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Settling Study of Titanium Dioxide in a Beverage

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Insinöörityön tarkoituksena oli tutkia titaanidioksidin laskeutumista jauheesta valmistetussa mehussa. Titaanidioksidia käytetään jauheesta valmistetuissa mehuissa tuomaan mehuun luonnollisen mehun kaltaista suuntuntumaa ja sakeutta. Työssä tutkittiin myös spraykuivauksen vaikutusta titaanioksidin laskeutuvuuteen. Työssä etsittiin myös reseptiä, jolla titaanidioksidin laskeutuvuutta mehussa pystyttiin estämään tai ainakin hidastamaan riittävästi.

Tutkimus aloitettiin kehittämällä reseptit laskeutuvuustutkimusta varten. Laskeutuvuuskoe tehtiin seuraavaksi. Laskeutuvuuskokeessa titaanidioksidin laskeutuvuutta seurattiin seitsemän päivän ajan. Spraykuivauksen vaikutusta laskeutuvuuteen selvitettiin toistamalla laskeutuvuuskoe mehuille, jotka oli valmistettu ”cloudista”, joka oli spraykuivattu jauheeksi.

Työssä löydettiin muutama resepti kuivamehulle, joiden avulla titaanidioksidin laskeutuvuus pystyttiin estämään melkein kokonaan seitsemän päivän seurantajaksolla. ”Cloudin” spraykuivaamisella jauheeksi ei tuntunut olevan paljoa vaikutusta titaanidioksidin laskeutuvuuteen.

Avainsanat	Titaanidioksidi, TiO_2, spraykuivuri, laskeutuvuus, elintarvike, juoma

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The aim of this thesis was to study the settling of titanium dioxide in juice made from a dry beverage mix and to determine whether the spray drying of the clouding agent has any effects on the settling of titanium dioxide. Titanium dioxide is used in beverages made from dry beverage mix to bring to the beverage mouthfeel and haziness common in natural juices. One goal was to discover a recipe for clouding agent which inhibits or decreases the descent of titanium dioxide in a beverage.

The research was executed by first developing the recipes for clouding agents and then testing the settling of titanium dioxide in juice for seven days. In order to find out whether the spray drying of clouding agent has an effect on the settling of titanium dioxide, the beverages compared were the ones, where the clouding agent used was first spray dried into a powder form.

In this thesis project a few recipes to decrease the settling of titanium dioxide was discovered. No significant difference in the settling of titanium dioxide was found between beverages where the clouding agent was used in liquid form or in powdered form. And since the settling of titanium dioxide was very little, in juices where the recipe for clouding agent was successful, spray drying did not seem to decrease the settling of titanium dioxide.

Keywords	titanium dioxide, TiO_2, spray dryer, descent, beverage, additive

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Appendix

Appendix 1: U.S: Patent no. 6,159,522: High Performance Titanium Dioxide Clouding Agent and Method of Manufacture Thereof

Abbreviations, Constructions and Definitions

Anatase	Crystal form of titanium dioxide
Clouding agents	Agents used to bring turbidity to beverage
DE	The proportion of the galacturonic acids that are in the methyl ester form, is called the “degree of esterification” (DE) or “degree of methoxylation” and is quoted as a percentage. DE affects the behavior of pectin.
DP	Degree of Polymerization
EU	European Union
Extracellular	Outside the cell
Genotoxicity	The property of chemical agents that damages the genetic information within a cell causing mutations.
Heteropolysaccharide	Heteropolysaccharides contain two or more different monosaccharide units.
Rutile	Crystal form of titanium dioxide
Starch hydrolysate	Starch hydrolysate is a collective term for products of the conversion of sugar into starch.
TiO_2	Titanium dioxide
U.S.	United States of America

1 Introduction

This thesis is a research about the settling of titanium dioxide (TiO_2) in a beverage made from dry beverage mix. The goal of this thesis project was to find a recipe for dry beverage mix where TiO_2 would not settle or settles very little. The purpose of this study was also to find out whether the spray drying of the clouding agent affects the settlement of TiO_2. In foodstuffs, titanium dioxide is used, for example to give whiteness to food. In beverage industry, TiO_2 is also used to bring opacity and haziness to juice in order to imitate the cloudiness of natural juices. The project was done for Huntsman Pigments (previously Sachtleben Pigments).

The recipe for the clouding agent was searched by experimentally testing different suspending agents in the cloud. The settlement study was done in a laboratory where two series of juices are made and the settlement of TiO_2 was observed for seven days. The first series of juices have clouding agent in liquid form and the clouding agent used in the second series of juices has been spray dried to powder.

2 Food Additives

2.1 Function of food additives

The two most basic functions of food additives are that they affect food safety by preserving it from bacteria and inhibiting oxidation and other chemical changes, they also make food taste or look better and/or give more pleasant mouth feel to food. People have had the need to preserve food for a long time. Many of the food preserving techniques we use now are relatively new such as canning or freezing. Before those techniques were discovered, the way of conserving for example, meat was salting, drying or pickling. And when the shortage of food ceased to be a problem, the taste and the appearance of food started to get more emphasis. However, the oldest additives being used are not preservatives. Our ancestors used additives such as vinegar and saltpeter which was for curing food [1]

2.2 Colorants in foodstuff

Food manufacturers use food colorants to enhance the visual properties of foods. Coloring foodstuff can be used also to bring the color back to food if it is lost in the food manufacturing process. The use of colors in food is controversial since some believe those are used to deceive the consumer, and also because some of the most brightly colored food products are made for children. The use of colorants is strictly controlled by legislation. [1, 2]

2.3 Emulsifiers, thickeners and stabilizers

Emulsion is a mixture of two liquids (or more) that do not mix without mixing. In order to stabilize the emulsion an emulsifier has to present in emulsion. Emulsifiers are substances used to stabilize an emulsion by increasing its kinetic stability. Emulsifiers do not let the two phases separate back to their own layers after mixing. [1, 3]

