Synthesis of Drying Oils by Thermal Splitting of Secondary Fatty Acid Esters of Castor Oil

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THE hydroxyl attached to the 12th carbon of ricinoleic acid in castor oil has the characteristics of a secondary alcohol function, and it can form esters with fatty acids. These esters, to distinguish them from those involving glycerol hydroxyls, will be designated here as secondary ricinolyl esters. An important reaction of these secondary esters of ricinoleic acid is their thermal splitting—the ester linkages can be disrupted, at elevated temperatures, to regenerate a free acid and produce another double bond in the original ricinoleic acid (7, 8). By comparison, the glyceryl ester linkages are far more stable.

The formation and decomposition of the secondary esters in a process where castor oil is dehydrated in the presence of free fatty acids is the subject of this research. This same reaction path is believed to be involved in the catalytic activity of strong acid catalysts such as sulfuric acid, except that the secondary esters of strong acids are so unstable that these do not accumulate in appreciable concentrations at the ordinary temperatures of commercial processes. The process using the weaker acids is divided easily into two stages: a) a lower temperature stage where fatty acids are reacted with the secondary hydroxyl of ricinoleic acid of the oil triglyceride, and b) a higher temperature stage where these secondary esters are decomposed to regenerate free acids. The splitting of the secondary esters converts the ricinoleic acid in the triglyceride to octadecadienoic acid isomers. Ester exchange reactions occur simultaneously, particularly in the high temperature stage of the reaction, which tends to homogenize the reaction mixture with respect to distribution of fatty acids. Even when nearly pure ricinoleic acid is used in the first esterification stage of the reaction, the iodine value of the regenerated and distilled free acids is about the same as that of the acids that remain in the oil triglyceride after the second stage of ester splitting. The final product after ester-splitting is a drying oil. Analytical data are reported here for the intermediate esters and final drying oil products obtained from this process.

Synthesis of Make-up Acids

The materials used were a commercial grade of raw castor oil and a mixture of fatty acids derived from raw castor oil. This mixture of acids contains ricinoleic acid, octadecadienoic acid isomers derived from ricinoleic acid, and such other fatty acids as occur in raw castor oil. Commercial realization of this process would require use of such acid mixtures rather than pure fractionated acids of one species, which might be preferred for a strictly theoretical study.

The apparatus consisted of a 250-gal., cylindrical, Monel, open-fire, varnish kettle fitted with a lid and a condenser. The kettle, charged with 660 lbs. of raw castor oil (Baker Castor Oil Company), was heated to 215°F. and agitated violently with a jet of steam while a solution of 127 lbs. commercial grade caustic (98% NaOH) in 229 lbs. of water was added slowly. This quantity of caustic represents a 5% excess of NaOH over what is required theoretically to saponify the oil. The reaction mixture was agitated with steam at 215 ± 20°F. until a clear solution was obtained when 100 g. of the soap product was mixed with 1,000 g. of distilled water at 160°F. Then 216 lbs. of 60° Baumé (at 68°F.) sulfuric acid (approximately 77.7% H_2SO_4) were diluted with 190 lbs. water and this acid solution (41.3% H_2SO_4—representing a 10% excess of acid) was pumped slowly into the steam-agitated batch of soap, and the heating continued until the free acids separated and visual observation indicated the aqueous layer to be soap-free.

The aqueous solution was discharged from the kettle and replaced with an equal volume of water. Agitation with steam was resumed. This washing operation was repeated with replacements of water until the wash water was neutral to methyl orange. The water was then allowed to settle, and the free acids were pumped to a storage tank.

This stock of acids was blended with process-recovered acids distilled from the dehydration mixture in a manner to be described later in proportion of 90 parts by weight of recovered acids to 10 parts of this saponification-derived, make-up acid. The make-up acid was required to compensate for acids lost because of decomposition reactions during the ester-splitting operation of the process that will be described in the following sections.

