

Description

Title of Invention: CRYSTALLIZATION ACCELERATOR FOR OIL AND FAT

Technical Field

[0001] The present invention relates to a crystallization accelerator for a fat/oil.

Background Art

[0002] In fat/oil-containing products, crystallization behaviors and properties of the fat/oil exert a significant influence in many situations including development, production, storage, and distribution of the products. Thus, a technique for controlling fat/oil crystals is one of the most important issues. In particular, a composition having a high ratio of fat/oil content therein is greatly affected by the crystallization behaviors of the fat/oil used, resulting in various problems.

[0003] As a method for, for example, inhibiting crystal coarsening during storage after production, Patent Literature 1 discloses a fat/oil-crystal adjustor containing a diglyceride for preventing deterioration of physical properties caused by the fat/oil crystal coarsening.

[0004] Patent Literature 2 discloses, as a method for producing a fat/oil composition in which no granulate crystal having a diameter of 20 μm or more is generated under even a long-term storage, a method for producing a fat/oil or fat/oil composition that generates no granulate crystal with generating unstable crystals by rapid cooling with a coolant at -20°C or less or by adding unstable crystal particles of a fat/oil.

[0005] Furthermore, use of a crystallization accelerator has also been proposed as a conventional technique, other than the method for inhibiting crystal coarsening. Non Patent Literature 1, for example, describes that a lipophilic emulsifier having a high melting point becomes a mold of a fat/oil crystal to accelerate the crystallization. In addition, a polyglycerol behenate ester is known to have a high crystallization accelerating effect and a reducing effect in a crystal size by Non Patent Literature 2 and the like.

Citation List

Patent Literature

[0006] Patent Literature 1: Japanese Patent Laid-Open No. 2000-345185

Patent Literature 2: Japanese Patent Laid-Open No. 2001-72992

Non Patent Literature

[0007] Non Patent Literature 1: Kiyotaka SATO and Satoru UENO, "Shishitsu no Kinosei to Kozo/Bussei -Bunshi kara Mascara/Chocolate made (Functionality and Structures/Physical Properties of Lipids -from Molecules to Mascaras/Chocolates-)" p. 91.

Non Patent Literature 2: Atsuyuki MIYAMOTO and Kazuo MATSUSHITA, "Properties of Polyglycerol Esters and Their Uses in the Food Industry", New Food Industry, 30 (11), pp. 12-18 (1988).

Summary of Invention

Technical Problem

[0008] However, since the conventional techniques focus on inhibiting crystal coarsening during a long-term storage, a fundamental issue of sufficiently crystallizing a fat/oil during a production process has not been solved. In addition, the crystallization accelerator requires sufficiently heating a fat/oil to be dissolved, and poor handling and being likely to cause deterioration of the fat/oil due to the heating are concerned; thus, unsuitable as a solution from the viewpoint of accelerating crystallization during a short time of a production process. Therefore, there is a fact that further development of a technique for accelerating crystallization is desired.

[0009] Hence, a main object of the present invention is to provide a novel crystallization accelerator for a fat/oil.

Solution to Problem

[0010] In other words, the present invention provides a crystallization accelerator for a fat/oil, including a polyglycerol fatty acid ester having an HLB of 5 to 9 and a melting point of 58 to 69°C.

In the crystallization accelerator according to the present invention, the polyglycerol may have an average degree of polymerization of 2 to 10.

The crystallization accelerator according to the present invention may have a degree of esterification of 20 to 60%.

Advantageous Effect of Invention

[0011] The present invention can provide a novel crystallization accelerator for a fat/oil.

An effect of the present invention is not necessarily limited to the effect described herein, and may be any effect described in the present disclosure.

Description of Embodiments

[0012] Hereinafter, preferable embodiments of the present invention will be described.

Embodiments that will be described hereinafter are described as representative embodiments of the present invention, and the scope of the present invention is not narrowly interpreted by the embodiments.

[0013] A polyglycerol fatty acid ester is obtained by an esterification reaction between a polyglycerol, formed by dehydrative condensation of glycerin molecules, and a fatty acid, and there are various polyglycerol fatty acid esters depending on the type of the polyglycerol (degree of polymerization), the type of the fatty acid (number of carbon atoms and number of double bonds), an ester composition, and the like. Each of the various esters is known to exhibit a distinct property.

[0014] The crystallization accelerator for a fat/oil according to the present invention includes at least a polyglycerol fatty acid ester, wherein the polyglycerol fatty acid ester has an HLB of 5 to 9 and a melting point of 58 to 69°C, wherein the polyglycerol fatty acid ester has a degree of esterification of 20 to 60%, and wherein a fatty acid constituting the polyglycerol fatty acid ester is a saturated fatty acid having 8 to 24 carbon atoms.

