• *Technical*

Confectionery Fats. I. Preparation by Interesterification and Fractionation on Pilot-Plant Scale[1]

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A cocoa butter-like fat has been prepared on a pilot plant scale by the interesterification of hydrogenated cottonseed oil and a triolein product or olive oil followed by fractional crystallization from acetone at two different temperatures. The coproducts—a fraction which consists primarily of trisaturates and is obtained by fractionation at 20 to 28°C., and a fraction which is primarily di- and triunsaturates and is obtained from the low temperature (0°C.) filtrate—are reused in the process. In five of the six pilot plant runs conducted, 100 pounds of 70:30 or 75:25 mixtures of the hard fat and liquid oil were used as starting materials. In the sixth run, 140 pounds were used. Yields varied from 25 to 35%.

Characteristics of the cocoa butter-like fat products are discussed. Variations in the products were made by changing the ratio of starting materials to 75:25 and by lowering the first crystallization temperature from about 28° to about 19°C.

Operational data obtained show that the process has commercial feasibility. Solvent-to-fat ratio was only 4 to 1. Filtration rates based on production of dry solids were 9 to 44 pounds per hour per square foot of filter area, respectively, for the first and second crystallizations. Although time to attain crystallization temperature was about 4 hours in the pilot plant operations, laboratory data indicate that comparable products can be obtained for crystallization times as low as one-half hour. The shorter crystallization time would be more applicable for commercial consideration. The steps in the process are considered conventional in commercial processing.

THE CONSUMPTION of cocoa fat, as cocoa butter and in the form of chocolate liquor, amounts to several hundred million pounds annually in the United States. The consumption of other confectionery fats, while difficult to estimate, amounts to many millions of pounds. A large proportion of these other confectionery fats are used in place of cocoa butter in chocolate-type confections or are used in pastel coating compositions, where cocoa butter-like fats are desired.

Prized characteristics of cocoa butter are an extremely short softening and melting range and a melting point a few degrees below body temperature. These characteristics are the result of a very high content of 2-oleodisaturated glycerides of palmitic and stearic acids.

Through the years many attempts have been made to modify natural fats and oils to resemble cocoa butter in its physical properties, and if possible, also in its composition. One approach to the problem consists of producing mixtures of glycerides containing a relatively high proportion of oleodisaturated triglycerides and then isolating this fraction.

In a report of earlier work in our laboratory, procedures were described for the preparation of cocoa butter-like fats from domestic oils. It was shown that cocoa butter-like mixtures can be prepared by the esterification of mixtures of oleic, palmitic, and stearic acids, or by the interesterification of their glycerides followed by fractional crystallization of the reaction products. One cocoa butter-like fat was prepared by the interesterification of 70 parts of completely hydrogenated cottonseed oil and 30 parts of olive oil, and subsequent fractionation.

It is the purpose of this paper to present data on the preparation of cocoa butter-like fats in laboratory and pilot plant quantities as a major step toward commercialization of the process using modifications of methods previously described (1). Hydrogenated cottonseed oil and a triolein product or olive oil were interesterified and then fractionally crystallized from acetone to yield the desired fats. Data show that the by-products can be used as starting materials in subsequent runs. The yield and properties of the cocoa butter-like fractions are shown as well as the effect of crystallization time and temperature, solvent ratios, and other processing variables on product yield.

Materials and Equipment

Materials. The starting fats used in 6 pilot plant runs and their analyses are given in Table I. The hydrogenated cottonseed oil, triolein, and olive oil were commercial grade products. The starting fats for Run No. 4 were by-products of previous runs, i.e., the hard fat was that produced in the first crystallization step, and the triolein-type fat was the oil present in the filtrates obtained after the low temperature crystallization step. This oil fraction was refined before being reused. Other materials used in this work were sodium ethylate, commercial grade acetone, oil pumped nitrogen, and glacial acetic acid. The acetone contained 0.4% water. The sodium ethylate catalyst was prepared by reacting sodium with absolute ethyl alcohol and evaporating the mixture to dryness.

