Silica Refining of Palm Oil

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The amount of bleaching earth required in the physical refining process of palm oil depends on the activity of the earth, quality of the oil and final color specification of the refined products. The use of silica (Trisyl) in combination with bleaching clay in palm oil refining has been investigated. The optimum conditions required for Trisyl and bleaching clay are 95–105°C for a period of 30–40 min. Improvements in color performance for palm oil products are noted with the addition of small quantities of Trisyl (0.06–0.24%) to the bleaching clay. Addition of 0.12% Trisyl to 0.4% bleaching clay improved the color of the refined oil by as much as 1.7 Red Lovibond units. Lower phosphorus levels (18.4 and 16.9 ppm) were obtained in the refined oils with an addition of 0.12 and 0.24% Trisyl, respectively, as compared to a level of 36.2 ppm of phosphorus when no silica was added to the earth. Better color stability was also obtained with oils treated with Trisyl. An additional advantage was the reduction in filtration time, leading to possible higher throughput in refining.

KEY WORDS: Bleaching earth, color stability, palm oil, phosphorus removal, silica refining.

Earth bleaching is one of the basic steps in the refining of crude palm oil. It involves addition of a bleaching clay to crude palm oil, which is then agitated under vacuum at a temperature of around 100–140°C for about 30–45 min, followed by separation of the earth from the oil by filtration. The bleaching earth is employed not just as an adsorbent of colored compounds (carotenoids in the case of palm oil), but it also adsorbs phospholipids, soaps and heavy metals and decomposes oxidation products, such as peroxides.

The amount of earth or clay required for bleaching palm oil is an important consideration. This will vary depending on the activity of the earth, quality of the crude oil and the final color specification required of the refined product. In general, the amount of earth used by refiners varies between 0.5 and 2.0%. When the clay is filtered from the oil, the rate of filtration decreases with high earth dosage, and the increased retention time makes the process uneconomical.

The refiner has a wide choice of earths and must decide which product will give optimum results. The ideal bleaching aid should be cost-effective and improve bleaching performance. Both natural and synthetic materials have been considered as possible bleaching adsorbents (1–3). Silica is one material that has potential application in the refining of oils and fats (4,5). A silica gel column is effective in removing polar impurities from oil (6). Among the silica materials that are commercially available for the refining of oils and fats are Trisyl products (W.R. Grace, Baltimore, MD) and Britesorb NC oil purifiers (The PQ Corporation, Valley Forge, PA). Trisyl silica has been evaluated for removal of color, phosphorus and sulfur (4,7,8). A novel refining process, known as modified physical refining (MPR), has been recommended with Trisyl silica. In MPR, soaps are generated by adding small amounts of caustic to crude or degummed oils to facilitate adsorptive removal of phospholipids (5).

The objectives of this study are to examine the use of Trisyl with bleaching earths in palm oil refining. This includes studying the conditions required when Trisyl is incorporated in bleaching earths, the performance of Trisyl with reduced dosages of bleaching earths in terms of color, phosphorus and iron removal from crude palm oil and the effect on the filtration time. It is also important to monitor color stability of the refined oils on storage and upon heating at 180°C (as in frying operations).

EXPERIMENTAL PROCEDURES

Evaluation of bleaching temperature. Crude palm oil with a free fatty acid level of 3.6%, and phosphorus and iron contents of 15 and 5.5 ppm, respectively, was used in the experiments. Degumming was carried out on all samples of 100 g crude oil at 90°C for 10 min with 0.05% (by wt of oil) phosphoric acid. The apparatus used consisted of a 250-mL three-necked, round-bottom flask fitted with an air condenser to a filter flask connected to a vacuum (9). A contact thermometer was used to regulate the temperature of the oil, which was heated to 90°C with a heating mantle. Nitrogen gas was bubbled through the oil during degumming and bleaching.

The degummed oil (100 g) was bleached with 0.27% (by wt of oil) Trisyl (W.R. Grace) and 0.8% (by wt of oil) bleaching clay (WAC Supreme; Wembley Activated Clay Sdn. Bhd., Parit Buntar, Perak, Malaysia). Bleaching temperatures were 85, 90, 95, 105, 115 and 125°C for 15 min. The oils were filtered under vacuum after bleaching. The filtered oils were heated to 260°C under vacuum (2–3 torr) and maintained for 20 min. The oils were analyzed for color (10), phosphorus (11) and iron content (12).

