Water repellency and loss of frothing ability in water developed after 6 and 7 weeks' storage, respectively.

In Examples 6 and 8, in which the glycerol monoester was prepared from hydrogenated soybean oil (ratio of stearic to palmitic acid ca. 90:10), a slower shift to the β-crystalline form occurred. The blend retained its water dispersibility and continued to froth even after 1½ years' storage.

In Examples 9 and 10, the source of glycerol monoester was a commercial mono and diglyceride product. These preparations showed poor α-crystalline stability, water dispersibility, and frothing ability when the mole per cents of the glycerol and propylene glycol monoesters were nearly the same (Example 9), but these properties were improved by using a 50% molar excess of propylene glycol monostearate over glycerol monostearate (Example 10).

1,3-Propanediol monostearate was ineffective in stabilizing the glycerol monoester of hydrogenated lard in the α-crystalline form, possibly because of its dissimilar crystalline modification (Example 11).

Glycerol monoesters from hydrogenated lard blended with ethylene glycol monostearate showed good stabilization of the glycerol monoester in the α-crystalline form and retention of frothing ability (Example 12).

It was concluded from these experiments that a composition of Conjoined Crystals, as judged by retention of the α-crystalline form during storage, and by retention of frothing ability, is obtained by melting and solidifying a blend of glycerol monostearate and 1,2-propanediol monostearate in approximately equal molecular proportions. With glycerol monoesters from hydrogenated soybean oil and hydrogenated lard, in which glycerol monostearate is mixed with other monoesters, such as glycerol monopalmitate, a blend containing a higher ratio of propylene glycol monoester to glycerol monoester gave better stability.

ACKNOWLEDGMENT

X-ray diffraction data by R. L. Dehm and R. R. Parmerter, Industrial Laboratory, Eastman Kodak Co.

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Conjoined Crystals. II. Applications[1]

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Abstract

Mixed crystals of glycerol monostearate and 1,2-propanediol monostearate (propylene glycol monostearate) (a useful composition of Conjoined Crystals, see Part I) disperse readily in water, retaining this property for long periods of time. The effect of composition on retention of the α-crystalline form of the glycerol monoester in such dispersions is discussed.

The water dispersions foam when shaken or when air is blown through the dispersion, a property which appears to be associated with the superior activity of the mixed crystals as a food emulsifier. A test method for measuring foam retention is described.

The crystals, or their water dispersions, are useful in the preparation of low-calorie, fruit "fluffs," such as whipped applesauce. Sponge cakes with fine grain, improved volume, and texture were prepared with the water dispersions. The crystals are effective emulsifiers in cake mixes and bread. These tests are described.

Introduction

IN PART I, the preparation and physical properties of a number of compositions of Conjoined Crystals were described. In Part II, we report on the properties of water dispersions and the application of the crystals and/or the water dispersions in fruit purees or "fluffs," sponge cakes, cake mixes and bread (3).

Experimental Procedures and Data

Monoester Preparation

Propylene glycol monoesters were made from commerical arachidic acid (75% arachidic, 25% stearic) and propylene glycol using 0.1% p-toluene sulfonic acid as a catalyst, reacting at 125C for 3 hr, and molecularly distilling to give a monoester having a purity of 92% as determined by the official AOCS method (2).

Glycerol monoesters were prepared from partially hydrogenated soybean oil having an iodine value (I.V.) of 15 by reacting the hydrogenated fat with glycerol and 0.1% strontium hydroxide catalyst for one hour at 245C and distilling in a molecular still to give a monester having a purity of 91% (1) and a melting point of 63–64.5C.

Propylene glycol monoesters were prepared from partially hydrogenated soybean oil having an I.V. of 15 by reacting the fatty acids, obtained from the hydrogenated fat by alkaline hydrolysis, with propylene glycol and 0.2% d-10-camphor sulfonic acid as a catalyst at a temperature of 165C for one hour and molecularly distilling to give a monoester having a purity of 94% with a melting point of 36.5–37.5C.

The preparation of glycerol monostearate, glycerol monopalmitate, 1,2-propanediol monostearate, 1,3-propanediol monostearate, and ethylene glycol monostearate were reported in Part I. Glycerol monoesters, mainly glycerol monostearate, were prepared by the molecular distillation of the monoesters from either hydrogenated soybean oil (stearic to palmitic acid ratio, approximately 90:10) or hydrogenated lard (ratio, approximately 70:30).

