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(54) Title: AQUEOUS CALCIUM CITRATE COMPOSITIONS

(57) Abrégé/Abstract:

An aqueous dispersion containing a finely divided special type of calcium citrate salt compositions and processes of making are provided to be used for opacifying and whitening aqueous food compositions.



AQUEOUS CALCIUM CITRATE COMPOSITIONS

2

ABSTRACT

4 An aqueous dispersion containing a finely divided
special type of calcium citrate salt compositions and
6 processes of making are provided to be used for
opacifying and whitening aqueous food compositions.

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16 LPATCASE:166

AQUEOUS CALCIUM CITRATE COMPOSITIONS

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This invention relates to aqueous compositions
4 comprising certain calcium citrate salts and the use
thereof, particularly in the food industry.

6

BACKGROUND OF THE INVENTION

8 The dietary importance of low-fat, low-calorie, no
cholesterol foods is well-documented in not only the
10 scientific literature but also in the lay press.
Considerable research effort has been, and is now being,
12 expended to meet the requirements of new food
technology. Thus, low fat food products such as cheeses,
14 mayonnaise, pudding, pastries, salad dressings,
margarines and the like have been developed based on
16 non-fat substitutions in whole or in part for the fat
content of classical foods. Such products necessitate
18 new food additives and constituents of the new dietary
food compositions. These new additives and constituents
20 are mainly designed to improve appearance, color,
mouth-feel, and induce other properties to assure public
22 acceptability of the new dietary compositions. To be
successful, such additives and constituents should be
24 food acceptable and compatible with the compositions in
which they are employed. For example, titanium dioxide
26 has been used as a whitener in low fat compositions and
is found to be compatible in these compositions.
28 However, the food-acceptability of titanium dioxide has

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been challenged and is rejected in many countries,
2 especially in Europe.

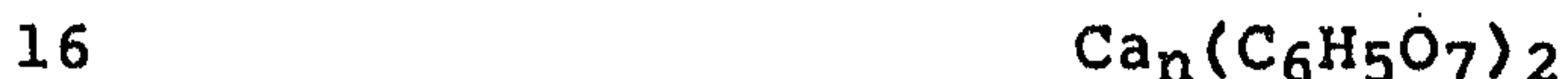
4 SUMMARY OF THE INVENTION

The present invention provides new and useful aqueous
6 dispersion calcium citrate salt compositions which are
readily adaptable for use in food compositions,
8 particularly as opacifiers, whitening agents, texture
modifiers and partial fat substitutes. These and other
10 uses of the present new salt compositions are described
hereinafter.

12

DETAILED DESCRIPTION OF THE INVENTION

14 The present new aqueous compositions comprise a
finely divided calcium citrate salt of the formula



wherein n is a value from 2.5 to 2.95, preferably
18 from 2.61 to 2.92, the dry form of the salt containing
not greater than 6% water dry weight, and an aqueous
20 slurry (1% by weight) of said salt in water at 25°C
showing a pH value of from about 4 to about 7, and
22 preferably from about 4 to about 5.5.

In general, these calcium citrate crystals are
24 prepared by spray drying a neutralization mixture
prepared by neutralizing citric acid with a slurry of
26 calcium carbonate or calcium oxide or hydroxide in water,
e.g., a slurry of calcium hydroxide under controlled
28 conditions to assure the production of the present new
calcium citrate salts. Temperature, slurry solid
30 content, rate of mixing of reactants and agitation time
before spray drying are critical parameters in
32 determining the physical characteristics of final product.

In particular, the calcium citrate crystals are
34 prepared by first neutralizing citric acid with calcium
hydroxide while controlling the rate and conditions of

the reaction as well as the degree of neutralization. In
2 the present process, a calcium hydroxide aqueous slurry
is reacted with a citric acid solution in water resulting
4 in a strong exothermic reaction. The rate of reaction,
concentration of reactants and varying conditions are all
6 important factors in producing calcium citrate salts of
the desired pH values, moisture content and particularly
8 the desired particle size.