[0015] When a polyglycerol fatty acid ester is added into an oil, a polyglycerol fatty acid ester having a low HLB (preferably, 3 or less), which is compatible with a fat/oil, is commonly

chosen. In addition, since a polyglycerol fatty acid ester having a high melting point is likely to crystallize to be a nucleus prior to the crystallization of the fat/oil, such polyglycerol fatty acid ester has been considered to be suitable for a crystallization accelerator. However, the present inventors have intensively investigated, and surprisingly found that setting the HLB within a range of 5 to 9 and the melting point within a range of 58 to 69°C can provide a crystallization accelerator enabling speedy crystallization to form fine crystals. In addition, since not having too high melting point, the polyglycerol fatty acid ester according to the present invention has also a good operability.

[0016] In the crystallization accelerator according to the present invention, the polyglycerol fatty acid ester has an HLB of 5 to 9. Here, the HLB, which is an index indicating a degree of hydrophilicity and lipophilicity, in the present invention is a value calculated by Atlas method. The HLB by Atlas method is calculated with the following expression (1).

[0017] [Expression 1]

$$\text{HLB} = 20(1-S/A) \dots (1)$$

S: Saponification value of the polyglycerol fatty acid ester

A: Acid value of the fatty acid constituting the polyglycerol fatty acid ester

[0018] In the present invention, a melting point and a freezing point can be measured by a conventionally known method, and for example, can be measured by using a differential scanning calorimeter (DSC).

[0019] In the crystallization accelerator according to the present invention, the melting point is 58 to 69°C, and preferably 58 to 66°C.

[0020] In the crystallization accelerator according to the present invention, the freezing point is preferably 53 to 65°C. Thereby, a sufficient crystallization accelerating effect can be obtained.

[0021] In the present invention, an average degree of polymerization of the polyglycerol constituting the polyglycerol fatty acid ester is preferably, but not limited to, 2 to 10, and more preferably 4 to 10. Here, the average degree of polymerization is an average degree of polymerization (n) of the polyglycerol calculated with a hydroxyl value by end-group analysis.

In detail, the average degree of polymerization is calculated with the following expression (2) and the following expression (3).

[0022] [Expression 2]

$$\text{Molecular Weight} = 74n + 18 \dots (2)$$

$$\text{Hydroxyl Value} = 56110(n+2)/\text{Molecular Weight} \dots (3)$$

[0023] The hydroxyl value in the expression (3), which is an index value for the number of hydroxyl groups contained in the polyglycerol, means a number of milligrams of potassium hydroxide required to neutralize acetic acid required to acetylate free hydroxyl groups contained in 1 g of the polyglycerol. The number of milligrams of potassium hydroxide is calculated in accordance with "The JOCS Standard Methods for Analysis of Fats, Oils and Related Materials (2003)" compiled by Japan Oil Chemist' Society.

[0024] The polyglycerol fatty acid ester can be produced by a conventionally known esterification reaction. The polyglycerol fatty acid ester can be produced by, for example, an esterification reaction between a fatty acid and a polyglycerol in the presence of an alkaline catalyst such as sodium hydroxide. The esterification is proceeded until a degree of esterification of the polyglycerol fatty acid ester reaches a desired value.

[0025] In the crystallization accelerator according to the present invention, the degree of esterification is preferably 20 to 60%, and more preferably 30 to 45%. Here, the degree of esterification is a value calculated with the following expression (4) where (n) denotes the average degree of polymerization of the polyglycerol calculated by the hydroxyl value, (n+2) denotes the number of hydroxyl groups that this polyglycerol has, and (M) denotes a molar number of the fatty acid to be added with the polyglycerol. The hydroxyl value is a value calculated with the expression (3).

[0026] [Expression 3]

$$\text{Degree of Esterification (\%)} = (M/(n+2)) \times 100 \dots (4)$$

[0027] As the fatty acid constituting the polyglycerol fatty acid ester, a saturated or unsaturated fatty acid having 8 to 24 carbon atoms is typically used, but not particularly limited thereto. The fatty acid may be a mixture, and specific examples of the fatty acid

include caprylic acid, pelargonic acid, capric acid, lauric acid, myristic acid, pentadecylic acid, palmitic acid, palmitoleic acid, margaric acid, stearic acid, oleic acid, vaccenic acid, linoleic acid, linolenic acid, arachidic acid, arachidonic acid, erucic acid, and behenic acid. Among them, a saturated fatty acid having 16 to 18 carbon atoms is particularly preferable in the viewpoint of a balance between meltability and solid fat content of the fat/oil composition and operability.

