reinforced cloth and on the outside of the spirals of the reinforced cloth. Thus in the former case the stream of liquid was in a relatively thick film; and because of this and its position inside the spiral the film presented a smaller surface to the stripping steam.

A comparison of column capacities when stripping to less than 0.02% trichloroethylene shows an increase from 45 pounds per hour of stripped oil, when using center feed with 1-inch Berl saddle packing, to 101 pounds per hour using the same packing but distributor feed. The substitution of the reinforced spiral weave metallic cloth spaced with ½-inch Berl saddles increased the column capacity to 221 pounds per hour and reduced injected steam requirements to 0.21 pounds of steam per pound of oil. This improved behavior was obtained in a column with a spaced cloth packing of only 78 inches in height compared with a Berl saddle height of 96 inches.

Summary

A study of the effect of liquid distribution on the performance of a packed column resulted in the development of a distributor head for feeding which not only improved the distribution but decreased the steam consumption by about 20% and increased the column capacity by about 30% when stripping soybean oil-trichloroethylene miscella from 20% to 0.02% residual solvent. Liquid distribution studies with rolled packing units composed of 10-mesh reinforced spiral weave stainless steel cloth with ½-inch Berl saddles as spacers between turns showed that these units maintained a very uniform distribution of liquid down the stripping column. A column 8 inches in diameter with packing units having a total height of 78 inches had a capacity, when operated with the distributor head on 20% soybean oil-trichloroethylene miscella, for stripping 229 pounds of soybean oil per hour to a residual solvent content of 0.02%, using 0.20 pound of steam per pound of oil.

REFERENCES

1. Arnold, L. K., and Hollowell, E. G., "The determination of small amounts of chlorinated hydrocarbons." Proc. Iowa Acad. Sci., *54*, 181-183 (1947).
2. Skow, M. L., "Spiral weave metallic cloth as a packing agent in rectification." Unpublished B. S. Thesis, Chem. Eng. Dept., Iowa State College (1938).
3. Sweeney, O. R., Arnold, L. K., and Hollowell, E. G., "Extraction of soybean oil by trichloroethylene." Iowa Eng. Exp. Sta. Bul. 165 (1949).
4. Tour, R. S., and Lerman, Frank, "Unconfined distribution in tower packing." Trans. Am. Inst. Chem. Eng., *35*, 719-742 (1939).
5. Tour, R. S., and Lerman, Frank, "Area source liquid distribution through unconfined tower packing." Trans. Am. Inst. Chem. Eng., *40*, 79-103 (1944).
6. Vilbrandt, F. C., Shuffle, E., and Row, S. B., "Metal knit cloth tower packing and its use in plate columns." Trans. Am. Inst. Chem. Eng,, *34*, 51-59 (1938).

[Received August 2, 1951]

The Effect of Trichloroethylene in the Hydrogenation of Soybean and Cottonseed Oils

F. A. NORRIS, K. F. MATTIL, and W. J. LEHMANN, Swift and Company, Chicago, Illinois

DESPITE the widespread use of hydrocarbon solvents for the extraction of oil-seeds there has been an increasing desire on the part of many processors to change to an essentially non-inflammable and non-explosive solvent such as may be found among the chlorinated hydrocarbons. This is mainly in the interest of safety. One large British mill changed over to trichloroethylene during World War II because of the danger of bombing, and results were entirely satisfactory. In this country the use of trichloroethylene in oil-seed extractions has been limited to a few plants processing soybeans. Further development has probably been hampered by the comparatively high cost of the solvent and, at least in the case of cottonseed, by certain technological difficulties requiring considerable research.

In addition to the foregoing, there has been a certain amount of misapprehension with regard to trichloroethylene as a solvent. An example of this is the belief held in some quarters that it is impossible to hydrogenate trichloroethylene-extracted oils because of residual solvent not removed during processing. This subject has been investigated in our laboratory and pilot plant, and we are presenting our findings herewith.

