Chlorophyll Removal During Earth Bleaching of Soybean Oil

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As is generally known, the bleaching of soybean oil for hydrogenated shortenings is more complicated and difficult to control than is that of cottonseed oil. This is because the treatment of the latter stock from a color standpoint is principally one of reducing the yellow and red pigments whereas the bleaching of soybean oil is governed largely by its chlorophyll content. Unless the chlorophyll content of hydrogenated fats containing substantial amounts of soybean oil is lowered sufficiently, the finished product will appear grey with a tendency toward green.

The yellow and red pigments in soybean oil appear to be reduced at a greater rate during hydrogenation than in cottonseed oil, and considerably faster than its chlorophyll content. The latter aspect complicates the bleaching of soybean oil as it necessitates knowing the chlorophyll content prior to hardening for the most successful operation.

The bleaching of soybean stock for salad oil is considered much less complicated than of that intended for hydrogenated shortenings because of the darker Lovibond color of the former which has a masking effect on the green.

In general, the Lovibond color system has been found quite adequate for the processing control of cottonseed oils. As those associated with the industry appreciate, however, this is not true with soybean oils. A considerable number of tests have been carried out in our laboratories relating to the estimation of chlorophyll and its removal from soya stock, and this paper reviews some of the more important practical aspects of this work. The discussion deals principally with the bleaching operation, but the influence of the other processing steps, that is, refining, hydrogenation, and deodorization, are also considered.

Our results show that substantially all of the chlorophyll in soybean oil is of the type A or its derivatives. This observation has been used in developing the following method for calculating the chlorophyll density. Furthermore, the assumption is made that the changes which the chlorophyllic bodies undergo during processing have no practical influence on the spectrophotometric evaluation.

All the chlorophyll figures given herein were determined with a Beckman spectrophotometer, employing a slit width of 0.05 mm. and a 10 cm. cell. The concentrations were then calculated, employing a formula derived from Beer's law as described by Comar (1) and modified by our laboratory as follows:

$$C = \frac{\text{Log}_{10}\dfrac{1}{T_1} - \text{Log}_{10}\dfrac{1}{T_2} \times 10^6}{92 \times \text{Cell Length} \times \text{Dilution Factor}}$$

where C = Concentration in micrograms per liter as chlorophyll A.

T_1 = Transmission factor at about 6600Å (Minimum).

T_2 = Transmission factor at about 6400Å (Maximum).

$$\text{Transmission Factor} = \frac{\%\ \text{Transmission}}{100}.$$

Cell Length is expressed in centimeters.

Dilution Factor is the fractional concentration of sample in solution of oil and solvent.

The constant 92 is the difference in the maximum specific absorption coefficient at 6600Å and minimum absorption coefficient at 6425Å of pure chlorophyll A.

The Effect of Refining

Normally, crude soybean oil contains about 1,500 micrograms of chlorophyll per liter. One would expect stock similar to that produced several years ago from green beans to have a much higher concentration. It may be recalled that the green beans during the season in question resulted as a consequence of a severe early frost.

Ordinary caustic-refining reduces the chlorophyll by about 25%, laboratory treatment being somewhat more effective in this respect than plant centrifugal operation, as may be seen from the following results.

TABLE NO. 1

The Effect of Caustic-Refining on the Chlorophyll Content of Crude Soybean Oil—μg./Liter

	Crude Oil	Plant Centrifugally Refined Oil	Laboratory Batch Refined Oil
Oil A	1130	880	795
Oil B	1123	885	847
Oil C	1078	847	804

As might be expected, our data also indicate that the higher the chlorophyll content of the refined stock, the greater the amount of bleaching earth generally required to reduce it to a level so as to result in satisfactory finished products.

The Effect of Hydrogenation

The hardening of soybean oil to a shortening consistency at moderate temperatures with ordinary catalysts appears to reduce the chlorophyll content by about two-thirds. This seems to be the case with both heavily as well as lightly bleached stocks. For instance, a well-bleached specimen having a chlorophyll concentration of only 15 μg. per liter contained 5 units after hardening to approximately 75 iodine value. Similarly, an underbleached sample with 546 μg. per liter had 180 units at 74.2 iodine value, as indicated in Table No. 2.

It may be seen from the results that substantially complete hardening reduces about 95% of the chlorophyll. The yellow and red pigments were also practically eliminated, the visual colors passing through the various shades of browns, yellows, yellowish-greens and greens to colorless during hardening to stearine.

