Solidification of Cocoa Butter[1]

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Abstract

Cocoa butter and other confectionery fats do not behave alike on molding. Explanations for the behavior of cocoa butter generally are unavailable. The linear contraction of molded cocoa butter on solidification under various conditions was determined. Maximum linear contraction of about 2% was measured when a well-seeded sample was solidified at 16C. Nearly all of this contraction occurred during the first half hour. A theoretical explanation for this contraction was developed. Linear contraction takes place after the well-seeded cocoa butter has solidified in the next-to-highest melting form and while this solid form is transforming to the most stable polymorph. Additional information was developed on the polymorphic forms of cocoa butter, the permanence of seed crystals at various temps, rates of solidification, and solidification characteristics of unseeded cocoa butter. The data were obtained by dilatometric examination of a small sample using a volumetric dilatometer and direct measurement of linear contraction during solidification in a mold.

COCOA BUTTER and chocolate or other products containing cocoa butter exhibit on solidification under optimum conditions a sizable contraction. Thus these products ordinarily are easy to demold.

On evaluating in our laboratory a cocoa butter-like fat derived from cottonseed oil (3), the fat was found to contract to an insufficient degree on solidification. This made demolding difficult under some conditions. The reason for the lack of contraction could not be explained on casual examination. A quantitative comparison with cocoa butter could not be made at that time because values on the actual amount of linear contraction could not be found in the literature.

The general properties of cocoa butter have been studied extensively over a large number of years, and practical procedures have been developed for handling cocoa butter and cocoa butter-containing products in the confectionery and pharmaceutical industry. Unfortunately, only in recent years have the fundamental physical properties of cocoa butter and its individual components been studied in a thorough manner. While the information obtained has been useful in explaining some of the behavior of cocoa butter and related fats, apparently no attempt has been made to relate these properties to contraction in molds.

The purpose of the present investigation was to measure the contraction of cocoa butter on solidification under various conditions and to develop a theoretical explanation for this contraction. To accomplish this purpose, additional information was developed on the polymorphic forms of cocoa butter, permanence of seed crystals at various temps, the solidification rates under various conditions, and the solidification characteristics of "unseeded" cocoa butter.

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Experimental

Dilatometric Procedure

Dilatometric melting and solidification were measured with a volumetric dilatometer consisting of a sample holder, made of glass tubing, 7 cm long × 0.51 cm inside diameter, sealed onto the end of a capillary tube, 0.55 mm inside diameter × 92 cm long. The capillary tube was bent through an angle of 180° at the sample holder. This single dilatometer was used throughout the investigation.

A single sample of about 0.87 g of a typical, commercial cocoa butter was used in the dilatometer throughout the investigation. This sample was put into the sample holder, and the latter was sealed onto the capillary tubing. The sample and dilatometer were deaerated with a good vacuum pump of the oil type, and enough mercury was introduced so that its level in the capillary tube was near the top when the sample holder was at 65C. A metric scale was attached to the capillary tube so that direct readings of mercury height could be made. (In using dilatometers of this type, the sample of fat must be deaerated by melting and solidifying it several times while under vacuum. If an air bubble is discovered after the mercury is introduced, the bubble can be removed by freezing the mercury and fat, cooling both to −65C, and pumping out the air. Care must be exercised in remelting the mercury. If a small steel ball bearing is sealed in with the fat, stirring using an external magnet will deaerate the fat rapidly while under vacuum.)

The sample of fat in the dilatometer was subjected to the desired thermal treatment, then the dilatometer was immersed in a water bath to the point where the top of the sample holder was just below the surface, and the level of the mercury in the capillary tube was noted as the temp of the water bath was raised or kept constant.

