

FIG. 1. Long spacings of thiol esters of C_{12} - C_{18} aliphatic acids.

tives are the projection of double the molecular length on [d 001]. Thus these aromatic thiol esters must crystallize in bimolecular layers like the methyl esters of the *n*-aliphatic acids. The increase in long spacing for each additional carbon atom is $2.30/2 = 1.15$ Å. and $1.85/2 = 0.92$ Å. for the benzyl and β -naphthyl derivatives, respectively. This is much lower than the expected projected distance, 1.27 Å., of a C-C bond. Thus these derivatives must be tilted with respect to the 001 plane.

On the other hand, the measured increase in long spacing for each additional carbon atom for the *n*-amyl and *n*-hexyl derivatives is 1.21 Å., slightly less than the expected projected C-C bond distance. Thus these *n*-aliphatic thiol acid esters, like the ethyl esters of the *n*-aliphatic acids, crystallize in apparent monomolecular layers. If the measured long spacings of these compounds are plotted against the total number of carbon atoms in the chain, the data form two separate, approximately parallel, lines. The only difference between the two sets of derivatives is in the number of carbon atoms; one, *n*-amyl, contains an odd number of carbon atoms while the other, *n*-hexyl,

contains an even number. This even-odd alternation in long spacing is characteristic for long chain compounds that possess tilted chains in the solid state (3). The previously reported long spacings of odd alternating compounds are always slightly greater, in proportion, than even. However in the present case the reverse is true. The reason for this is not apparent at the present time.

Because of the multiplicity of lines in the low angular region, it is difficult to isolate the side spacings of these derivatives. However a side spacing common to each derivative in a particular series can be found for the β -naphthyl-, *n*-amyl-, and benzyl-derivatives. For example, in the four β -naphthyl derivatives each show a relatively strong diffraction line at about 3.83 Å. However for the *n*-hexyl series there appears to be no correspondence. This probably results from the difficulty in obtaining the material in good crystalline form because of the low melting temperatures of the myristate and palmitate members of the series, 20.5 and 28.5°C., respectively.

Summary

X-ray diffraction powder data were obtained for 14 thiol esters of long chain fatty acids including benzyl, β -naphthyl, *n*-amyl, and *n*-hexyl thiol myristates; thiol palmitates; thiol stearates; and in some cases thiol laurates. All the individual compounds can be readily distinguished and identified by the diffraction data. Long spacings increase regularly with increase in hydrocarbon chain length. The benzyl and β -naphthyl thiol esters crystallize in tilted bimolecular layers while the *n*-amyl and *n*-hexyl thiol derivatives crystallize in tilted monomolecular layers.

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[Received July 9, 1956]

Some Laboratory Investigations of Degummed Cottonseed Oil

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IN A PAPER presented by W. C. Whittecar at the April, 1955, meeting of the American Oil Chemists' Society in New Orleans (7) the mechanics of cottonseed oil degumming, its primary and secondary benefits were discussed. There has been little change in the mechanics of the operation since that time, and we now believe that the principle is a thoroughly sound and profitable one.

One innovation however has been tried experimentally, that of miscella degumming, or degumming the oil while still in the miscella stage. Oil was taken from a French basket-type of extractor to the usual pre-evaporator but, instead of going directly to the final still to remove the last of the hexane, the oil went to the degumming stage. This miscella contained 8.0% hexane. The oil was degummed in the

usual way, *i.e.*, it was mixed with 2.5% water, heated to 120°F. (49°C.), and centrifuged through two De Laval VO 194 hermetically sealed machines. Oil was pumped from the centrifuges to the vacuum still to remove the hexane and finally to a four-car dryer to remove the moisture.

This process worked quite well. The cup loss of the oil produced by this method is comparable to straight degumming but is somewhat more stable in color, as verified by an eight-month storage test. This results, we assume, from the fact that the total gossypol content of the miscella-degummed oil is lower than that of regularly degummed oil, as shown in Table I.