Laboratory-scale Hydrogenation

In some early experiments cottonseed oils containing 0.0-0.1% trichloroethylene (extreme levels were deliberately selected for testing so as to show up any effects) were subjected to hydrogenation in a small glass laboratory reactor,[1] in which hydrogen at atmospheric pressure is blown through an oil-catalyst mixture agitated by a high speed stirrer and maintained at any desired temperature. In this and all subsequent hydrogenations a commercial, reduced nickel catalyst containing approximately 25% metallic nickel was used. The catalyst concentration employed in the present experiments was 0.12%, and the reaction temperature was maintained at 165°C. (329°F.). Oil samples were prepared by adding various amounts of trichloroethylene to refined and bleached oil, mechanically expressed. In each test 190 grams were hydrogenated. Results are shown in Figure 1.

It is seen that oils containing .007% trichloroethylene hydrogenated as well as the trichloroethylene-free oil used for a control. Also it is apparent that oils containing as much as 0.1% trichloroethylene still hydrogenated reasonably well. The explanation for this is probably that trichloroethylene is continuously distilled from the oil under the conditions employed in this type reactor. It evidently does not form an irreversible adsorption complex with the catalyst. Reasoning from this, one would expect that the effect of any concentration of trichloroethylene in oil would vary with the operating conditions employed in the hydrogenation and, at least theoretically, oil containing any quantity of trichloroethylene could be hydrogenated under suitable conditions.

---

[1] Baker Instrument Company, Orange, N. J.

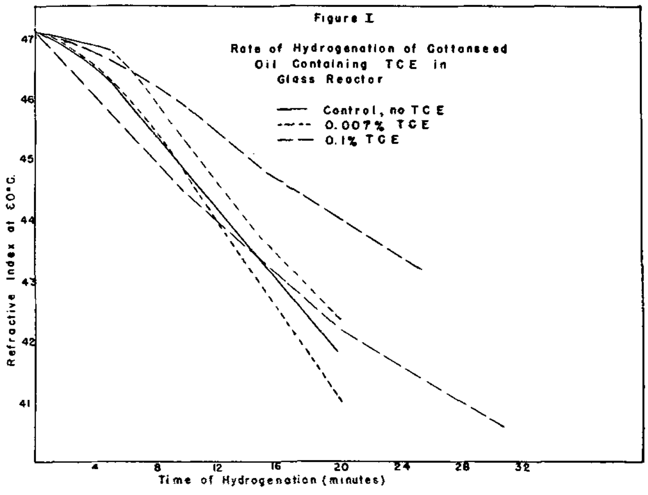


Figure I

Rate of Hydrogenation of Cottonseed Oil Containing TCE in Glass Reactor

Further laboratory experiments were conducted in a 3-liter metal converter (dead-end type) which, previous experience had shown, gives results comparable with those obtained in plant production. Varying percentages of trichloroethylene were added to refined and bleached, mechanically expressed, soybean oil, and the hydrogenations were carried out at 385°F., with 25 pounds of hydrogen pressure and 0.08% nickel catalyst. As routine practice the oils were heated, with vigorous agitation, to 385°F. under 25 inches of vacuum prior to the addition of the catalyst. During the course of the hydrogenation the reactor was evacuated at least once every 10 minutes.

It may be seen from the data in Figure 2 that in this dead-end type apparatus as little as 0.01% trichloroethylene exerted a marked inhibitory effect and 0.1% stopped hydrogenation entirely after a brief initial period. It was found with the oil containing 0.03% trichloroethylene that the addition of another 0.04% of catalyst greatly accelerated a lagging rate of hydrogenation.

