Pretreatment of Soybean Oil for Physical Refining: Evaluation of Efficiency of Various Adsorbents in Removing Phospholipids and Pigments

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ABSTRACT

A study was conducted on the efficiency of several adsorbents (Tonsil L80, Tonsil ACC, Fuller's earth, Celite, Kaoline, silicic acid, and Florosil) in removing phospholipids and color bodies from phosphoric acid degummed soybean oil. Best results under the conditions of the experiments were obtained with Tonsil L80 at a 2% concentration and 100 C (reduction in phosphorus content from 17.3 to 3.1 μg/g oil, and in photometric color from 21.6 to 2.4). Removal of phospholipids from the oil by Tonsil L80 and Tonsil ACC follows the Freundlich equation. A colorimetric method for determination of microamounts of phospholipids and a spot test for their quantitative evaluation were also developed.

INTRODUCTION

In recent years there is a trend to replace the alkali neutralization process of free fatty acids with steam refining (1-5). Sullivan (4) pointed out the advantages of physical refining (steam distillation) in reducing operating costs of the process in comparison to chemical refining. When compared with processes of chemical refining, physical refining uses higher amounts of bleaching earth and steam, but savings can be made on equipment, space, time, and labor. Also, oil losses are reduced and fatty acids of higher grade are obtained, and those pollution problems which arise from acidulation of soapstock are eliminated.

Present experience shows that oils cannot be deodorized satisfactorily unless most of the phospholipids have been removed. Soybean oil, rich in phospholipids, poses a special problem in physical refining. In the degummed oil, the nonhydratable phospholipids still remain, which may be subsequently removed in the alkali refining. Hvolby (6) discusses this problem and also suggests other chemical treatments for removal of those phospholipids (e.g., solutions of EDTA, of surfacants). Other authors (2,4,5) recommend acid degumming and pretreatment of the oil with bleaching earths prior to steam distillation.

Abundant literature is available on bleaching earths and their effect on oil pigments (7,8). However, little information is available on the effect of bleaching earths on removing phospholipids from oil.

The present study is confined mainly to evaluation of efficiencies of several adsorbents in removal of phospholipids from degummed soybean oil. Colors of the bleached oils were also determined.

EXPERIMENTAL PROCEDURES

Partly degummed soybean oil was obtained from industry. Two hundred g portions of that oil were degummed in the laboratory at 60 C by a method similar to that described by Evans et al. (9). The oil was placed in a blender and mixed at high speed with 2% water for 4 min. The gums were removed by centrifugation. Phosphoric acid (85%) was then added to the oil (0.05-0.1% v/w) and mixed as above. That step was followed by addition of 2% water and mixing as above. The gums were removed by centrifugation. The oil was washed in a separating funnel with hot (80 C) water until essentially free of acid. The residual water was removed by centrifugation. The oil was then dried in the presence of nitrogen.

Treatment of the degummed oil with different adsorbents (Table I) was conducted in the presence of nitrogen; the oil-adsorbent mixture was agitated with a magnetic stirrer. Fifteen g oil were placed in a 50 ml beaker. The oil was heated to 70 C. The required amount of adsorbent was then added, and the oil was heated to the desired temperature (Table I). After 30 min the oil was cooled to 80 C and the solids were filtered off.

Determination of phospholipids was carried out by a spot test and by colorimetry (see below). Preliminary determination of phospholipid content in the treated oil was carried out by thin layer chromatography (TLC), using visual comparison of the spots with those obtained from standard solution of phospholipids. Controlex (Central Soya) soybean lecithin (minimum 95% acetone insolubles) was used for preparing the standard solutions in chloroform. Amounts of standard solution applied to the TLC plate corresponded to 0.5-2.0 μg phospholipids. Ten μl of the oil solution in chloroform (corresponding to 4 mg oil) were applied to each plate, alternately with the solutions of the standards. Chromatograms were developed in chloroform until the solvent front advanced 7 cm, (a distance sufficient for separation of triglycerides from the phospholipids). Plates were dried and subsequently sprayed with molybdenum blue reagent (10). The phospholipids remained at the origin and were stained blue. Intensities of the spots from the investigated oil were compared to those of the spots from standard solutions of phospholipids, and the phospholipid content in the oil was estimated.