Esterification of Raw Castor With Free Oil Acids

A 38- x 38-in. Monel kettle was charged with a mixture of 184 lbs. of raw castor oil and 253 lbs. of fatty acids. The characteristics of the components and of the blend are given in Table I. The aluminum lid of the kettle was fitted with a sampling port, a goose-neck connection to an air condenser, a varnish maker's thermometer, and the riser of an immersed, 36-in.-diameter, perforated, stainless steel coil which served as a gas sparger. The input of carbon dioxide to the sparger was measured with a Fischer-Porter Flowrator.

TABLE I

Original and Final Properties of Fatty Acid-Castor Oil Reaction Mixture

	Original	Final
Saponification value	189.8	191.0
Acid value	101.2	38.7
Acetyl value	76.9	38.7
Ester-split value	1.2	60.5
Specific gravity 60°F./60°F.	0.9338	0.9350
Viscosity (Stokes at 77°F.)	1.7	2.7
Gardner color (1933)	4	10

The kettle was heated over a coke-fire pit. The temperature was elevated to 482°F. over about a 2- to 3-hr. period while the carbon dioxide input was controlled at 1.12 $ft.^3/min$. The first sample of Table II represents the condition of the reaction mixture when

TABLE II

Synthesis of Secondary Ester of Castor Oil-Rate Data-Comparison of Changes in Oil Properties

ΔT(°F.)	Δt (min.)	Acid value decrease	Acetyl value decrease	Ester-split value increase
284 to 482°F.	160	23.6	22.0	21.9
0	60	21.7	21.0	22.7
0	20	4.6	4.3	4.7
482 to 300°F.	225	4.7	4.2	5.5
Totals	345	54.6	51.5	54.8

the temperature reached 482°F. At this time the gas flow was reduced to 0.72 ft.^{3}/min. Samples were withdrawn at 10-min. intervals while the temperature was maintained at 482°F. for 80 min. The batch was allowed to cool to 300°F. over a period of about 3 to 4 hours. The hot reaction mixture (418.1 lbs., or 95.7% yield) was transferred to storage containers and used for subsequent experiments. The characteristics of this reaction product are given in Table I. Table II shows the close equivalence between acid number and acetyl value decrease and ester-split value increase. This confirms the theory regarding formation of secondary esters. The drop in acetyl value indicated in Tables I and II and Figure 1 corresponded to the loss of one molecule of water per ester linkage formed.

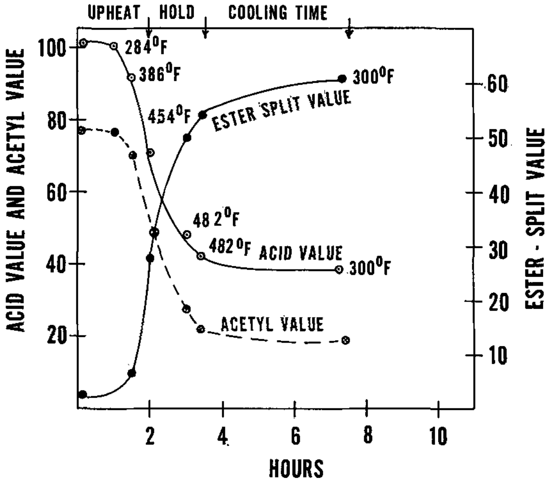

FIG. 1. Change of acid, acetyl and ester split values with process time and temperature.

The formation of secondary esters caused a slight increase in viscosity of the mixture. The color change indicated in Table I may not be a necessary consequence of the process. The color might be improved if Inconel or some other more corrosion-resistant alloy were used instead of Monel for the reactor. More uniformly distributed heating, and lower peak temperatures might further retard discoloration.

The reaction rate is shown in Figure 1. All the experimental points are not shown—in the range of 482°F.(hold time 80 min.), the curves are smoothed through data for samples taken every 10 min.