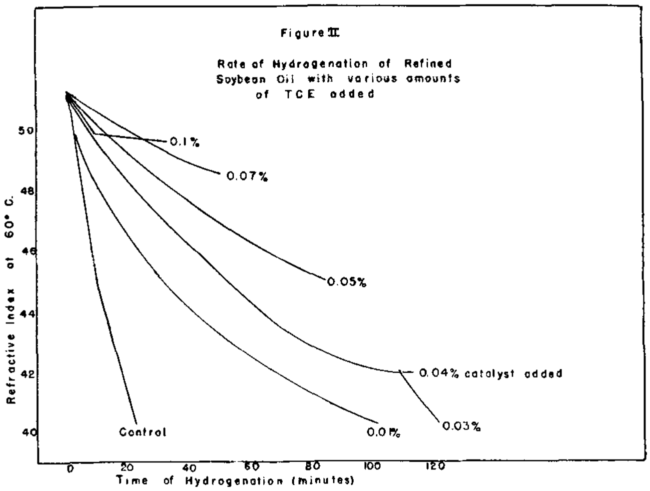


Figure II

Rate of Hydrogenation of Refined Soybean Oil with various amounts of TCE added

Somewhat similar results were obtained in the hydrogenation of refined and bleached, mechanically expressed, cottonseed oil to which trichloroethylene had been added (Figure 3). In this case less catalyst (0.05%) was used, and the batch was purged every three rather than every 10 minutes during the early stages of hydrogenation. Although 0.005% trichloroethylene was tolerated quite well by the cottonseed oil, 0.01% had a very serious retarding effect. It was found however that by using more catalyst (0.1%) oils containing 0.01% trichloroethylene hydrogenated much more rapidly. Also it was observed that the addition of the catalyst in two portions gave results superior to those obtained when the catalyst was all added at one time. Further reference will be made to this point later.

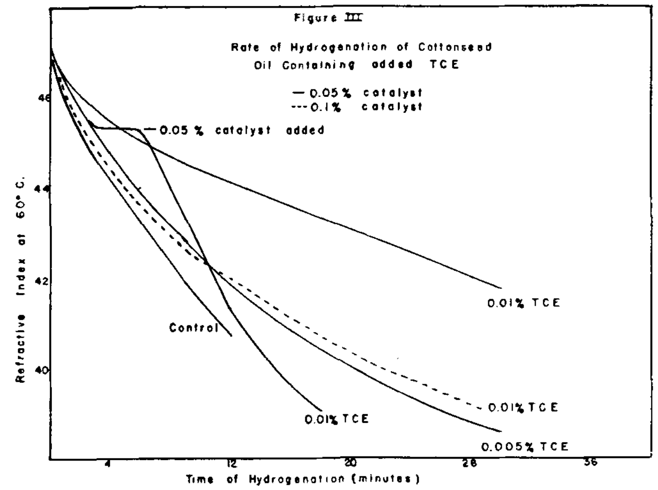


Figure III

Rate of Hydrogenation of Cottonseed Oil Containing added TCE

These data and the results obtained with the glass hydrogenator previously described indicated that it should be possible to hydrogenate cottonseed oil containing relatively large quantities of trichloroethylene in a dead-end type converter, provided proper conditions of hydrogenation were employed. For example, if an oil were known to contain excessive quantities of trichloroethylene, it should be helpful to hold the oil for some time under vacuum at hydrogenation temperature before adding the catalyst. That such is the case can be seen from the data in Figure 4. Holding the oil containing 0.1% trichloroethylene under vacuum at 385°F. apparently reduced the concentration to less than half that quantity, based on comparative rates of hydrogenation.

A series of experiments was conducted in order to compare the relative merits of the split catalyst addition technique with the improvement by prelim-