Emulsifiers are surfactants which lower the surface tension between two surface (liquid and liquid or liquid and solid). Surfactant accumulates at the interphase between the phases and does not dissolve well in either one of the bulk phases. A typical surfactant consists of a long hydrocarbon tail that dissolves in hydrocarbon and other non-polar materials, and a hydrophilic head group that dissolves in polar solvent (typically water). [1, 3]

In foodstuff thickeners are applied to substance in order to increase viscosity of the solution. Thickeners in can also improve the suspension of other ingredients or emulsions which increases the stability of the product. Some thickening agents are gelling agents which for a gel in liquid phase. Thickeners used in food are mainly based on polysaccharides or protein. [1]

Stabilizers are used in food to maintain its physical and chemical condition by stabilizing the emulsion. In emulsion, stabilizers function is to inhibit the separation of phases. [1]

3 Titanium Dioxide

Titanium dioxide is inorganic natural pigment. It has two forms which are used commercially, anatase and rutile. Anatase form of titanium dioxide is used to provide whiteness and opacity in foods and it has an E code E171. [4]

3.1 Properties

Titanium dioxide is an amorphous white powder and it is characterized by brightness and a very high refractive index (2.4). Refractive index is a measure of bending of a ray of light when passing from one medium into another. Titanium dioxide is opaque mineral which is insoluble to water and organic solvents and is stable material; it is resistant to light, pH variations, oxidation and heat. TiO_2 is available in oil-dispersible and water-dispersible forms, and it naturally occurs in main three forms, which are rutile, anatase and brookite. TiO_2 which is used in food industry is pure titanium dioxide and it is anatase form. Titanium dioxide is used in paints, inks, plastics, paper, textiles, toothpaste, and in food to provide whiteness and opacity. [4, 5]

3.2 Occurrence

Titanium dioxide is extracted from natural ores and milled to the correct particle size to provide optimum opacity and whiteness. In nature, titanium dioxide exists in three different crystalline forms; rutile, anatase and brookite. Anatase are form is permitted to be used in foodstuff. The form of titanium dioxide can be determined by processing conditions. [4]

3.2.1 Anatase

Anatase in nature is found small, isolated and sharply developed crystals that are relatively pure titanium dioxide. The anatase form of titanium oxide is used in the food industry. The common pyramid of anatase, parallel to the faces of which there are perfect cleavages, has an angle over the polar edge of 82°9', the corresponding angle of rutile being 56°52½'. The structure of anatase is presented in Figure 1. [4, 6]

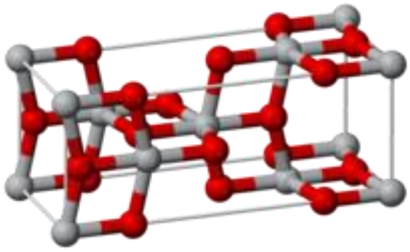

Figure 1 Picture of titanium dioxide's anatase form's crystal structure

The mineral was named on account of this steeper pyramid of anatase, by René Just Haüy in 1801, from the Greek anatasis, "extension", the vertical axis of the crystals being longer than in rutile. One of the differences between the physical characters of anatase and rutile is that the anatase is less hard (5.5–6 vs. 6-6.5 Mohs) and dense (specific gravity about 3.9 vs. 4.2). The other difference of anatase and rutile is that anatase is optically different than rutile; it scatters more UV-light than rutile and rutile appears bluer white than anatase. [4, 6]

3.2.2 Rutile

Rutile is a mineral composing primarily of titanium oxide all though in nature it may contain in up to 10 % iron and notable amount of niobium and tantalum. As mentioned earlier, rutile is harder and denser form of TiO_2 then anatase. It is the most common form of TiO_2 and it has among the highest refractive indices at visible wavelengths of any known crystal, and also exhibits a particularly large birefringence and high dispersion. With these properties, it is useful for the manufacture of certain optical elements, especially polarization optics, for longer visible and infrared wavelengths up to about 4.5µm. The name rutile comes from the Latin rutilus, red, which is a reference to the deep red color observed in some specimens when viewed by transmitted light. The structure of rutile is presented in Figure 2. [4, 7]

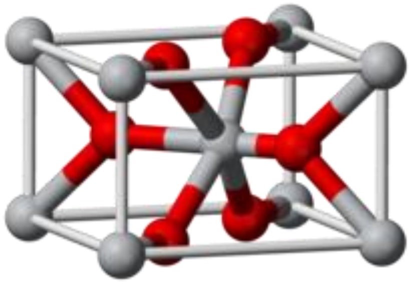

Figure 2 Picture of titanium dioxide's rutile form's crystal structure

3.3 Production

World widely 4 million tons of titanium dioxide is being produced per year and it is used widely in industrial applications, such as in paints, inks, plastics and in textiles, and a small proportion is used as a food colorant. Titanium dioxide is produced chiefly from ilmenite, a titaniferous ore ($FeTiO_2$). The production of titanium dioxide's rutile form is done by chloride or sulfate processes via the treatment of the TiO_2 ore with chlorine gas or sulfuric acid, and the process is followed by a series of purification steps. Anatase form production is done by sulfuric acid treatment followed by series of purification steps. [4]

3.4 Use in foodstuff

Titanium dioxide is mainly used in such food applications as dairy products, icings, confectionery, and toppings. TiO_2 is also used in dry beverage mixes. Dry beverage mix is a powder which can be dissolved into a water in order to manufacture a beverage, which duplicates natural beverage. Dry beverage mix must easily and instantaneously go into solution and give the impression of natural-looking product. It is used in food to color to foodstuff, to give the food opacity and to give a light background for other colorings. TiO_2 is used to give mouth feel and creaminess to low-fat products. [1, 4, 8]

Titanium dioxide is the only true white pigment that is allowed to be used in foodstuff in the EU. Anatase form of TiO_2 is preferred for utilization in the food industry consequently it's high-purity. [1, 4]

