This rise is not significant with $SP_2$ and $DX_2$, and thus the assumption made earlier in the calculations that all dienes present in these fractions are completely estimated by the ultraviolet absorption method is valid. With the the fraction $DX_3$ the rise is not serious, and the total isomerizable diene (sum of *cis,cis* and *cis,trans*), about 2.9%, agrees admirably with the total diene calculated from iodine value about 2.9% (Table I), further supporting the assumption made under calculations that all dienes present are estimated by the ultraviolet absorption method. In interpreting the results with $SP_5$, the fact that it was not recrystallized must be borne in mind. If the *trans,trans* 9,12-isomer was present, it must have appeared in either of these fractions (cryst $-50$ or cryst $-70°C.$) beause of its higher melting point 28°C. (11). The almost constant $k_{232}$ value, even after 4–5 hrs. of isomerization with these fractions, shows that this isomer, even if present, is negligible. With $SP_4$ and $DX_4$ the increase in the values is considerable, revealing the presence of isomerizable geometric isomers of linoleic acid. With a synthetic mixture of linoleic and linolelaidic (*trans* 9, *trans* 12) acids Jackson *et al.* (11) noted that the values increased even after 150 min. of isomerization and became steady beyond 4.5 hrs. In our study we note that, with $SP_4$ and $DX_4$, the values at the end of 150 min. and 4.5 hrs. are about the same. Therefore it is concluded that no *trans,trans* isomer is present and the only conjugatable isomer present is of the *cis,trans* or *trans,cis* type. The contents of *cis,cis* and *cis,trans* diene were calculated on this basis. It is noted that the values for linoleic acid by this calculation are higher than that by the tetrabromide method. From the empirical nature of the $k_{232}$ m$\mu$ values for the *cis,trans* isomers of linoleic acid, as pointed out by Jackson *et al.* (11), this is about the best agreement that can be expected. However, for the content of linoleic acid, the tetrabromide method is the one to be relied upon as this is a direct estimation. A comparison of the proportions of total *trans* ($SP_4$ - 42.9%, $DX_4$ - 43.8) and that of *cis,trans* ($SP_4$ - 18.0, $DX_4$ - 22.4) shows that considerable amounts (24.9, 21.4) of isolated *cis,trans* dienes are present. Placing reliance on the tetrabromide method for estimation of linoleic acid, it can be concluded that for all practical purposes these isomers, 9,12 *cis,trans* or *trans,cis* and isolated *cis,trans* are present in about equal amounts.

## Summary

A scheme is described to separate the fatty acids of shortenings and margarines into four fractions, the final filtrate of which contains most of the polyunsaturated acids. The nature of the unsaturated acids in these fractions is discussed. It is observed that these fats contain 25–40% of *trans* monoethenoic acids and 2–8% of linoleic acid and considerable proportions of both 9,12-*cis,trans* or *trans,cis* and isolated *cis,trans* isomers of linoleic acid.

## Acknowledgment

Our thanks are due to P. F. Urone and H. K. Anders of the Industrial Hygiene Division of the Department of Health, State of Ohio, for the use of their infrared spectrophotometer.

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[Received February 6, 1956]

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# Refining Cottonseed Oil at High Rates of Shear[1]

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A LARGE PERCENTAGE of the cottonseed oil being produced does not readily refine and bleach to the light color demanded in present-day shortening and other edible oil products. Any one or several of a number of factors may be responsible for a given oil having an unsatisfactory color after processing. Adverse environmental conditions during the growing of the cottonseed may result in immature or damaged seed being harvested. Prolonged storage or storage at a relatively high temperature or storage of seed having a high moisture content may be responsible. Finally the conditions under which an oil is extracted from the seed and stored may have an adverse effect on the ease with which color bodies can be subsequently removed. It is certain that cottonseed oils which are difficult to process to a light color by standard methods will continue to be produced.