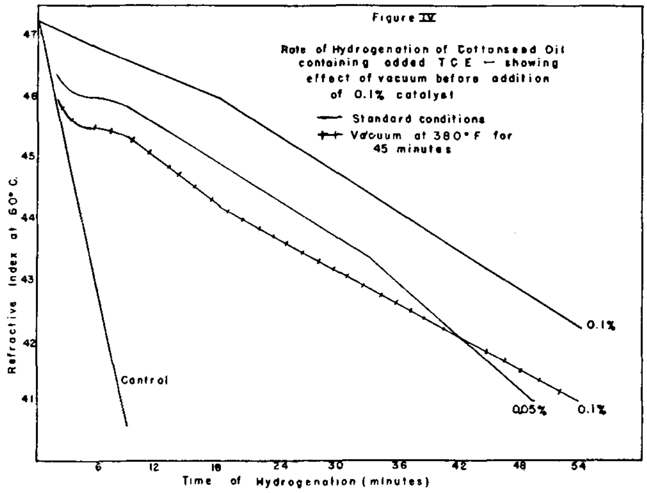
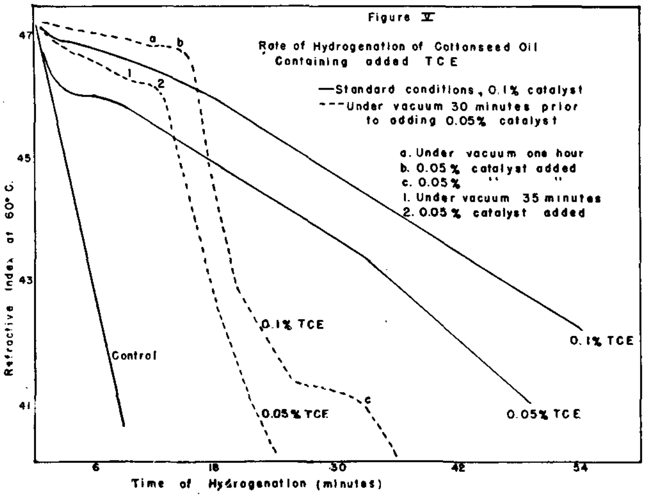


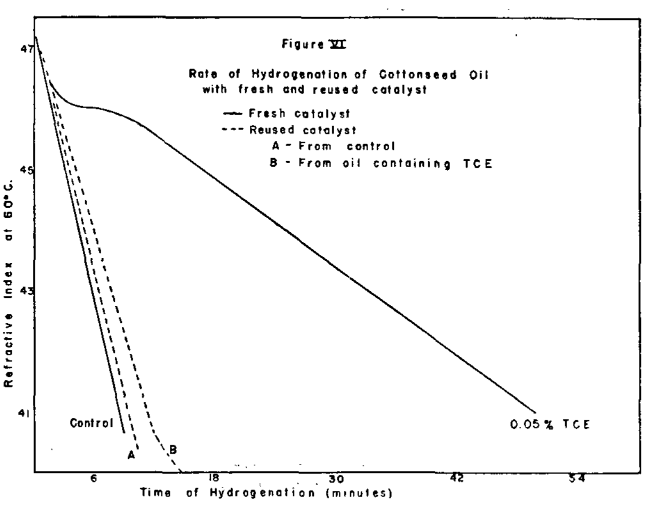
Figure IV

Rate of Hydrogenation of Cottonseed Oil containing added TCE — showing effect of vacuum before addition of 0.1% catalyst



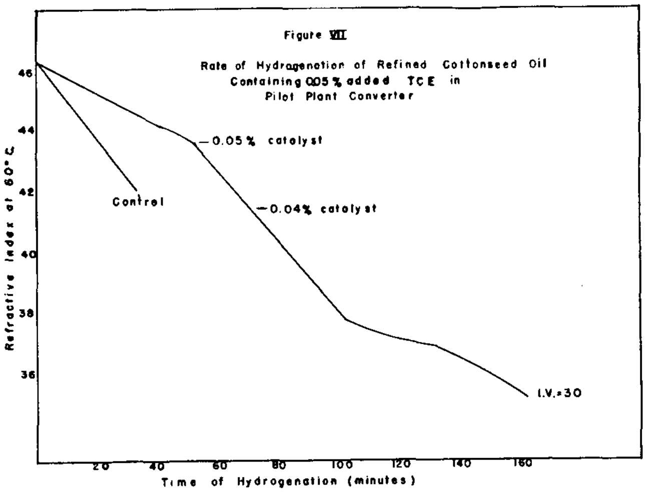
inary evacuation (Figure 5). As controls, three oils containing 0.1%, 0.05%, and no trichloroethylene were hydrogenated under standard conditions, using 0.1% catalyst added in a single portion at the beginning of hydrogenation. The two test oils, containing 0.05% and 0.10% trichloroethylene, were held under 25 inches of vacuum at 385°F. for 30 minutes prior to the addition of 0.05% catalyst. It will be noted that in both cases the rate of hydrogenation was quite slow at the beginning and was not noticeably improved by holding the oils under vacuum a second time at points a) and 1) in the two curves. However the addition of another 0.05% catalyst at points b) and 2), which brought the total catalyst concentration up to that used in the control run, caused a marked increase in the rate of hydrogenation and the slope of the curve for the oil containing 0.05% trichloroethylene paralleled that of the control containing no trichloroethylene. In the case of the oil which had contained 0.10% trichloroethylene, the rate was equally as fast until a drop of 5.5 refractive index units (corresponding to approximately 33 iodine number units) had occurred. However it was again accelerated at point c) when another 0.05% catalyst was added.