Evaluation of optimum bleaching time. In the second set of experiments, the optimum temperature was selected with reaction times of 10, 15, 20, 30, 40 and 50 min. The bleached oils were deodorized at 260°C and analyzed for color, phosphorus and iron content.

Degumming requirements. In these experiments, acetic acid (0.05 and 0.1% by wt of oil), water (2% by wt of oil) and phosphoric acid (0.05 and 0.1% by wt of oil) were evaluated as degumming agents. Degumming was carried out at 90°C for 10 min on 100 g crude oil. Bleaching was carried out at 105°C for 20 min with a combination of 0.27% (by wt of oil) Trisyl and 0.8% (by wt of oil) bleaching clay. The earths used were WAC Supreme and WAC 100 (Wembley Activated Clay Sdn. Bhd.), SBE 01 (Southern Bleaching Earth, Selangor, Malaysia), Fulmout AA (Laporte, Johore Bahru, Johore, Malaysia) and Pure Flo (Oil-Dri, Chicago, IL). The oils were deodorized at 260°C for 20 min under vacuum (2–3 torr) and analyzed for phosphorus and color. The degumming and bleaching method was as described by Rice (9). Control experiments without any phosphoric acid degumming were included. The oils were treated with 0.27% (by wt of oil) Trisyl and 0.8% (by wt of oil) bleaching earth (WAC Supreme and WAC 100) for 20 min at 105°C.

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Performance of Trisyl with bleaching clay. The experiments were carried out in a glass refining unit. Crude palm oil (1 kg) was degummed in a 2-L jacketed vessel with 0.1% (by wt of oil) phosphoric acid at 85°C. The oil was stirred for 15 min, and varying combinations of bleaching clay with Trisyl were added. Bleaching was performed at 90°C for 30 min. The bleached oil was filtered under vacuum through a Buchner funnel with a Whatman No. 1 filter paper. The filtered oil was transferred to a 2-L, three-necked, round-bottom flask, where it was deodorized at 260°C for 2 h at 2–3 torr. The refined oil was cooled to 60°C. Color was read in a Lovibond Tintometer with a 5.25-inch cell (10). Phosphorus levels were analyzed as described in the procedures of the International Union of Pure and Applied Chemists (11), and iron was analyzed by atomic absorption spectroscopy (12).

Monitoring of color development at 180°C. This was carried out with 50 mL oil heated in a 50-mL tall beaker at 180°C in an oven for 16 h and cooled to 60°C. Color of the oil was read in a Lovibond Tintometer in a 1-inch cell. The sample was placed in the oven again for another 16 h at 180°C. Color readings were taken at the end of each 16-h heating period (13). This test represents the color stability of the refined oil when used at frying temperatures.

Monitoring of color development at 60°C. The sample (400 g) was stored for 10 wk in a 600-mL beaker in an oven set at 60°C. The color of the oil was measured weekly in a Lovibond Tintometer in a 5.25-inch cell (14). This accelerated test represents the stability of refined palm oil during storage and transportation.

Filtration. Crude palm oil (100 g) was heated to 90°C in the apparatus described earlier and degummed with 0.05% (by wt of oil) phosphoric acid for 10 min. The required dosage of clay or clay/silica mixture was added, and the temperature of the oil was raised to 105°C. The reaction was carried out for 20 min with stirring. The hot oil/clay mixture was vacuum-filtered into a Buchner flask through No. 1 Whatman filter paper. The filtration rate is taken as the time required to filter the oil through until no oil is observed on the clay surface.

Repeatability of experiments. The robustness of the experiments is demonstrated on a set of samples (0.8% by wt of oil of WAC Supreme and 0.06% by wt of oil of Trisyl). Duplicate experiments showed little variation as given by color [1.9 red (R), 19 yellow (Y), 2.0 R 20Y], iron (0.3, 0.4 ppm) and phosphorus (14.8, 15.3 ppm). The repeatability standard deviation of the color test is ±0.07 for a mean value of 2.3R units and ±1.2 for a mean of 21.0Y units. The repeatability standard deviation of the iron and phosphorus test is ±0.7 (4.4 ppm) (12) and ±0.7 (4.5 ppm) (Siew, W.-L., unpublished data) where the mean value is given in the parentheses. The standard deviation of the filtration test is ±10 s for a mean of 105 s (Siew, W.L., unpublished data).

RESULTS AND DISCUSSION

Processing conditions for bleaching with clay and Trisyl. The results in Table 1 show that optimum colors were obtained at temperatures between 90–105°C. Greater color was obtained at higher temperatures of 115° and 125°C. A period of between 30–40 min appeared to be optimum for color, iron and phosphorus removal. Too short a reaction time (10 min) was inadequate for phosphorus removal. Thus, the temperatures and reaction times normally used in earth bleaching are still applicable when silica is incorporated into the process.