It is preferred to form two separate aqueous systems,
10 one, a solution of citric acid and the second, a slurry
of calcium hydroxide, oxide or carbonate and then mix the
12 uniform slurry of calcium hydroxide or carbonate with the
aqueous citric acid. The temperature of the mixture is
14 not allowed to exceed about 60°C. The pH of the slurry
so produced after thorough mixing should fall within the
16 range of 4-6 and, if needed, should be adjusted to this
range of pH. The slurry can be used as such or can be
18 spray-dried or dried by other known drying steps.

The produced calcium citrate salt is very insoluble
20 in water providing about 0.1% by weight solution at
ambient temperature and slightly more soluble in hot
22 water. During preparation of a batch and while waiting
for spray drying of the batch, the salts are present in
24 the insoluble form, a slurry of tiny crystals which form
aggregates of varying particle size ranging from 5 to 100
26 microns. In present experience, the best products are
obtained by using the following conditions.

28 The solids level of the aqueous slurry of calcium
citrate salt is maintained at 20-26% and preferably at
30 22-24% by weight based on anhydrous salt. The slurry
temperature during spray drying is from 80°C-100°F and
32 preferably 80°-90°F. To avoid gel formation in the
aqueous slurry, especially at temperatures below 70°F,
34 and recrystallization which can occur on prolonged
storage, spray drying of the aqueous slurry is effected

within about 4-5 hours after slurry preparation. The
2 slurry is spray dried at an inlet temperature of from
about 425°F to about 460°F to deliver a free-flowing
4 white powder with a moisture content of less than 6% and
bulk density of from about 0.3 to about 0.7 g/cc.
6 Extensive mixing and especially homogenization prior to
spray drying should be avoided since the particles of
8 salt may be broken down into fine particles.

The calcium citrate crystals generally have the
10 following characteristics:

	Bulk Density	0.33-0.66 g/cc
12	Granulation	95% through U.S. 100 mesh or 150 microns
14	Rotatap, 8. min.	10% maximum through U.S. 400 mesh or
16		38 microns
	pH (1% by weight solution)	4.0-6.5
18	Appearance	free-flowing, white powder

20
These salts are neutral or slightly acidic and have a
22 well-defined crystal size. The salt can be employed in
the form of the anhydrous salt or the hydrated salt. In
24 the hydrated form, the salt can usually contain up to
about 13-15% by weight of water of hydration. In
26 general, it is preferred to use the salt in lower
hydrated form with less than about 10% by weight of water
28 of hydration. Of course, the hydrated salt can be dried
to any level of water of hydration using known methods.
30 On standing, the salt does not undergo any loss or gain
of water during storage.

32 The concentration of salt in the present new
compositions can range from about 0.2% to about 22% by
34 weight of the composition. Particularly desirable are
compositions wherein the concentration of salt is from

about 15% to about 20%. Such compositions have a high ratio of salt to water and can be used most efficiently in providing desired levels of the salt in the food compositions to which they are added, as described hereinafter.

The calcium citrate employed in the present invention is in the form of small platelet crystals. The average length of the crystals is below 3.0 microns, preferably about 1.5 microns, width below 2.0 microns, preferably about 1 micron and thickness below 1 micron, preferably 0.1 to 0.2 micron. During preparation, clusters of these tiny platelets aggregate together to form spherical particles that range from about 2 to about 50 microns in diameter. Such clusters are readily separable by mechanical stirring in water or by merely allowing the clusters to stand in water for protracted periods of time, e.g., overnight at room temperature. A most efficient method for reducing the clusters to the individual platelets is the use of mechanical shear, as provided by a ball mill. Other mechanical stirring means that can be employed include homogenizers, microfluidizer or colloid mills, but the ball mill product is smoother and more viscous at a given salt/water content.

When mixed with water, particularly at levels above about 10% by weight, the present spray-dried calcium citrate salt platelets cause a significant increase in the viscosity of the mixture. Thus, at 15% to 20% by weight the aqueous calcium citrate compositions are in the form of thick pastes resembling soft cheeses and margarines in consistency. At 20% and higher levels, the mixtures tend to solidify, especially when highly efficient mechanical shear is used.