The powdered emulsifier used in the "Applications" section was prepared by spray cooling, as described in Part I, and contained a molar ratio of 45:55 of the glycerol monoesters from hydrogenated soybean oil and the propylene glycol monoesters prepared from a commerical stearic acid (Humko Products Division, National Dairy Corp., Hystrene S-97, stearic acid to palmitic acid ratio, approximately 90:10).

Water Dispersions

Water dispersions were made by two methods. In

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[1] Communication no. 294 from the Research Laboratories of Distillation Products Industries, Division of Eastman Kodak Co.

TABLE I

Formation of β-Crystalline Form of Glycerol Monoester in 40% Water Dispersion of Conjoined Crystals Preparations

Example	Composition[a]—Molar Percentage		Age[b]	% β-form of glycerol monoester
	Glycerol monoester from	Propylene glycol monoester from		
1	55 Hydrogenated soybean oil	45 Stearic acid[c]	1 month	23
2	48 Hydrogenated soybean oil	52 Stearic acid	2 years, 8 months	6
3	40 Hydrogenated soybean oil	60 Stearic acid	2 years, 5 months	0
4	50 Hydrogenated lard	50 Stearic acid	4 months	8
5	45 Hydrogenated lard	55 Stearic acid	1 year	3
6	50 Hydrogenated lard	50 Stearic acid	2 weeks	74

[a] In Examples 1–5, the monoesters were melted together and spray chilled prior to addition to water. In Example 6, the monoesters were spray chilled separately before addition to water.

[b] In Examples 1–5, the initial preparations contained less than 5% β-form of glycerol monoester. In Example 6, the initial preparation contained 15% β-form of glycerol monoester.

[c] Hystrene S-97.

one method, the powder was dispersed in water by stirring at room temperature. Four parts of powder were usually blended with six parts of water, but the concentration can be varied.

Water dispersions containing 40 or 50% Conjoined Crystals preparation (which formed soft pastes) were also made by melting the crystals, adding the melt to water at 60–65C, stirring in a household mixer at #2 speed (slow mixing) until the temperature dropped to 46C, and increasing the mixing speed to #4 (creaming) until the temperature reached 38C. The product was smooth and soft. Concentrations of 30%, 20%. and 10% were made by adding water, with stirring. to a 50% product. The 30% product remained quite fluid for several days and then became a very soft paste. The 20% and 10% products remained fluid.

The percentage of β-crystalline form in the water dispersions was determined by infrared analysis of a small sample, dried under reduced pressure, at room temperature, just prior to analysis. The infrared method is described in Part I.

Discussion

Change to β-Crystalline Form in Aqueous Dispersions

Aqueous dispersions of freshly melted glycerol monostearate alone, showed a rapid change from the α to β-crystalline form. Distilled monoesters from hydrogenated lard were melted and spray chilled. Infrared analysis showed that the powder was 85% in the α and 15% in the β-crystalline form. When dispersed immediately in water in 40% monoester concentration, and stored at room temperature, there was a shift to 66% and 78% β-crystalline form in 4 and 7 days, respectively.

Aqueous dispersions of a number of Conjoined Crystals preparations showed only a slow change from the α to β-crystalline form. In Table I (Examples 2–5) is listed the percentage β-form of the glycerol monoester in a number of such dispersions after storage for periods for nearly three years. Infrared analysis indicated only 3–8% β-form to be present.

TABLE II

The Effect of Other Acids and Glycols on the Formation of β-Crystalline Form of Glycerol Monoester in 40% Water Dispersions

Example	Composition—Molar Percentage		Age	% β-form of glycerol monoester
	Glycerol monoester from	Glycol monoester from		
1	48 Palmitic acid	52 Propylene glycol monostearate	5 weeks	54
2	50 Hydrogenated lard	50 Propylene glycol monoarchidate	1 month	70
3	50 Hydrogenated lard	50 Ethylene glycol monostearate	1 month	20
4	50 Hydrogenated lard	50 1,3-Propanediol monostearate	1 month	34

TABLE III

Effect of Unsaturation on the Formation of the β-Crystalline Form of Glycerol Monoester in 40% Aqueous Dispersions of Glycerol and Propylene Glycol Monoesters

Example	Glycerol monoester	Propylene glycol monoester	Age	% β-form of glycerol monoester
	I.V.	I.V.		
1	0.9	0.9	2 years, 8 months	6
2	0.9	5	3 weeks	40
3	5	0	3 weeks	6
4	5	5	3 weeks	36
5	15	0	1 month	55
6	0.9	15	1 week	54
7	15	15	1 week	65

Formation of the β-crystalline form of the glycerol monoester was retarded when the preparation contained greater than 50 molar precent of propylene glycol monoester (Examples 1, 2, and 3). This was reported for the powdered preparations (Part I).