TABLE 1

Evaluation of Temperature and Time Required for Refining with Trisyl[a] and WAC Supreme[a]

Conditions	Color (5.25-inch cell)[b] R	Y	P (ppm)	Fe (ppm)
Temperature (°C)				
85	1.7	20	4.9	0.2
90	1.8	21	5.4	0.3
95	1.7	21	7.0	0.2
105	1.7	21	4.6	0.3
115	1.9	29.1	5.2	0.2
125	1.9	27	3.9	0.3
Time (min)				
10	1.7	23.1	5.3	0.4
15	1.7	21.1	3.9	0.4
20	1.7	21	3.8	0.6
30	1.7	21	3.0	0.4
40	1.7	21	3.1	0.4
50	1.7	21	4.3	0.6

[a] Trisyl from W.R. Grace (Baltimore, MD), WAC Supreme from Wembley Activated Sdn. Bhd. (Parit Buntar, Perak, Malaysia).
[b] R, red; Y, yellow.

In the absence of a degumming agent, bleaching clays alone gave poor performance with respect to color removal (Table 2). A combination of 0.27% Trisyl and 0.8% bleaching clay showed reduced colors as compared to that obtained with 1% of the earth alone. When degumming was carried out either with water, phosphoric or acetic acids, the Trisyl-treated oils showed good colors of 1.8–2.1R in a 5.25-inch Lovibond cell. The phosphorus content in the

TABLE 2

Degumming with Trisyl and Bleaching Clays[a]

Treatments	Color (5.25-inch cell) R	Y	B	P (ppm)
		No degumming		
Clay with Trisyl[b]				
WAC Supreme	2.0	28	—	3.0
WAC 100	2.8	31	—	5.3
SBE 01	2.0	28	—	5.2
Fulmont AA	2.1	31	—	3.3
Pure Flo	2.1	31	—	3.5
Clay alone (1%)				
WAC Supreme	3.4	36	0.1	4.4
WAC 100	3.6	41	0.1	5.7
		Degumming[c]		
2% Water	1.9	28	—	4.0
0.05% Phosphoric acid	1.8	26	—	3.8
0.1% Phosphoric acid	1.8	27	—	22.5
0.05% Acetic acid	2.1	28	—	4.8
0.1% Acetic acid	2.1	28	—	4.5

[a] Sources and abbreviations as in Table 1; B, blue.
[b] 0.27% Trisyl and 0.8% clay.
[c] 0.27% Trisyl and 0.8% WAC Supreme.

refined oils was low, with the exception of the oils treated with 0.1% phosphoric acid. The high phosphorus level retained in the oil was due to the retention of the residual phosphoric acid. A similar effect is generally noted with bleaching earths (Zschau, W., private communication). It is thus important to regulate the correct dosage of phosphoric acid in the process for effective removal of impurities. Acetic acid did not perform as well as phosphoric acid or water. Water degumming was, in fact, as effective as phosphoric acid in removing color and phosphorus from the oil.

The data in Table 2 show that although the use of bleaching clays alone requires an acid degumming step, the use of Trisyl in addition to the bleaching clays allows omission of the degumming step. This suggests that Trisyl has the capability of adsorbing phospholipids and enhancing the clay's ability to adsorb pigments. The efficiency of the process also depends on the activity or quality of the clays used (Table 2).

Data showing the effect of treatment of oil with bleaching clay and Trisyl in different proportions on the color, phosphorus and iron contents are illustrated in Table 3. Refining with 1% clay resulted in a color of 2.0R in the oil. On lowering the amount of adsorbent from 1% to 0.8, 0.6 and 0.4%, the color of the refined oil increased significantly, from 2.0R to 3.8R. The low dosage of clay is therefore not sufficient to effect an efficient removal of the color. Addition of Trisyl to the clays improved the color. For example, the addition of 0.12% Trisyl to 0.6% clay showed no increase in color as compared to using only 0.6% clay alone. If the clay dosage is further reduced to 0.4%, the color obtained is 3.8R. An addition of 0.12% Trisyl to the clay considerably improved the refining capabilities, as the color remained at 2.1R. Further additions of Trisyl to the clay, for example with 0.18% and 0.24% Trisyl, resulted in the lowering of the "yellow" tinge but did not affect the red color of the oil. It is possible to further reduce the color of oils by adding larger quantities of Trisyl. This is shown from studies on canola oil, where the addition of 2 and 4% Trisyl to canola oil with 4% American Oil Chemists' Society bleaching earth shows a reduction of color from the control of 7.0R 57.5Y (no Trisyl) to 4.0R 35.4Y and 2.6R 36.7Y, respectively (7). On the other hand, it may not be economically feasible to do this for refining palm oil because the cost of Trisyl is three times that of bleaching earths.