In one preferred modification, the calcium citrate platelets are coated with a water-dispersible, food-acceptable additive capable of coating the

platelets. A wide variety of such coating additives can
2 be used for this purpose and include, for example,
protein coatings such as casein, sodium caseinate and
4 zein; polysaccharide gums such as xanthan gum, gum
arabic, locust bean gum, guar and similar gums; higher
6 fatty acids, e.g., C₁₂-C₂₂ such as lauric acid, stearic
acid, oleic acid, linoleic acid, or sodium or potassium
8 salts of these higher fatty acids; natural food solids
such as starches and skim milk solids and fruit juices
10 such as orange juice solids; and modified cellulose gum
such as methyl cellulose, ethyl cellulose and
12 carboxymethyl cellulose. Coating of the calcium citrate
platelets can be effected during preparation of the
14 present new aqueous compositions by the mere expediency
of adding the coating agent to the water of the present
16 new aqueous compositions prior to or during preparation
by intimate mixing of the salt with water.
18 Alternatively, before spray-drying of the calcium citrate
suspension in water during preparation of the new salt,
20 the water-dispersible coating agent can be added to the
reaction mixture and the spray-dried product obtained in
22 coated form. A further procedure involves addition of
the coating agent to the food composition to which the
24 present new food additive aqueous compositions are added
and the salt platelets are coated in situ during
26 dispersion in the food composition.

The present new aqueous compositions are particularly
28 effective as opacifier and whitening agents for aqueous
food compositions. Exemplary such food compositions
30 include puddings, mayonnaise, salad dressings and similar
products in which oil is replaced by water and other food
32 ingredients and the products are described as non-fat or
low-calorie foods. When used as an opacifier-whitener,
34 the levels of salt should be from about 0.2% to 5.0% of
the food composition.

To attain such levels of salt for opacifier-whitener
2 uses, the salt can be added neat to the water used to
form the aqueous food composition or directly to the
4 aqueous food composition. Alternatively, and preferably,
the salt is added in the form of the new aqueous calcium
6 citrate pastes of this invention. The use of the paste
assures the highly desirable form of platelets of the
8 calcium citrate which are responsible for the
opacifier-whitener results in the aqueous food
10 composition. The paste is preferably comprised of from
about 15% to about 20% by weight salt.

12 In either form of addition, the calcium citrate
crystals are distributed uniformly throughout the food
14 composition by usual mixing methods and no special
handling is required to accomplish this result.

16 In addition to use as a whitener and opacifier, the
present new aqueous food compositions are useful as
18 potential fat substitutes due to the fat mimetic property
thereof. This use may be restricted due to chalky taste
20 of the calcium citrate crystals and is preferably
restricted to not greater than about 5% by weight and
22 most preferably less than about 3% of salt based on the
finished composition.

24 A further use of the present new aqueous calcium
citrate compositions is as an anti-sticking agent,
26 particularly for baking products such as cookies, breads
and cakes. In this use, the aqueous paste is merely
28 applied to the surface of baking trays in contact with
the product to be baked and serves as an effective
30 anti-sticking agent. The layer of paste applied can be a
very thin layer formed by merely spreading the aqueous
32 salt composition substantially uniformly across the
baking surface. The baked products are easily removed
34 without contact surface disruption. Even of greater
significance is the avoidance of fat-based anti-sticking

coatings on the baking surface with the accompanying
2 inclusion of the fat coating in the baked product.

The present new aqueous dispersions of calcium
4 citrate have also been used in place of roll-in margarine
for the production of fat-free baked goods without
6 adversely affecting appearance, taste or size of the
baked products when compared with products made with
8 margarine. As is well known, margarine is comprised of
hydrogenated oils which contain trans fatty acids.

10 In contrast with the results obtained with the
calcium citrate crystals of this invention commercial
12 calcium citrate, whether in hydrated form (13% H₂O) or
after rigorous drying, does not exhibit the same
14 properties and is ineffective when tested side-by-side
with the present new compositions, or as an additive to
16 aqueous food composition. Without being bound to any
theory of operation of the present invention, the
18 phenomena observed with the present new salts is
attributable to the particle size of the salt crystals,
20 relying almost completely on the shape, number and
geometrical arrangement of the calcium citrate crystals
22 as they disperse in the water phase of the new food
compositions of this invention.