In order to determine whether or not trichloroethylene permanently affects hydrogenation catalysts, two tests were run comparing catalyst recovered from trichloroethylene-free cottonseed oil with that recovered after the hydrogenation of a cottonseed oil containing 0.05% trichloroethylene (Figure 6). In the preliminary work the original oils were hydrogenated under standard conditions using 0.1% catalyst and 3-minute purges. Once again the oil containing 0.05% trichloroethylene hardened much more slowly than did the control. The catalyst was then removed from the two hydrogenated oils by filtration through a pad of diatomaceous earth. For the test hydrogenations the total sum of catalyst and earth separated from each oil was added to sufficient fresh cottonseed oil to represent a 20% excess over that initially used. This was done in order to compensate for any loss of catalyst and catalyst activity. The curves show that the difference between the two catalysts, although slightly in favor of that from the control oil, was relatively insignificant. It thus appears that the catalyst was not permanently harmed by having been used to hydrogenate oil containing trichloroethylene.



Pilot Plant Scale Hydrogenations

In order to approximate more closely actual plant conditions, a pilot plant hydrogenation test was also carried out using 2,500-pound batches of refined and bleached cottonseed oil. The converter used was a batch, dead-end type equipped with a pump for circulating hydrogen. Two oils were used, one a control and the other containing 0.05% added trichloroethylene. In each case the oil was heated to temperature (375°F.) under a 27-inch vacuum and with good agitation. At 300°F. the oil was purged twice for 15 seconds and 5 times for 60 seconds each at 3 pounds hydrogen pressure. The catalyst (0.11%) was added at 340°F. and the oil purged twice more for 15 seconds each time.



As seen from Figure 7, although 0.05% trichloroethylene retarded the rate of hydrogenation of the cottonseed oil, the oil did hydrogenate without serious difficulty. On the basis of the initial rate of hydrogenation it would have taken about 2½ times as long to reach shortening consistency as was required for the control run. However this rate was accelerated by the addition of another 0.05% catalyst. It was found that the hydrogenation continued reasonably well until the oil reached an iodine value of about 30. From this point on further progress was quite slow, and the hydrogenation was discontinued when the iodine number was 19.9. The final product had an F.A.C. melting point of 136°F. and a titer of 56.7°C.

Analysis of various selected products of the above hydrogenations has indicated that trichloroethylene does not significantly affect the selectivity of hydrogenation even when a sufficient quantity is present to produce an inhibitory effect on the rate of hydrogenation. Typical data are shown in Table I.

TABLE I

Composition of Hydrogenated Oils

	Control	0.005% Trichloroethylene	0.007% Trichloroethylene	0.01% Trichloroethylene	Pilot Plant Control	Pilot Plant Test[a]
Time of hydrogenation (min.)	12	12	21	30	33	62
Iodine number	69.5	76.1	72.8	75.0	77.0	77.1
% linoleic acid	7.3	10.2	8.1	8.5	13.4	12.8
% linolenic acid	0.04	0.04	0.04	0.00	0.05	0.07
% conjugated diene acid	0.65	0.58	0.27	0.85	1.1	0.84

[a] 0.05% trichloroethylene.

Plant Scale Hydrogenations

In plant equipment, using 25,000-pound batches and 10- to 30-minute purging intervals, the critical level of trichloroethylene added to the oil in the converter appears to be approximately 0.003%. At this level there was little or no effect on the rate of hydrogenation whereas 0.005% trichloroethylene increased the length of time to obtain a given degree of hydrogenation twofold and 0.01% threefold.

