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[54] **METHOD OF PREVENTING THE CAKING OF HARDENED OIL COATED PARTICLES**

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[58] **Field of Search** ..... 117/100 A, 167, 16; 99/140, 156, 83, 140, 2 F, 143, 159

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[57] **ABSTRACT**

A method of preventing the caking of hardened oil coated particles which comprises allowing particles consisting of a core material coated with a coating agent predominantly of a hardened oil having a melting point of 45°–85°C., to stand for at least 20 hours at a temperature exceeding 25°C. but lower than the softening point of the hardened oil to thereby stabilize the crystal structure of the hardened oil and thereafter adding to the coated particles a caking inhibitor, in an amount of 0.3 – 5 percent by weight based on weight of the coated particles.

6 Claims, 2 Drawing Figures

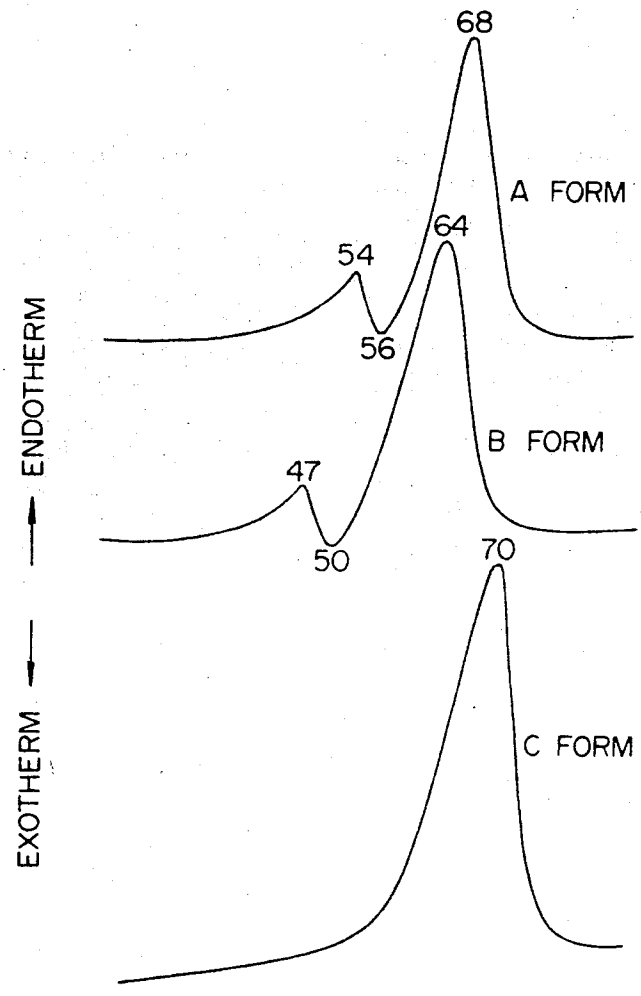


Fig. 1

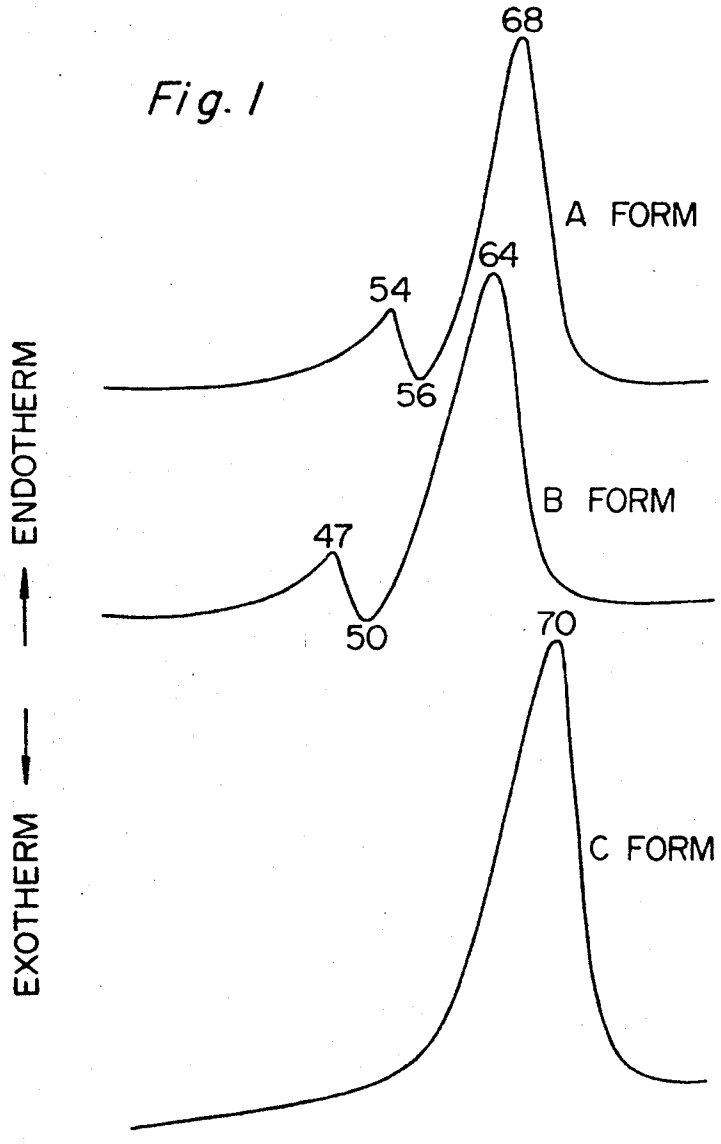
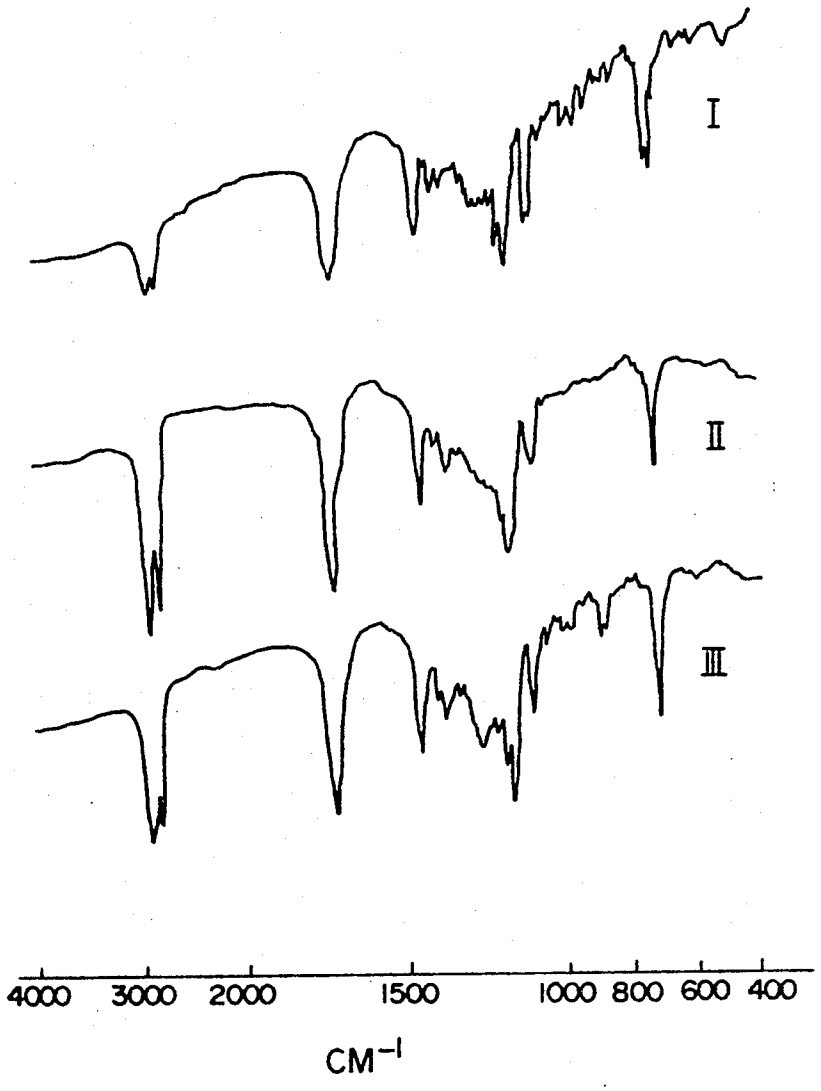


Fig. 2



METHOD OF PREVENTING THE CAKING OF HARDENED OIL COATED PARTICLES

This invention relates to a method of preventing the caking of particles consisting of a core material coated with a coating agent whose principal ingredient is a hardened oil.