Linear Contraction

Linear contraction was measured on a small strip of the cocoa butter solidified in an aluminum mold (Fig. 1). The latter consisted of a block, 76 mm long × 76 mm wide × 19 mm high, under a plate,

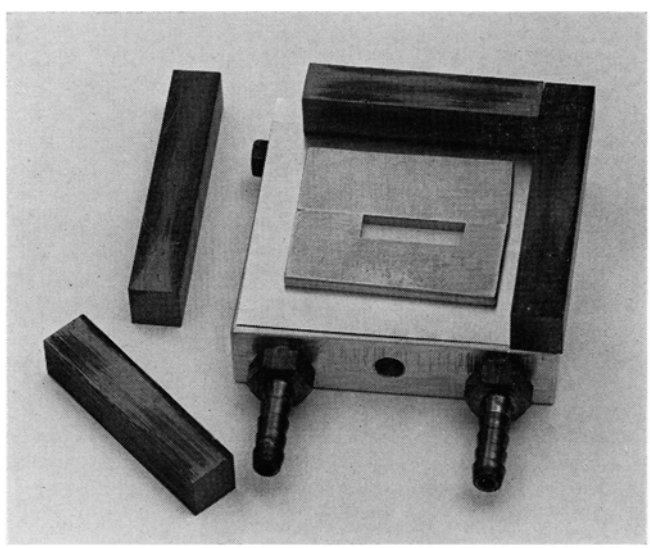

FIG. 1. Aluminum mold used to measure linear contraction.

1/8 in (3.18 mm) thick, in which a rectangular slot 25 mm long × 7 mm wide had been cut. The plate, which was not as long and wide as the block, was surrounded by four lengths of brass bar (12.7 × 12.7 mm) to help in maintaining a constant temp. The temp of the fat and mold was controlled by circulating water through passageways drilled in the block. Linear contraction from the mold was measured in the long dimension by observations through a microscope having a calibrated scale in the eyepiece. Usually the linear contraction at both ends was nearly identical.

Results and Discussion

Dilatometric Melting

Cocoa butter consists of a mixture of triglycerides, but ca. 80% is composed of 2-oleopalmitostearin and 2-oleodistearin which behave much as a single compound (2). Therefore, cocoa butter is referred to in this discussion as though it were a single triglyceride. Dilatometric melting curves obtained for the polymorphs of cocoa butter are shown in Fig. 2. Initially the highest melting polymorph, Form I, was obtained by melting and heating to 50C the sample in the dilatometer, then immersing the sample successively in ice water and a water bath at 24C, then repeating the immersion cycle numerous times, and finally aging the sample for 65 hr at room temp (about 25C). Dilatometric curve *B* was obtained on slowly warming the sample in a water bath while the temp and scale readings were noted.

Dilatometric curves *A* and *C* also represent the highest melting polymorph, but were obtained under different conditions. Curve *C* was obtained by solidifying the sample after it had been melted by heating to about 34C. Thus, this sample contained much seed or crystal nuclei of the highest melting form. After solidification the dilatometer was held overnight at room temp and dilatometric curve *C* was obtained.

Curve *A* was obtained after aging the fat sample about 8 weeks at room temp.

Some values calculated from the three dilatometric curves of the stable form of cocoa butter are given in Table I. Vaeck (4) concluded that a sample of cocoa butter well seeded with the stable crystal form will change completely into the highest melting crystal form when held at room temperature for perhaps 0.5 hr. Our data tend to confirm this. Yet, small changes in the point of complete melting did occur with passage of time, and the melting range tended to become shorter.

Possibly changes in crystal size or orientation with time could account for much of these differences. It must be remembered that cocoa butter contains a few minor components, some of which are liquid at room temp. These may complicate the number and types of phases present and thus contribute to the changes observed above.

Dilatomettric melting curves *D* and *E* represent the next-to-highest melting polymorph, Form II, and correspond to the beta prime form reported by Vaeck (4). To obtain this form, the sample was melted and heated to 47C and then chilled in ice water. Curve *E* was obtained on slowly warming the sample.

Curve *D* was obtained by melting and heating the sample to 47C, solidifying and holding it at 20C for 3 hr and then obtaining the dilatometric melting curve. In this case a slight amt of tempering occurred and caused the melting range to become shorter, although the point of complete melting was not changed.