[0028] The application of the crystallization accelerator according to the present invention is not particularly limited, and it can be widely used in the fields of, such as, foods and beverages, cosmetics, quasi-pharmaceutical products, and pharmaceuticals containing a fat/oil. The crystallization accelerator according to the present invention can exert the effect of the present invention particularly in a fat/oil composition requiring the crystallization accelerating effect during a short time of a production process such as whipped cream, coffee whitener, margarine, shortening, chocolate, a milk-based beverage, and a functional fat/oil.

[0029] A fat/oil contained in the fat/oil composition is also not particularly limited, and examples thereof include: plant fats/oils such as rapeseed oil, soybean oil, sunflower seed oil, cottonseed oil, peanut oil, rice bran oil, corn oil, safflower oil, olive oil, kapok oil, sesame oil, evening primrose oil, palm oil, sheer butter, sal butter, cocoa butter, coconut oil, and palm kernel oil; a single or mixed oil of animal fats/oils such as milk fat, beef tallow, lard, fish oil, and whale oil; and processed fats/oils thereof in which hardening, fractionation, interesterification, or the like is performed. Among these, the crystallization accelerator according to the present invention is particularly suitable for a palm-based fat/oil, an interesterified fat/oil, and the like, which have a low crystallization speed. As an interesterified oil, lauric interesterified oil and the like are preferable.

[0030] The method for using the crystallization accelerator according to the present invention exhibits the crystallization accelerating effect by melting the crystallization accelerator in a desired fat/oil and undergoing a crystallization process from a state where the fat/oil and the crystallization accelerator are completely melted. In this time, preferably 0.02 to 5 weight%,

based on the fat/oil, of the crystallization accelerator according to the present invention is added to enable to obtain a sufficient crystallization accelerating effect.

Examples

[0031] Hereinafter, the present invention will be described based on Examples.

Examples that will be described hereinafter are described as an example of representative examples of the present invention, and the scope of the present invention is not narrowly interpreted by the Examples.

[0032] In the polyglycerol according to the present invention, "Diglycerin-S", manufactured by Sakamoto Yakuhin Kogyo Co., Ltd., was used as a polyglycerol having an average degree of polymerization of 2; "POLYGLYCERIN #310", manufactured by Sakamoto Yakuhin Kogyo Co., Ltd., was used as a polyglycerol having an average degree of polymerization of 4; "POLYGLYCERIN #500", manufactured by Sakamoto Yakuhin Kogyo Co., Ltd., was used as a polyglycerol having an average degree of polymerization of 6; and "POLYGLYCERIN #750", manufactured by Sakamoto Yakuhin Kogyo Co., Ltd., was used as a polyglycerol having an average degree of polymerization of 10.

[0033] <Synthesis Example 1>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 2 and 239 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 35%.

[0034] <Synthesis Example 2>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 4 and 157 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 31%.

[0035] <Synthesis Example 3>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 4 and 191 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 37%.

[0036] <Synthesis Example 4>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 6 and 123 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 30%.

[0037] <Synthesis Example 5>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 6 and 184 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 45%.

[0038] <Synthesis Example 6>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 6 and 225 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 55%.

[0039] <Synthesis Example 7>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 10 and 153 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 38%.

[0040] <Synthesis Example 8>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 10 and 184 g of stearic acid were added, and the mixture was reacted at

245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 45%.

[0041] <Synthesis Example 9>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 6, 31 g of palmitic acid, and 101 g of stearic acid were added, and the mixture was reacted at 245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 33%.

[0042] <Comparative Example 1>

A polyglycerol behenate ester, trade name: HB-750 (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0043] <Comparative Example 2>

A polyglycerol behenate ester, trade name: DDB-750 (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0044] <Comparative Example 3>

A polyglycerol stearate ester, trade name: MS-3S (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0045] <Comparative Example 4>

A polyglycerol stearate ester, trade name: PS-3S (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0046] <Comparative Example 5>

A polyglycerol stearate ester, trade name: TS-5S (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0047] <Comparative Example 6>

A polyglycerol stearate ester, trade name: DAS-7S (manufactured by Sakamoto Yakuhin Kogyo Co., Ltd.)

[0048] <Comparative Example 7>

To a reaction vessel, 100 g of the polyglycerol having an average degree of polymerization of 4 and 157 g of palmitic acid were added, and the mixture was reacted at

245°C under alkalinity by sodium hydroxide and a nitrogen flow to obtain a polyglycerol fatty acid ester having a degree of esterification of 33%.