Hardened oils have been used for such purposes as the prevention of moisture absorption, maintenance of effectiveness of prevention of reaction of such drugs and chemicals as medicines for man as well as animals, agricultural chemicals, food additives, etc., by serving as a surface coating with these drugs and chemicals as the core material. Especially when a food additive is the core material, the application of a hardened oil coating has been frequently practiced to achieve a unique end, i.e., to prevent the additive from eluting at room temperature but permitting it to elute during the step of heating the food product, in order to prevent the decomposition of the core material in the foodstuff material and any adverse effect of the core material on the foodstuff material.

A hardened oil to be used for the above described purposes is one having a melting point ranging from 45° to 85°C. In the case of a hardened oil whose melting point is below the foregoing range, there is the possibility of its softening at high temperatures experienced in summer. Especially desirable hardened oils are, for example, hardened beef tallow (m.p. 59° – 61°C.), hardened whole oil (m.p. 55° – 60°C.), hardened rape seed oil (m.p. 50° – 62°C.), hardened soybean oil (m.p. 60° – 69°C.), hardened cottonseed oil (m.p. 55° – 61°C.) and hardened castor oil (m.p. 82° – 85°C.)

As methods of coating such core materials as medicines for man as well as animals, agricultural chemicals and food additives with a hardened oil numerous methods are known such as the following :

1. The spraying method which comprises heat-melting the hardened oil, dispersing the core material therein and thereafter spraying this dispersion into a gas of a melting point below that of the hardened oil (e.g. air, nitrogen and carbon dioxide) thereby accomplishing the coating of the core material and at the same time the cooling and solidification of the particles.

2. The coating pan method in which the coating of the particles is carried out by repeating an operation consisting of placing the core material in a coating pan, spraying a solvent-dissolved hardened oil onto the core material while tumbling same in the pan, and thereafter evaporating and removing the solvent by blowing, for example, hot air against the coated particles.

3. The suspension-in-air coating method which comprises floating the core material in a stream of air and coating the so floating core material by spraying a solution of a hardened oil against the material.

4. The vacuum vaporization method which comprises heating the hardened oil in a vacuum and evaporating it against the core material to thereby effect the vapor deposition of the hardened oil onto the surface of the core material.

5. The electrostatic coating method which comprises impressing the particles of the core material and the particles of the hardened oil solution with opposite electric charges to thus unite these particles.

6. The meltable-dispersion method which comprises heat-melting the hardened oil in a liquid which does not dissolve the same, dispersing the core material in the melt, forming the dispersed core material into small particles, and thereafter cooling and solidifying the same.

While the particle size of these coated particles consisting of a core material coated with a hardened oil will vary depending upon the intended use of the core material, the coated particles are usually prepared so as to have a suitable particle diameter ranging from 50 to 2,000 microns. It is most desired that these coated particles are independent from each and have fluidity. If the coated particles are caked and in a lumpy state, their use is not only inconvenient but also this makes them unfit for use at times. Especially in the case where the core material happens to be a food additive, it is necessary that these particles are uniformly mixed in the foodstuff material. Therefore, a food additive in which the particles are in a caked state rather than achieving its purpose has the opposite effect of degrading the quality of the food, since it becomes incorporated in the food product in a nonuniform state.

In view of the foregoing reason, in order to prevent this caking which causes an excessive degradation of the merchandise value of the product, the addition of about 0.3 – 5 percent by weight based on the hardened oil coated particles of a finely divided inorganic substance such as silica, magnesium alumino silicate, magnesium carbonate, and calcium tertiary phosphate or alkaline earth metal salts of higher fatty acids, such as calcium stearate or magnesium stearate is being practiced. However, notwithstanding the addition of these caking inhibitors, it frequently happens that the product becomes caked after shipment of the product from the manufacturer's plant and by the time it reaches the consumer.

The object of the present invention is to therefore provide hardened oil coated particles in which the hereinbefore noted caking does not occur.