24 The following examples are proved to further
illustrate the invention.

26

EXAMPLE 1

28 A calcium citrate sample was prepared by reacting
2763.8 lbs. of citric acid with 1600 lbs. calcium
30 hydroxide (97-98% Ca(OH)₂ by analysis) in the presence of
1433 gallons of water. The mole ratio of calcium
32 hydroxide to citric acid was very slightly less than 3:2,
actually 2.92:2. The citric acid (Pfizer fine granular,
34 food grade) was mixed in a large batch tank with
675 gallons of cold water. The calcium hydroxide

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(Mississippi Lime, hydrated lime food code) was mixed in a separate batch tank with 675 gallons of cold water. The calcium hydroxide slurry is then pumped into the citric acid solution at a rate to deliver the entire slurry in 10-15 minutes. It is necessary to have good agitation during the entire reaction and mixing process. The remaining 83 gallons of water is used to rinse the calcium hydroxide tank and transport lines. Due to the heat of reaction, the temperature of the resultant slurry was increased from an initial value of 15°C (60°F) to a maximum of 57°C (134°F). After the reaction is complete, the batch is cooled to 80-90°F. The final pH of this concentrated slurry (22% calcium citrate, dry basis) should fall within the range 3.8-4.6 or can be adjusted up or down using the reacting ingredients. The slurry is then dried via spray drying utilizing a rotary wheel (7600 rpm). The outlet temperature was adjusted to 225°F and the inlet temperature was 450°F.

The calcium citrate powder obtained after spray drying was a free-flowing white powder with a moisture less than 6.0% and a bulk density in the range 0.33-0.65 g/cc. The pH of 1% slurry in water was 5.5. 95% of the powder passed through U.S. 200 mesh.

24

EXAMPLE 2

Spray-dried calcium citrate produced in accordance with Example 1 was mixed with water and then micromilled to obtain a fairly thick paste which does not require refrigeration using the following procedure.

Calcium citrate (2265 g.) was added to 9656 g. of water at room temperature. A fairly gritty slurry was obtained (19% calcium citrate, 81% water) that was maintained in suspension by using an electric stirrer. The suspension was then pumped and milled using a *Dyno-Mill filled with glass beads (Type KDL, manufactured

*Trade-mark

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by Willy A. Bachofen, AG Maschinenfabrik,
2 Basel-Switzerland). One pass through the Dyno-Mill was
sufficient to produce a fairly smooth paste. This sample
4 is stable for several months whether refrigerated or
stored at room temperature. There was no crystal growth
6 or loss of smoothness.

8 EXAMPLE 3

The procedure of Example 2 was repeated but with 1%
10 sodium caseinate added to the water used to produce a
product in which the calcium citrate is coated with the
12 sodium caseinate.

The product is smoother with a more shiny appearance
14 due to the sodium caseinate coating. Again a paste type
texture was obtained when the calcium citrate (19 weight
16 percent) was micromilled in an aqueous phase.

If not pasteurized, the product requires
18 refrigeration.

20 EXAMPLE 4

The precipitated calcium citrate produced in
22 accordance with Example 1 without spray drying was coated
with sodium caseinate using the procedure of Example 3 to
24 obtain a product of the following composition:

22% calcium citrate
26 1.1% sodium caseinate
76.9% water

28

This sample also requires refrigeration, if not
30 pasteurized.

To produce this product, 1920 g. of anhydrous citric
32 acid was dissolved in 6000 ml. water. Sodium caseinate
(143 g.) * (Alanate 155, New Zealand Milk Products) was
34 dissolved in 1500 ml. hot water; this solution was then
cooled to room temperature and mixed with the citric acid

*Trade-mark

solution. A slurry of 1110 g. of calcium hydroxide in
2 1870 ml. water was added quickly with stirring to the
citric acid-sodium caseinate solution. Within two
4 minutes of mixing, the temperature of the mixture
increased from 70°F to 150°F. A coarse caseinate-coated
6 calcium citrate suspension was obtained that was
continually stirred for about 45 minutes. During this
8 period, the temperature dropped to 100°F. The suspension
was homogenized for 10 minutes using a Ross laboratory
10 homogenizer followed by one pass through the Dyno-Mill as
in Example 2. The homogenization step facilitated the
12 even pumping of the suspension through the Micromill.