3.5 Regulations and toxicology of titanium dioxide

In the U.S. the utilization of titanium dioxide is limited to 1 % by weight, in the EU there is no limitation TiO_2 utilization in foodstuff. Animal studies have showed low acute toxicity in rats (LD_{50} > 25 g/kg body weight/day) and mice (LD_{50} > 10 g/kg body weight/day) and non-carcinogenicity and genotoxicity in long-term studies. It was considered that TiO_2 is poorly absorbed in mammals, but it was found in human gut-associated lymphoid tissue. [4]

4 Clouding Agents in Beverages

4.1 Clouding agents

Clouding agents are used in aqueous beverages produced from dry beverage mixes to imitate the opacity of a natural juice. Most clouding agents are manufactured by mixing a spacing agent, a suspending agent and titanium dioxide. The agent that provides the opacity to the juice is titanium dioxide. It is important that the clouding agent is at least partially soluble or dispersible in the beverage and that the clouding agent remains dispersible in the beverage for some period of time without settling out of the liquid. [9]

A dispersion is a mixture of two substances which do not mix together, but the particles are dispersed in the solution. Mixture of water and titanium dioxide is a colloid dispersion. A colloid is a substance in which microscopically dispersed insoluble particles are suspended throughout another substance. Dispersion can be stabilized with emulsifiers, stabilizers or thickeners. [3, 9]

4.2 Suspending agents and spacing agents

A suspending agent helps reduce the sedimentation rate of particles in suspension by increasing the viscosity of the solution and thereby slowing down settling in accordance with Stokes Law. Emulsifiers, thickeners and stabilizers are used as suspending agents in clouding agents. [10, 11]

The Spacing agent's function in the clouding agent is to disperse and maintain the titanium dioxide as a separate particles. The suitable spacing agent is a water-soluble, polymeric substance, such as maltodextrin or other starch hydrolyzates. Suitable spacing agent is bland in flavor and without appreciable sweetness. [10]

5 Substance Descent on a Medium

5.1 Fluids viscosity

Fluid is a substance that continues to deform when it is subjected to a tangential or shear force. The rate at which the fluid deforms continuously depends on the magnitude of the applied force and also on a property of the fluid called its viscosity or resistance to deformation and flow. The viscosity of a fluid measures its resistance to flow under applied shear stress. For liquids, the more viscose the liquid is, thicker it is. Fluids can be broadly classified according to the relation between the applied shear stress and the rate of deformation. [10, 12]

5.1.1 Newtonian fluids

Newtonian fluids are those fluids which obey Newton's law of viscosity. A Newtonian fluid's viscosity remains constant regardless any external stress that is placed upon it, such as mixing. Newtonian fluids have a linear relationship between viscosity and shear stress. Regardless of the shear stress applied to a fluid, its viscosity remains the same. For example water is a Newtonian fluid. [13, 14]

5.1.2 Non-Newtonian fluids

Fluid which viscosity is variable based on applied stress is called a non-Newtonian fluid. For example, a cornstarch dissolved in water is a non-Newtonian fluid. Non-Newtonian fluids become thicker or thinner when stress is applied. Non-Newtonian fluids are classified to pseudoplastic, shear thickening fluids, Bingham plastic fluids, rheopetric or anti-thixotropic fluids. [15]

Pseudoplastic fluid, or shear thinning fluid, is a fluid, which gets thinner when stress is applied to it. For example a paint is a pseudoplastic fluid. Shear thickening fluids viscosity increases, when stress is applied to it. Bingham plastic fluids require a finite yield stress before they begin to flow. For example, mayonnaise is a Bingham plastic fluid. Rheopectic or anti-thixotropic strain rate is a function of time, a fluid which are rheopectric thickens when shaken. They get more viscose, the more they are under shearing force. Thixotropic fluid thins out with time when it is under shear stress. [15]

5.1.3 Stokes law

Stokes law is a mathematical equation that expresses the settling velocities of small spherical particles in a fluid medium. The Stokes law is presented in Equation (1). The force of viscosity in which the particle is moving through a medium is influenced by radius of the spherical object, R (in m), dynamic viscosity of the surrounding medium, μ (in N), and the particle's velocity, v (in m/s). [3, 16]

$$F_d = 6\pi \, \mu \, R \, v \tag{1}$$

6 Polysaccharides

6.1 Chemical structures and properties

Polysaccharides are polymers of monosaccharides. Polysaccharides are composed of glycose units in linear or branched arrangements. Most polysaccharides much larger than the 10- or 20-unit limit of oligosaccharides. The number of polysaccharide units in a polysaccharide, which is termed its degree of polymerization (DP) varies. Only a few have DPs less than 100, most have DPs in the range 200-3000. The larger ones, such as cellulose, have a DP of 7000- 15.000. Starch amylopectin has even larger DP (>60.000). [17]

6.1.1 Degree of polymerization

The degree of polymerization, or DP, is a number of monomeric units in polymer molecule. DP uniquely determines the weight of a macromolecule of known composition. Synthetic polymers comprise a set of macromolecules of varying degrees of polymerization and, accordingly, molecular weight. [17]

The physical and chemical properties of oligomer change with increasing molecular weight. There is a certain critical value beyond which further increase in the molecular weight no longer significantly affects these properties. This value characterizes the transition from the oligomer to the polymer, and it differs for different properties. Polymers with identical composition but different total molecular weights may exhibit different physical properties. In general, increasing degree of polymerization correlates with higher melting temperature and higher mechanical strength. [17, 18]

6.2 Solution viscosity and stability

Polysaccharides (gums, hydrocolloids) are used in foods primely to thicken and gel aqueous systems and otherwise to modify and to control the flow properties and textures of liquid products and the deformation properties of semisolid products. They are generally used in food products at concentration of 0.25-0.5%, indicating their great ability to produce viscosity and to form gels. [17]

7 Effects of Additives on Titan dioxide Descent in a Beverage

7.1 Effects of high shear mixing and heating on clouding agent

Subjecting particulate titanium dioxide and water alone to high shear mixing to form first an aqueous mixture, the resulting TiO_2 particles have preferred small size and physical structure that is not achieved when a spacing agent and suspending agent is also present. The preferred TiO_2 particles may be able to bind with the subsequently introduced spacing agent and suspending agent in a manner that cannot be achieved earlier. [10]

When preparing the clouding agent, the heating of the mixture while subjecting it to high shear mixing, makes the clouding agent mix smoothly. Heating of the mixture also helps the suspending agent to dissolve in the mixture better. [10]

7.2 Viscosity of the selected suspending agents

In this published version of this thesis project, suspending agents are not mentioned by name. They are referred by code, A, B, C or D.