The level of phosphorus in refined oils represents the efficiency of the degumming and bleaching stages. In refined palm oil, phosphorus levels vary from 0.9–8.9 ppm (15). The phosphorus in refined palm oil is the residue of the phosphoric acid from the degumming process (15). The wide range of phosphorus retained in refined oils is attributed to the earth dosage used and the activity of the bleaching clays. Reduction in bleaching clay from 1 to 0.4% resulted in an increase of phosphorus from 10.8 to 36.2 ppm (Table 3), indicating the reduced capacity of the lower clay dosage for removing phosphoric acid. Addition of a small percentage of Trisyl product to the clay showed an improvement in the phosphorus removal. However, the phosphorus level in the oils treated with a combined low amount of bleaching clays and Trisyl were still higher than the oil treated with 1% clay alone. This can be overcome by reducing the phosphoric acid dosage used in the degumming stage. Furthermore, our degumming experiments have indicated that the silica can act as a degumming agent. Too much phosphoric acid usage may be redundant in this treatment. As palm oil contains only low amounts of nonhydratable phospholipids as compared to most other oils (16), it is important to optimize the stoichiometric amount of phosphoric acid required. Welsh *et al.* (4) have reported the high capacity of Trisyl for phospholipids and soaps. This experiment confirmed that Trisyl is also capable of adsorbing the phosphoric acid moieties in the oil, as shown by Bogdanor (17). Although increasing the amount of phosphoric acid from 500 to 1000 ppm improved the removal of phosphorus in soybean and sunflower oils (17), this effect was not observed in palm oil because of low phospholipid content in palm oil. The use of Trisyl did not show any significant increase in the iron removal from the oil because iron levels in Trisyl-treated oils were similar to those with bleaching earths alone.

Color stability at 60 and 180°C. The test at 60°C was carried out to assess the long-term storage performance of the oils. Color stability of oils refined with bleaching clays and Trisyl showed higher stability than those of oils refined with bleaching clays alone. With a lower dosage of bleaching clay (for example, with 0.6% clay), the best stability was obtained with 0.18% Trisyl. Clay alone (at 0.6%) showed poor stability (Fig. 1). Similarly, at 0.4% dosages, the best stability was obtained with higher addition of Trisyl products (0.24%). The oils with 0.4% clay

TABLE 3

Use of Trisyl (T) and Bleaching Clay in Palm Oil Refining

	Color		Fe	P	Filtration
Treatments	R	Y	(ppm)	(ppm)	time (s)
1% Clay[a]	2.0	29	0.6	10.8	135
0.8% Clay	2.0	28	0.5	15.1	101
0.8% Clay + 0.06% T	2.0	28	0.4	15.1	105
0.6% Clay	2.9	34	0.5	25.1	115
0.6% Clay + 0.12% T	2.0	31	0.5	14.9	110
0.4% Clay	3.8	62	0.6	36.2	116
0.4% Clay + 0.12% T	2.1	43	0.5	22.9	110
0.4% Clay + 0.18% T	2.1	34	0.6	18.4	108
0.4% Clay + 0.24% T	2.0	28	0.5	16.9	92

[a] WAC Supreme. Sources as in Table 1.

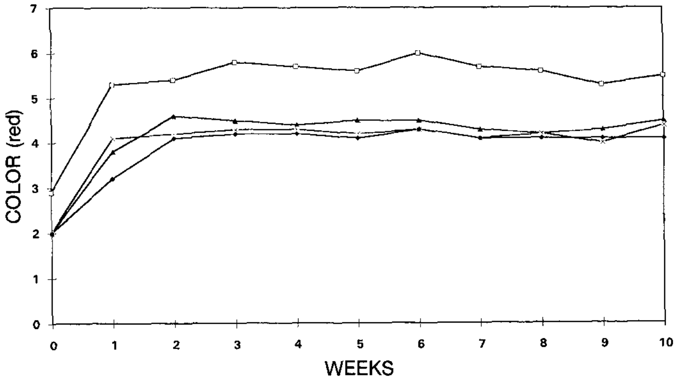

FIG. 1. Color stability of palm oil at 60°C with 0.6% bleaching clay (BC) and Trisyl (T). ▲, 1% BC; □, 0.6% BC; X, 0.6% BC + 0.12 T; ◆, 0.6% BC + 0.18% T. Trisyl from W.R. Grace (Baltimore, MD).

and 0.24% Trisyl showed comparable stability to oils refined with 1.0% clay alone (Fig. 2).