TABLE I
Fats Used in Pilot Plant Runs[1]

Starting fats	Used in pilot plant (Run No.)	Iodine value	FFA (%)	*Trans* bonds as trielaidin (%)
Hard fats				
Hydrogenated cottonseed oil. 1st precipitate	1,2,3,5,6	1.8	0.06	.....
Runs No. 2,3	4	5.1	0.2	.....
Triolein type				
Triolein[2]	1,2,3,5	85.0	0.11	10.9
2nd filtrate, Runs No. 1,2 (refined)	4	48.0	0.2	.....
Olive oil (refined, bleached, and deodorized)	6	82.8	0.03	2.4

[1] For each run 100 lbs. of starting fats were used, except in Run 6 in which case 140 lbs. were used.
[2] Saponification No. 195.4.

[1] Presented at the Fall Meeting of the American Oil Chemists' Society, Los Angeles, California, September 28–30, 1959.
[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.

Equipment. For the laboratory scale phase of this work standard laboratory equipment was used. The pilot plant operations included the use of the following equipment units: a 30-gallon interesterification tank equipped with heating and cooling coils, perforated pipe for bubbling nitrogen, and variable speed stirrer; two stainless steel, jacketed crystallization tanks each with sufficient capacity to hold about 70 gallons below the jacket line; two gravity filter units, each large enough to hold about 35 pounds of product and one of which was jacketed to maintain low temperatures; brine supply system; stainless steel trays 3 ft. x 4 ft. for air drying the products; and auxilliary equipment such as pumps, stirrers, and recorders.

Procedure

Theoretical Yields. It is generally recognized that when a trisaturated glyceride is interesterified with a triunsaturated glyceride a random rearrangement of the saturated and unsaturated fatty acid groups occurs and the proportions of trisaturated and mono-, di-, and triunsaturated glycerides can be calculated from the mole ratio of the starting materials. Curves for the yields of the several classes of glycerides for different mole percentages of triunsaturated glycerides are reproduced in another publication (1). From these curves it is evident that in order to have the highest possible yield of monounsaturated glycerides (cocoa butter-like fat) the mole percentage of triunsaturated glycerides used as starting material should range between about 20 and 40%. Mole percentages of approximately 25 and 30 were used in this work. The theoretical yields of monounsaturated glycerides for 25 and 30% triunsaturated glycerides in the starting materials are 42.2 and 44.1 mole per cent, respectively.

Operating in the region of 25 to 30% of triunsaturated glycerides in the interesterification mixture has other advantages. The largest by-product consists mostly of trisaturated glycerides which are relatively easy to remove from the desired fraction and are very resistant to deterioration. The smaller by-product consists of the di- and triunsaturated fractions which can be recovered from the final filtrate for reuse.

Pilot Plant Procedure. With some modifications, the general procedure used in the pilot plant operations to produce the cocoa butter-like material was comparable to that reported by Feuge, Lovegren, and Cosler (1). Two fats were interesterified in the presence of an alkaline catalyst and then crystallized from acetone at two different temperatures. The first crystallization was conducted at about room temperature to remove a predominantly saturated triglyceride fraction and a second crystallization at near 0°C. to produce the cocoa butter-like product. A flow diagram of the pilot-plant operations is shown in Figure 1.

A mixture of hydrogenated cottonseed oil and triolein or olive oil, totaling about 100 pounds, was heated to about 104°C. for about one hour while bubbling nitrogen through it to remove traces of moisture. After cooling, the hard fat and liquid oil were interesterified at 65–70°C. for 30 minutes in the presence of a sodium ethylate catalyst (0.13% on basis of sodium). The mixture was washed once with equal volumes of a 4% acetic acid solution and then three times with tap water. For each wash the water