Suspending agent A forms a very pseudoplastic, high viscosity solution; therefore it is excellent emulsion and suspension stabilizer. Suspending agent A forms a solution which has viscosity that is unaffected by temperature or pH change. [19]

Suspending agent B is stable and has good gelling ability at relatively low pH such as pH 3-4, suspending agent B is the dominating gelling agent in modern production of jams as well as other products which are gelled, acidulous, and sweet. [19]

Suspending agents, C and D, form viscose solutions and are stable even in low pH such as at pH 3. [19, 22]

7.3 Effects of spray drying on particles descent in medium

Typically in spray drying, the product will be fed to the drying tower under working pressures of 500 psi and 3000 psi. Such pressures inflict additional shearing force on the mixture and further serve to homogenize and reduce the particle size of the product. Since the particle size becomes smaller it will not settle as fast as a larger particle. [8]

8 Spray Dryer

8.1 Usage

Spray dryer is often used to produce powders from liquid foods, concentrates or pulps. It is commonly used for milk powder, coffee, and tea. Spray drying includes a suspended particle processing operation that consists of particle formation as well as drying. The liquid food is first atomized or sprayed into heated air within a drying chamber and after that the moisture from the food is removed. The input which is in a fluid state is first processed into droplets that are dried into particles by exposing them to hot air. Dryer walls are being cooled to 38 to 50 °C by feeding cold, dry air at the outlet end of the dryer. Obtained dry powders can be immediately used as constituents of dry mixtures, soups, etc. [20, 21, 22]

8.2 Spray drying process

Three subsequent steps of the drying process can be divided1) the atomization of the feed; 2) the spray-air mixing and moisture evaporation, and 3) the separation of dry product from the outlet air. [21]

Most critical phase of the drying operation is the atomization. Food products such as slurries are dispensed into a fine spray in the atomizer. There are three general types of atomizer available commercially. Rotary wheel atomizers and single-fluid pressure nozzle atomizers are the two most commonly used types. Rarely, for some special applications such as slurries and pastelike materials, a pneumatic two-fluid (compressed air and liquid feed) can be used. [21]

Co-current, counter-current, or mixed flow of droplets and drying air can vary in typical spray-drying system. The geometry of drying chambers depends mainly of the type of atomizer being used. The chamber is usually short and wide (conical type), for rotary wheel atomizers and for nozzle atomizers the chamber is usually long and narrow (tall type). [21]

Fine droplets that are produced dispense a very large surface area for evaporation. Due to the high velocity of hot air, a forced convention is normally generated that will favor, together with the direct contact of air and product, a very high heat transfer. Therefore in short contact time, in a few seconds, a very fast drying rates are obtained. For heat sensitive foods this technique is highly desirable, because the rapid drying keeps the product cool. The dry product is collected at the bottom of the drying chamber and is separated from the air using cyclones, bag filters, or electrostatic precipitators. The final separation of the powder from the exhaust air is provided in wet scrubbers, wet cyclones, or irrigated fans. [21, 22]

In order to achieve proper conditions for spray drying, several problems must be overcome. Stickiness, caking, and hygroscopicity of final product should be avoided and monitored. Instant dried powders must possess several properties for their further use in formulated food products: a desirable wettable surface, a high sinkability (i.e. product must float upon rehydration), a high dispersability, and a high resistance to sedimentation. To generate these properties, an agglomeration process is often performed after spray drying. It involves a controlled humidification to form small clumps, usually carried out in a fluidized bed dryer. Spray-dried particles that are agglomerated rehydrate better than spray-dried powders. [21]

8.3 Composition

Spray drier typically consists of large volume drying chamber, feed atomizer, hot air supply, and dry product recovery and dust collection systems. The composition of spray dryer is presented in Figure 3. [21]

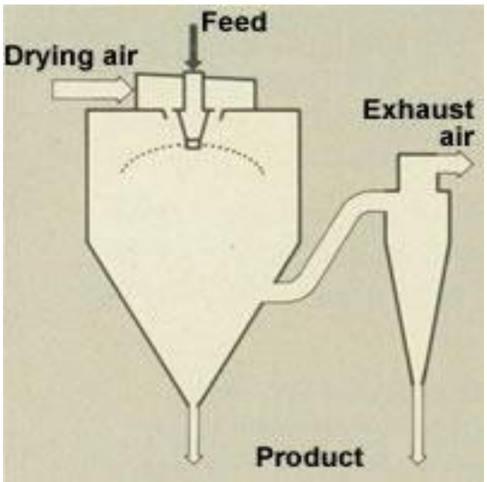

Figure 3 Composition of a spray dryer

9 Experiment

The experiment was done to discover if the spray drying has effects on the decent of titanium dioxide in beverage and to find out which of the selected suspending agents functions better in two series of tests that are made to compare the descend of TiO_2. The method of this experiment was based on U.S. patents no 6,159,522. Patent is found in Appendix 1.

The method was adjusted in some parts since the patent was made for industrial usage. The machinery listed in the patent were replaced by laboratory equipment. The suspending agents and the spacing agents used were chosen based on discussions with Huntsman Pigments.

The experiment was done by comparing clouding agents which have been spray dried to powder form to the ones that are still in liquid form. The clouding agents were prepared by the same method, based on the patent mentioned earlier, and the second series of test clouding agents were spray dried before the descent test. The settling of TiO_2 was being tested by following the settlement of the cloud in the juices for seven days. The spray dryer used in this study was a Büchi Mini Spray Dryer B-290, which shows in Figure 4.