A fairly viscous, smooth and shiny paste was obtained.

14

EXAMPLE 5

16 An oil-free mayonnaise was prepared with the
following composition:

18	water	642.1 g.
	whole egg	113.5 g.
20	starch	60.5 g.
	sugar	46 g.
22	vinegar	30 g.
	dry egg white	29.9 g.
24	maltodextrin	19.7 g.
	lemon juice	18.1 g.
26	salt	10 g.
	gums	2.69 g.
28	flavor	as needed

30 To each of five samples of this oil-free mayonnaise
as added:

- 32 (a) titanium dioxide (0.38%) control
(b) the Example 1 spray-dried calcium citrate
34 (2% salt)

2 (c) calcium citrate paste micromilled at the
level of 19% in H₂O using the Dyno-Mill. The paste
was added at the level of 10 parts per 100 parts
4 mayonnaise (1.73% salt)

6 (d) calcium citrate micromilled in H₂O in the
presence of 1% sodium stearate and added at the level
of 15 g./150 g. mayonnaise (1.73% salt)

8 (e) calcium citrate (19 parts) micromilled in
80 parts H₂O and 1 part sodium caseinate. Ten grams
10 of this paste was added to 100 g. of mayonnaise
(1.73% salt).

12 In all cases, samples b-e exhibited an opacifying
effect on the mayonnaise substantially the same as
14 sample a (TiO₂). When compared to the mayonnaise mixture
containing no opacifier additive, the samples a-e were
16 quite opaque.

18 EXAMPLE 6

An instant pudding was prepared from the following
20 dry blend:

22	sugar	75	g.
	pregelatinized starch	20	g.
	sodium pyrophosphate	2	g.
24	sodium orthophosphate	2	g.
	mono and diglyceride emulsifiers	0.5	g.
26	vanilla flavor	as needed	

28 These ingredients were combined with 500 ml. of skim
milk. After shaking for one minute, the resultant
30 product was poured in 2 cups to set. The pudding lacked
opacity and the appearance of a good quality appetizing
32 product.

An opaque pudding was produced by dispersing 1.2 g.
34 of spray dried calcium citrate (the Example 1 product)

into the dry blend described above and the product
2 produced by the same procedure.

Better opacity was obtained when the spray-dried
4 calcium citrate of Example 1 was first mixed with water
(19:81) and micromilled using a Dyno-Mill and then 6.3 g.
6 of the micromilled salt paste (1.2 g. calcium citrate)
was dispersed in the skim milk with the dry blend being
8 then added.

In both cases, the calcium citrate addition was at a
10 level of 0.2% which did not adversely affect the texture
or eating quality of the pudding but did greatly enhance
12 the appearance and opacity of the product.

14

EXAMPLE 7

The spray dried product of Example 1 when mixed with
16 water at from room temperature up to about 70°C swells
and with shear it increases the viscosity of the blend
18 quite rapidly due to the breakdown of the crystal
clusters described hereinbefore.

20 Sodium caseinate was dissolved in water at a level of
1% up to 5%. Spray-dried calcium citrate produced
22 according to Example 1 was then added to a level of 18 to
20 parts by weight to the caseinate solution. The
24 suspension was then mixed and then sheared in a
homogenizer to produce a product with a viscosity higher
26 than mayonnaise.

This procedure can be repeated with skim milk or
28 regular milk in lieu of plain water to obtain milk
products of high viscosity. When employed to produce
30 products such as non-fat mayonnaise or milk products such
as various cheeses, flavorants may be added to the
32 aqueous system at any point in the preparation of the
final food product. In addition, pH adjustments of the
34 aqueous systems can be effected by addition of food grade
reagents, e.g., citric acid, to provide desired pH

levels. As indicated herein, the pH of the calcium
citrate produced in Example 1 procedures is in the range
of 4.5 to 6.0 depending on concentration. Other
additives present in the aqueous composition may also
affect the pH.