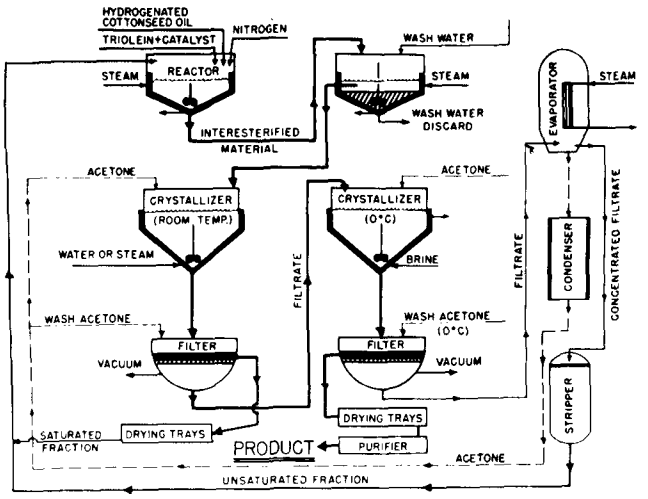

FIG. 1. Flow diagram of pilot plant process for producing cocoa butter-like fat.

was stirred with the mixture at about 80°C., settled, and the water layer drained. The pH of the water from the final washing was 5.0. The remaining moisture was removed from the fat by stripping with nitrogen.

For the first crystallization, the interesterified fat was added to 64 gallons of acetone (1:4 by wt.), and the mixture heated until dissolved. The mixture was cooled gradually over a period of four hours to either about 19 or 28°C. and filtered. The first precipitate or trisaturated fraction was washed with five gallons of acetone. The filtrate was cooled to −2 to +1°C. in about four hours and the resulting slurry filtered through the jacketed filter to produce the second precipitate or cocoa butter-like fat. This precipitate was washed with 15 gallons of chilled acetone. Acetone was removed from both the first fraction and the second product fraction by air drying under a hood. The oil in the final filtrate which contained primarily the di- and triunsaturated glycerides was recovered in conventional pilot plant evaporation equipment.

Pilot Plant Scale Investigations

Processing Conditions. The processing conditions for the pilot plant runs are shown in Table II. The ratios of hydrogenated cottonseed oil to liquid oil (triolein or olive oil) were selected on the basis of the high yield of monounsaturated glycerides indicated by the theoretical yield curves in (1). In Runs 5 and 6 the ratio was changed from 70:30 to 75:25 to decrease the proportion of diunsaturates which in turn decreased the "oily" characteristic of the cocoa

TABLE II

Processing Conditions for Pilot Plant Runs

Pilot plant Run No.	Starting fats[1]		Crystallization temperatures	
	Hydrogenated cottonseed oil (%)	Liquid oil (%)	1st(°C.)	2nd(°C.)
1	70	30	28	−1.5
2	70	30	27	−2.0
3	70	30	28	−2.0
4	54[2]	46[2]	28	−1.0
5	75	25	19	−1.0
6	75	25[3]	17	+1.0

[1] Solvent-to-fat ratio, 4 to 1.
[2] Used by-products of Runs 1, 2, and 3, i.e., 1st ppts. for the "hard" fat, and oil from final filtrates as the "liquid oil."
[3] Olive oil, all others triolein product.

butter-like product. Although the amount of trisaturates was increased by this change in ratio, the trisaturates were readily separated in the filtration step.

The interesterification reaction temperature and time, as well as the conditions for washing the interesterified material, were essentially the same for all runs. These conditions are given in the section on pilot plant procedure.

The crystallization temperatures for Runs 5 and 6 were based on the yield curves shown in Figures 2 and 3, respectively. The first crystallization temperatures were decreased to just below 20°C. to lower the trisaturate content of the final product, thereby decreasing the melting point of the product. For the second crystallization step, temperatures between −1 and −2°C. were used except for Run No. 6 in which case the temperature was changed to +1°C. This was done to decrease the amount of diunsaturated components in the cocoa butter-like fat products.