Figure 4 Picture of the Büchi Mini Spray Drier B-290

9.1 Method for making the clouding agent

Making of the clouding agent started with high shear mixing of the TiO_2 and water. Water amount used to make a clouding agent was 200 ml, mixing was continued for 30 minutes. After that a spacing agent was added to a mix and the high shear mixing was continued for 30 minutes. A suspending agent was added to the mix and the high shear mixing was continued for 10 minutes. After that the mix was heated to 66 - 72° C and the high shear mixing was continued for 90 minutes. Mixer used in this study was called Ultra-Turrax T25, which is presented in Figure 5.

Figure 5 Picture of the mixer used in the experiment

9.2 Test series of clouding agents

Test clouding agents where there were no spacing agent and/or suspending agent were done in the same way apart from phases that were excluded. The second series of clouding agents were spray dried after mixing the solution. Table 1 shows the different suspension made for this experiment listed. Clouding agents for the test were prepared in random order as was the selection of repetition test.

Table 1 Test series

Test no.	
1	TiO_2 + H_2O (no mixing with mixer)
2	TiO_2 + H_2O
3	TiO_2 + H_2O + maltodextrin
4	TiO_2 + H_2O + suspending agent A
5	TiO_2 + H_2O + maltodextrin + suspending agent A
6	TiO_2 + H_2O + maltodextrin + suspending agent B
7	TiO_2 + H_2O + maltodextrin + suspending agent C
8	TiO_2 + H_2O + maltodextrin + suspending agent D
9	TiO_2 + H_2O + maltodextrin + A + C + D
10	Repetition of test no 7

Test no. 1 was done to find out whether the mixing has an influence on settling of TiO_2 and tests no. 1 and 2 were done to find out how the titanium dioxide acts out on its own on the experiment.

Test no. 3 was done to find out how the used spacing agent works without a suspending agent and the test 4 to found out whether to suspending agent works without the spacing agent.

Tests no. 5, 6, 7, 8 were executed to find out which of the suspending agent selected works the best and in test no. 9 a combination of selected suspending agents was used to determine how a mixture of suspending agent acts out.

Test no. 10 was a repetition of the test no. 7 to find out how repeatable the test is.

9.2.1 Clouding agent

The spacing agent used in this study was maltodextrin (DE60) and suspending agents were A, B, C and D. The ratio of the components the clouding agent was modified of the following ratio found in U.S. patent no. 6,159,522. Table 2 presents the ratio of components in the clouding agent presented.

Table 2 Ingredient proportions in cloud

Ingredient	Amount (% by weight)
TiO2	25–30 %
spacing agent	40–70 %
suspending agent	10–30 %

Usage of the spray dryer determines how thick the clouding agent could be. If the clouding agent was not runny enough it would not have come through the nozzles of the spray dryer. The amount of suspending agent was therefore determined experimentally by making a suspension of suspending agent and water. The percent of suspending agent needed to give the wanted thickness to clouding agent are presented in the following Table 3.

Table 3 Suspending agents' amounts in the thesis project

Suspending agent	Amount (%)
A	0.5
B	5
C	1
D	3

The recipe for clouding agent where xanthan was being used (test no.5) as a suspending agent is presented in Table 4. Water amount being 200 ml the percentage of suspending agent A in the final suspension was therefore 0.5 %.

Table 4 Recipe for test beverage with suspending agent A

Ingredient	amount (g)
TiO2	2.24
Maltodextrin	7.07
Suspending agent A	1.12

9.3 Prepares for the descent test

The first series of tests were made from the liquid clouding agents. The TiO_2 content wanted in the juice was 0.010 %. For example in the descent test of test clouding agent no. 5 the amount of the liquid clouding agent pipetted was 1.1 ml and therefore the TiO_2 concentration in the juice was 0.010 %.

The second series of tests were conducted after spray dying the suspension. The wanted titanium dioxide content in final juice was also 0.010%. The yield after spray drying the clouding agent no. 5 was 3,19 g and the content in spay dried cloud was 21 % in order to get 0.010 % TiO_2 content in the final juice the amount of the cloud weighed for the test of clouding agent no. 5 was 0,047 g.

9.4 Descent test

The descent test were completed in a juice that had glucose content of 40 g/l and the pH was adjusted with citric acid to 3. The clouding agent were first measured to the juice then stirred thoroughly and poured into a 100 ml measuring glass. The same procedures were done the test series made from liquid clouding agent and clouding agent spray dried to powder. The measuring glasses were then left in a laminar flow cabinet to lay in peace for seven days. The descent of TiO_2 in was observed in those seven days by photographing the progress of the TiO_2 descent and the progress of descent was estimated and valued by visual perception.

10 Results

Measuring glasses with beverages containing cloud were first photographed on the day the juices were poured to the glasses (day 0). Beverages were photographed the second time after seven days (day 7).

10.1 Cloud in liquid form

Figure 6 shows measuring glasses which contain test juices that has clouding agent in liquid form on day 0.