Some tests were run to determine the solubility of gossypol in *n*-hexane, commercial grade, in an effort

TABLE I
Comparison of Total Gossypol in Regular and
Miscella Degumming Processes

	% in oil	% in gums
Regular degumming.....	.63	5.83
Miscella degumming.....	.49	6.33
Crude oil.....	.83	

to explain this reduction of gossypol. As shown in Table II, gossypol is fairly soluble in commercial hexane at the temperatures encountered in the miscella degumming process. It is not as soluble at room temperature. Some of the gossypol dissolved in the hot hexane is carried over from the oil phase to the gum phase. Hexane evaporating from the gums before they reach the desolventizer-toaster and also the remaining hexane dropping in temperature would be responsible for the deposition of this extra gossypol in the gums.

The gums produced by this process are in all respects the same as gums produced by regular degumming except that they are somewhat more diffi-

TABLE II
Solubility of Gossypol in Commercial n-Hexane

Temp. °C.	% Recovery of 10 mg./100 ml.
25.....	25.0
30.....	28.2
40.....	39.1
50.....	50.0
60.....	62.5
70.....	66.6

cult to handle in the laboratory because they are tough and rubbery. Thorough mixing with gentle heat, then chilling before weighing the samples for the acetone-insoluble test (3) have proven helpful. Also, extra acetone rinses are necessary.

THE BIG PROBLEM remaining to be solved satisfactorily is that of a laboratory method for refining degummed cottonseed oil. We think that, since we initiated the degumming of cottonseed oil on a commercial scale, we should be able to devise a laboratory method of handling it. Consequently for the past 18 months we have experimented with various methods and techniques. A "suggestion list" has been prepared and distributed to processors of our oil and also to members of the A.O.C.S. Official Methods Committee and Refining Committee, setting forth our findings. These are merely suggestions and do not represent a departure from existing official methods (1).

The problem in handling degummed cottonseed oil is that of black lye and suspended soap. It is difficult, using existing methods, to separate these components and keep them out of the oil. To leave any of either fraction in the oil causes erratic color readings. A brownish discoloration masks the true red color and makes reading of the colors extremely difficult. These components must not be allowed to get into the refined oil. Since in degumming the natural binder is removed, great care must be taken in refining so that the soapstock is not unduly broken up once it forms.

The following is typical of what happens in the laboratory. The oil is being refined. In perhaps five minutes after the oil is in the hot bath with slow agitation, the soapstock forms and drops. Continued agitation according to instructions in the Official Method (1) only serves to break up the soapstock again. The longer the agitation, the more finely di-

vided the soap becomes. Only upon prolonged agitation will the stock again agglomerate and settle out with a slight increase in loss. Thus, regarding a modification of the time for refining, we conclude that the answer will be either in a very short time in the hot bath (5 min.) or a very long time (90 min.). The short time is preferred since it gives a lower loss figure without sacrificing color.

With regard to the strength and amount of lye to use, we have done many actual cup tests on fresh oil and oil of different ages, using a geometric progression by days in order to gain the greatest amount of information with the fewest determinations.¹

ANOTHER DEVICE which we pressed into service was that of a short, approximate refining, using a laboratory centrifuge. This method is short and easy, taking only about two hours. The free fatty acid is determined as usual. The amount of lye used is measured volumetrically into a 100-cc. centrifuge tube. Oil is added to the 100-cc. mark. Violent agitation by hand mixes oil and lye. The mixture is heated in the tube for about 10 min. in a water bath at 70° C., then centrifuged. A high rate of centrifugation is necessary, at the highest speed the glassware can stand. For this reason, and also because of the heating involved, we use Pyrex centrifuge tubes. A speed of 2,500 r.p.m. is best if your equipment will stand it. Also it is helpful to agitate the oil and soapstock in the centrifuge tube immediately before centrifuging because this has proven to give more even, compact soap levels and therefore more results that can be duplicated. The soap level is read and subtracted from 100. A factor, applied to the difference, is derived from the relationship of the specific gravity of the lye used to the specific gravity of the oil in order to convert volumes to weights since in this test nothing is weighed. After multiplying by the correct factor, this product is again subtracted from 100 to give the percentage of refining loss. The factors are worked out in advance and are derived from the specific gravities of the various strengths of lye likely to be used, assuming an average figure as a constant for the specific gravity of cottonseed oil.