It has been demonstrated that re-refining, the accepted method of treating off-color cottonseed oils,

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[1] Presented at the 28th fall meeting of the American Oil Chemists' Society, Minneapolis, Minn., Oct. 11–13, 1954.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

TABLE I

Comparison of Ordinary and High-Shear Refining[a]

| Oil No. | Free fatty acids, % | Ordinary refining | | | High-shear refining | | |
|---|---|---|---|---|---|---|---|
| | | Color, Lovibond red units | | Refining loss, % | Color, Lovibond red units | | Refining loss, % |
| | | Refined | Bleached | | Refined | Bleached | |
| 1 | 1.4 | 24.5 | 8.4 | 6.2 | 14.8 | 5.6 | 6.7 |
| 2 | 1.1 | 5.5 | 1.2 | 5.7 | 5.4 | 1.2 | 5.2 |
| 3[b] | 6.1 | 23.4 | 13.1 | 17.3 | 15.5 | 9.2 | 20.4 |
| 4[b, c] | 5.3 | 12.2 | 4.1[d] | 18.4 | 11.5 | 3.5[d] | 26.9 |
| 5[b] | 0.8 | 7.4 | 2.3[d] | 7.4 | 5.7 | 1.3[d] | 6.1 |
| 6 | 1.3 | 5.6 | 1.6 | 4.4 | 5.2 | 1.3 | 4.8 |
| 7 | 5.2 | 32.0 | 26.0 | 12.6 | 9.5 | 3.3 | 14.7 |
| 8[b] | 8.3 | 19.9 | 10.2 | 22.8 | 17.4 | 7.5 | 24.2 |
| 9[b] | 1.6 | 9.6 | 4.7[d] | 9.9 | 7.8 | 3.2[d] | 10.8 |
| 10 | 5.2 | 10.9 | 3.9 | 12.1 | 10.3 | 3.5 | 16.1 |

[a] Unless otherwise noted, all samples were refined with 20°Bé. caustic soda solution in amount sufficient to neutralize free fatty acids and supply 0.5% of excess caustic soda; high-shear agitation, when employed, was for 15 min. at 1,720 r.p.m. All colors were determined in the presence of 35 Lovibond yellow units; and the refined oils were bleached according to A.O.C.S. method.

[b] Strength of caustic soda solution was 26°Bé. for these oils.

[c] Subjected to high-shear agitation for 10 min.

[d] Bleached with 6% of neutral, activated clay.

can be made more effective through the use of high-shear agitation (3). Also the use of high-shear agitation during the wash with caustic soda in the continuous soda ash process of refining results in a finished oil of much lighter color (2). The term "high-shear," as used here, means the efficient mixing of the oil and caustic soda solution accompanied by a violent shearing of the elements of the mixture. These actions are induced by an impeller revolving in a well-baffled vessel and at a rate far above that used in ordinary refining. In the earlier work on re-refining at high shear some of the mixing and shearing was sufficient to increase the temperature of the mixture at a rate of 0.8 Centigrade degree per minute.

In re-refining cottonseed oil it was believed that the use of high shear made it possible to bring the acidic color bodies in the oil into intimate contact with the aqueous solution of caustic soda before the alkalinity of the latter was reduced through reaction with the oil.

Because once-refined oil contains practically no surface-active agents or free fatty acids which can readily be converted into soaps, high shear apparently was a substitute for emulsifiers and was found to be quite effective in reducing the amount of color bodies in the oil.

It might be expected that the use of high shear would be of no advantage in the refining of crude cottonseed oil. When a solution of caustic soda is mixed with the crude oil, a fine water-in-oil emulsion forms immediately; very little agitation is required. Violent agitation of such an emulsion might promote the saponification of neutral oil and the occlusion of excessive amounts of neutral oil in the aqueous phase. However, on the basis of experimental work, the indicated possibilities were shown to be unsupported in fact (4). The present article will show that the use of high shear is desirable in the refining of crude cottonseed oil with caustic soda.

## Procedure and Materials

The refining tests involving high shear were carried out, insofar as possible, according to the A.O.C.S. cup method for hydraulic-pressed cottonseed oil (1), except that changes were made in the amounts and strengths of the caustic soda solutions which were used and that mixing at a high rate of shear for various lengths of time was substituted for the standard 15 min. of mixing at 250 r.p.m. The mixing at high shear was carried out in the stainless steel apparatus previously described (3) in connection with the high-shear re-refining of cottonseed oil. The impeller of the type used to reduce and disperse solids in slurries was used in all of the tests.