On the basis of a finding that the hereinbefore described caking of the hardened oil coated particles was due to a change taking place in the crystal structure of the hardened oil used as the coating agent, it was possible to achieve the above object of the invention by operating in the following manner. The particles consisting of a core material which have been coated with a coating agent whose principal ingredient is a hardened oil of a melting point 45° – 85°C. are allowed to stand for at least 20 hours at a temperature higher than 25°C. but lower than the softening point of the hardened oil, thereby stabilizing the crystal structure of the hardened oil, following which the particles are incorporated with a caking inhibitor, in an amount of 0.3 – 5 percent by weight based on the weight of the coated particles.

Changes in the crystal structure of a hardened oil occur as a result of its temperature history. That is, the solidified mass of hardened oil is made up of a plurality of crystals, i.e., a congregation of small crystals and, thus, changes in the crystal structure take place as a result of the temperature history of these small crystals. The solid hardened oil obtained by either cooling and solidifying or precipitating from a solvent a hardened oil which is in a molten state as a result of heating is of a structure in which a plurality of small crystals in an unstable form are collected together in a relatively loose arrangement. Now, when these crystals are allowed to stand for a prolonged period of time in a state where heat is applied from the outside, the unstable crystal structure is tranformed to a stable crystal struc-

ture and moreover the small crystals which were in a relatively loose arrangement become disposed orderly and in a state, with a consequence that they become exceedingly stabilized. The crystal structure which has been stabilized in this manner no longer changes at a temperature lower than the softening point of the hardened oil.

The changes, such as discribed, in the crystal structure of a hardened oil due to its temperature history have been examined in detail by means of differential thermal analysis or X-ray or infrared absorption analysis. However, no studies have been made which relate the prevention of the caking of the hardened oil coated particles to the crystal structure of the hardened oil. The studies concerning the prevention of caking have completely ignored the crystal structure of the hardened oil but have been exclusively directed to inquires with regard to the classes and amount of the caking inhibitor to be used. Further, the explanation that was given regarding the cause of the caking was merely that a part of the hardened oil melts on approaching a temperature close to the softening point, thereby causing a fusion to take place between the particles and thus result in a caked state. As a result of research concerning the relationship between the changes in the crystal structure of the hardened oil and caking, it has been found that the caking of the hardened oil coating particles was not only affected by the temperature at which the particles were allowed to stand but that the temperature history of the coated particles also had a great effect on this caking phenomenon.

When the relationship of the changes in crystal structure and caking is described with reference to the accompanying drawings, taking as an example hardened beef tallow, it is as follows :

In the accompanying drawings,

FIG. 1 is a graph illustrating the results of a different thermal analysis of hardened beef tallow; and

FIG. 2 is a graph illustrating the results of an infrared absorption analysis of hardened beef tallow.

When a differential thermal analysis is carried out on hardened beef tallow (m.p. 59° – 61°C.) after heat-melting it and then cooling and solidifying it, three classes of curves are obtained as shown in FIG. 1 depending upon the method employed for the cooling treatment. The crystal forms of the hardened oil which provide these three classes of differential thermal curves are referred to as A, B and C forms. The A form crystal is a crystal form obtained when a heat-melted hardened oil is rapidly cooled and solidified in cold water, and while it is stable at low temperatures, it gradually transform to the B form crystal when the temperature rises finally becoming transformed to the C form crystal. The B form crystal is one which is obtained when the hardened oil has been cooled and solidified under relatively mild conditions, i.e. by being allowed to stand at room temperature. Under these conditions, the B form crystal is obtained without passing through the A form crystal stage. The B form crystal, as in the case with the A form crystal, is unstable and therefore gradually transforms to the C form crystal. The C form crystal is a crystal form which is obtained when the A and B form crystals have been allowed to stand either for 15 or more days at 25°C. or 3 or more days at 30°C. This C form crystal being exceedingly stable does not change at temperatures below the softening point. Further, concurrently with this transformation, a change in the disposition of the small crystals from a loose arrangement to an orderly arrangement takes place. Therefore, not only is the crystal form stabilized but also the stability of the overall structure is increased. Referring to the graph of FIG. 1, the maximum peak temperature of the A form crystal is 68°C., that of the B form crystal is 64°C. and that of the C form crystal is 70°C., that of the C form crystal being the highest, while that of the B form crystal being the lowest. That is, in the case of the hardened beef tallow, the transformation takes place first from the A form crystal to the B form crystal having a lower maximum peak temperature and then to the C form crystal which is the most stable. This sort of transformation is a phenomenon which is generally seen in the case of the higher fatty acids and higher alcohols. In FIG. 2, graph I illustrates the infrared analysis results of the C form crystal and graph II shows that of the A form crystal. The form of graph I is more complicated than that of graph II, and it can be clearly seen a difference exists.