Figures 2 and 3 were used to predict the type and amount of fat obtained when the interesterified fat was crystallized from acetone. The amount of fat remaining in the acetone solution was plotted *versus* the crystallization temperature. Above 38°C. the solution was clear. Between 38° and 30°C. the majority of the trisaturated glycerides precipitated whereas much smaller amounts precipitated between 30° and 15°C. Most of the monounsaturated glycerides precipitated over the range 15°C. to −10°C. Di- and triunsaturated glycerides precipitated at lower temperatures. Unfortunately, there is some overlapping with each of these products with the glyceride above and below it.

Practical considerations permitted the use of only the upper portion of the monounsaturated product because the fat that precipitates between 0 and−10° C. contains too great a proportion of fat which is liquid at room temperature. The difference in position of the curves in Figures 3 and 4 is probably due to the greater insolubility of glycerides of elaidic acid and other iso-oleic acids containing *trans* bonds. The triolein used contained 10.9% *trans* bonds which could mean that as many as 30% of the triglycerides contain at least one *trans* bond. The *trans* bond content of the olive oil was only 2.4%.

If the ratio of acetone to interesterified fat is increased to 5:1 the percentage of fat crystallized at various temperatures is nearly the same as when a 4:1 solvent ratio is used. Consequently, the composition of the product is not affected significantly by small changes in solvent ratio.

A series of laboratory tests was run at 20°C. and 0°C. to determine the effect of holding time at these two temperatures on the yield of fat crystallized from an acetone solution. The holding times, which were varied from one-half hour to 23 hours, showed no significant effect on product yields.

Pilot Plant Products. Theoretically these cocoa butter-like products contain some of all the different monounsaturated triglyceride isomers produced by interesterification. With only stearic, palmitic, oleic, and elaidic acids present, there are 14 possible different monounsaturated isomers present in various amounts. By changing the starting materials and processing conditions, products can be obtained which have various proportions of these different triglycerides and, consequently, different physical properties.

Table III shows the yields and analyses of the cocoa butter-like products produced in the pilot plant runs. In Run 4, in which by-products were used as the starting materials, a decrease in yield of about 3% was obtained. Otherwise the characteristics of the product were comparable to those of Runs 1, 2, and 3. The slight difference in crystallization temperatures and the aging and thermal history of the samples may be responsible for the small differences observed in the physical properties of the products. Since the products from Runs 1 through 4 were similarly prepared and had similar properties, they were combined into one sample. As shown in the table, the amount melted at 35°C. was about 75% and the *trans* bond content calculated as trielaidin was 4.3%.

Changing the processing conditions for Run 5 resulted in a decrease in yield, but the amount of the product melted at 35°C. increased to about 90%. The *trans* bond content increased slightly. In Run 6, in which olive oil was used and processing conditions were comparable to Run 5, the yield dropped appre-

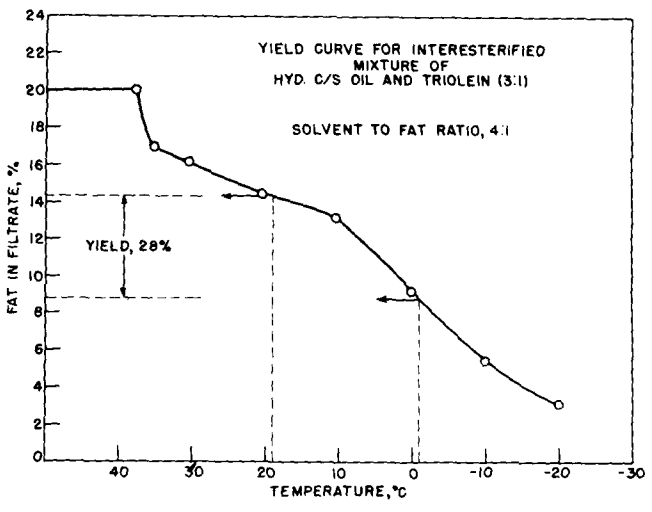

FIG. 2. Curve for determining yields of cocoa butter-like fat and by-products obtained at various crystallization temperatures using hydrogenated cottonseed oil and triolein as starting materials.