Splitting of Secondary Esters to Yield Dehydrated Castor Oil

This series of syntheses was performed in a three-neck Pyrex flask fitted with variable speed agitator, condenser, thermometer, and glass tubing for input of inert gas or steam. A Glas-Col Mantle heater was fitted to the top of the flask to minimize condensation; the bottom of the flask was heated with one or more high pressure gas burners. Two Liebig condensers in series were connected through a condensate receiver to a Cenco Hyvac pump. At the specified temperature of distillation the input of carbon dioxide was maintained at a rate which permitted the pump to hold a reduced pressure of about 9 to 15 cm. of mercury. The average rate of distillation of fatty acid was about 2 ml./min. Some data from the first experiment on the distillation splitting at 500°F. of fatty acids from the castor oil-fatty acid reaction product are given in Table III for one 2,400-g. batch, which produced 1,855 g. of product and 545 g. of volatile material. The low viscosity of the oil indicated that very little polymerization had taken place. At 500°F. the distillation failed to remove a sufficient quantity of the split acids in a reasonable period of time. The poor color indicated that the over-long reaction time caused excessive decomposition. The iodine value was rather low as compared with commercial dehydrated castor, indicating the presence of unsplit secondary esters. The difference between total and partial iodine values and the fairly high diene number showed the presence of appreciable conjugation. The extensive amount of thermal decomposition was reflected also in the high unsaponifiable content of both the product and distillate. Even if allowance is made for some acid value increase due to the splitting of glyceryl esters (to be discussed later), the ester split value of this product showed that at least 19% of the total fatty acids occur as secondary ricinolyl esters. This trial run demonstrated the necessity of employing shorter distillation times at reduced pressures and higher temperatures.

TABLE III

Data for Product and Condensate
(3.5 hrs. distillation at 500°F. and 16 mm. of Hg)

	Product	Condensate[a]
Viscosity (Stokes at 77°F.)	8.0	0.84
Acid value	31.1	182.0
Specific gravity 60°F./60°F	0.9432	0.9056
Color—Gardner, 1933	15	4
Iodine value (Wijs, 1 hr.)	110	131.8
Iodine value (Woburn—Total)	145	....
Diene number	11	....
Refractive index $N_D^{77°F.}$	1.4853	....
Acetyl value	0.3	3.3
Ester-split value	47.3	....
Unsaponifiable matter, %	3.28	8.57

[a] Data refer to only the non-aqueous part of the condensate, and these data are typical for the acid fraction recovered in other experiments (Table IV). This recovered acid plus some make-up ricinoleic acid is recycled into the esterification stage of the process.

The next stage of the study was to establish at what temperatures a satisfactory product could be produced in one hour of distillation time and at reduced pressures of 5 to 10 cm. of mercury. The results for various temperatures are shown in Table IV and Figure 2. The substitution of low pressure steam (212°F.) for the carbon dioxide sparging used in the trial run of Table III allowed for a reduction of the acid numbers of the products 4 to 11 (Table IV) to values of about 20. However other experiments showed that the rate of distillation of the liberated fatty acids had no rate limiting effect on the rate of ester splitting. The use of steam instead of carbon dioxide sparging improved the efficiency of

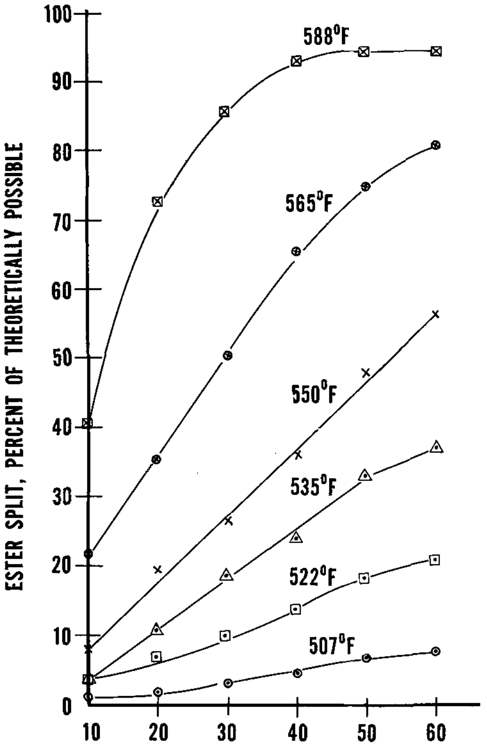

FIG. 2. Total interval of time at splitting temperature, minutes.

fatty acid distillation without having much influence on the rate of ester-splitting.