Effect of Refining Operations on Trichloroethylene Content of Oils

Since the trichloroethylene content of an oil just prior to hydrogenation is likely to be different from that of the crude oil as a result of the processing steps employed, a study was made to the effect of refining and bleaching on the trichloroethylene content of the final oil.

In one series of experiments varying quantities of trichloroethylene were added to crude soybean oils and the oils then refined and bleached in the laboratory. Figure 8 illustrates the hydrogenation curves on these oils. Comparing these results with those obtained when trichloroethylene was added to the refined and bleached oils, it is seen that .03% trichloroethylene in the crude oil gives a faster rate of hydrogenation than does .01% in the refined and bleached oil. Also .3% trichloroethylene in crude oil hydrogenates equally as well as .05% in refined and bleached oil.

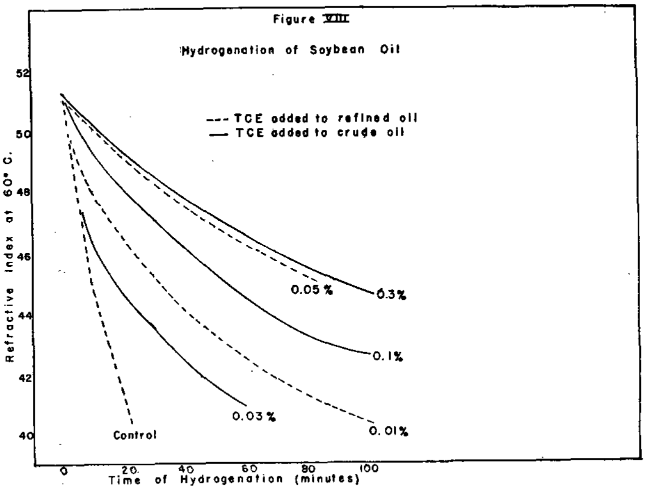


TABLE II

Effect of Processing on Trichloroethylene Content of Cottonseed Oil

	Kettle	Centrifugal (a)	Centrifugal (b)
Crude oil	0.078%	0.038%	0.056%
From centrifuge	....	0.017	0.051
From water wash	....	0.016	0.046
From drier	....	0.011	0.025
Refined oil	0.047	....	....
Bleached oil	0.009	0.003	0.009

Table II shows analytical results obtained on crude oils to which trichloroethylene had been added and on samples taken at various stages in the refining of these oils by two different centrifugal methods (plant scale) and by kettle refining (pilot plant scale). All these crudes would be considered poorly stripped oils (0.01% has been guaranteed by one manufacturing concern), yet all three produced refined oil which could be hydrogenated with no serious difficulty. The kettle-refined oil was hydrogenated in the pilot plant with no difficulty or retarded rate to 60°C. titer hard fat. The centrifugal a) oil was split into two batches for hardening in plant scale equipment; one batch hardened at normal rate and the other was slightly slower than normal. The oil from centrifugal b) refining required about twice the usual length of time for hardening to shortening consistency.

In future solvent extraction plants trichloroethylene removal from oils can probably be made as complete as is necessary. Present commercial levels for soybean oils appear to be in the range of .005-.02%. These levels were undoubtedly selected without carrying out an exhaustive investigation of hydrogenation and therefore do not represent the ultimate stripping possible but rather what was decided upon early in the work on the use of trichloroethylene as an oil-seed solvent.

Summary

It has been found that at concentrations greater than .003% trichloroethylene retards the rate of hydrogenation of vegetable oils without any apparent effect upon selectivity of hydrogenation. However it is not an irreversible catalyst poison, and oils containing relatively large amounts of trichloroethylene have been successfully hydrogenated in the laboratory and pilot plant.

In those cases where the concentration in the refined oil was sufficient to inhibit the rate of hydrogenation, it was possible to increase the rate considerably by means of additional purging of the converter, addition of extra quantities of catalyst, or the addition of normal quantities of catalyst in divided portions. These are considered to be emergency measures inasmuch as it is believed that efficiently operated solvent extraction plants should produce stripped oils which, after refining, can be hydrogenated under normal conditions without difficulty.