Various aqueous calcium citrate compositions were
prepared and the stability of these compositions
determined, as shown in the following Table where the
respective parts of tricalcium citrate and coating, if
present, are indicated, the balance being water.

	<u>Tricalcium Citrate</u>	<u>Coating</u>	<u>Observations</u>
12	(in parts per 100 of aqueous composition)		
(a)	18.5	0	Remained pasty for months
14 (b)	20	xanthan gum (0.3)	Remained pasty for months
(c)	18	sodium stearate (0.18)	Remained pasty for months
16 (d)	18.9(I)	gum arabic (1.89 and orange juice solids (2.45)	Remained pasty for months, yellow tint and glossy
18			
(e)	18.9	gum arabic (1.89) and orange juice solids (2.45)	same as (d)
20			
22 (f)	19	pineapple juice solids (7.9)	

Note I: precipitated calcium citrate produced as in Example 1 without
spray-drying.

26

For samples a, b, c, e and f, the calcium citrate
used is the spray dried product of Example 1, treated as
indicated for each sample.

In the foregoing examples, the original crystals
produced in accordance with Example 1 range from 0.5 to
1 micrometer. However, during actual precipitation and
handling, these crystals may form clusters that grow in
size up to 50 micrometers. Thus, some kind of post
grinding or high shear is recommended to reverse cluster

formation. The Dyno-Mill is particularly well-adapted
2 for the purpose of producing optimum size reduction. The
microfluidizer or the colloid mill are other typical
4 particle size reducing equipment.

With the procedures of Examples 4-6 were repeated
6 with a homogenizer, e.g., Ross homogenizer, in lieu of
the Dyno-Mill, the resulting products were not always as
8 smooth as those obtained with the very efficient
Dyno-Mill, ball mill.

10 When the shearing method is very effective, the
resulting product may tend to become a solid mass when
12 high levels of calcium citrate are used, e.g., more than
20:80 H₂O. Reducing the level of calcium citrate will
14 obviate this problem.

16

EXAMPLE 8

CHEESE

18 A fat-free/processed cheese loaf without opacifiers
added was obtained. The opacifier calcium citrate was
20 used to impart whiteness to the product in the following
manner.

22 100 g. of the processed cheese was transferred to a
300 ml. beaker and 16 g. of micromilled tricalcium
24 citrate paste (19% TCC, 81% water) produced in accordance
with Example 2 was added to the cheese block. The beaker
26 was covered by Saran Wrap and microwaved for a total time
of 60 seconds. It was mixed lightly at 30 sec. and then
28 given a good mixing with a spatula at the end of the
microwave treatment. The melted cheese was then covered
30 and let stand to cool at room temperature. The weight of
dry TCC in final product = 2.6%.

32 To 100 g. of the same processed cheese was added 3 g.
of spray dried calcium citrate of Example 1. The same
34 melting/mixing procedure was followed exactly as in
Sample 1 above.

As controls, a 100 g. block of the starting
2 unopacified cheese was used as well as a commercially
available cheese containing the opacifier titanium
4 dioxide.

The cheeses treated with calcium citrate are
6 definitely very white (opaque) as compared with the
original untreated cheese starting material. The
8 experimental samples are as opaque as the titanium
dioxide treated cheese and all treated samples look much
10 better than the untreated cheese.

12

EXAMPLE 9SALAD DRESSING

14	A buttermilk dressing dry mix was prepared from	
	Whey Solids, sweet	25.0 g.
16	Gum arabic	12.5
	Lactic acid	4.2
18	Salt	15.7
	Buttermilk	10.0
20	Sugar	7.5
	Citric acid	1.8
22	Xanthan gum	0.5
	Flavor/spices	As needed

24

These ingredients were mixed thoroughly and the blend
26 was subdivided into four equal portions by weight. To
two of them was added 2 g. each of clouding agents TiO₂
28 (titanium dioxide) as controls. To the other two
portions was added to each 5 g. of our spray dried
30 clouding agent calcium citrate, (Example 1 product).
These are the test samples.

32 One control and one test dry sample were mixed each
with a mixture of one cup of Kraft Mayonnaise and one cup
34 of skim milk. Both dry samples produced on
reconstitution fairly thick dressings. No significant

differences in opacity (white color) and other
2 physical/taste attributes can be noticed between the TiO₂
control and the test sample product.