The preparation in Example 3 was also analyzed by X-ray diffraction after storage for two years and five months. Only the α-form of glycerol monoester and propylene glycol monoester could be detected.

The two monoesters must be blended before crystallization to retard formation of the β-form. In Example 6, the glycerol and propylene glycol monesters were spray chilled separately, blended as powders in 50/50 molar proportion, and the powder was dispersed in water at room temperature. The glycerol monoester changed to the β-crystalline form in two weeks.

Aqueous dispersions from mixtures of glycerol and propylene glycol monoesters made from different fatty acids were investigated (Table II). The glycerol monoester reverted relatively quickly to the β-crystalline form (Examples 1 and 2).

Aqueous dispersions from mixtures of glycerol monoesters and other glycol monoesters such as ethylene glycol monostearate or 1,3-propanediol monostearate were studied. The glycerol monoester again reverted relatively quickly to the β-crystalline form (Examples 3 and 4).

The effect of unsaturation in the monoester was investigated using combinations of glycerol and propylene glycol monoesters from partially hydrogenated soybean oil (Table III). Unsaturation increased the rate of formation of β-form of glycerol monoester. Unsaturation in the propylene glycol monoester apprepared to be more deleterious than in the glycerol monoester (Examples 5 and 6).

Froth Test

The ability of Conjoined Crystals preparations to froth in water was tested with carbon dioxide from baking powder. Two-tenths of a g of powdered emulsifier and 3 g of baking powder were blended, put in a 250 ml graduate and 50 ml of water was added. Froth was measured by its volume at times up to 1 hr.

In Table IV are given the results of a froth test

TABLE IV

Froth Test—Ml Froth at Times Indicated

Time	Control	β-Form glycerol monostearate	α-Form propylene glycol monostearate	Conjoined Crystals preparation
7 sec	1	5	5	12
30 sec	0	0	7	15
1 min	....	....	0	17
5 min	....	....	....	27
20 min	....	....	....	45
60 min	....	....	....	60

TABLE V
Fruit Fluff

Minutes of Whipping	Applesauce with 2% added Conjoined Crystals preparation		Applesauce whipped, dried, reconstituted
	% Overrun 0 days	% Overrun 24 days	% Overrun
1	40	30	220
2	100	120	410
3	190	220	660
4	270	320	750
5	370	450	840
6	510	570	870
7	610	665	920
8	670	700	920
9	720	780	910
10	740	780	890

for a control, β-crystalline form of glycerol monostearate, α-crystalline form of propylene glycol monostearate and a Conjoined Crystals preparation made from the two monoesters. The β-crystalline form of glycerol monostearate and the α-crystalline form of propylene glycol monostearate showed little tendency to froth. The Conjoined Crystals blend maintained a good volume of froth for more than an hour.

Applications

Fruit "Fluff"

Fruit purees, such as applesauce, in which air is incorporated by whipping, promise to find many applications, e.g. in low-calorie frozen desserts. Conjoined Crystals preparations proved to be superior to distilled monoesters in preparing such fluffs.

Distilled monoesters of hydrogenated lard, when melted and freshly solidified, were found to be predominantly in the α-crystalline form. A 40% water dispersion was added to finely ground applesauce at a level of 1–2% of monoester. The applesauce was then whipped immediately in a Hobart mixer to give a fluff with an increase in volume (overrun) of 700–800%.

However, when the applesauce was whipped after storage at room temperature for a few days prior to whipping, little air was incorporated. The loss in whipping ability was attributed to the change of the monoester from the α to the β-crystalline form. The applesauce, after storage, could be whipped after reheating, which presumably reconverted the monoester to the α-crystalline form, but this is inconvenient.

The Conjoined Crystals preparation (1–2%, composition described in Experimental Procedures section) was added to applesauce either as a powder or as a water dispersion. The mixture was then warmed to 160F or higher and cooled to 115F during stirring in a mixer. Air was readily incorporated (Table V).

In Table V are given the percentage overruns for whipping times of 1–10 min. One sample was whipped shortly after preparation, the other after 24 days of storage at room temperature. It is evident that there was no loss of "whippability" after this storage period. Further experiments showed that the same volume of whip was obtained after 12 months' storage of the treated applesauce.