It has been demonstrated that each of the three most common methods of refining crude oils greatly reduces the concentration of trichloroethylene in the oils so that crudes containing excessive amounts of added trichloroethylene hardened with little or no difficulty after being refined by any one of the three methods.

Acknowledgment

The analyses for trichloroethylene reported in this paper were run by I. Eisdorfer, who used a distillation and infra-red absorption method devised in these laboratories. In this method 400 g. of oil are distilled with 200 ml. of deodorized kerosene and the first 40 ml. of distillate examined for infra-red absorption at 10.8 microns. This method has been superseded in our laboratories by the method of Eisdorfer and Mehlenbacher (1), which has proven to be superior in many respects.

REFERENCE

1. Eisdorfer, I., and Mehlenbacher, V. C., J. Amer. Oil Chem. Soc., *28*, 307 (1951).

[Received August 22, 1951]

ABSTRACTS . . . . Don Whyte, Editor

• Oils and Fats

R. A. Reiners, Abstractor

Molecular rotation in some long-chain fatty acid esters in the solid state. R. W. Crowe and C. P. Smyth (Princeton Univ.). *J. Am. Chem. Soc.* **73**, 5401(1951). A plot of the measurements of the dielectric constant of very pure stearic acid at various temperatures shows a sharp break at the freezing point. Due to its strong tendency to form non-polar dimers, the dielectric properties of this compound resemble closely those of a long-chain hydrocarbon. Dielectric constants and loss factors were also measured on a series of high molecular weight alcohol esters of stearic and palmitic acids.

A study of the n-octadecenoic acids. III. X-ray diffraction behavior of 6,7- through 12,13-dihydroxystearic acids. E. S. Sutton, W. F. Huber, A. J. Mabis and C. B. Stewart (Procter & Gamble Co.). *J. Am. Chem. Soc.* **73**, 5206(1951). Both the low-melting and the high-melting series of 6,7- through 12,13-dihydroxystearic acids show alternation of properties. By m.p.'s and interplanar spacings it is possible to classify these acids into 4 subgroups, namely, the even (6,7-, 8,9- etc.) and the odd (7,8-, 9,10-, etc.) low-melting and the even and odd high-melting isomers. Within each subgroup the individual members cannot be satisfactorily distinguished by means of m.p. and interplanar spacings. They can be distinguished, however, by the relative intensities of the different orders of their long spacings. Polymorphism was detected in the 6,7-acids and the 9,10-acids.

Displacement analysis of lipids. VI. Separation of unsaturated acids. R. T. Holman and W. T. Williams (Texas A. and M. College System, College Station). *J. Am. Chem. Soc.* **73**, 5285 (1951). Separations of saturated and various unsaturated fatty acids of the same chain length have been made with acids varying in chain length from 4-18 carbon atoms using charcoal as adsorbent and aqueous ethanol as solvent. Non-conjugated unsaturation decreases adsorption, carboxyl conjugated conjugation increases adsorption. Linoleic and oleic acids are separable, but they both lie between myristic and palmitic acids in adsorbability. Impurities in fatty acid preparations which were not removed by repeated distillation were detected by chromatographic separation.

VII. Carrier separation of unsaturated fatty acids. R. T. Holman. *Ibid.* 5289. The positions of a series of single unsaturated fatty acids in a carrier displacement chromatogram have been determined using methyl esters of even saturated acids in one series and methyl esters of odd saturated acids in another. Darco G 60 was the adsorbent and 95% ethanol was the solvent. It was found that increasing the number of isolated double bonds decreases the adsorption, changing a saturated acid to an unsaturated acid to an acetylenic acid decreases adsorption, and conjugation of double bonds increases adsorption. Differences in adsorbability of *cis-* and *trans-*isomers are slight. One isolated double bond in the molecule decreases adsorption roughly equivalent to 2 less carbon atoms. Separation of stearic and linoleic acids and of linoleic acid and its conjugated isomer by carrier displacement are demonstrated.