TABLE I

Changes in Melting Characteristics of Well-Tempered Cocoa Butter on Storage at 25C

Storage time at 25C	Temperature at which fat contained the indicated percentage of liquid			
	20%	50%	80%	100%
16 hr	26.0	28.9	31.2	.....
2.5 da	....	30.3	32.2	34.5
8 wk	29.8	31.8	33.2	35.5

Curve *F*, Form III, was obtained by a "thrust-in" technique. For each point shown on the curve, the sample was melted completely by heating to about 50C and solidified by cooling for 5 min in the dilatometer bath at the indicated temp. This time was more than sufficient to cool the sample to the bath temp but insufficient to convert it to Form II.

Dilatometric Solidification

Permanence of Crystal Nuclei at Various Temperatures

The ability of seed crystals of the highest melting form of cocoa butter to withstand various temps was established. The dilatometer containing the highest melting form was held in a water bath for 30 min at each test temp and then solidified by placing the dilatometer in a water bath at 16C. This solidification temp was used because it is about the optimum for best contraction. Dilatometer readings were taken each minute. The results are shown in Figure 3. Heating temps up to 34C do not appear to slow the rate of solidification appreciably, but at 35C a definite retardation is evident. At 36C apparently the bulk of the seed crystals has been destroyed. On the basis of the data in Figure 2, just a little over 0.9% of solid fat remains unmelted at 35C, while at 36C virtually none remains. From the data in Figure 3, most of the few

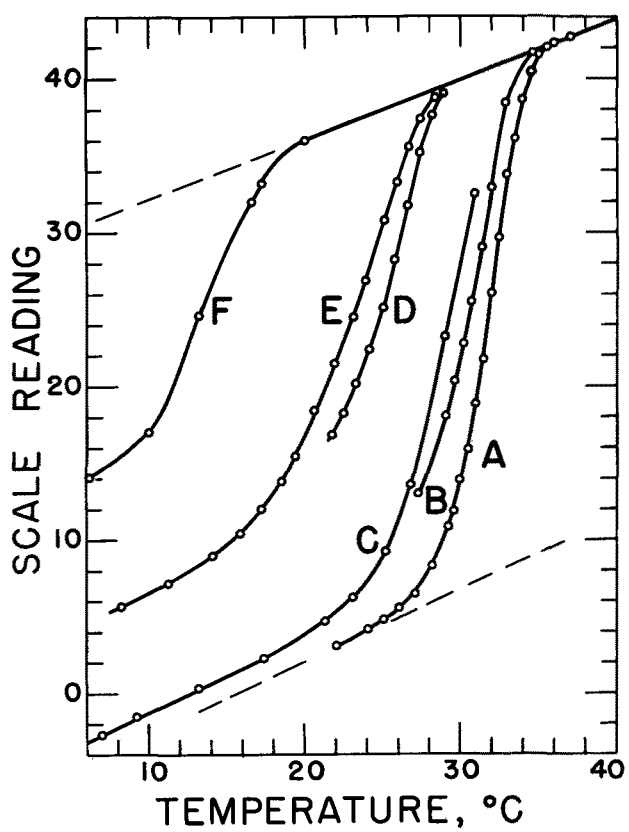

FIG. 2. Dilatometric curves for cocoa butter obtained under various conditions. *A*, *B*, *C*, Form I; *D*, *E*, Form II; *F*, Form III.