[0049] Using the polyglycerol fatty acid esters of Synthesis Examples 1 to 9, produced by the above, and Comparative Examples 1 to 7, the following measurements were performed.

[0050] <Measurement of Freezing Point and Melting Point>

A freezing point and melting point of each of the polyglycerol fatty acid esters were measured by a differential scanning calorimeter (model number: DSC8320, manufactured by Rigaku Corporation). To an aluminum cell, 5 mg of each sample was weighed to be sealed with a sample sealer. As a reference, 5 mg of alumina was used. The cell was cooled from 85°C to 25°C at 5°C/min., retained for 5 minutes, and then heated to 85°C at 5°C/min. In this time, an on-set temperature of an exothermic peak during the cooling was determined as the freezing point, and an off-set temperature of an endothermic peak during the heating was determined as the melting point.

[0051] <Sample Preparation for Measurement of Solid Fat Content (SFC) and Microscope Observation>

To each fat/oil of refined palm oil, hardened palm kernel oil, and an interesterified oil, 0.5 weight% of each of the polyglycerol fatty acid esters was added, and then homogeneously dissolved at 80°C. The interesterified oil, specifically lauric interesterified oil, being a mixed fat/oil of palm kernel oil, palm oil, and extremely hardened rapeseed oil, and having a melting point of 27.2°C was used.

[0052] <Measurement of Solid Fat Content (SFC)>

In accordance with AOCS Official Method Cd 16b-93 (1999), an SFC was measured by a benchtop NMR (model number: minispec mq20, manufactured by BRUKER Corporation). The SFC, an abbreviation for Solid Fat Content, means a content (%) of a solid fat present in a fat/oil at a constant temperature. Therefore, a higher SFC of a fat/oil after a constant time from the beginning of the crystallization indicates faster crystallization of the fat/oil and higher crystallization accelerating effect.

[0053] The sample was introduced into a sample tube for measurement to a height of about 5 cm, and heated at 80°C for 10 minutes to melt. Then, the sample tube was moved into a circulating constant-temperature water bath (model number: NCB-1200, manufactured by EYELA) in which the temperature was regulated at 25°C in a case of the refined palm oil, 25°C in a case of the hardened palm kernel oil, or 20°C in a case of the interesterified oil; and an SFC was measured 10 minutes later in a case of the refined palm oil, 3 minutes later in a case of the hardened palm kernel oil, or 10 minutes later in a case of the interesterified oil. The evaluation was performed using the indices of a sample without additive (Blank) and a sample of HB-750 or DDB-750, a common crystallization accelerator.

[Evaluation Criteria]

×: Equal to or lower than the SFC without additive.

△: Higher than the SFC without additive, and lower than the SFC of HB-750.

○: Equal to or higher than the SFC of HB-750, and lower than the SFC of DDB-750.

◎: Equal to or higher than the SFC of DDB-750.

[0054] <Measurement of Crystal Size>

On a microscope slide, 10 µL of each sample was dropped, and covered with a coverslip to make a preparation. The preparation was heated to 80°C at 20°C/min. with a cooling-and-heating stage (model number: 10030, manufactured by Linkam Scientific Instruments Limited); then cooled at 5°C/min to 25°C in a case of the refined palm oil, 25°C in a case of the hardened palm kernel oil, or 20°C in a case of the interesterified oil; and a crystalline form was observed 20 minutes later in a case of the refined palm oil, 10 minutes later in a case of the hardened palm kernel oil, or 15 minutes later in a case of the interesterified oil, with a polarizing microscope (model number: BX50, manufactured by Olympus Corporation) to take a photograph with an attached digital camera (model number: DP20, manufactured by Olympus Corporation). A crystal size was measured with the image. The evaluation was performed using the indices of a sample without additive (Blank) and a sample of HB-750 or DDB-750, a common crystallization accelerator.

[Evaluation Criteria]

×: Equal to or larger than the crystal size without additive.

△: Smaller than the crystal size without additive, and larger than the crystal size of HB-750.

○: Equal to or smaller than the crystal size of HB-750, and larger than the crystal size of DDB-750.

◎: Equal to or smaller than the crystal size of DDB-750.

[0055] <Measurement Results>

Measurement results, HLBs, and degrees of esterification (%) of the polyglycerol fatty acid esters of Synthesis Examples 1 to 9 and Comparative Examples 1 to 7 are shown in the following Table 1.