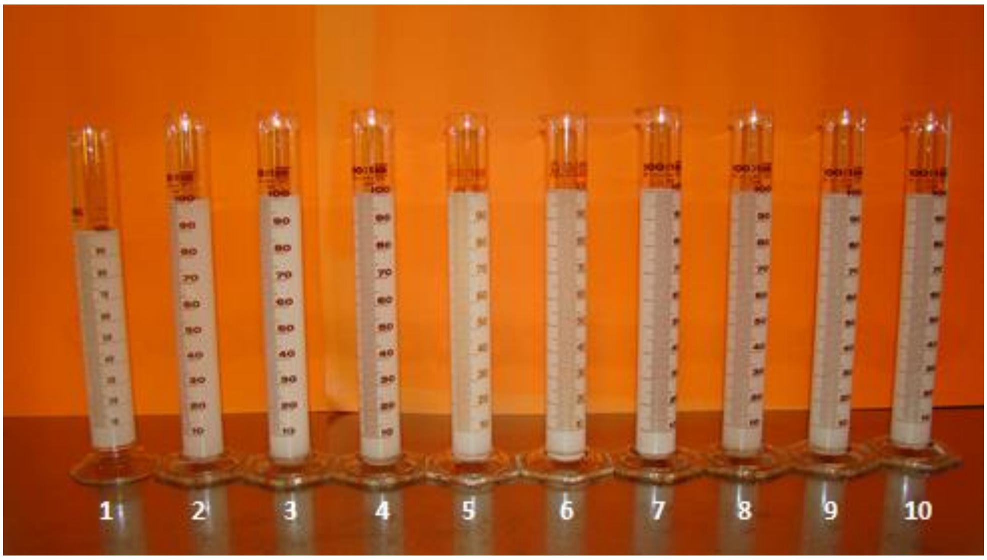

Figure 6 Picture of juices which contain clouding agent in liquid form.

As can be seen in Figure 6, there is no settling of the clouding agent in any of the measuring glasses. When preparing the test beverages, there were not any problems with the mixing of the cloud with juice.

Figure 7 which was taken on day 7, shows both more and less settling of the clouding agent in almost all of the measuring glasses.

Figure 7 Picture of beverages where clouding agent is used in liquid form

Table 5 gives the results of the settling test visually evaluated.

Table 5 Visual evaluations of the settling test

Test no 1	Visual evaluations
1	a visible layer in the bottom of the measuring glass, the beverage is quite transparent
2	a visible layer in the bottom of the measuring glass, the beverage is quite transparent
3	some settling in the bottom of the measuring glass, the beverage is not as transparent as the first two
4	no visible layer of sediment in the bottom of the glass, beverage has the opacity left
5	no visible layer of sediment in the bottom and the beverage has the opacity left
6	no visible layer in the bottom of the measuring glass, beverage has opacity, but is a little more transparent than the beverage no 5
7	a visible layer of sediment in the bottom, the beverage has still some opacity left
8	totally transparent beverage, all of the cloud has settled in the bottom of the measuring glass
9	a little visible layer of sediment in the bottom, the beverage has still opacity left
10	a visible layer of sediment in the bottom, the beverage has still some opacity left

10.2 Cloud in powder form

Figure 8 shows beverages made from powdered cloud on day 0. There were some difficulties of mixing the cloud to juice. All clouds needed shaking, they all seemed to mix well after a while part from juices no 7 and 10, in which the suspending agent, used in the cloud, was suspending agent D.

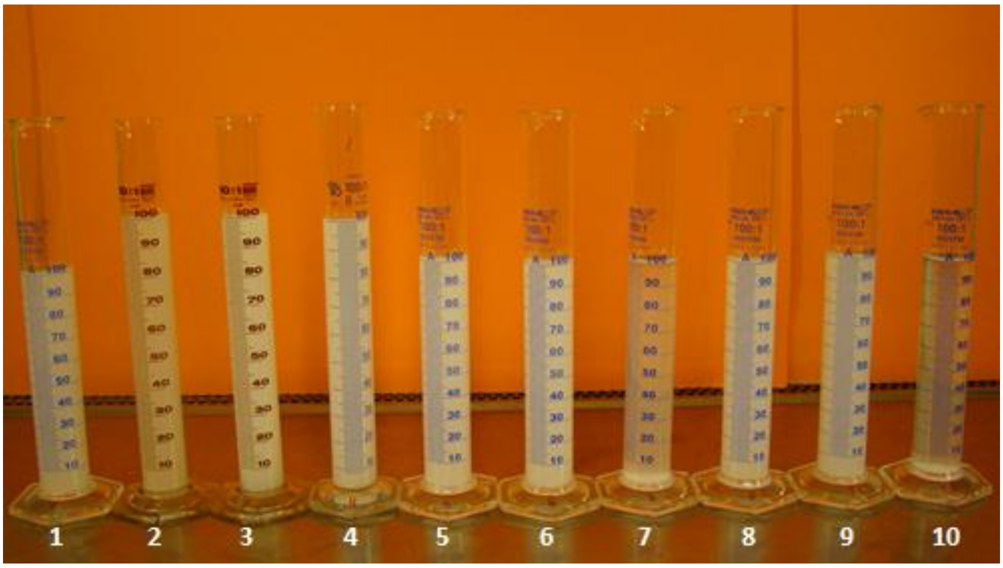

Figure 8 Picture of juices on day 0 which contain clouding agent in powder form-

Figure 9 shows juices, in which the cloud is in powdered form, after settling for 7 days.

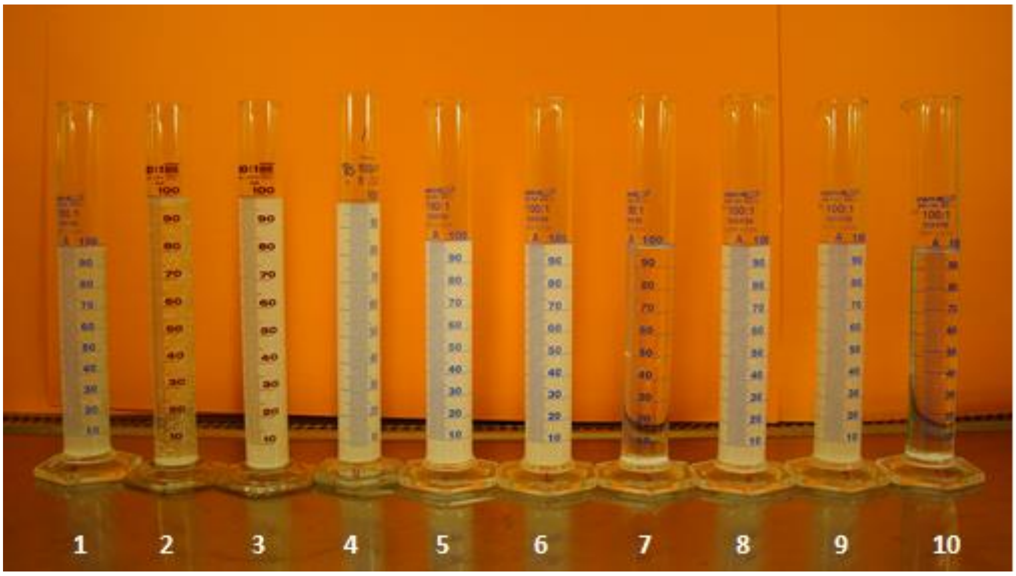

Figure 9 Picture of juices containing clouding agent in powder form on day 7

Table 6 shows the visual evaluations of the settling test to beverages which had the clouding agent in powder form.