The colorimetric method which was used for phospholipid determination was a modified procedure of Harris and Popat (11). Weight of the oil to be taken for the determination was estimated from preliminary results obtained by the spot test above. The procedure involved charring of 0.2-1 g oil in a 80 ml narrow crucible on an electrical digestion rack, followed by ashing the residue in a muffle furnace at 525 C for a minimum of 2 hr and until free of carbon. The ash was dissolved in 2 ml perchloric acid and 3 ml of distilled water. The crucible was heated on a steam bath for 10 min, while covered with a watch glass. The digest solution was transferred to a 10 ml volumetric flask and the volume adjusted with distilled water. Five ml of the solution were placed in a 20 ml tube followed by 0.5 ml ammonium molybdate solution [5%, w/v of $(NH_4)_6\ Mo_7O_{24} \times 4\ H_2O$ in 5 N H_2SO_4] and 0.5 ml of reducing solution [2 g methol (methyl p-aminophenol sulfate), 20 g of $Na_2SO_3 \cdot 7\ H_2O$ and 300 g $NaHSO_3$, made up to 1 liter with distilled water]. The content of the tube was mixed on a Vortex mixer while the tube was covered with a small beaker. The molybdenum blue color was developed by heating the tube in a boiling water bath for 10 min. The tube was subsequently cooled in an ice bath and brought to room temperature. The extinction was read after 5 min at 820 nm. For calibration, 1-5 μg phosphorus standards were

TABLE I

Phosphorus (or Phospholipid) Content and Photometric Color of Soybean Oil after Treatment with Various Adsorbents

Adsorbent	Adsorbent used (%, w/w)	Temperature (C)	Colorimetric method[a]		Spot test	Photometric[b] color
			Phosphorus (μg/g oil)	Phospholipids (μg/g oil)	Phospholipids (μg/g oil)	
Tonsil L80	2	100	3.1	93	125	2.4
Tonsil L80	2	90	3.3	98	125	3.1
Tonsil L80	2	80	3.5	106	---	3.5
Tonsil L80	1.5	100	5.2	156	175	3.7
Tonsil L80	1	100	8.2	245	250	4.8
Tonsil ACC	2	120	4.2	125	125	2.5
Tonsil ACC[c]	2	100	---	---	125	2.2
Tonsil ACC	1 + 1[d]	100	4.6	137	125	2.2
Tonsil ACC	2	100	3.9	118	125	2.2
Tonsil ACC	2	90	4.2	126	125	3.9
Tonsil ACC	2	80	5.0	150	---	4.4
Tonsil ACC	1.5	100	5.5	164	200	3.9
Tonsil ACC	1	100	7.7	230	250	6.7
Fuller's earth[c]	2	120	8.9	266	250	12.0
Fuller's earth	2	120	12.3	370	350	16.3
Fuller's earth	2	100	16.3	490	400	21.1
Fuller's earth[c]	1 + 1[d]	120	---	---	250	17.2
Fuller's earth[c]	1.5	120	10.4	312	---	16.4
Fuller's earth[c]	1	120	11.8	355	---	20.3
Kaoline[c]	2	120	8.8	264	250	18.1
Kaoline	2	100	13.7	410	350	20.5
Celite[c]	2	120	8.5	256	250	13.6
Celite	2	100	13.3	400	300	18.9
Silicic acid[c]	2	100	6.3	190	250	20.8
Florosil[c]	5	120	5.3	160	200	21.6
None	---	---	17.3	520	---	21.6

[a]Factor 30 was used for conversion of phosphorus to phospholipids (12).
[b]Calculated according to AOCS Official Method Cc 13c-50 (13).
[c]The adsorbent was dried at 120 C for 2 hr before use.
[d]Two increments of 1% adsorbent (dual stage treatment of the oil).

carried simultaneously through the same procedure. (Beer's law was valid in that range). One μg phosphorus in 6 ml assay solution gave an extinction of ca. 0.1. The factor 30 was used for conversion of phosphorus to phospholipids (12).

The photometric color of the oil was determined according to AOCS Official Method Cc 13c-50, with a combined Gilford-Beckman Spectrophotometer (13).

RESULTS AND DISCUSSION

One of the difficulties encountered in this study was the determination of microamounts of phospholipids in edible oils. To overcome this, a rapid spot test for phospholipids was developed, and the colorimetric method of Harris and Popat (11) was modified to increase its sensitivity. There was a good agreement between the results obtained for phospholipid content in the oil by the spot test and the colorimetric method, mainly in the lower range [125-250 μg phospholipids/g oil (Table I)]. The spot test served for preliminary evaluation of efficiencies of the investigated adsorbents.

Degumming of the oil with different amounts of water and with either 0.1 or 0.05% (v/w) phosphoric acid reduced the phospholipid content from 5,100 to 520 μg/g phospholipids (see Experimental). It seems that slight changes in the procedures of degumming did not significantly affect the concentration of the residual phospholipids (ca.500 μg/g). That results was in agreement with the findings of Hvolby (6). The above concentration of phospholipids was still too high for an oil to be satisfactorily processed by physical refining.