The Effect of Deodorization

The deodorization of hydrogenated soybean oil has little, if any, influence on the chlorophyll content,

TABLE NO. 2

The Effect of Hydrogenation on the Color and Chlorophyll Content of Lightly Bleached Refined Soybean Oil

	Iodine Value	Visual Color	Lovibond Color	Chlorophyll µg./Liter
Refined Oil	133.6	Brown	70Y-11.0R	1,295
Bleached	133.0	Lt. Brown	70Y-10.0R	546
Hardened Sample 1	110.5	Yellowish	70Y-4.5R	256
Sample 2	74.2	Greenish Yellow	70Y-2.9R	180
Sample 3	55.8	Lt. Green	70Y-1.7R	108
Sample 4	33.3	V. L. Green	8Y-0.5R	65
Sample 5	2.3	Almost Colorless	4Y-0.5R	40*

* Approximated graphically. Oil was too hard to determine spectrophotometrically.

providing the concentration is within practical limits. This operation may, however, appear to increase the chlorophyll content, but this apparent increase in green is due to the removal of the yellow and red pigments.

The Effect of Bleaching

As mentioned, hydrogenation of soybean oil to a shortening consistency usually reduces the chlorophyll content by a more or less uniform percentage whereas ordinary deodorization has no influence in this respect. It follows, therefore, that the chlorophyll content of the finished product must be controlled by the bleaching and/or postbleaching steps. The remarks in this paper are confined to the bleaching prior to hardening.

Bleaching with earth adsorbents still remains the most effective means of removing chlorophyll from soybean oil. Hinners *et al.*, of our laboratories, showed in their evaluation of bleaching earths (2) that activated materials adsorb chlorophyll very efficiently and that the adsorptive capacity of such a material for this pigment is directly proportional to the acidity of the earth. They likewise pointed out that chlorophyll is adsorbed in accordance with Freundlich's equation (3, 4) which states that the ratio of the amount of pigment adsorbed per unit of adsorbent to the amount of residual dissolved pigment raised to the power "n" (earth characteristic factor) is constant. In addition, they demonstrated that the Lovibond color determination cannot be used to measure the adsorptive capacity of various earths for chlorophyll. For example, a sample of soybean oil bleached to the same Lovibond color with different earths varied widely in chlorophyll content. The foregoing statements serve to illustrate the complexity of the problems encountered in the bleaching of soybean oil.

Tests carried out in the laboratory to determine the influence of varying times, temperatures, and pressures on the chlorophyll removal have indicated the following:

Time. Increased times at bleaching temperature appear to be of no material benefit. In some cases, indications are that the efficiency of the chlorophyll removal tends to fall off with longer bleaching periods, as may be seen from the results in Tables No. 3 and No. 4. These data also show that chlorophyll removal is quite rapid, the maximum adsorption being obtained during the heating-up period or shortly thereafter.

TABLE NO. 3

The Effect of Varying Times and Amounts of Activated Adsorbents on the Chlorophyll Content of Refined Soybean Oil Bleached at 125°C. and 55 mm. Hg Pressure

	Chlorophyll Content µg. per Liter		
	Bleaching Time—Minutes		
	0	15	30
Original Unbleached Oil	925	......	......
Oil Bleached With			
1. 0.75% Earth X	82	98	104
2. 0.75% Earth Y	78	92	108
3. 0.75% Earth X + 0.25% Carbon S	56	78	78
4. 0.75% Earth Y + 0.25% Carbon S	63	83	85
5. 0.25% Earth X + 0.25% Carbon S	74	89	85
6. 0.25% Earth Y + 0.25% Carbon S	80	77	93
7. 0.25% Carbon S	238	191	166

Temperature. The temperature appears to exert no consistent or practical influence on the chlorophyll removal throughout the range covered, as may be seen from the results given in Table No. 4.

Pressure. Pressure variations within the range of 10 mm. to 55 mm. also seem to have little, if any, practical influence on the chlorophyll removal. This is likewise indicated by the data in Table No. 4.

In the previously mentioned article by Hinners, there appeared isotherms defining the adsorption power of various earths with the same soybean oil. These were developed on the basis of the logarithmic form of Freundlich's equation, that is,

$$\text{Log}\,\frac{x}{m} = \text{Log}\,k + n\,\text{Log}\,c.$$

where x = Amount of chlorophyll adsorbed.
m = Amount of adsorbent.
c = Amount of residual chlorophyll.
k and n are constants.