Table V lists also product No. 12, which is equivalent to product No. 6, except that it is produced from the original, undistilled oil stock by removal of the free acids by liquid phase extraction with ethyl alcohol. The original oil-ester was twice extracted with about equal volumes of denatured alcohol at 80°F., washed four times with equal volumes of warm water (147°F.), and finally dried at 250°F. at a reduced pressure of 10 cm. mercury until no more volatile condensate could be recovered.

Sample 13 of Table V represents another comparison oil prepared from commercial, catalytically-dehydrated castor oil. In the still which was used for the preparation of the other products the commercial oil was bodied at 575°F. in a carbon dioxide atmosphere until the viscosity had increased from 1.4 to 5.9 stokes and the acid number had increased from 4 to about 5.2. Sufficient of the fatty acid by-product of batches 1 to 11 was added to bring the acid value to about 21, which is about equal to the acid value of the split-acid products of this process.

TABLE V

Comparison of Reference Oil Mixtures With Process Products 5, 6, and 9

	Process oil	Reference oil	Process Oil	Reference oil	Process oil	Reference oil
Product	6	12	5	14	9	13
Viscosity— Stokes, 77°F.	4.6	3.4	5.9	6.3	62.2	5.9
Acid value	18.1	20.0	20.7	21.0	18.5	20.3
Acetyl value	3.5	17.0	3.0	13.0	1.6	16.9
Ester-split value	65.4	65.6	55.1	53.0	14.0	10.0
Iodine value (Wijs—1 hr.	109	109	110	112	108	123
Iodine value, total (Woburn)	130	129	135	136	152	150
Diene number (maleic)	9.5	11.0	10.1	12.0	12.6	12.0

The high acetyl value of product 13 is the result of the commercial process by which the oil was made (original acetyl value before bodying and blending with acids was 26). The ester split value of 10, reported for oil product No. 13, might represent a blank determination on the analytical method. The ester-split value of this oil should be zero if no glyceryl ester linkages had been split. The blank correction might be applied to the reported ester-split values for the products of this process.

Product No. 14 is another reference oil mixture designed to be compared with product No. 5 of this process. Oils numbered 12 and 13 (Table V) and the original ester stock used for batches 1 to 11 were blended in the proportions 760/500/740 to give product No. 14, which is similar to product No. 5 in secondary ester content, acid value, and viscosity, but differs in iodine value and acetyl value. The oil series 1 to 14 (Tables IV and V) now represents a variety of products of varying properties, prepared in a number of ways. Drying tests were performed on this product series. Included also is a typical sample of commercial dehydrated castor oil, which was not modified by the addition of other materials.

Analytical Methods

The acid value, iodine value (Wijs-1 hour), saponification number, viscosity, specific gravity, refractive index, and unsaponifiables were determined from the appropriate sections of ASTM, D555-51T, while the acetyl value was determined from ASTM, D-960-48T (1). The total iodine value determination followed von Mikusch and Frazier (11). The diene value was established by maleic addition by the procedure of