In general, the hardened oils precipitated from a solvent are of the C form crystal, but in this case it is still an unstable C form crystal. In addition, its crystal structure is also one not disposed in an orderly manner but is one which is of loose arrangement. However, when this hardened oil is allowed to stand at above a certain temperature, the crystals are changed to C form crystals having stability and its crystal structure becomes one which has an orderly arrangement.

Graph III of FIG. 2 is the result of an informed analysis of hardened beef tallow which has been crystallized by the evaporation of chloroform from a chloroform solution at 20°C., a clear difference being seen from this graph when compared with graphs I and II. When this hardened oil crystal is allowed to stand at above a certain temperature, it changes to a stable crystal equalling that of graph I.

The speed with which the crystal structure transforms from the A or B form to C form is influenced by the temperature at which the crystals stand, the speed becoming faster in proportion as the temperature becomes higher. At low temperatures at which the transformation does not progress (generally, the speed becomes very slow when the temperature falls to below 15°C.), caking of the particles coated with a hardened oil of the A form or B form crystals does not take place even though the particles are allowed to stand for a prolonged period of time.

The caking of the hardened oil coated particles, which takes place when the crystal structure transforms from the A or B form to the C form, can be explained as being a phenomenon wherein particles combine by mutually taking in the crystals of the other particles at the surfaces thereof during the time when the transformation of the A form and B form crystals to the stables C form crystal is taking place or when a change in the loose disposition of the small crystals to an orderly arrangement is taking place.

In carrying out the stabilization of the hardened oil crystal structure in accordance with the present invention, i.e., the transformation from the A form and B form crystals to the C form crystal as well as the change in the loose disposition of the small crystals to an orderly arrangement, the hardened oil coated particles are suitably allowed to stand at a temperature above 25°C., and preferably above 30°C. At low temperature of below 25°C., either the speed of transformation is

exceedingly slow or no transformation takes place at all. For example, the change to a completely stable form of crystal takes place in 15 days at 25°C., 3 days at 30°C., 24 hours at 40°C., and 20 hours at 45°C. Thus, the time that the particles must be allowed to stand for completion of their stabilization becomes shorter as the temperature becomes higher. The hardened oil coated particles, which have been stabilized in this manner, are passed through a sieve and any slight caking that has occurred during the transformation is eliminated. The particles, which have in this way been rendered independent of each other, as then incorporated with 0.3 – 5 percent by weight, and preferably 0.5 – 3 percent by wieght, based on the particles, of a caking inhibitor, and as a result the product of the present invention of improved fluidity, which does not cake at temperatures lower than the softening point of the hardened oil, and is therefore of high merchandise value is obtained. While any substance may be used as the aforesaid caking-inhibitor as long as it is one which does not impede the function of the core material, usually silica, magnesium alumino silicate, magnesium carbonate, calcium tertiary phosphate, calcium stearate or magnesium stearate is conveniently used.

The operation for carrying out the stabilization treatment is simple. For example, the coated particles immediately after their preparation need only be allowed to stand in a room of a temperature higher than 25°C. but lower than the softening point of the hardened oil until transformation of the crystal structure to the form C form is completed. This is done with the particles spread thinly in a vessel, such as a pan, in such a manner that the particles are subjected to a minimum of load. The reason not to impose a load more than the minimum on the particles is to reduce as much as possible the occurrence of caking during the transformation stage. Since it is impossible to avoid caking from taking place during the transformation, a pressure which tends to increase the contact area between the particles at this stage must be avoided as much as possible to reduce to a minimum the possibility of caking.

The operation involved in incorporating the caking inhibitor is also simple. A procedure consisting of admixing the prescribed amount of caking inhibitor with the coated particles using a customary mixer will do. The slight caking which has occurred during the stabilization treatment is completely eliminated during this mixing while at the same time the caking inhibitor becomes uniformly mixed with the coated particles. Thus, coated particles having fluidity and in which caking does not take place can be readily obtained.

The following non-limitative examples are given for more specifically illustrating the invention. The percents in the example are on a weight basis.