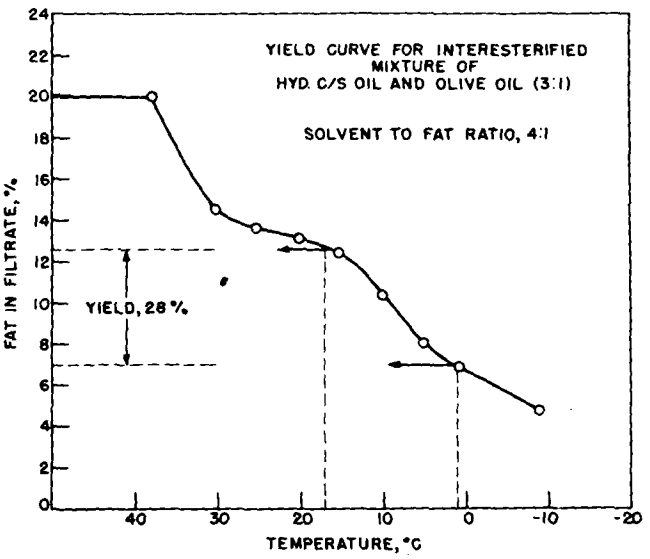

FIG. 3. Curve for determining yields of cocoa butter-like fat and by-products obtained at various crystallization temperatures using hydrogenated cottonseed oil and olive oil as starting materials.

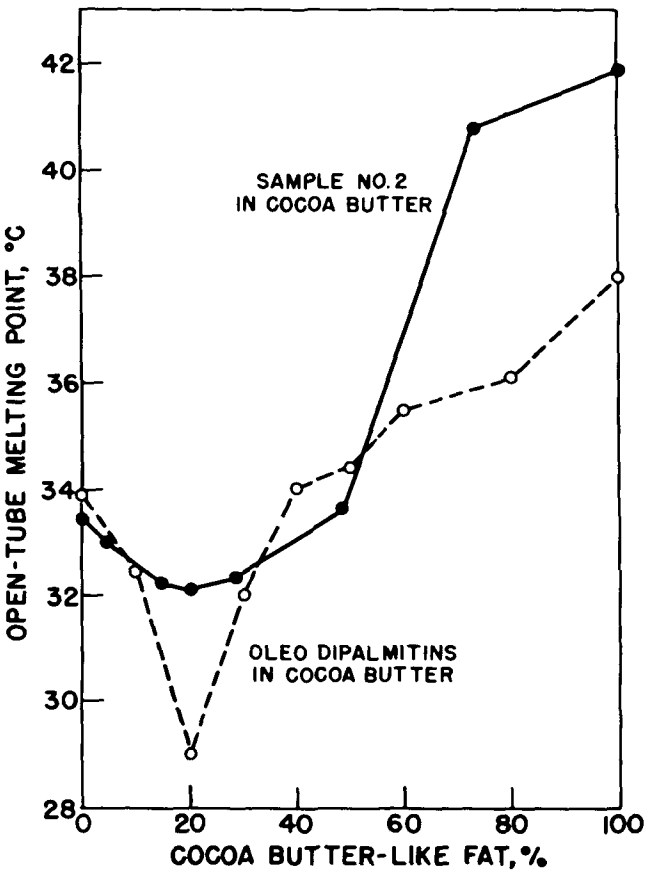

FIG. 4. Open-tube melting points (softening points) of mixtures of cocoa butter-like fat with cocoa butter.

ciably; however, *trans* bond content was one-half of that of Run 5.

The iodine value of these products is slightly lower than the theoretical for the monounsaturated triglycerides (about 29) due to the presence of some trisaturated glycerides. The clear melting points appear high; however these are due to the small amounts of trisaturated glycerides. Dilatometric studies show that up to 75% of products from Runs 1 through 4, and 90% from Runs 5 and 6, melt over the same short melting range as that of cocoa butter.