Component fatty acids of rapeseed oil. C. G. Youngs, T. M. Mallard, B. M. Craig and H. R. Sallans (Nat. Res. Labs., Saskatoon, Sask.). *Can. J. Chem.* **29**, 871(1951). The fatty acid composition of the oil from Argentine rapeseed grown in Western Canada was investigated by converting the glyceride esters to methyl esters and distilling the latter in a Podbielniak Heligrid column. Results indicated that the erucic acid content of this oil was 40% and the eicosenoic acid content 12% as compared with 47-50% and 3-6% reported by previous investigators. The methyl esters were prepared by the conventional method in 88% yield and by the use of dimethyl sulfate in 99.4% yield. Essentially the same results were obtained on distillation of these esters indicating that a representative sample was obtained in the former case.

Polymerizable derivatives of long-chain fatty acids. IV. Vinyl esters. W. S. Port, J. E. Hansen, E. F. Jordan, Jr., T. J. Dietz and D. Swern (Eastern Reg. Res. Lab., Philadelphia, Penna.). *J. Polymer Sci.* **7**, 207(1951). Vinyl esters of saturated fatty acids polymerize readily and rapidly. Vinyl oleate, when present in excess of 5%, and oxygen exert marked retarding effects. Properties of the polymers and polymerization techniques are described.

Hydrolysis of wool wax and related high molecular weight esters. I. Homogeneous reactions. E. V. Truter (Univ., Leeds, 2). *J. Applied Chem.* **1**, 452(1951). The homogeneous alkaline hydrolysis of the acetates, caprylates, and palmitates of n-octadecanol and cholesterol in alcohols has been studied. The constants of the reactions are within the anticipated range indicating that any difficulties encountered in the heterogeneous saponification of wool wax must be due to surface phenomena.

II. Heterogeneous reaction: oil-in-water emulsions. *Ibid.*, 454. The aqueous alkaline hydrolysis of wool wax, n-octadecylcaprylate and palmitate and cholesteryl acetate and caprylate as oil-in-water emulsions stabilized by various agents, has been examined. When about one-third of the wax has been saponified the rate of reaction is considerably diminished because the alcohols liberated in the reaction compete with the esters for places in the interface and the latter are excluded by a mass-action effect. Complete saponification as an oil-in-water emulsion will only be possible if these alcohols can be removed from the interface.

Residual oil in extracted soybean flakes is 0.5% using solvent-flake ratio of 0.85. Anon. *Chem. Proc.* 14(11), 46(1951). Operation of the Rotocel extractor installed in the Indianapolis plant of Glidden Co. is described.

Develop new type traveling screen extractor for cotton seed. Anon. *Oil Mill Gaz.* **56**(5), 13(1951). A total immersion countercurrent type extractor is described in which the flakes are passed in a zig-zag pattern down the rectangular extraction column by means of a series of horizontally traveling stainless steel screens. High efficiency is claimed.

Selective extraction of a fish oil with furfural. Ma. A. de Lamo, R. Montequi and A. Doadrio. *Pubs. inst. quim. "Alonso Barba"* (Madrid) **4**, 295-301(1950). Striped-tunny oil of good quality and furfural were heated on a water bath until in solution, and the temperature was noted. After standing 24 hours the two layers were separated, and the percentage oil and furfural in each was determined before and after vacuum distillation. It was most convenient to segregate at 40° with a furfural: oil ratio of 4:1. The iodine no. of the residue oil was 184.6 while that of the extracted oil was 220. The iodine no. of extracted oil diminished with rise in extraction temperature. (*Chem. Abs.* **45**, 9283)

Indian edible oils. Unsaponifiable matter. K. Ramamurti and B. N. Banerjee (Indian Inst. Sci., Bangalore). *Indian J. Med. Research* **38**, 377-83(1950). The unsaponifiable matter from peanut oil, sesame oil, and coconut oil were studied. As rancidity increases (1) the iodine no. of both alcohol-soluble and insoluble fractions of the unsaponifiable matter increase; (2)