A sample of the treated applesauce was dried to a powder in a stream of air. It was then reconstituted with warm water. The percentage overruns observed (Table V) indicated that no loss of whippability had occurred.

TABLE VI
Sponge Cake Formula

Ingredients	Parts by weight
Water (130F)	43
Sugar	143
Milk powder	10.75
Whole eggs	143
Flour	100
Baking powder	1.75
Salt	1.75

TABLE VII
Sponge Cakes

Emulsifier[a]	Batter density	Baked cake	
		Porosity[b]	Volume ml/lb batter
None	0.69	1	1520
Aqueous dispersion of Conjoined Crystals preparation	0.46	3	2300
Aqueous mixture of glycerol monostearate (β-crystalline form)	0.53	1	2350
Aqueous dispersion of propylene glycol monostearate (α-crystalline form)	0.39	0	2400

[a] Each 40% aqueous dispersion added to sponge cake batter at a level of 0.5% (0.2% dry emulsifier basis) of the weight of flour.

[b] Visual estimation, increasing from "0" for "poor" to "3" for "excellent."

Foam-Type Cakes

Sponge cakes promised to be a good application for aqueous Conjoined Crystals preparations. Foam-type cakes are so-called because the "body" of the cake batter as well as the major supporting framework of the baked cake depends on the aeration or beating of eggs into a "foam-like mass."

Three emulsifier preparations were tested in sponge cake. The Conjoined Crystals preparation, molecularly distilled glycerol monoesters from hydrogenated lard and propylene glycol monostearate were each dispersed in water at 40% concentration. The three emulsifiers were tested in the sponge cake formula shown in Table VI.

The monoesters were added at the first stage during the mixing of the water, sugar, milk powder, and eggs. The ingredients were mixed with a wire whip in a Hobart mixer for 5 min at high speed. Flour, baking powder, and salt were then added and mixing continued for 2 min at low speed. The cakes were baked in 8-in. round layer tins containing 200 g of batter for 17 min at 360F.

The results of the baking tests are sumarized in Table VII.

The cake baked with the Conjoined Crystals preparation had excellent porosity or texture and volume and the batter had the desired low density. In the experiments, neither the β-form of glycerol monostearate nor propylene glycol monostearate improved the texture over that obtained when no emulsifier was added.

TABLE VIII
White Cake Mix

Mix	Emulsifier	Batter[a]		Baked cake	
		Density	Appearance	Porosity	Volume ml/lb
Package Mix A	....	0.85	V. smooth, sl. thick	2	1405
Package Mix B	....	0.85	V. smooth, sl. thick	3	1350
Mix base, less shortening and emulsifier[b]	Conjoined Crystals preparation	0.85	Smooth, sl. thick	3	1435
Mix, less shortening and emulsifier[c]	Conjoined Crystals preparation	0.90	V. smooth, sl. thick	3	1420

[a] Blend 1 min; beat 4 min.

[b] Shortening—rearranged lard containing 12% tallow flakes; total shortening level including emulsifier, 12% of base. Conjoined Crystals preparation level—5% of rearranged lard preparation. Emulsifier added to mix base.

[c] Same as (b), except Conjoined Crystals preparation melted and incorporated in rearranged lard preparation.

TABLE IX
Cake Mix

Mix	Emulsifier	Batter[a]		Baked cake	
		Density	Appearance	Porosity	Volume ml/lb
Package mix, white	....	0.88	Sl. thin, smooth	3	1170
A white cake base, less shortening and emulsifier	10% Conjoined Crystals preparation[b]	0.77	Thick, smooth	4	1410
Package mix, yellow	....	0.82	Sl. thick, smooth	2	1150
A yellow cake base, less shortening and emulsifier	10% Conjoined Crystals preparation[b]	0.70	V. thick, V. smooth	5	1430

[a] Blend 1 min; beat 2 min.
[b] Shortening—rearranged lard containing tallow flakes; total shortening level including emulsifier, 12% of base. Conjoined Crystals preparation level, 10% of rearranged lard preparation, added half to shortening and half to cake mix base.

Cake Mixes

Conjoined Crystals preparations promised to be useful in cake mixes and they were evaluated in both yellow and white cakes. The purpose of the emulsifier is to enhance the ability of the cake batter to hold and retain air incorporated in the mixing step as well as the gas released by the baking powder. A further purpose is to simplify preparation of the cake, reducing the time of preparation and permitting greater tolerance in varying from specified directions.