Three samples, one of which was the combined products of Runs 1 through 4 and the other two from Runs 5 and 6, were designated samples 1, 2, and 3, respectively. Samples 1 and 2 were submitted to commercial concerns for evaluation in chocolate formulations. Sample 1 was too waxy due to its high (20%) trisaturated glyceride content. This waxiness characteristic could be eliminated by use of emulsifiers but generally this is not desirable. Sample 2 was much improved over the original sample from the standpoint of both decreased waxiness and oiliness. Mold release properties were not as good as with cocoa butter.

One of the requirements of a satisfactory cocoa butter-like fat is that it not change significantly the melting characteristics of cocoa butter with which it is mixed. A measure of compatibility of the two fats is the degree of the melting point depression. The compatibility of cocoa butter-like fat No. 2 with cocoa butter is indicated in Figure 4. A maximum softening point depression of only 1.3°C. was obtained at about 20% added fat. Normal use of a cocoa butter-like fat would be above 20% on a fat basis when used with cocoa or chocolate liquor flavoring. Also shown in Figure 4 is a fat, essentially oleodipalmitin, which was previously prepared in this laboratory (1) and which is not nearly as compatible as Sample 2.

TABLE III

Cocoa Butter-Like Products from Pilot Plant Runs

Run No.	Yield (%)	Iodine value	FFA (%)	Slip point (°C.)	Melting point (°C.)	Amount melted at 35° C.	*Trans* bond as trielaidin (%)
1	36.2	28.0	0.28	47.7	56.0	75[1]	4.3[1]
2	36.4	27.4	0.24	45.2	57.0	75	4.3
3	35.8	27.2	0.20	51.2	58.4	75	4.3
4	32.9	26.7	0.18	49.2	56.7	75	4.3
5	30.0	26.3	0.28	42.1	47.0	90	5.0
6	24.0	27.5	0.32	43.5	49.0	90	2.5

[1] Combined products from Runs No. 1, 2, 3, and 4.

These cocoa butter-like products, due to their different composition from cocoa butter, no doubt require a different tempering procedure. Cocoa butter requires melting at a particular temperature, seeding, quick cooling, and optimum storage conditions. Although actual tempering conditions have not been determined, it is known that the cocoa butter-like products, due to their type of polymorphism, do not require melting at a particular temperature or seeding.

Slow polymorphic changes over a period of days following solidification tend to increase the hardness and raise the melting point. Because of these different properties, new solidification and tempering conditions may have to be used to produce the best confectionery products with these new fats.

By-products. The yields, iodine values, and free fatty acid contents of the by-products produced in the pilot plant runs are shown in Table IV. In commercial operations these by-products would be used as starting materials in subsequent preparations. The increased yield of first precipitate for Runs 5 and 6 is due to the greater proportion of hard fat used as starting material as well as the decreased temperature of the first crystallization (Table II). This lower temperature of the first crystallization in Runs 5 and 6 also causes a slight increase in the iodine value of the first precipitates due to a slight increase in overlapping of monounsaturated triglycerides into the first precipitate.

The small amounts of free fatty acids, which are produced when the acetic acid is added to neutralize the interesterification catalyst, appear primarily in the final filtrate due to the solubility of these free fatty acids in acetone. Color also tends to concentrate in this final filtrate. Because of the concentration of free fatty acids and color, only the oil recovered from the final filtrate need be refined before reusing the by-products in subsequent batches.

TABLE IV

By-Products from Pilot Plant Runs

Run No.	First precipitate[1]			Oil recovered from final filtrate[2]		
	Yield (%)	Iodine value	FFA	Yield (%)	Iodine value	FFA
1	34.1	5.0	0.15	24.1	47.5	2.5
2	30.5	.....	0.07	26.3	48.5	2.1
3	31.7	5.1	0.34	24.8	48.4	1.8
4	30.6	4.6	0.52	31.6	45.5	1.5
5	41.0	6.3	0.21	24.0	41.0	2.7
6	46.7	6.8	0.23	24.5	41.8	3.5

[1] % *Trans* bond for Runs No. 5 and 6 were 3.8 and 2.2, respectively.
[2] % *Trans* bond for Runs No. 5 and 6 were 4.2 and 0.3, respectively.