4 The two remaining dry mix samples (TiO₂ control and
text sample) were blended each with two cups of water.
6 Fairly fluid dressings were obtained as compared with
these prepared using the mayonnaise and skim milk blend
8 above, but the opacity of these two water bases are
almost undistinguished. An unexpected result was that
10 the calcium citrate remained in suspension much longer
than the fairly dense TiO₂ in the fluid (non viscous)
12 dressing. It is clear that the present calcium citrate
salt can replace TiO₂ as an opacifier in a salad dressing
14 whether a viscous or a fairly fluid dressing is needed.

The pH of these dressings was 3.7 for the water substrate
16 and 4.1 for the mayonnaise skim milk system.

18

EXAMPLE 10

NON-FAT RELEASE AGENTS FOR BAKED GOODS

20 a) 200 g. of spray dried calcium citrate of
Example 1 was weighed and added to 881 g. of
22 deionized water and thoroughly mixed to obtain an
18.5% calcium citrate paste. This sample was then
24 passed through the Dyno-Mill three times. Kimwipe
was used to apply a small thin coat of the milled
26 material to the outer surface of an aluminum foil
before applying a bread dough. After baking, there
28 was no stickiness of product to the surface of the
coated aluminum foil (easy release).

30 b) 200 g. of the same calcium citrate was
added to 800 g. of deionized water and 0.3 g. of
32 xanthan gum. Sample was used and dispersed without
heating and micromilled as in a). Sample was
34 similarly coated on aluminum foil as in a).

- 18 -

2 Significant stickiness of product to aluminum foil
was found after baking with this coating.

4 c) 400 g. of the same calcium citrate and 4 g.
of sodium stearate was added to 1824 g. of deionized
water and micromilled. The resultant material was
6 coated on aluminum foil as described in a). The
dough was applied and after baking, there was no
8 stickiness of the baked product to the surface of the
coated aluminum foil.

10 d) Dough was applied to the untreated surface
of the aluminum foil as a control. After baking,
12 significant stickiness was found between this product
and the foil.

14 e) A commercial fat-containing releasing
agent, *PAM, was sprayed on the aluminum surface and
16 dough was applied and baked. No stickiness of
product to aluminum foil was found.

18 It is evident that untreated calcium citrate
(Example a)) or calcium citrate made more hydrophobic
20 with sodium stearate (Example c)) act as non-fat release
agents for baked goods.

22

EXAMPLE 11

REPLACEMENT FOR ROLL-IN MARGARINE IN BAKED GOODS

24 Micromilled calcium citrate of Example 4 (348 g.) was
26 spread over a Sweet Danish dough (1500 g.) and rolled
in. The sample was then retorted for 30 minutes,
28 flattened and rolled. This procedure was repeated three
times in order to form multiple layers. The viscosity of
30 the micromilled calcium citrate sample was high enough
(close to roll-in margarine) that there was no squeezing
32 of paste out of the dough.

The dough was then made into Swiss Rolls and proofed
34 for 45 minutes. The dough was baked for 20 minutes.

After baking and allowing to cool to room temperature,

the Swiss rolls that resulted were stored in boxes at
2 room temperature. Samples were compared to control made
with margarine the second day. There was no discernible
4 difference found between the margarine control and that
made with micromilled calcium citrate in appearance,
6 taste, and baked size.

This example shows that calcium citrate aqueous paste
8 compositions can be used to replace margarine, a
hydrogenated oil that is highly saturated with trans
10 fatty acids. In addition, the calcium citrate sample
would provide no extra fat calories since equal weight of
12 margarine and TCC were used to produce the Sweet Danish.

What is claimed is:

1. An aqueous dispersion comprising from about 0.2% to about 22% by weight of a finely divided calcium citrate salt of the formula:



wherein n is a value from 2.5 to 2.95, said salt being in the form of small platelets of a length of below about 3 microns, a width of below about 2 microns and a thickness of below about 1 micron.