The heat stability test at 180°C shows the color stability of the oil at frying temperatures. The test indicated that acceptable color stability can be obtained with Trisyl (Table 4). The effect was significant, especially when low earth dosage was used. It is quite clear from both tests that a low earth dosage results in instability of color. This could be due to an inadequate amount of active sites available on the earth for removal of all the color bodies present in the oil (18). The mechanism for the improved color stability is not known, but may be due to removal of color components and other polar impurities present in crude oil. In this respect, polar impurities, such as phenolic acids, have been identified as components responsible for color instability at high temperature (13). The results suggest that Trisyl silica has the capability of enhancing the earth's ability to remove color bodies, phosphorus and other minor components that affect the color stability of the oil. This effect is synergistic because silica on its own does not cause any color removal from palm oil (Siew, W.L., unpublished data). Color stability after use of silica in refining oils has not been reported, although better oxidative stability had been reported for silica-treated soybean oils (19).

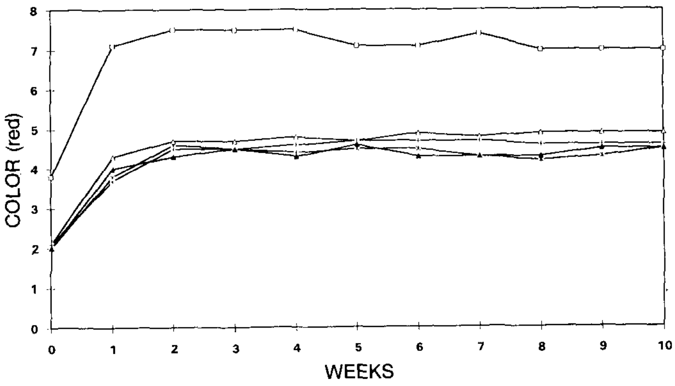

FIG. 2. Color stability of palm oil at 60°C with 0.4% bleaching clay and Trisyl. *, 1% BC; □, 0.4% BC; △, 0.4% BC + 0.12 T; +, 0.4% BC + 0.18% T; ▲, 0.4% BC + 0.24% T. Source information and abbreviations as in Figure 1.

TABLE 4

Heat Stability at 180°C

	Color of refined oil (1-inch cell)			
Treatments	Day 0	Day 1	Day 2	Day 3
1% Clay[a]	0.8	1.6	1.9	1.8
0.8% Clay	0.8	2.0	1.9	2.0
0.8% Clay + 0.06% T	0.8	1.4	2.0	2.0
0.6% Clay	1.0	2.0	2.3	2.8
0.6% Clay + 0.12% T	0.7	1.3	2.0	2.0
0.4% Clay	1.1	2.2	2.1	2.8
0.4% Clay + 0.12% T	0.7	1.5	2.0	2.1
0.4% Clay + 0.18% T	0.6	1.4	1.9	2.0
0.4% Clay + 0.24% T	0.7	1.4	2.0	2.1

[a] WAC Supreme. Sources as in Table 1. T, Trisyl.

Filterability. Filterability is measured as the time taken to filter 100 g of oil through the clay/Trisyl until no oil is visible on the surface. The time was generally lower when Trisyl was incorporated in the clay. The time taken for 1% clay was 135 s, and for 0.4% clay it was 116 s. Introducing silica to the 0.4% earth dosage level at 0.12, 0.18 and 0.24% reduced the filtration time to 110, 108 and 92 s, respectively, as compared to 116 s (Table 3).

The results of this study indicate the possible application of silica-type materials, e.g., Trisyl, in the bleaching step of physical refining of crude palm oil. A lower earth dosage is possible when Trisyl is incorporated at low concentration in the process. This incorporation should be performed with efficient bleaching earths and optimized for high removal of pigments and other trace impurities while retaining good stability in the finished products. The degumming step should be fully evaluated because the amount of degumming agents needed can be reduced. Ease of filtration is an added advantage. As in all processes, an economic evaluation of this alternative procedure should be undertaken, taking into consideration the relative cost of materials and the derived advantages or benefits.

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