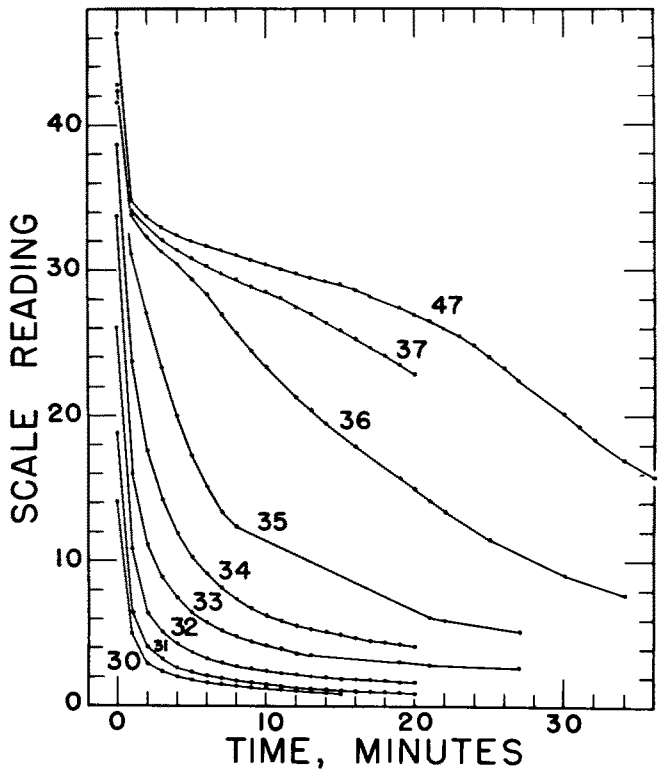

FIG. 3. Contraction of cocoa butter after heating to various temps and cooling in a bath at 16C.

seed or nuclei remaining at 36C are destroyed on heating to 37C, as there is very little change in rate of solidification when the melted sample is heated to 47C instead of 37C.

In Figure 3, the 36, 37 and 47C curves all indicate a scale reading of about 34 at the end of 1 min. This is approximately the scale on extending the liquid line in Figure 2 to 16C. Thus, in these three cases the liquid

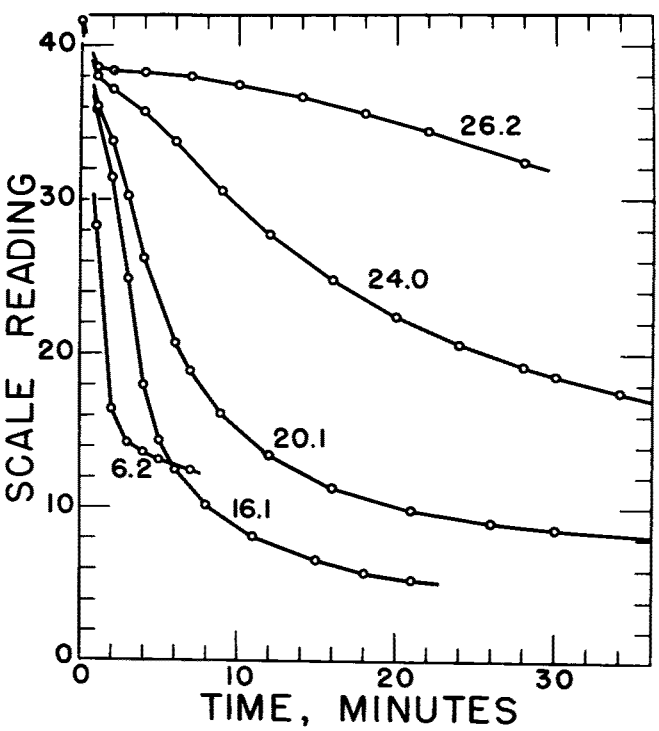

FIG. 4. Contraction of seeded cocoa butter when cooled at various temps.

sample has for practical purposes only been cooled to 16C. The curves representing the other temps indicate solidification actually started within 1 min. At 35C this solidification was slight, but was greater at the successively lower temps. It may be concluded that the presence of a small amt of unmelted cocoa butter in the highest melting form is necessary for rapid solidification at 16C.

Solidification of Seeded Cocoa Butter at Various Temps

To help establish the effect of solidification temp on contraction, the well-tempered (Form I) sample of cocoa butter in the dilatometer was partially melted by heating to 33.6C. Under these conditions a well-seeded sample was obtained. It was then solidified by immersion in a water bath maintained at various temps. Dilatometric scale readings were obtained each minute. Some of the results are shown in Figure 4. (Readings at 22C and 18C not shown).

Solidification temps of 22C or lower were necessary for fairly rapid solidification. Temps of 24 and 26C are below the melting range of the highest melting polymorph. From this it must be concluded that the direct solidification of cocoa butter to Form I is slow even when seed crystals of Form I are present.