2. A dispersion according to claim 1 wherein the average length of the crystals is about 1.5 microns, average width is about 1 micron and the average thickness is from about 0.1 to about 0.2 micron.
3. A dispersion according to claim 1 or 2 wherein the value of n is from about 2.61 to about 2.92.
4. A dispersion according to any one of claims 1 to 3, wherein a 1% aqueous solution of said salt shows a pH value of from about 4 to about 7.
5. A dispersion according to any one of claims 1 to 3, wherein a 1% aqueous solution of said salt shows a pH value of from about 4 to about 5.5.
6. A dispersion according to any one of claims 1 to 5, wherein the amount of said salt is from about 15% to about 20% by weight of the composition.
7. A dispersion according to any one of claims 1 to 6, wherein said calcium citrate salt particles are coated with a food-acceptable additive.

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8. An aqueous food composition comprising an aqueous dispersion of a finely divided calcium citrate salt of the formula:



wherein n is a value from 2.5 to 2.95, said salt being present at a level from about 0.2% to about 3% by weight of the composition, said salt being in the form of small platelets of a length of below about 3 microns, a width of below about 2 microns and a thickness of below about 1 micron.

9. A composition according to claim 8 wherein the average length of the crystals is about 1.5 microns, average width is about 1 micron and the average thickness is from about 0.1 to about 0.2 micron.

10. A composition according to claim 8 or 9 wherein the value of n is from about 2.61 to about 2.92.

11. A composition according to any one of claims 8 to 10, wherein a 1% aqueous solution of said salt shows a pH value of from about 4 to about 7.

12. A composition according to any one of claims 8 to 10, wherein a 1% aqueous solution of said salt shows a pH value of from about 4 to about 5.5.

13. A composition according to any one of claims 8 to 12, wherein said calcium citrate salt particles are coated with a food-acceptable additive.

14. A composition according to any one of claims 8 to 13, which comprises salad dressing.

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15. A composition according to any one of claims 8 to 13, which comprises cheese.
16. A composition according to any one of claims 8 to 13, which comprises pudding.
17. A composition according to any one of claims 8 to 13, which comprises margarine.
18. A composition according to any one of claims 8 to 13, which comprises mayonnaise.
19. A process of opacifying and whitening an aqueous food composition which comprises intimately mixing an opacifying and whitening amount of a finely divided calcium citrate salt of the formula:
- $$\text{Ca}_n(\text{C}_6\text{H}_5\text{O}_7)_2$$
- wherein n is a value from 2.5 to 2.95 said salt being in the form of small platelets of a length of below about 3 microns, a width of below about 2 microns and a thickness of below about 1 micron.
20. A process according to claim 19 wherein a 1% aqueous solution of said salt in water shows a pH value of from about 4 to about 7 and the value of n is from about 2.61 to about 2.92.
21. A process according to claim 19 or 20, wherein the opacifying and whitening amount of salt is from about 0.5% to about 3% by weight of the composition.

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22. A process according to any one of claims 19 to 21, wherein the salt is in the form of small platelets of an average length of about 1.5 micron, average width of about 1 micron and average thickness of about 0.2 micron.

23. A process according to any one of claims 19 to 22, wherein the calcium citrate salt is coated with a food-acceptable additive.

24. A process according to any one of claims 19 to 23, wherein the calcium citrate salt is in the form of an aqueous dispersion according to claim 1.

25. A process of producing finely-divided crystals of calcium citrate which comprises reducing crystal agglomerates of calcium citrate salt of the formula:



wherein n is a value from 2.5 to 2.95 in an aqueous medium at a pH from about 3.5 to about 7.0 to the form of small platelet crystals of a length of below about 3 microns, a width of below about 2 microns and a thickness of below about 1 micron.

26. A process according to claim 25 wherein said crystal agglomerates are reduced by grinding.

27. A process according to claim 25 wherein said crystal agglomerates are reduced by agitation in an aqueous medium for sufficient time to effect the desired reduction.

28. A process according to claim 25 wherein said crystal agglomerates are reduced by standing in an aqueous medium for sufficient time to effect the desired reduction.

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29. A process according to claim 25 wherein said crystal agglomerates are reduced by homogenizing in an aqueous medium.