EXAMPLE 1

Four kg of hardened beef tallow were heat-melted and maintained at a temperature of 70°C. After adding 1 kg of powdered sorbic acid to the melted hardened beef tallow, the mixture was mixed with thorough stirring using a homo-mixer to obtain a homogeneous dispersion. The dispersion was sprayed into air of 20°C., and on cooling and solidification hardened oil coated sorbic acid particles useable as a food preservative were prepared. The following caking test was carried out on the so obtained coated particles.

The several classes of caking inhibitors indicated in Tables 1—1 to 1–5 were added separately to the coated particles, following which the coated particles were allowed to stand under the various conditions indicated in Tables 1–1 to 1–5. This was followed by packing the coated particles in a cylindrical tube 40 mm in diameter and 60 mm in height and subjecting the particles to a pressure by placing a 500-gram weight atop the packed particles. The particles were allowed to stand for 7 days in this state at the prescribed test temperatures indicated in Tables 1—1 to 1–5. Next, the coated particles contained in the tube were taken out therefore ensuring that in doing so the caked condition of the particles was not disturbed, after which the so withdrawn particles were lightly sieved with a 10-mesh sieve. The amount of coated particles remaining on the sieve relative to the total amount was then calculated and expressed in percent. This value, which is designated the degree of caking (%), is indicated in Tables 1—1 to 1–5. The larger this value is, the greater the caking of the particles. Also shown in Tables 1—1 to 1–5 are the crystal forms of the hardened beef tallow before and after the test.

TABLE 1-1

Conditions under which particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature ° C.)	Degree of caking (percent)	Crystal form	
				Before test	After test
Tested immediately after preparation		10	15–20	A	A
Do		30	90–95	A	C
Do	Calcium tertiary phosphate, 3%	10	Below 1	A	A
Do	do	30	80–90	A	C
Do	Silica, 3%	30	70–80	A	C
Do	Magnesium alumino silicate, 3%	30	70–80	A	C

TABLE 1-2

Condition under which particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature ° C.)	Degree of caking (percent)	Crystal form	
				Before test	After test
Left standing 3 days at 25° C. after preparation		10	15–20	B	B
Do		30	90–95	B	C
Do	Calcium tertiary phosphate, 3%	30	80–90	B	C
Do	Silica, 3%	30	70–80	B	C
Do	Magnesium alumino silicate, 3%	30	70–80	B	C

TABLE 1-3

Condition under which particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature ° C.)	Degree of caking (percent)	Crystal form: Before test	Crystal form: After test
Left standing 15 days at 25° C. after preparation		10	15-20	C	C
Do		30	15-20	C	C
Do	Calcium tertiary phosphate, 2%	10	Below 1	C	C
Do	do	30	do	C	C
Do	Silica 1%	30	do	C	C
Do	Magnesium alumino silicate, 1%	30	do	C	C

TABLE 1-4

Condition under which particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature ° C.)	Degree of caking (percent)	Crystal form: Before test	Crystal form: After test
Left standing 3 days at 30° C. after preparation	Calcium tertiary phosphate, 0.5%	30	5-10	C	C
Do	Silica, 0.5%	30	1-5	C	C
Do	Magnesium alumino silicate, 0.5%	30	1-5	C	C
Do	Calcium tertiary phosphate, 2%	30	Below 1	C	C

TABLE 1-5

Condition under which particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature (° C.)	Degree of caking (percent)	Crystal form: Before test	Crystal form: After test
Left standing 20 hours at 45° C		10	15-20	C	C
Do		35	15-20	C	C
Do	Calcium tertiary phosphate, 2%	35	Below 1	C	C
Do	Silica, 2%	35	do	C	C
Do	Magnesium alumino silicate, 2%	35	do	C	C

EXAMPLE 2

The three kilograms of hardened castor oil (m.p. 80° - 85°C.) were heat-melted. After adding 4 grams of soya-lecithin thereto as a surfactant, one kg of finely divided fumaric acid was added, following which the mixture was commingled with thorough stirring to obtain a dispersion. While maintaining this dispersion at 90°C., it was sprayed into air of 30°C., wherefrom it was cooled and solidified. As a result hardened castor oil coated fumaric acid particles were prepared.

The so obtained coated particles were incorporated separately with the various caking inhibitors indicated in Table 2 to adhere the caking inhibitors to the surface of the hardened caster oil coated fumaric acid particles, and a caking test was carried out as in Example 1 under the various conditions indicated in Table 2. The results obtained are shown in Table 2.