The strengths of lye are roughly correlated with the lye tables in the official method, but instead of a free fatty acid increment of 0.1% an increment of 0.5% is used. To determine the color the oil is simply poured off into a color tube and read. Some clearing with diatomaceous earth and filtering is often desirable.

Of course, there is not enough oil to determine a bleach by the usual method. Scaling down the weight of bleaching earth to correspond to the reduced volume of refined oil (90 cc. *versus* the customary 300 g.) did not prove very satisfactory. Perhaps good mixing with the ordinary refining equipment was not possible at such reduced volumes.

Some modifications of the short refining method have been made. For instance, if duplicate raffinings are desired or necessary to balance the load in the centrifuge, then the oil is measured in a graduate and poured into a refining cup. Lye is pipetted into the oil, and the mixture is stirred on a conventional refining machine for 10 min. at 250 r.p.m. Oil is quickly transferred to two centrifuge tubes and treated as described above. Good checks can be ob-

¹ These data are not presented here as most of them have no direct bearing on the subject at hand.

tained, and results agree rather closely with the official cup method. This is especially true of color. The color of the same oil refined by the short method and by the official cup method is almost invariably the same. The losses tend to be somewhat lower than by the cup method, although agreeing remarkably close at times, considering the fact that no correction is made for black lye or entrained oil in the soapstock. The latter will be less in the short method than in the cup method because centrifugation does a better job of separating oil and soapstock. The short method more nearly duplicates what actually happens in a modern continuous refining process employing centrifuges.

SOME DIFFICULTY was encountered when this method was applied to degummed oil until it was discovered that the same constant factor used for the specific gravity of cottonseed oil would not work for both a degummed and a regular crude oil. The specific gravities are not the same. The specific gravity of a crude oil at 23°C. is 0.9226. A degummed oil made from this same crude has a specific gravity of 0.9180 at 23°C. Two sets of volume-to-weight factors are needed if this method is to be used on both types of oil.

This centrifuge method is a handy tool to use for certain purposes. Since it is so rapid, it can be useful for checking the effect of changes in processing in the mill. For instance, the effect that the amount of moisture in cooking has on the color and loss of the oil may be checked by this method. In a short time the operator knows whether his change helped or hindered.

We used this method to help us arrive at a lot of answers quickly in connection with the problem of determining what strength and amount of lye to use in the refining of degummed cottonseed oil. With the same sample of oil we made 96 determinations by the short method, using a wide variety of strengths and amounts of lye. This same test run by the official method would have taken 288 cups. The short method has been tested and proved enough in four years of use so that we can rely on the results as being fairly accurate.

Figure 1 shows what we attempted to do with the short method. Using every strength of lye recom-