Table 6 Visual evaluations of the settling test

Test no 1	Visual evaluations
1	a visible layer in the bottom of the measuring glass, the beverage is almost transparent
2	a visible layer in the bottom of the measuring glass, the beverage is almost transparent
3	some settling in the bottom of the measuring glass, the beverage is not as transparent as the first two
4	no visible layer of sediment in the bottom of the glass, beverage has the opacity left
5	no visible layer of sediment in the bottom and the beverage has the opacity left
6	no visible layer in the bottom of the measuring glass, beverage has the opacity left
7	the beverage is totally transparent and the cloud has settled in the bottom of the glass
8	has the opacity left and there is not any sediment seen in the bottom of the glass
9	the beverage has some opacity left, but there is a visible layer of sediment seen in the bottom
10	the beverage is totally transparent and the cloud has settled in the bottom of the glass

11 Evaluation of the Results

From the settling test it can be concluded that the suspending agents that works best in both series of test are xanthan and pectin. There seems to be no benefit of spray drying them since the liquid form works as well as the powder. The use of suspending agent A can be justifiable since the amount needed is ten times less then suspending agent D. However, suspending agent B is more natural choice to be used in juice.

This thesis also shows that spray drying was not a suitable procedure for some suspending agents selected. Suspending agent C did not react well to spray drying and the result on preventing titanium dioxides settling was not as good as in liquid form. However, spray dying seems to make suspending agent D work little bit better as a suspending agent since the settling of TiO_2 is less in beverage where powder form of clouding agent is used. The yield from spray drier would be higher in industrial spray drier, since it has larger chambers in which the powder does not stick to the walls of the chambers so much.

In the measuring glasses of descent test, some microbiological contamination was seen in juices, which turned out in microscopic research to be mold. The spoilage of beverage could have been prevented by usage of food preservative.

The settling of TiO_2 could have been monitored better if the measuring glasses used would have been for example such as are used to study the decomposition of pectin. Those tubes are narrow in the bottom, and there is a scale in the bottom of the tube; hence the settling of the clouding agent is easy to determinate, and the results are easy to compare. To save time the settling test could have been done faster than in seven days if a centrifuge would have been used.

12 Summary

The purpose of this thesis project was to find out, whether the spray drying affects the settling of titanium dioxide in juice made from dry beverage mix. The results shows there is not much difference in the descent of titanium dioxide; whether the cloud was spray dried or if it was still in liquid form.

This thesis project was done also to find out a recipe for a cloud which inhibits or reduces the settling of titanium dioxide in juice made out of a dry beverage mix. In this project, two of the test clouding agents, proved to reduce the sedimentation of titanium dioxide well. Those two were suspending agents A and B. Suspending agent A worked well even when the content of A in the final beverage was only 0.005 %, and while suspending agent B worked as well with the 0.05 % content.

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Appendix 1. U.S. Patent no. 6,159,522; High Performance Titanium Dioxide Clouding Agent and Method of Manufacture Thereof

US006159522A

United States Patent [19]
Chuang et al.
[11] **Patent Number: 6,159,522**
[45] **Date of Patent: Dec. 12, 2000**

[54] **HIGH PERFORMANCE TITANIUM DIOXIDE CLOUDING AGENT AND METHOD OF MANUFACTURE THEREOF**

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[73] Assignee: **Kraft Foods, Inc.**, Northfield, Ill.

[21] Appl. No.: **09/388,849**

[22] Filed: **Sep. 2, 1999**

[51] **Int. Cl.**[7] **A23L 2/62**
[52] **U.S. Cl.** **426/590**; 426/519; 426/573; 426/575; 426/599; 426/661
[58] **Field of Search** 426/590, 599, 426/573, 575, 661, 519

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Primary Examiner—Helen Pratt
Attorney, Agent, or Firm—Thomas R. Savoie; Thomas A. Marcoux

[57] **ABSTRACT**

A clouding agent for dry beverage mixes is prepared by first forming a mixture of titanium dioxide and water and then subjecting the mixture to high speed shear. A spacing agent and suspending agent are then added to the mixture and the mixture is again subjected to a high speed shear, followed by spray drying. The resultant clouding agent may contain higher quantities of titanium dioxide than conventional clouding agents to thereby provide increased opacity without increased sedimentation. Further, the method of the invention provides higher throughput through the spray dryer and better yields than conventional methods of preparation.

15 Claims, No Drawings

HIGH PERFORMANCE TITANIUM DIOXIDE CLOUDING AGENT AND METHOD OF MANUFACTURE THEREOF

FIELD OF THE INVENTION

The present invention is directed to a titanium dioxide-containing clouding agent for particulate dry beverage mixes and to a method of producing the clouding agent which provides a higher throughput better yield and higher titanium dioxide content than conventional methods of manufacturing such clouding agents.

BACKGROUND OF THE INVENTION

Dry beverage mixes, particularly imitation fruit juice beverage mixes, are typically formulated with a particulate clouding agent in order to imitate the opacity of a natural juice. Most clouding agents are prepared by combining a spacing agent such as maltodextrin, a suspending agent such as gum arabic, and titanium dioxide. Titanium dioxide is the key ingredient which provides opacity in the clouding agent. U.S. Pat. No. 4,187,326 to Serafino et al. discloses a particulate clouding composition for dry mix beverages containing TiO_2. U.S. Pat. No. 4,529,613 to Mezzino et al. describes a particulate, dry beverage mix clouding agent containing up to 20% by weight TiO_2.