The hardened castor oil coated fumaric acid particles are added to the starting food material, and by preventing the elution of the fumaric acid at room temperature but by causing the acid to elute during the heating step, they are used for the purpose of lowering the pH of the food product. Since as shown in Table 2 the degree of caking of the invention coated particles is low, they are especially suitable for this purpose.

TABLE 2

Conditions under which the particles are allowed to stand	Class and amount of caking inhibitor added	Test temperature (° C.)	Degree of caking (percent)
Tested immediately after preparation.		10	55-10.
Do		35	80-85.
Do	Magnesium alumino silicate, 2%.	35	70-80.
Do	Calcium tertiary phosphate, 2%.	35	70-80.
Do	Silica, 2%	35	70-80.
Left standing 2 days at 45° C. after preparation.		10	5-10.
Do		35	5-10.
Do	Magnesium alumino silicate, 2%.	35	Below 1.
Do	Calcium tertiary phosphate, 2%.	35	Do.
Do	Silica, 2%	35	Do.

EXAMPLE 3

A glutamic acid powder of 40-mesh was placed in a coating pan and while being tumbled the powder was sprayed with a 30 percent chloroform solution of hardened beef tallow (m.p. 59 - 61°C.) After continuing the tumbling of the powder particles for a while and having accomplished the uniform wetting of the surface of the glutamic acid powder particles, the chloroform was evaporated by means of hot air. The foregoing operation was repeated until the content of the hardened beef tallow in the particles became 40 percent. As a result coated glutamic acid particles which could be used as a seasoning as well as a pH lowering agent of food products were prepared.

The so obtained coated glutamic acid particles were allowed to stand under the conditions indicated in Table 3, after which the various caking inhibitors were added and the caking test was carried out. The results obtained are shown in Table 3.

TABLE 3

Conditions under which the particles were allowed to stand	Class and amount of caking inhibitor added	Test temperature (° C.)	Degree of caking (percent)
Tested immediately after preparation.		10	10-15.
Do		35	60-70.
Do	Calcium stearate, 3%.	35	40-50.
Do	Magnesium stearate, 3%.	35	40-50.
Do	Magnesium carbonate, 3%.	35	40-50.
Left standing 3 days at 37° C.		10	10-15.
Do		35	10-15.
Do	Calcium stearate, 3%.	35	Below 1.
Do	Magnesium stearate, 3%.	35	Do.
Do	Magnesium carbonate, 3%.	35	Do.

From the results presented in the foregoing tables, it is seen that the caking of the hardened oil coated particles is pronounced at the time the crystal structure changes, with the consequence that unless the crystal structure of the hardened oil has been stabilized the

caking inhibitor which has been incorporated in the coated particles is practically powerless in demonstrating its effectiveness. On the other hand, it is seen that in accordance with the invention method wherein the caking inhibitor is incorporated in the hardened oil coated particles after having stabilized the crystal structure of the hardened oil by allowing the coated particles to stand at a temperature higher than 25°C. but lower than the softening point of the hardened oil, the effectiveness of the caking inhibitor can be fully demonstrated and stable hardened oil coated particles which have fluidity and do not cake at normal temperatures can be obtained.

We claim:

1. A method of preventing the caking of hardened oil coated particles which comprises allowing particles consisting of a core material coated with a coating agent predominantly of a hardened oil having a melting point of 45–85°C., to stand for at least 20 hours at a temperature exceeding 25°C. but lower than the softening point of said hardened oil and thereafter adding to the stabilized hardened oil-coated particles a cake inhibitor, in an amount of 0.3–5 percent by weight based on the weight of the stabilized hardened oil-coated particles.

2. The method of claim **1** wherein said caking inhibitor is a finely divided inorganic substance.

3. The method of claim **1** wherein said caking inhibitor is an alkaline earth metal salt of a higher fatty acid.

4. The method of claim **1** wherein said caking inhibitor is silica, magnesium alumino silicate, magnesium carbonate, tertiary calcium phosphate, calcium stearate or magnesium stearate.

5. The method of claim **1** wherein said core material coated with said hardened oil is allowed to stand at a temperature exceeding 30°C.

6. The method of claim **1** wherein said caking inhibitor is added in an amount of 0.5–3 percent by weight based on the weight of the stabilized hardened oil-coated particles.

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