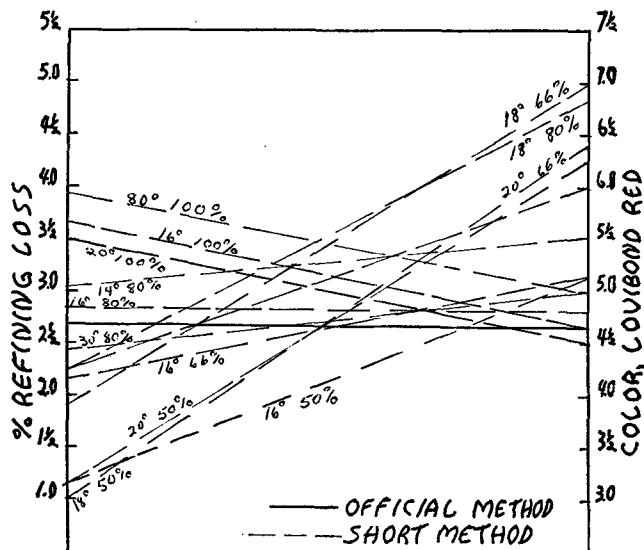


FIG. 1

mended in the Official Methods for any and all types of oil, we varied the amount used of each. Percentages of 50, 66.6, 80, and 100 were used of each strength. The results are compared with the official cup test results on the same oil. Since any refining loss higher than that obtained by the existing method would prove of no benefit, this method was set as the standard. Any strength and amount of lye producing a lower loss shows promise, providing the color can be controlled.

On this basis then, the 16° and 20° lyes look promising, with the 18° lye behaving very strangely. This appears to be nothing new since the 18° Bé. strength is the least used of any lye in the official tables. Perhaps the best strength for free fatty acids below 1.5% is 16° (80%). One thing is apparent. With higher strength lyes this oil saponifies very readily and is sensitive to slight changes in amounts. For instance, note the widening between lines where 22° or 26° Bé. strength were used in practically any amounts (Figure 2).

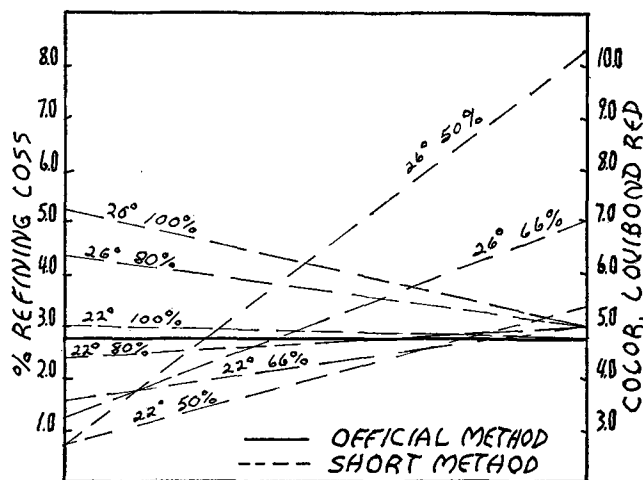


FIG. 2

It would seem that the best lye to use would be either a 16° Bé. or a 20° Bé. with a short time in the hot bath when refining. Concerning the lye strength however, the refiners tell us that the 16° or 20° strength does not work as well for them as a 12° Bé. About a 0.3% excess of 12° Bé. lye appears to give the best results for oils having a normal free fatty acid range. The reason for this, we believe, is obvious. In the refinery the suspended soap can be spun out in the centrifuge while with the cup method in the laboratory this is not possible. Also the refiners feel that the presence of additional water in the lower strength of lye aids in getting a better oil and higher yield. One helpful technique is to use colder water in the chilling stage after remelting the soapstock. Ice water is best. Short, successive remelts with shorter drainage and longer time in the chilling bath at colder temperature will control the suspended soap and black lye problem pretty well. Also agitation of the stock between remelts is helpful in reclaiming the oil entrained in the stock.

Quite a new and different approach to the problem is that of the chromatographic adsorption method of determining the refining loss (5, 6). The loss is determined by measuring the loss in weight of an oil sample diluted with anhydrous diethyl ether and poured through a carefully prepared column of pow-

dered alumina. After several rinsings with 25-ml. portions of diethyl ether, the solvent is evaporated over a water bath and the oil is weighed again. In all chromatographic determinations a solution of 975 cc. of anhydrous diethyl ether and 25 cc. of anhydrous (absolute) ethyl alcohol was used.