In contrast with this, at lower temps the solidification to lower-melting polymorphs and their subsequent transformation is rapid. For example, at a solidification temp of ca. 20C, only 8 min is required to give a scale reading of about 17 (Fig. 4) corresponding to solidification to Form II (Fig. 2). Thus, in the course of a few minutes rapid solidification occurs and the fairly rapid conversion of Form II to Form I must be taking place. At 22C or lower, the solidification of cocoa butter seeded with the highest-melting polymorph apparently is a two-step process of (1) solidification of seeded liquid to Form II followed by (2) conversion of this Form II to the Form I. For about the first 5 min the first step of this process apparently predominates; after about 5 min a sufficient amount of Form II is present so that the second step then predominates.

On transferring the scale readings at the end of 20 min for each of the solidification runs represented in Figure 4 to scale readings at equal temps in Figure 2, it is noted that for the 26C run the scale reading is above the curve for Form II (Fig. 2). At 24C it is just below this curve. At 22C and lower temps the readings approach that of the curve for Form I (Fig. 2). However, at 6C the scale reading is above the curve for Form II. Probably at a temp this low the alpha polymorph, Form III, is obtained and the rate of transformation of Form III to Form II to Form I is too slow to have much effect in 20 min. At the higher temp, 24 to 26C, direct conversion of liquid to Form I was not as fast as the conversion of the liquid at 22C and lower to Form II and then the transformation to Form I. From these data, 16C appears to be the best solidification temp because: (1) little if any of the alpha form is produced; (2) a rapid crystallization rate is obtained; (3) crystals of small size result from the rapid crystallization rate; and (4) the highest-melting or beta form is obtained quickly when seed are present.

Solidification of Unseeded Cocoa Butter at Various Temps

The procedure described in the preceding section was used with unseeded cocoa butter. In these tests the sample in the dilatometer was melted and heated

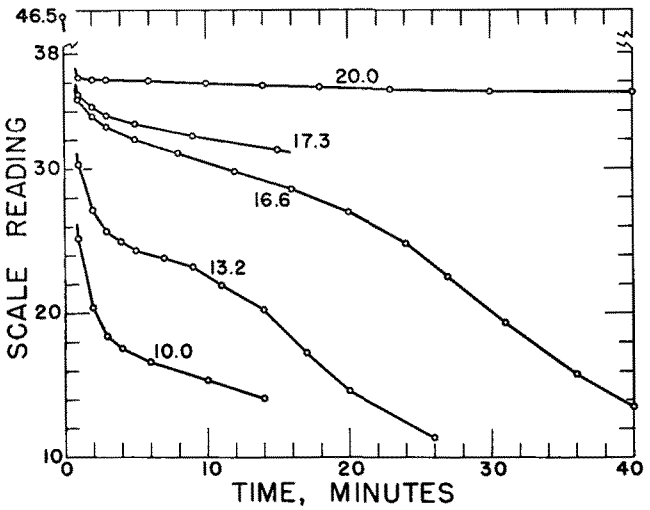

FIG. 5. Contraction of unseeded cocoa butter when cooled at various temps.

to about 47C before solidification at various temps. The results obtained are shown in Figure 5.

At a temp of 20C practically no solidification occurred in 2 hr. As the temp decreased, the solidification rate increased.

The solidification process resembled that of cocoa butter seeded with the highest melting form except that the cocoa butter solidified, when possible, to Form III (melting range about 10 to 18C) and then converted to Form II. This Form III to Form II conversion appears to be about proportional to the content of Form III at the solidification temps of 20, 16, and 13C. In this experiment one-half conversion to Form II required the following times:

Solidification temperature, °C	Time required for one-half of fat to be converted to Form II, min
20.0	140
16.6	32
13.2	17

Linear Contraction of Cocoa Butter

A sample of well-tempered cocoa butter in the small aluminum mold was melted by careful heating to 35C by circulating water at 35C through the temp control block. Cool water at the desired solidification temp was then circulated. Linear contraction was measured each minute with the aid of the microscope. The data obtained are plotted in Figure 6.

Most of the linear contraction occurred from about the fifth to the fifteenth minute for all solidifications except that at 22C. Comparison of the measurements made over these periods of time with the dilatometric data in Figures 2 and 4 indicates that the contraction in the mold started when Form II was the predominant solid and stopped when about one-half of Form II had been converted to Form I. Apparently, the initial conversion of Form II to Form I was accompanied by a reduction in volume which caused the entire sample to pull away from the mold. The conversion of the residual portion of Form II to Form I did not cause a similar, proportionate contraction, possibly because a rigid structure produced by the initial conversion to Form I prevented it.