TABLE IV

Summary of Chemical Constants for Dehydrated Castor Oils

	1	4	5	6	8	9	10	11
Splitting temp., °F.	500	550	522	507	574	588	565	535
Viscosity (Stokes, 77°F.)	8.0	24.2	5.9	4.6	11.6	62.2	13.3	8.3
Acid value								
I. Oil	31.1	20.7	20.7	18.1	23.3	18.5	19.7	21.6
II. Distillate	182.0	181.0	169.0	165.0	182.0	182.0	180.0	178.0
Ref. index, $N_D^{25°C.}$	1.48527	1.48856	1.48435	1.48258	1.48799	1.49055	1.48755	1.48570
Color—Gardner								
I. Oil	15	16	13	13	14	15	15	14
II. Distillate	4	3	3	3	2	2	2	2
Sp. Gr. 15.5/15.5°C.	0.9432	0.9510	0.9405	0.9387	0.9485	0.9550	0.9485	0.9419
Iodine No. (Wijs—1 hr.)	110.2	108.9	109.9	109.0	111.5	107.7	110.5	109.9
Iodine No. (Woburn)	144.6	147.2	135.4	130.5	151.1	151.8	147.8	145.5
Diene value (maleic addition)	10.8	12.2	10.1	9.5	12.4	12.6	11.6	11.0
% Unsaponifiables								
I. Oil	3.3	3.0	2.3	2.2	2.8	2.5	2.2	2.2
II. Distillate	8.6	7.9	9.2	10	7.2	7.9	7.0	7.7
Acetyl value	0.3	1.4	3.0	3.5	2.3	1.6	1.1	2.0
Ester-split value[a]	47.3	26.6	55.1	65.4	25.1	14.0	31.7	41.2

[a] Defined as the mg. KOH required to neutralize the free acids split from 1 g. of sample after heating 30 minutes at 316°C.

Overholt and Elm (6). Color ratings were established with a Hellige Comparator Model 605-V fitted to conform to the 1933 Gardner Color Standards. The ester-split value was established by determining the acid value of a sample before and after a 5-ml. oil sample was heated in a 15- x 1.6-cm. test tube for 30 min. in a 316 ± 2°C. oil bath. The ester-split value is the difference between initial and final acid value. The maleic-addition diene value tends to have its indicated theoretical significance only for oils that have a low acetyl value (4).

Drying Tests

All the oil samples were thinned to a viscosity of 1 stoke with mineral spirits (KB-36, distillation range 302 to 394°F.), and films were drawn down on 3- x 5-in. glass plates with a 0.015-in. wet-film gage. The films were exposed horizontally in the center of a well-ventilated, draft-free room, in diffused daylight, at temperatures of 87 ± 6°F. The relative humidity varied between 46 and 64% during the exposure period. Drying tests were made in duplicate, with and without metallic driers. Where indicated in Table VI naphthenate driers were used in proportions of 0.3% lead and 0.03% cobalt, based on weight of oil. The data for different films are given in Figure 3 for the air drying times without catalyst as a function of the ester-split value to iodine value ratio. With the exception of sample No. 14, the reference oils cannot be correlated with the process products. Sample 1, which received the longer heat treatment, has somewhat better drying properties than other oils that resemble it in other properties. There seems to be a correlation between ester-split value and drying times for the process oils if one compares the effect at unit iodine value. Secondary ester content seems to retard the drying rate in oils without driers. In the presence of driers (not necessarily the optimum proportions for each oil) the drying behavior of the oils changes and the correlation of drying rate with ester content is not as obvious. Table VI shows however that some effects are apparent even for the oils with driers.

TABLE VI

Drying Time of Dehydrated Castor Oil Products, With and Without Driers

Product No.	I.V. range	Ester-split value	Drying time (hours)			
			With driers		Without driers	
			Dust-free (finger-touch)	Tack-free to Al-foil	Tack-free (finger-touch)	Frosting[c]
5	133±3	55	0.75	1.6	42	None
14[b]	133±3	53	1.0	2.0	40	None
6	133±3	65	1.2	1.9	47	None
12[b]	133±3	66	1.5	After tack	72	None
4	145±4	27	0.40	0.67	28	Slight
10	145±4	32	0.66	0.94	29	Severe
11	145±4	41	0.77	1.7	39	None
1	145±4	47	0.68	0.97	22	None
8	153±3	25	0.45	0.72	20	None
9	153±3	14	0.42	0.72	27	Slight
13[b]	153±3	10	0.82	1.7	49	None
Commercial D.C.O.[a]	......	10	0.50	1.1	30	Severe

[a] Heat bodied—viscosity 1.4 stokes, I.V. (Wijs) 135, acetyl value 26.
[b] Comparison oils—to be distinguished from products of ester-splitting.
[c] None of the oils containing driers showed frosting or wrinkling in 24 hrs.