For purposes of comparison refining tests were made as described above except that the standard 15 min. of mixing at 250 r.p.m. was used instead of mixing at high shear.

The refined oils were bleached according to the official A.O.C.S. method for cottonseed oil, except that in several instances the amount and type of clay used was changed.

The crude oils used in the experiments were samples obtained from several mills and refineries in the South and Southwest. The history of the samples generally was not known. It is believed however that the oils in nearly every instance were either of the screw-pressed or hydraulic-pressed type.

## Results and Discussions

The refining losses and colors obtained when the various crude oils were refined with and without the use of high-shear agitation are recorded in Table I.

From the data recorded in the table it is evident that in every case the use of high shear resulted in the refined oil having a Lovibond color lower than that obtained without the use of high shear. In most instances the improvement was slight, but in several of these marked improvement could hardly be expected. When the Lovibond red color of a refined cottonseed oil is reduced below about 9 units by ordinary refining, not much can be done to improve the removal of color by changes in the refining technique; and generally such oils present no color problem. On the other hand, oils which ordinarily refine to a red color appreciably greater than 9 units do present a color problem. Apparently a good proportion of these latter oils respond to a marked extent to high-shear refining. Of the six oils (Nos. 1, 3, 4, 7, 8, and 10) having a red color of 10 units or higher after ordinary refining, three (Nos. 1, 3, and 7) improved to a marked extent when high shear was employed.

The improvement in the color of refined oils through the use of high shear is still evident in the oils after bleaching, according to the data in Table I. Even an oil like No. 5, which refines by the ordinary method to a low and entirely acceptable color, has a significantly better bleach color when high-shear agitation is used in place of ordinary agitation in the

TABLE II

Effect of Operating Variables on Color of Oil Obtained on High-Shear Refining Crude Oil No. 1[a]

| Temperature, °C. | Color, Lovibond red units | Strength of caustic, °Bé. | Color, Lovibond red units | Excess caustic, % | Color, Lovibond red units | Time at high shear, min. | Color, Lovibond red units | High-shear agitation, r.p.m. | Color, Lovibond red units |
|---|---|---|---|---|---|---|---|---|---|
| 20 | 10.7 | 8 | >32 | 0.1 | >32 | 2.5 | 15.1 | 370 | 20.6 |
| 40 | 12.8 | 14 | >32 | 0.3 | 22.0 | 10.0 | 15.1 | 650 | 14.2 |
| 50 | 15.1 | 20 | 15.1 | 0.5 | 15.1 | 30.0 | 14.7 | 1720 | 15.1 |
| 65 | 17.7 | 26 | 11.6 | 0.9 | 12.5 | 50.0 | 13.7 | 2940 | 12.6 |
|  |  |  |  |  |  |  |  | 5100 | 13.7 |
|  |  | 30 | 11.3 |  |  |  |  |  |  |

[a] All colors were determined in the presence of 35 Lovibond yellow units. Unless otherwise noted, all refinings were carried out using 20°Bé. lye in an amount to provide an excess of 0.5% of solid caustic soda, and high-shear agitation at 1,720 r.p.m. was employed for 10 min. at room temperature.

refining process. Such a substitution results in lowering the bleach color from 2.3 to 1.3 Lovibond red units.

The substitution of high-shear agitation for ordinary agitation generally increases the refining loss though these increases are mostly moderate. In two instances there was an actual decrease in refining loss. It is possible that the increases shown were caused by air being trapped in the soapstock in the course of the high-shear refining, thereby making it difficult to separate cleanly the soapstock from the oil. There may not be any difference in losses when the two procedures are carried out in suitable equipment on a plant scale.

To establish the effect of the operating variables on the color of the refined oils obtained by the high-shear method, a number of experimental tests were made. Typical results obtained with one of the oils (No. 1) are recorded in Table II.

It is evident from the table that the amount of color in the refined oil decreased as the temperature decreased and the strength and amount of the caustic soda solution increased. Ordinary changes in the magnitude of each of these variables produced relatively large differences in the color. Increasing the time at high shear definitely lowered the color of the refined oil but by amounts so small that prolonged agitation probably would not be justified.

