rapeseed oil in some details, such as in the effect of added water.

In the bleaching process, the pigments are transferred from the oil to the surfaces of the clay particles together with the stabilizer. They form a colored coating on the clay particles that can be seen in the microscope. The accumulation of stabilizer and pigment particles on the surfaces of the clay particles constitutes a concentration of the colloid in the form of a gel.

In the first period of the bleaching process, the pigment particles with stabilizer deposit themselves onto the clay particles and in the second period, onto the coat on the clay particles. The kinetics are the same in both periods but the rate constant is smaller in the second period.

The oscillations shown in Figures 2 and 3 of the adsorption process are characteristic of the gel. Reference may be made to the periodic formation of precipitate known as Liesegang's rings. Periodic chemical reactions have been treated by Hedges and Myers (14) and in a more recent symposium of the Faraday Society (15). A case in point has been encountered in an experimental study of the reversible gel $\rightleftarrows$ colloid transformation by Berg and Ohlsson (16). Berg (10) attributes the oscillation to a delay of the restoring force (reduction) in the oxidation-reduction system. He says that oscillations occur only at low concentrations of stabilizer. When the stabilizer is abundant, the damping of the system is great enough to make the system aperiodic.

In addition to producing oscillations, the manipulation of the initial water content and the preparation of a slurry reduced the adsorption capacity of the clay so that, in both cases, the final state—state of saturation—was reached at a higher level of pigment concentration in the oil. In the slurry, the effect was temporary, and the normal adsorption capacity was restored after some time, about 2 hr. It is notable that the initial adsorption rate was not affected.

Bleaching is a complex process, but its rate-determining step is fairly simple. The pigment has the state of a stable colloid in the oil. In order to separate the pigment from the oil, it is necessary and sufficient to break the stability of the colloid. This is the primary function of the bleaching clay.

REFERENCES

1. Norris, F.A., in "Bailey's Industrial Oil and Fat Products," 3rd Edn. edited by D. Swern, Interscience Publishers, New York, NY, 1964, pp. 769-792.
2. Kaufmann, H.P., and K.D. Mukherjee, Fette Seifen Anstrichm. 68:651,896 (1966); 64:128, 463 (1967).
3. Stout, L.E., D.F. Chamberlain and J.M. McKelvey, JAOCS 26:120 (1949).
4. Drap, C., and M. Naudet, Rev. Fr. Corps Gras 7:495 (1960).
5. Naudet, M., and C. Drap, Fette Seifen Anstrichm. 62:487 (1960).
6. Rich, A.D., JAOCS 41:315 (1964).
7. Tollenaar, F.D., and H. Hockmann, Fette Seifen Anstrichm. 66:430 (1964).
8. Guillaumin, R. and J.F. Pertuisot, Rev. Fr. Corps Gras 14:449 (1967).
9. Brimberg, U.I., Fette Seifen Anstrichm. 83:184 (1981).
10. Berg, T.G.O., prepared for publication.
11. Brekke, O.L., in "Handbook of Soy Oil Processing," American Soybean Association and AOCS, 1980, p. 116.
12. Zsigmondy, R., and P.A. Thiessen, "Das kolloide Gold," Akademische Verlagsges., 1925.
    Zsigmondy, R., "Über Kolloidchemie," Verlag J.A. Barth, Leipzig, 1925.
13. Khoo, L.E., F. Morsingh and K.Y. Liew, JAOCS 56:672 (1979).
14. Hedges, E.S., and J.E. Myers, "The Problem of Physico-Chemical Periodicity," Edward Arnold Co., London, 1926.
15. Symp. Farady Soc. No. 9 (1974) "Physical Chemistry of Oscillatory Phenomena," The Chemical Society, London, 1975.
16. Berg, T.G.O., and A.Ohlsson, prepared for publication.

[Received May 28, 1981]