[0056]

[Table 1]

Polyglycerol Fatty Acid Ester	Average Degree of Polymerization of Polyglycerol	HLB	Degree of Esterification (%)	Melting Point (°C)	Freezing Point (°C)	SFC (%)				Crystal Size (µm)			
						(a)	Evaluation	(b)	Evaluation	(c)	Evaluation	(d)	Evaluation
Synthesis Example 1	2	5	35	64.0	59.4	8.4	◎	6.9	○	7.4	○	15.3	◎
Synthesis Example 2	4	7	31	61.6	57.3	10.7	◎	10.9	◎	19.5	◎	20.1	◎
Synthesis Example 3	4	6	37	61.4	56.9	10.8	◎	9.3	◎	12.7	○	20.3	◎
Synthesis Example 4	6	8	30	60.9	56.3	10.8	◎	12.1	◎	21.9	◎	19.2	◎
Synthesis Example 5	6	6	45	61.6	56.7	11.0	◎	10.4	◎	6.4	○	13.8	◎
Synthesis Example 6	6	5	55	61.6	56.2	10.9	◎	9.9	◎	0.8	△	10.7	◎
Synthesis Example 7	10	7	38	58.5	53.6	10.6	◎	8.5	◎	10.5	○	18.5	◎
Synthesis Example 8	10	6	45	58.8	53.9	11.2	◎	8.4	◎	6.2	○	16.1	◎
Synthesis Example 9	6	7.6	33	58.2	53.7	10.0	◎	10.6	◎	19.9	◎	20.6	○
Blank	-	-	-	-	-	0.4	-	0.2	-	0.1	-	42.0	-
Comparative Example 1	10	4.2	58	69.6	65.2	6.4	-	6.6	-	6.1	-	20.7	-
Comparative Example 2	10	2.5	100	73.2	66.8	6.5	-	7.1	-	18.2	-	20.4	-
Comparative Example 3	4	8.4	17	55.9	51.9	9.0	◎	7.1	○	20.2	◎	31.9	△
Comparative Example 4	4	2.6	83	55.0	48.9	2.6	△	1.9	△	0.7	△	17.0	◎
Comparative Example 5	6	7.4	38	56.6	51.9	10.2	◎	9.7	◎	22.4	◎	27.3	△
Comparative Example 6	10	3.8	83	53.8	46.9	4.5	△	2.1	△	0.5	△	20.0	◎
Comparative Example 7	4	7	33	50.9	46.5	7.0	◎	3.2	△	1.1	△	39.1	△

(a) Refined Palm Oil (b) Hardened Palm Kernel Oil (c) Interestified Oil

[0057] <Consideration>

It has been confirmed that the polyglycerol fatty acid esters of Synthesis Examples 1 to 9 have an equivalent or high crystallization accelerating effect in comparison with the polyglycerol behenate esters (Comparative Examples 1 and 2), which have a crystallization accelerating effect, using any fat/oil of the refined palm oil, the hardened palm kernel oil, and the interesterified oil, and also have larger SFC values and finer crystals than those of the polyglycerol fatty acid esters of Comparative Examples 3 to 7. Therefore, the polyglycerol fatty acid ester having a good operability and a high crystallization accelerating effect on a fat/oil has been obtained by setting the HLB to 5 to 9 and the melting point to 58 to 69°C.

Industrial Applicability

[0058] The present invention can provide a novel crystallization accelerator for a fat/oil. The crystallization accelerator according to the present invention can be widely used, based on its excellent crystallization accelerating effect, in the fields of, such as, foods and beverages, cosmetics, quasi-pharmaceutical products, and pharmaceuticals containing a fat/oil.

CLAIMS

[Claim 1]

A crystallization accelerator for a fat/oil, comprising at least a polyglycerol fatty acid ester,

wherein the polyglycerol fatty acid ester has an HLB of 5 to 9 and a melting point of 58 to 69°C,

wherein the polyglycerol fatty acid ester has a degree of esterification of 20 to 60%,
and

wherein a fatty acid constituting the polyglycerol fatty acid ester is a saturated fatty acid having 8 to 24 carbon atoms.

[Claim 2]

The crystallization accelerator according to claim 1,

wherein a polyglycerol constituting the polyglycerol fatty acid ester has an average degree of polymerization of 2 to 10.

[Claim 3]

The crystallization accelerator according to claim 1 or claim 2,

wherein the polyglycerol fatty acid ester has a freezing point of 53 to 65°C.

[Claim 4]

The crystallization accelerator according to any of claims 1 to 3,

wherein the HLB is a value calculated by Atlas method.

[Claim 5]

The crystallization accelerator according to any of claims 2 to 4,
wherein the polyglycerol constituting the polyglycerol fatty acid ester has an average degree of polymerization of 4 to 10.