The effect of degree or rate of high shear agitation appears to be somewhat erratic, which may be attributed in part to the fact that this variable is complex and cannot be clearly defined in terms of revolutions per minute. However it probably can be concluded that increasing the rate of shear improves the color of the refined oil until a rate is reached beyond which further increases are without effect.

There is an apparent discrepancy in Table II. According to the data on the effect of temperature, a refining at room temperature (about 26°C.) would have produced a refined oil having a red color of about 11 Lovibond units, which is somewhat lower than that indicated for comparable conditions in the remainder of the table. The only explanation that can be made is that the effect of temperature was determined at a different time and by a different operator.

To obtain an indication of the type of color bodies most affected by high-shear refining, spectra were obtained in the near ultraviolet and visible regions (300–700 mμ) for Oil No. 3 and the several processed oils derived from it and represented in Table I. The spectral measurements were made in iso-octane solutions, using a Cory recording spectrophotometer. Absorbtivities were calculated from the data and were used to establish the relative quantities of four types of color bodies found in cottonseed oil. In establishing these quantities, it was assumed that in the region of maximum absorption for each type of color body the amount of absorption of the other color bodies present was negligible. The relative quantities which were established are recorded in Table III.

TABLE III

Relative Quantities of Color Bodies in Crude Oil No. 3 after Processing[a]

| Oil | Content of color bodies[b] |  |  |  |
|---|---|---|---|---|
|  | Gossypol-like (400 mμ) | Carotenoid (450 mμ) | Gossypurpurin (560 mμ) | Pheophytin (670 mμ) |
| Crude | 100 | 100 | 100 | 100 |
| Ordinary refined | 10 | 14 | 6 | 18 |
| Ordinary refined and bleached | 8 | 15 | 9 | 16 |
| High-shear refined | 4 | 7 | 8 | 13 |
| High-shear refined and bleached | 3 | 6 | 5 | 12 |

[a] Processed samples are those represented in Table I.

[b] Assuming the amount in the original crude oil to be 100.

From the values given in the table there is an indication that high-shear refining is more effective than ordinary refining in eliminating gossypol-like color bodies and yellow, nonacidic carotenoids while this is not entirely true for gossypurpurin and pheophytin. These results appear to be consistent because similar ones were obtained with Oil No. 8. However the differences are so small and the color system in cottonseed oils is so complex that at the present time no detailed explanations can be given for the differences observed.

## Summary

Ten crude cottonseed oils obtained from different areas in the South and Southwest were refined with and without the use of high-shear agitation in the step involving the initial mixing of the crude oil and caustic soda solution. In each instance the use of high shear produced a lower color in the refined oil. The improvement with some oils was not marked because they either refined very well by the ordinary method or failed for some unexplained reason to respond readily to high-shear mixing. However a good proportion of the oils which were quite dark after refining by the ordinary method refined to a much lighter oil when high shear was used.

It was established that in high shear refining the color of the refined oil decreased as the temperature at which high shear was used decreased, the time at high shear increased, and the rate at which shear was applied increased. However an increase in the latter above a certain value had no effect. Also it was found that the color of the refined oil decreased as the amount and strength of the caustic soda solution increased.

Absorption spectra of some of the processed oils indicated that high shear was more effective than ordinary mixing in removing from an oil the gossypol-like and carotenoid color bodies.

### Acknowledgment

The authors wish to thank Donald Mitcham for determining the absorption spectra and the South Texas Cotton Oil Company and the Buckeye Cotton Oil Company for the oils used in the investigation.

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[Received May 16, 1955]

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# The Kinetics of the Hydrogenation of Pure Fatty Esters. I. Mono-Olefinic Systems: Methyl Oleate

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A RECENT PAPER by Swicklik *et al.* (11) has presented, along with their own interesting contribution, a survey of the literature concerning the kinetics of fatty oil hydrogenation. The considerable confusion which existed in this field of research prior to 1941 was complicated, as they pointed out, by unsatisfactory data. As evidenced by the more recent publications on the subject, this state of affairs is being corrected gradually by studying the hydrogenation of simple, pure unsaturated compounds, carried out under well-controlled conditions, thus allowing the basic features of the problem to emerge. A further step would be to make use of the fact that the reactions involved are taking place on the surface of a catalyst and, as such, are governed by the laws of adsorption. These should be involved in any attempt at setting up rate equations.