Theoretically, if solidification of a fluid proceeds by the growth of spherical particles at many random points in the fluid, between about one-half and three-quarters will be solid when the growing spheres meet to form a rigid structure. The exact percentage depends upon the assumptions which must be made.

The experimental data which were developed when

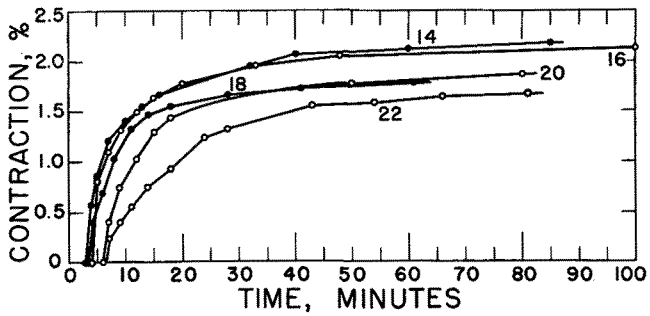

FIG. 6. Linear contraction of seeded cocoa butter when solidified at various temps.

coupled with the idea of rigid particles growing in a relatively plastic mass serve well to explain why cocoa butter contracts after molding under conditions used in the confectionery industry. When cocoa butter seeded with crystal nuclei of the highest melting polymorph solidifies at 16C, the immediate effect is the formation of Form II with perhaps some Form III, which quickly converts to Form II. Each nucleus of Form I starts to grow as soon as FormII is present, but the growth is at a slower rate than the conversion of Form III to Form II or the solidification of the liquid to Form II. As the content of Form I increases the whole mass contracts because the density of Form I is greater than that of Form II (2) and Form II is relatively plastic (1). When the Form I crystallization centers meet and form a continuous solid structure, linear contraction ceases for practical purposes.

To provide further data in support of this mechanism, the linear contraction of an unseeded cocoa butter was measured. The sample was melted and heated to 47C to destroy all crystal nuclei. It was then solidified in the mold at 16C. The linear contraction observed was as follows:

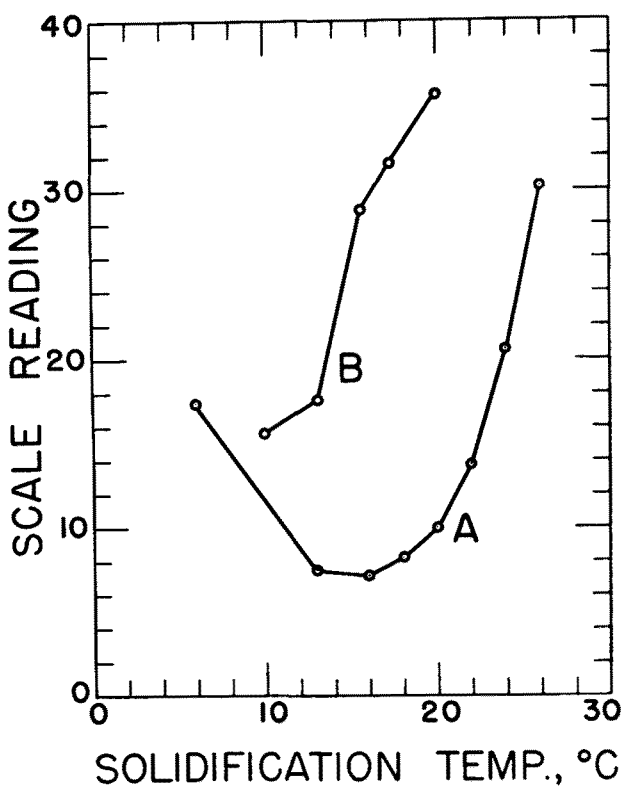

FIG. 7. Volumetric contraction (corrected to 20C) after 20 min at the solidification temp, *A*, seeded cocoa butter; *B*, unseeded cocoa butter.