Treatment with adsorbents was therefore tried to reduce further the phospholipids concentration in the oil. Such treatment gave satisfactory results as can be seen from Table I. Tonsil L80 and Tonsil ACC were found to have the highest capacity for both adsorbing residual phospholipids and for removing the coloring substances from the oil. Best performance was obtained for Tonsil L80 at a 2% concentration and at 100 C (93 μg of residual phospholipids per g of oil). That temperature and concentration were also optimal for Tonsil ACC (118 μg of residual phospholipids per g of oil). The values obtained for phospholipid content and photometric color of the degummed oils treated by us with either 2% Tonsil L80 or Tonsil ACC at 90 and 100 C were similar to those reported by Ohlson and Svensson (14) for neutralized and bleached oils, and the values obtained for phospholipid content were in the range reported by Evans et al. (9). These results (max 150 μg phospholipids/g oil) also meet requirements of the local plants. However, when the concentration of the Tonsil L80 was reduced from 2% to 1.5% or 1%, the results for phospholipid content were significantly worse (93 μg/g at 2% clay vs. 156 and 245 μg/g oil at 1.5% and 1% clay, respectively).

One experiment was performed at 80 C with Tonsil L80 at a 2% concentration in the oil, while all other conditions were kept as described above, to see if that earth is active enough at a temperature lower than that used in the other experiments (Table I). The result obtained was satisfactory: 106 μg phospholipids were left per g of oil as compared to 93 μg/g oil at 100 C. The photometric color of the oil treated at 80 C, however, was higher than that of the oil treated at 100 C (3.5 and 2.4, respectively). But for Tonsil ACC at a 2% concentration lowering, the temperature of adsorption from 100 C to 80 C reduced its adsorption capacity for phospholipids (150 vs. 118 μg phospholipids/g oil were left when the treatment took place at 80 and 100 C, respectively).

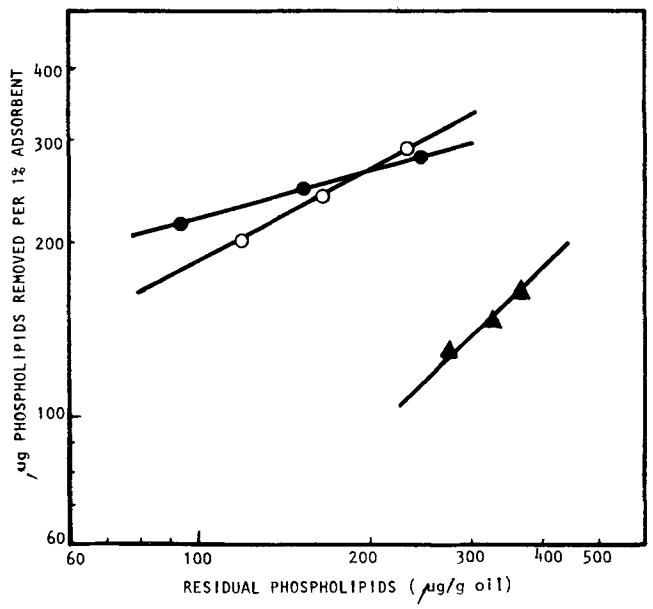

FIG. 1. Adsorption isotherms of phospholipids for Tonsil L80 (solid circles) and Tonsil ACC (open circles), at 100 C; and for Fuller's earth (triangles), at 120 C.

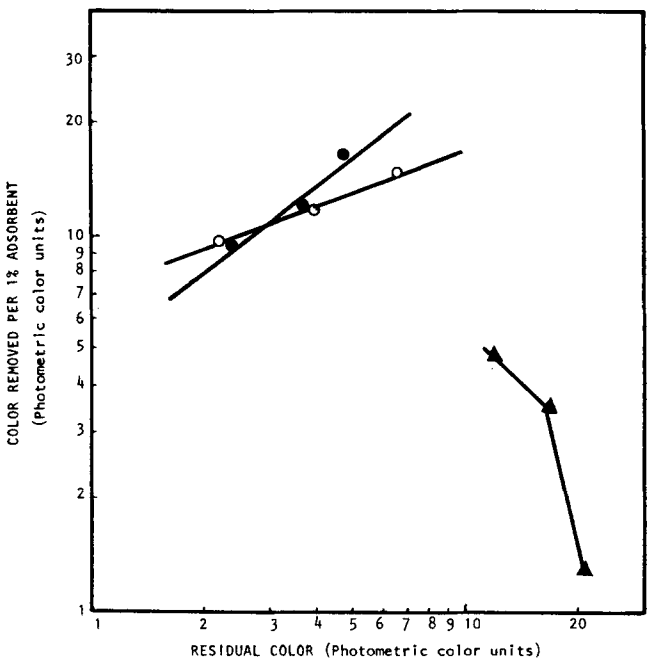

FIG. 2. Adsorption isotherms of color bodies for Tonsil L80 (solid circles) and Tonsil ACC (open circles) at 100 C; and for Fuller's earth (triangles) at 120 C.