The present series describes work accomplished with simple alkyl esters under conditions designed to suppress complicating side reactions and to permit accurate measurement of the rate of hydrogen absorption. Absorption rate data obtained in this way reflect the simple kinetics involved in the reaction.

The present article discusses data obtained on hydrogenating methyl oleate. Their implications are basic in interpreting the more complicated systems described in the following articles of this series.

## Experimental

### REAGENTS

*Methyl oleate* was obtained from olive oil through methanolysis, fractional molecular distillation of the crude esters, several fractional crystallizations from acetone, and a final fractional distillation, using the Podbielniak semi-automatic microanalyzer. The product showed the following analysis:

hydrogen value, 0.680 (13); required, 0.680.
refractive index at 20°C., 1.4515; reported, 1.4515 (7).

Spectrophotometric analyses (before and after alkali-isomerization) detected no conjugated or polyunsaturated impurities.

Stored under nitrogen in sealed ampoules kept in the refrigerator, the ester was transferred to hypodermic syringes for weighing according to a technique already described (14).

*Ethyl alcohol* was obtained by refluxing under nitrogen 95% fermentation alcohol over caustic soda for several hours and fractionally distilling the product under nitrogen. The water content was 5%; transmittance against distilled water was 60% at 220 mμ.

*Dibutyl-ether* was obtained by careful fractional distillation over sodium of Eastman Kodak (white label) product. Found: B.P. 142.5°C. under 760 mm.; reported, 142.4°C. (12).

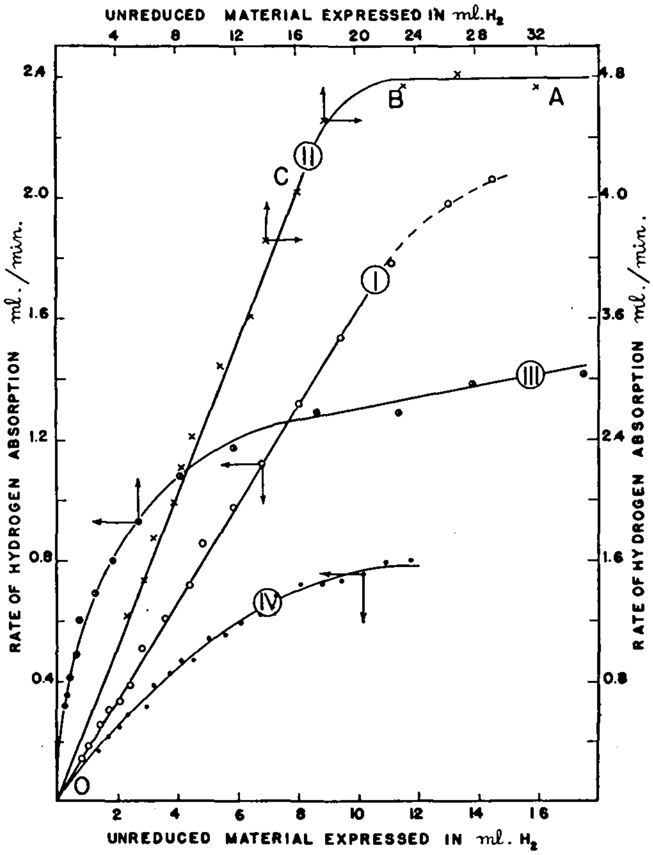

FIG. 1. Hydrogenation Rate Curves.

Curve I: Methyl oleate in 95% ethyl alcohol with Raney nickel showing first order relationship.

Curve II: Same system as for Curve I but with larger amounts of both methyl oleate and Raney nickel resulting in zero order kinetics (AB) during the early stages.

Curve III: Methyl oleate in 95% ethyl alcohol with a platinum catalyst.

Curve IV: Methyl oleate in dibutyl ether with a platinum catalyst.

Related coordinates for the various curves are indicated by the arrows.