To say that this loss is refining loss in the ordinary sense is not entirely true. It is not the loss that would be expected in caustic refining. Instead it is the removal of all non-lipid fractions in the oil. What remains is neutral oil. The chromatographic method simply removes the free fatty acids, pigments, and other non-lipid bodies. In this respect it is similar to the Wesson loss (Table III).

TABLE III
Chromatographic Loss Method
% Loss (Duplicates)

	1	2
Degummed.....	2.04	2.02
Degummed.....	2.48	2.42
Crude.....	4.28	4.28
% Free fatty acid (av.).....		.08
% Total gossypol (av.).....		.06
Color (av. Lovibond Red).....		5.5

Here we see a comparison of the chromatographic loss with the regular cup method, using the same oil in each case. In every case the chromatographic loss is lower than the cup loss and in most cases considerably so. Judging from the very close checks with duplicate samples, shown in Table IV and the lower

TABLE IV
A Comparison of Refining Methods
(% Loss)

Crude		Degummed	
Official Method	Chromatographic	Official Method	Chromatographic
8.3.....	4.7	5.2	2.6
9.3.....	4.6	5.7	3.0
8.7.....	4.8	6.3	2.8
8.3.....	3.8	5.2	2.3
10.3.....	4.1	4.9	2.3
7.9.....	4.8	3.6	2.1
9.7.....	4.2	4.1	2.5

loss figures, it would seem that in this method practically 100% of the neutral oil is recovered. The oil is in every respect a refined oil. The color is very low, as is the free fatty acid and the gossypol content. The colors approach the bleached oil figures in some cases. Since very small samples are used, usually 2-3 g., reading of individual colors, using the Lovibond glasses, is impractical. Colors can only be read by diluting with 25 ml. of anhydrous diethyl ether and placing the mixture in a Beckman DU or other suitable spectrophotometer, using selected wavelengths in much the same manner as is done in the A.O.C.S.

spectrophotometric method to convert wavelength readings into comparable Lovibond Red figures (2).

Since the chromatographic method is a true measure of what is actually oil and what is not, it would seem that it would be a more accurate basis for accounting for losses and gains in the refinery. Heretofore the refiner has been able to realize savings over the laboratory cup loss of from 25% to 50%. In other words, he has always, since the advent of continuous centrifuge refining, been able to beat what the laboratory says he should do with a given oil. This seems to be a rather archaic way of doing business. The laboratory should be the one to set the pace and let the refiner try to shoot for the mark it sets.

If this were to come about, a re-evaluation of our laboratory-refinery relationship would necessarily ensue. Instead of the refiner being able to beat what the laboratory says, he would then try to approach the figure that the laboratory says is perfection. Then instead of savings over cup loss of 25 to 50%, he would perhaps do only 95-98% as well as the laboratory does.² A revamping of present accounting systems would be a natural by-product if this came about.

Summary

In the foregoing we have set forth our views and findings on possible ways of handling degummed cottonseed oil in the laboratory. Foreseeing the day when degummed cottonseed oil will come into prominence, we offer these suggestions and findings as an incentive to spur collaborative efforts in a search for a better laboratory method. Two possibilities have been explored. One is a centrifuge method of refining, approximating actual refining conditions in present-day refineries. The other is a chromatographic determination of total neutral oil. It is indeed heartening to know that the A.O.C.S. total neutral oil subcommittee is actively engaged in a collaborative program of work on such methods as the chromatographic loss method. This is good evidence that we are making a realistic approach to the problem of better laboratory methods.

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[Received April 23, 1956]

²The only actual figure is from one refinery showing an average figure of 90%.

Erratum

ACCORDING to Thomas F. Boyd of the Industrial Test Laboratory, Philadelphia Naval Shipyard, Philadelphia, Pa., a correction should be made as follows: "in the article, 'An Investigation of the Adsorption of Detergent and Builders onto Cotton and Soil by Radio-tracer Methods,' 33, 614-619 (1956), under Table I, lines 15 20, 27 58, and 30 38 should read >15 20, >27 58, and >30 38."