Time, min	Contraction, %
Up to 20	zero
40	0.23
60	0.40
130	0.46
300	0.49

After standing overnight at 25C, no contraction was evident and the texture had become sponge-like.

In comparison, samples of cocoa butter solidified after seeding with Form I maintained their good contraction and appearance on aging.

Practical Conditions for Maximum Contraction

In commercial operations with cocoa butter the maximum contraction is desired over a reasonably short period of time. With this in mind, the scale reading obtained in the experiments represented in Figures 4 and 5 were examined. The values at the end of 20 min were plotted against solidification temp. So that these values would be comparable, they were corrected to 20C to eliminate the vol change caused by the expansion or contraction of the solid cocoa butter between 20C and the temp of each experiment. The calculated results are plotted in Figure 7.

With the seeded cocoa butter, max volumetric contraction was found at or near 16C. Max volumetric contraction of unseeded cocoa butter was less and occurred at a lower temp.

It should be remembered, of course, that to maintain solidification at 16C in a large block of cocoa butter, an ambient temp below 16C must be used after the surface has solidified.

Good gloss is believed to be due to the presence of minute crystals. This gloss is maintained only if this minute crystal structure remains unchanged. For this reason, solidification procedures which produce minute crystals of the highest melting polymorph will also produce products which have good gloss. The conditions of max linear contraction from the mold are the same as those required for good gloss. This was confirmed by experiment.

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Effect of Saline Electrolyte on Particle Sizes in Fat Emulsions by Electronic Counting[1]

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Abstract

The number of particles of specific diams in in the fat emulsions SR-151, Intralipid, and Lipofundin, by electronic counting, was critically dependent upon the elapsed time of contact of the emulsions with the diluting saline electrolyte. The most pronounced change in the number of particles as a function of time occurred with the particles of smallest diams, those less than 2μ. Increases in the number of particles by approx 100% occurred within 20 min of mixing the emulsions and electrolyte. Apparently coalescence or aggregation of smaller particles caused the increases in numbers. By extrapolation to zero time, accurate counts were obtained.

Introduction

FAT EMULSIONS which have been developed for intravenous nutrition consist of very fine dispersions of oil particles in aqueous media. Measurement of the diametric sizes of some of the dispersed oil particles in such emulsions by oil immersion light microscopy, while tedious, can be accomplished to provide an approximation of the gross range of particle sizes present. Such observations are very subjective, however, and depend to a great extent on the skill of the observer and the number of representative fields which are examined. If it is desired to determine the number of particles in incremental diametric size ranges as a basis for calculating size distribution approaching statistical significance, the task becomes formidable. Fischer and Harkins (5) made such an analysis of a hydrocarbon emulsion, and observed at least 1,000 particles to determine the relation between diams of oil spheres and the percentage number of particles of the respective diams. King and Mukherje stopped the Brownian motion in soap-stabilized emulsions of olive oil and kerosene in water and used a projection microscope to observe particle distribution in a like number of particles (6). Pinter and Zilversmit employed a gradient centrifugation method to obtain the distribution of particles below 1μ in diam in an "anhydrous" fat emulsion (10). The latter publication presents no information as to the distribution of particles of larger diam, although by oil immersion light microscopy particles of larger sizes are known to be present in similar fat emulsions (13).

An electronic instrument for determining the volume and number of particles in dispersions has recently become available (4), which provides size distribution data in a fraction of the time required by microscopy. There are a number of literature references to the theoretical aspects and reliability of this method (3, 14, 1, 15), and to the use of the instrument for determination of the distribution of particle sizes in a variety of liquid systems (8, 2, 7, 9, 12). As yet there have been no systematic studies of the use of the electronic counting method in determining the particle sizes in fat emulsions, nor of the possible physical effects of this method, particularly the required electrolyte, on the dispersed oil particles of a fat emulsion. This report presents the results of such an investigation.

Experimental

Emulsions. Three oil/water emulsions were used. One of these, designated SR-151, contained 20 wt % of soybean oil, 1.0 wt % of purified egg lecithin, and an aqueous solution of 2.5% glycerol as the isotonic aqueous phase. This emulsion has been fully

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