TABLE NO. 4

The Effect of Varying Times, Temperatures, and Pressures on the Adsorption of Chlorophyll From Refined Soybean Oil

	Bleaching Time Mins. at Temp.	Chlorophyll Content, µg./Liter, After Bleaching at:								
		Temperature								
		100°C.			125°C.			150°C.		
		Pressure—mm. Hg								
		10	25	55	10	25	55	10	25	55
Extracted Oil Bleached With 0.5% Activated Earth	0	209	135	132	95	78	98	118	95	91
	15	91	88	85	80	101	90	87	91	85
	30	100	89	100	78	102	84	87	78	87
Expeller Oil Bleached With 1% Activated Earth	0	132	50	63	82	48	39	58	68	63
	15	76	61	60	98	63	74	65	68	70
	30	78	80	54	102	63	78	65	73	67

Isotherms have likewise been developed to show the adsorptive power of a given earth for the chlorophyll removal from different samples of soybean oil. These are given in Fig. 1.

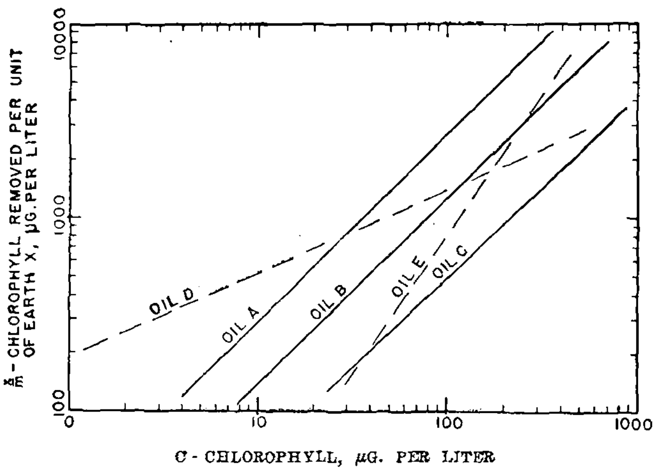

FIG. 1. Chlorophyll adsorption isotherms for various soybean oils bleached with activated earth.

When the value of n (the slope of the isotherms) is the same, the adsorptive capacity of the earth for the chlorophyll is inversely proportional to the constant k. It follows, therefore, that the amount of earth necessary to reduce the chlorophyll content of an unknown sample to a given level can best be determined by analyzing the stock for chlorophyll before and after bleaching it with one or more different amounts of earth. Two points are necessary except when the slope of the isotherm is known. In the latter case, only one bleach evaluation should be sufficient.

Although many soybean oils conform to a type and hence give absorption isotherms with practically the same slope (Oils A, B, and C, Fig. 1), there are noteworthy exceptions, as illustrated by D and E. This further emphasizes the difficulties of controlling the bleaching of this stock.

Discussion

Our observations with respect to the effects of refining and hydrogenation seem somewhat at variance with previous findings. According to the literature (4, 5) chlorophyll is very stable to caustic, whereas the results given herein show that as much as 25% of the chlorophyll present in crude soybean oil is removed by refining with alkali. This apparent anomaly may be explained by the possibility that although pure chlorophyll is stabilized by caustic, it or its derivatives may be more soluble in the soap stock and thus reduced during refining. No attempts have been made to investigate this point.

Bailey (4) states that the green color of oils is not reduced by hydrogenation but appears to be accentuated by the removal of the reds and yellows. Visual observation of the green color of a partially hydrogenated soybean oil may lead to such a conclusion but as is shown in Table No. 2, it has been found that the chlorophyll content is reduced appreciably even on partial hydrogenation and that when the oil is completely hardened, the chlorophyll is almost entirely destroyed so that the product appears green-free to the eye.

No attempt has been made to investigate the mechanism of chlorophyll removal or to explain the shift in the absorption band on hydrogenation. Crude and refined as well as bleached soybean oils exhibit an absorption maxima at 6600-6700Å but on hydrogenation, the absorption band shifts to 6400Å corresponding to a conversion of chlorophyll A to chlorophyll B. Since hydrogenation shifts the absorption band to the B position, it is possible that the theoretical absorption maxima are also changed, in which case the calculations as chlorophyll A may underestimate the chlorophyll content of hydrogenated oil.

This possibility is of little commercial importance, however, because the visual greenness of the oil at any stage of hardening appears to correlate fairly well with its chlorophyll density. Furthermore, the concentration of chlorophyll in a green-free or satisfactory sample is so low that the significance of an error in hardened stocks is of no practical concern.

Summary

A spectrophotometric procedure for determining and calculating the chlorophyll content of unhardened as well as hardened soybean oil has been given. This procedure has proven satisfactory from a practical standpoint for controlling the greenness imparted to finished shortenings by chlorophyll. The influence of the refining, hydrogenation and deodorization operations on the chlorophyll content has also been reviewed.

Isotherms have also been presented which illustrate the complexity encountered in bleaching soybean oil with respect to chlorophyll.

Acknowledgments

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