The Conjoined Crystals preparation was added to a white cake mix base obtained from a commercial firm at a level of 5% of the shortening. The shortening was rearranged lard containing 12% tallow flakes. The emulsifier was either incorporated in the mix as a powder or was melted and incorporated in the shortening. The cake mix batters were made by the 1-step method (all ingredients added prior to mixing), blending 1 min and beating 4 min. The results are given in Table VIII.

It was found that the cakes made with the Conjoined Crystals emulsifier compared well in volume and texture (porosity) with cakes made with the two commerical package mixes.

Conditions were adjusted so as to reduce the time of mixing in the 1-step method to blending for 1 min and beating for 2 min. This is a severe test of the emulsifier. In the experiments, 10% of Conjoined Crystals preparation was used, based on the shortening. Half of this was added to the shortening and half was added as a powder to the cake mix base. Both yellow and white cakes were prepared. The results are given in Table IX. Both in batter density, texture and volume, the cakes containing the Conjoined Crystals preparation were equal to or superior to those we prepared with the two commercial 1-step mixes tested.

TABLE X
Bread Formula

	Parts by weight	
Sponge		Mix time: 4½ min
Flour	65	Ferment time: 4½ hr at 87F and 80% humidity
Water	40.5	
Yeast	1.75	
Yeast food	0.5	
Dough		
Flour	35	Mix time: 9½ min
Water	27	Floor time: 30 min
Sugar	6	Proof time: 1 hr, 5 min at 98F and 95% humidity
Salt	2.25	Bake time: 20 min at 450F
Milk powder	4	
Lard	2.0	

TABLE XI
Emulsifiers Added to Bread to Retard Firming

Emulsifier additive	Baker Compressimeter data Bread age[a] in days					
	1	2	3	4	5	6
None	4.8	6.8	7.6	9.0	13.2	13.4
4 oz glycerol monoester from hydrogenated soybean oil	4.2	6.8	8.2	9.8	10.6	12.2
4 oz propylene glycol monostearate	3.6	3.8	6.2	6.6	9.0	10.2
4 oz Conjoined Crystals preparation	2.8	4.0	5.6	5.4	6.8	8.0

[a] Wrapped in wax paper and stored at 72F and 60% relative humidity.

TABLE XII
Conjoined Crystals as a Dry Powdered Bread Emulsifier Extended Shelf-life Studies

Sample	Baker Compressimeter data Bread age[a] in days					
	1	2	3	4	5	6
32 oz lard—Control	5.8	8.0	10.6	13.4	14.8	14.2
32 oz Conjoined Crystals preparation	2.6	5.2	4.6	5.2	5.0	5.4
2nd week of storage tests	7	8	9	10	11	12
32 oz lard—Control	14.4	19.2	21.6	22.0	24.6	24.8
32 oz Conjoined Crystals preparation	6.0	6.6	7.2	7.6	8.2	8.8

[a] Wrapped in wax paper and stored at 72F and 60% relative humidity.

Bread

The U.S. standards of identity for bread do not presently permit the use of the propylene glycol monoester component of Conjoined Crystals preparations, but one preparation was tested in bread because this type of emulsifier may find uses in bread mixes.

Three emulsifiers were prepared in powder form by spray chilling and tested in a typical bread formula (Table X).

The emulsifiers were 1) molecularly distilled glycerol monoesters of hydrogenated soybean oil, 2) propylene glycol monostearate, and 3) the Conjoined Crystals preparation. Each was added at a level of 4 oz/100 lb of flour. The baked bread was wrapped, stored, and tested for the development of firming with the Baker Compressimeter. This instrument measures the number of grams required to press a disc 36 mm in diameter to a depth of 3 mm on a slice 1 cm in thickness. The results are given in Table XI.

The Conjoined Crystals preparation was more effective than the other two emulsifiers tested in retarding the development of firmness.

In a separate experiment, the Conjoined Crystals preparation was substituted for the lard normally used in making bread. The results are given in Table XII.

Bread containing the Conjoined Crystals preparation did not become undesirably firm for 11 days (g stress = 8.2) whereas the bread containing lard alone reached this stress value in two days. These favorable results suggest that the Conjoined Crystals preparation may find applications in nonstandardized breads, such as Army Quartermaster canned bread or in yeast raised bread mixes.

ACKNOWLEDGMENT

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