With regard to the other adsorbents listed in Table I, bleaching powers of silicic acid and Florosil under the condition tested were very low and much worse than their abilities to adsorb phospholipids. Fuller's earth, Celite, and Kaoline which were activated before use (Table I, footnote c) showed better performance at an oil temperature of 120 C than at 100 C. However, the results obtained for both phospholipid content and photometric color after treatment with these clays were poor in comparison with those obtained with Tonsil clays. No attempt was made to increase concentrations of Fuller's earth, Celite, and Kaoline above 2%, as that would increase oil losses to an impractical level.

A comparison was made between single vs. dual stage treatment of the oil with Tonsil ACC at 100 C and with Fuller's earth at 120 C; 1 x 2% or 2 x 1% clay were used with the treated oil (Table I). It was concluded that the dual stage treatment showed no advantage.

It is interesting to note that, as in the case of color substances, removal of phospholipids from the oil by adsorption on Tonsil clays and Fuller's earth followed Freundlich's adsorption equation (15): $x/m = Kc^n$ (or $\log x/m = K + n\log c$); where x is the amount of substance adsorbed, m the amount of adsorbent, c is the amount of residual substance, and K and n are constants. The adsorption isotherms for phospholipids by Tonsil clays for the data at 100 C and for Fuller's earth at 120 C are presented in Figure 1. The following equations have been described for these earths (using linear regression):

$$\text{Tonsil L80: } x/m = 66.6\ c^{0.26}$$
$$\text{Tonsil ACC: } x/m = 14.5\ c^{0.55}$$
$$\text{Fuller's earth: } x/m = 0.8 \times c^{0.91}$$

The equations were derived only for Tonsil clays (best adsorbents for phospholipids) and also for Fuller's earth (which performed quite poorly), for comparison. K calculated for Fuller's earth was found to be extremely small as compared with K's of the Tonsil clays (0.8 vs. 66.5 and 14.5); that was not surprising in view of the poor adsorbtivity of that earth for phospholipids.

For the two Tonsil clays that were investigated in this study, the larger K of Tonsil L80 (66.6) and the smaller n (0.26), vs. K = 14.5 and n = 0.55 for Tonsil ACC, indicate that the first clay may perform better, and through its application, phospholipid content in oil can be reduced to a lower level.

Figure 2 presents adsorption isotherms derived for the color bleaching activities of Tonsil clays and Fuller's earth. The following Freundlich equations have been derived for the two investigated Tonsil clays:

$$\text{Tonsil L80: } x/m = 4.7\ c^{0.78}$$
$$\text{Tonsil ACC: } x/m = 7.2\ c^{0.38}$$

It also may be seen from Figure 2 that under the conditions of this study, Fuller's earth as bleaching agent does not obey Freundlich's equation. A similar phenomenon was also reported by King and Wharton (16) who explained the shape of the curve by the darkening of the oil due to the catalytic effect of the adsorbent when the latter was used at too low concentrations. When bleaching was carried out with 1% and 1.5% Fuller's earth, the shape of the adsorption isotherm of Fuller's earth was influenced mainly by the anomalous increase in absorption at 550 nm [one of the parameters for calculation of photometric color (13)].

It may be seen from this study that activated clays (Tonsil clays) have higher adsorbing capacities than a natural earth (Fuller's earth) for both color bodies and phospholipids.

It should be stressed that behavior of the activated clays (Tonsil L80 and Tonsil ACC) is not the same when the adsorbables are phospholipids or color bodies (see the derived Freundlich equations above, and Figs. 1 and 2). It has been pointed out above that Tonsil L80 is a better adsorbent for phospholipids than Tonsil ACC. However, as an adsorbent of color bodies, Tonsil ACC is more efficient [it has a larger K than Tonsil L80 (7.2 vs. 4.7), and a smaller n (0.38 vs. 0.78)]; nevertheless, the photometric color of the oil which has been treated with Tonsil L80 was sufficiently low (2.4).

The acceptable phospholipid levels in the treated oil were between 93-164 µg/g oil, and the residual photometric colors of those oils were 2.2-3.9 (Table I). Consideration of Figure 1 would reveal that reduction in phospholipid concentration was achieved to the left of the intersection point of the Tonsil L80 and Tonsil ACC isotherms, and in the

region in which Tonsil L80 undoubtedly adsorbs phospholipids better than Tonsil ACC.

It may be seen from Figure 2, that the residual colors of the oils which had been treated with the Tonsils lie near and around the intersection point of the Tonsil's isotherms; it seems of no difference therefore which of the Tonsils (L80 or ACC) will be used for removal of the color bodies. It appears that when both phospholipids and color bodies should be removed from the oil, Tonsil L80 would be preferred.

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