Trans bonds are present in all three fractions from Run 5. In Run 6 they tend to concentrate only in the first two fractions, possibly due to lower *trans* bond content of the starting material. When the by-products are reused as starting products, the ratio of the amount of first precipitate to oil recovered from final filtrate is determined by the iodine values of the two products. Sufficient amounts of the two by-products are used so that the iodine value of the resultant mixture would be the same as the iodine value of the original mixture of hydrogenated cottonseed oil (hard fat) and triolein-type product.

Acetone-to-Fat Ratio

For pilot plant operations and for practical commercial considerations it was desirable to decrease the acetone-to-fat ratios of 30:1 and 15:1, previously used in laboratory scale work. The results of a series of tests, in which ratios of 15:1, 8:1, and 4:1 were investigated, showed that there were no appreciable differences in yields and iodine value of the cocoa butter-like products. Yields decreased from 32.5% to 31.2% and iodine values increased from 25.2 to 26.8. The 4:1 ratio was consequently used in pilot plant studies and can be used in commercial scale operations.

A lower solvent-to-fat ratio such as 2:1 may in some cases introduce a two-phase liquid-liquid system in the second crystallization step. This liquid-liquid system is encountered at increased temperatures as the water content of the acetone is increased above about 0.4%.

Filtration Rates

A standard 0.1 sq. ft. Eimco [3] filter leaf test apparatus was used to determine filtration rates of the fat-acetone slurries of materials crystallized at 18°C. and 2°C. The procedure for testing was that recommended by filter manufacturers for simulating actual operating conditions of a rotary cylindrical vacuum filter. The filter medium was a cotton material with the following specifications: weave 2/2 twill; thread count 36 x 25; and air flow 12.6 CFM per sq. ft.

The filtration rates were determined and calculated in terms of pounds of dry solids per hour per square foot of filter area. The cycle time is the total time required for forming, washing, and drying the filter cake. "Drying" refers to the time that air is pulled through the filter cake. Cycle times were varied from 30 to 80 seconds for the 18°C. slurries, and 15 and 30 seconds for the 2°C. slurries. For practical commercial application, the determined filtration rates were recalculated on the basis of a 90-second cycle time and multiplied by a factor of 0.8 to allow for differences in conversion from test results to commercial practicability.

Filtration results were as follows:

Actual		Practical		
Cycle time (seconds)	Filtration rate	Cycle time (seconds)	Filtration rate	Filtration rate x 0.8
For 18°C. slurry				
30	25.7	90	8.6	6.9
45	17.1	90	8.6	6.9
80	12.6	90	11.2	9.0
For 2°C. slurry				
15	118.5	90	19.8	15.8
30	164.0	90	54.7	43.8

It is apparent that the filtration rate for the low temperature slurry which contains the cocoa butter-like fat is two to five times greater than that for the higher temperature slurry which contains the first precipitate by-product. These data will be used in recommending filter sizes for a commercial process for producing a cocoa butter-like fat.

Solvent Retention in Filtered Cocoa Butter-Like Fat

Three experiments were conducted to determine the effect of the amount of solvent retained in the filtered cake on the appearance of the final material after air drying. A low temperature slurry (0°C.) was filtered on a fritted glass funnel. Samples were taken after normal drainage without vacuum, after draining for 10 seconds at a reduced pressure of four inches of mercury, and after draining for 30 seconds at a reduced pressure of 27 inches of mercury. The resulting residual acetone in the cakes was 79.0, 76.5, and 67.8%, respectively. After air drying, the materials that originally had the higher solvent retention appeared more "plastic." Also the more "plastic" materials required more time for drying which was out of proportion to the solvent content. Based on these tests, and experience with other tests in this study, it appears that solvent in the low temperature filter cake should be less than 70% before air drying. In the filter leaf tests discussed under filtration rates, solvent retained in the cakes was about 50% for the first and 60% for the second precipitates.

[3] *Mention of names of firms or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.*

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[Received April 21, 1961]