Evaluation of the Process and Products

This investigation has established the feasibility of the ester-splitting process for preparation of a variety of dehydrated castor oil products of low acetyl value and a wide range of variation in iodine and ester-split values. The preferred conditions of the process are *a)* the formation of the secondary ricinolyl esters of castor oil and fatty acids at temperatures below 500°F., followed by *b)* the splitting of these esters at temperatures exceeding 500°F. under conditions of steam distillation at reduced pressures of 15 cm. of Hg or less. The recovered free acids can be recycled to stage *a* of the process. Analytical data are reported in Table IV for eight process oils. The data here obtained confirm the theories advanced in the literature regarding the mechanism of castor oil dehydration (2, 3, 5, 7, 8, 9, 10).

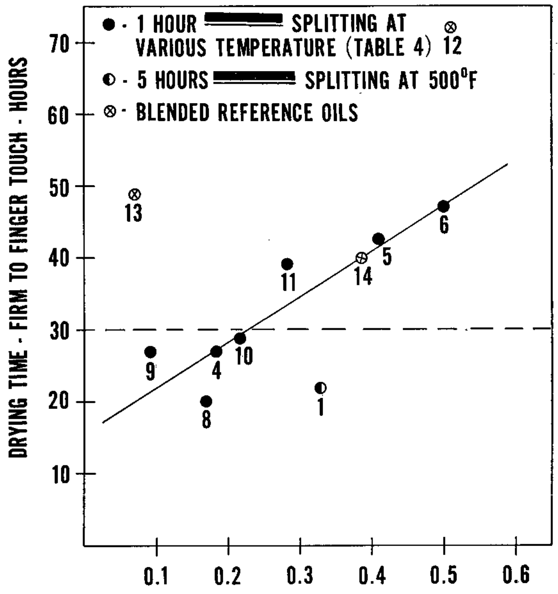

Fig. 3. Ratio-ester-split value/iodine value (Woburn).

As compared to commercial grades of catalytically dehydrated castor oils, these products are of higher acid value and are obviously inferior in color. These faults might be corrected at least in part if the oils are handled throughout in less corrosive metal equipment and in more inert atmospheres, also if improved methods of acid distillation at lower pressures can be devised. The rate of removal of the split acids seems to have no rate-limiting effect on the ester-splitting reaction of the process. The unsaponifiable content of the fatty acid distillates (7 to 10%) indicates the formation of some decomposition products in either or both stages of the process. However the unsaponifiable content is sufficiently low to permit recycle of these acids, along with about 10% of some make-up fatty acids, to the first esterification stage of the process. If the higher acid value of the final oil product can be tolerated, or possibly reduced by more efficient distillation, this process leads to comparatively efficient recovery of at least 90% of the theoretical yield of dehydrated castor oil and eliminates the problem of removing strong acid catalysts employed in some alternate processes. Generally the ester-splitting process produces higher viscosity oils, which feature may or may not be an advantage, depending on the intended use for the oil.

The drying properties of oils produced by ester-splitting are compared with certain reference oil compositions (Table VI and Figure 3). At comparable degrees of unsaturation, residual secondary esters seem to inhibit drying properties less than do residual hydroxyls, and the drying oils obtained from nearly completely split oil-fatty acid esters seem to show some superiority as compared to catalytically dehydrated and thermally bodied oils of comparable, iodine number, viscosity, and acid number. This conclusion however need not be general since the drying properties are sensitive to other variables. For example, as indicated by process product 1, prolonged processing at high temperatures can improve drying rates even though the conditions are insufficient to cause much change in secondary ester content, iodine value, or diene value. Possibly other mechanisms, such as ester exchange and other isomerization reactions, are important, the effect of which cannot be detected by the methods of analysis here employed.

The differences in drying rates of dehydrated castor oils of this process and other processes are minimized greatly by the introduction of metallic drier catalysts hence, from the viewpoint of comparing the commercial worth of dehydrated castor oils, the quality of drying rate differences may not be very important. Dehydrated castor oil is seldom used as the sole nonvolatile component of the binder in paint vehicles, and hardly ever in any form without the aid of drying catalysts.

Apart from the subject of drying rate comparisons for different process oils, the data of this paper should have considerable qualitative significance in the formulation of other vehicles where castor oil products are used to modify polyesters or other varnish resins. The esterification possibilities of secondary hydroxyls of ricinoleic acid and the extent of thermal stability of such esters in the presence of weak acids are facts important to the science and art of the resin formulator.

Acknowledgment

Appreciation is expressed to the Sherwin-Williams Company of Cleveland, Ohio, who generously provided the materials and equipment for this experimental study. The yet unpublished analytical method for determination of ester-split value is credited to the research laboratory of the Sherwin-Williams Company.

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[Received December 3, 1953]

Report of the Seed and Meal Analysis Committee, 1953-1954

THE work of the Seed and Meal Analysis Committee is conducted by eight subcommittees. They are: Screen Test for Soyflour, Analysis of Tung Fruit and Meal, Analysis of Copra and Copra Meal, Analysis of Castor Beans and Pomace, Foreign Matter in Lint, Residual Lint on Cottonseed, Analysis of Flaxseed and Linseed Meals, and Bulk Sampling of Meals. Development of methods for the analysis of sesame seed has been requested of the committee. A subcommittee will be organized for the work on such methods as soon as success in the development of an instrument by which the seed can be ground in a solvent is assured. It appears that the subcommittee may be named soon. Reports and recommendations of two subcommittees are as follows:

Analysis of Flaxseed and Linseed Meal

METHODS for sampling and for the determination of moisture and volatile matter and of oil in flaxseed, and of moisture and volatile matter, oil, protein, ash, and crude fiber in linseed meal have been studied collaboratively by the subcommittee. Methods proposed are based on the collaborative tests and the judgment of the members of the subcommittee and others experienced in the sampling and analysis of both flaxseed and linseed meal. The one for sampling flaxseed is essentially the federal procedure written in A.O.C.S. format. Those for the flaxseed are as follows:

Sampling

Scope: Applicable to flaxseed.

A. Apparatus

1. Trier, double-tube, separate compartment, grain trier or probe *ca.* 60 in. long.
2. Bag trier.
3. Sampling canvas 5 ft. x 2 ft.
4. Boerner sample divider, 36-pocket size.
5. Water-proof sample sacks.
6. Air-tight containers for preserving samples.
7. Spout sampler or "Pelican" for sampling bulk grain from running streams.
8. Carter dockage tester for flaxseed containing a No. 000 riddle, No. 1 riddle, a top No. 4 slotted sieve (0.064 x $\frac{3}{8}$ in.) in the middle, a No. 2 round hole sieve ($\frac{5}{64}$ in. dia.), and a No. 7 round hole sieve (4 1/2/64 in. dia.) in the bottom carriage.
9. Hand sieves 0.064 by 0.375 in. perforations, $\frac{3}{64}$ by $\frac{3}{8}$ in. perforations, $\frac{1}{12}$ in. round hole, 4 1/2/64 in. round hole, and 4 x 16 mesh to sq. in.

B. Procedure

a) *Flaxseed in bulk*

1. Probe in seven or more places with a standard trier in well distributed parts of the car. Insert the probe at an angle of 10 degrees with the vertical, with the slots closed and faced up. Open the slots and give the probe several gentle up and down movements. Then close the slots and withdraw the probe.
   a. Probe in center of car.
   b. Probe 3 to 5 ft. back from door-post toward the end of the car and approximately 2 ft. out from one side of the car.
   c. Probe from 3 to 5 ft. from same end of the car and approximately 2 ft. from opposite side of car, as described in b.
   d. Repeat b and c above in opposite end and sides of car.
   e. Probe 2 ft. from each end of car in center.
2. Place contents of each probe on the sampling cloth and mix by lifting alternate edges of the cloth. A minimum sample of 2,500 g. shall be collected and stored in an air-tight container.