In typical methods of preparing a clouding agent, including the methods described in U.S. Pat. Nos. 4,187,326 and 4,529,613, the spacing agent and suspending agent are added to water and subjected to high shear mixing. The titanium dioxide is added after the spacing agent and suspending agents are dispersed by the initial high shear mixing and the mixture is again subjected to further high shear mixing. The resulting slurry is then dried, typically by spray drying. The resulting co-dried clouding agent may then be included in a dry beverage mix, particularly a fruit flavored dry beverage mix.

There are several drawbacks associated with conventional clouding agents and methods of preparation thereof. One problem is that while it is desirable to have a relatively high level of titanium dioxide to provide the right opacity, the amount of titanium dioxide which may be included in the clouding agent is limited because of its tendency to precipitate out and create sedimentation in the reconstituted beverage. Another problem is that in conventional methods of preparing clouding agents, the processing rates are slowed because the inner surfaces of the processing vessels tend to become caked, requiring significant cleaning efforts before subsequent batches may be manufactured. Loss of the ingredients in this way also reduces yield. It has been found that in these prior art processes, higher titanium dioxide content in the slurry made it harder to spray dry the slurry, further reducing yield and lowering throughtput.

Accordingly, there is a need for a clouding agent having increased opacity on an equal weight basis and a process of manufacture thereof which reduces undesirable buildup of material on the sides of the mixing tank thereby improving the throughput and yield of the process.

SUMMARY OF THE INVENTION

The foregoing and other objects which will be apparent to those of ordinary skill in the art are achieved in accordance with the invention by providing a method of making a particulate clouding agent for a dry beverage mix comprising: (a.) subjecting particulate titanium dioxide and water to high shear mixing to form a first aqueous mixture; (b.)

adding a spacing agent and a suspending agent to said first aqueous mixture to form a second mixture; (c.) subjecting the second mixture to high shear mixing to form a further aqueous mixture; and (d.) spray drying the second aqueous mixture to form a particulate clouding agent, thereby providing an improved particulate dry mix beverage clouding agent comprising TiO_2, spacing agent, and suspending agent in which the TiO_2 content is from 21 to 30% by weight based on the total weight of the clouding agent on a dry weight basis, and by providing a particulate dry beverage mix including the improved clouding agent.

The particulate titanium dioxide and other constituents of the clouding agent are food grade. The titanium dioxide has an average particle size of 0.3 microns with a particle size distribution of 100% through a 200 mesh screen. Mesh size referred to in the present specification is U.S. mesh size unless indicated to the contrary. The TiO_2 is preferably a purified inorganic white, named by the 1971 Colour Index, 6 pigment white 6, C.I. 77891, and available commercially from Wittaker, Clark & Daniels, Inc., South Plainfield, N.J. or Warner-Jenkinson, St. Louis, Mo.

The spacing agent, which is also referred to in the art as a carrier or bulling agent or filler, functions to disperse and maintain the titanium dioxide as separate particles. The spacing agent, which typically has a particle size distribution of 90% minimum through 140 mesh and 50% maximum through 325 mesh, is suitably a water-soluble, polymeric substance, including maltodextrins and other starch hydrolyzates. Suitable spacing agents are described in U.S. Pat. No. 4,187,326 and U.S. Pat. No. 4,529,613, the disclosures of which are herein incorporated by reference. Maltodextrins, which are starch hydrolyates produced by converting refined corn starch into nutritive saccharides through the use of acids or enzymes, are preferred. Suitable maltodextrins are bland in flavor and without appreciable sweetness. Preferred maltodexrins have a DE of less than 20, and more preferably from 10 to 20. Other suitable spacing agents, when employed, are preferably used in combination with the preferred maltodextrin spacing agent.

The suspending agent is suitably a gum, such as gum arabic, xanthan gum, or a pectic substance such as pectin. Suitable suspending agents are described in U.S. Pat. No. 4,187,326 and U.S. Pat. No. 4,529,613.

In the method of this invention, the solids are subjected to high shear mixing with water. Various types of high shear mixers may be employed such as those described in U.S. Pat. No. 4,187,326 and U.S. Pat. No. 4,529,613. A homogenizer is preferred, and an in-line 3-stage homogenizer is particularly preferred. A suitable shear rate of mixing is generally in the range of 3000 rpms to 4000 rpms. In general, a mixing time of from 10 to 60 minutes for each high shear mixing step is suitable.

It is a key aspect of the invention that a TiO_2-water mixture is formed first and subjected to high shear mixing as described above before addition of the spacing agent or suspending agent. The spacing and suspending agent may then be added either simultaneously or sequentially, in which case the spacing agent may be added prior to the suspending agent or vice versa. In each of these process variations, however, the mixture is subjected to high shear mixing as described above as each ingredient is added.

The total amount of the key ingredients (TiO_2 spacing agent, and suspending agent) is suitably from 20 to 45% and preferably 25 to 35% by weight based on the aqueous mixture. The total amount of the TiO_2, based on the total weight of the key ingredients, is at least 21% by weight, on a dry weight basis. As mentioned above, it has previously proven difficult to obtain a satisfactory clouding agent having a high TiO_2 content. Preferably, the total amount of TiO_2 based on the total weight of the key ingredients for the clouding agent of this invention, is from 23 to 30% by weight, on a dry weight basis. The spacing agent is suitably present in an amount of 40 to 70% by weight and preferably in an amount of 50 to 60% by weight, on the same basis. The suspending agent is suitably present in an amount of 10 to 30% by weight and preferably from 15 to 25% by weight, on the same basis.

Water content of the aqueous mixture is suitably 55 to 80%, and preferably 65 to 75% by weight, based on the weight of the aqueous mixture.

After preparation of the aqueous mixture by high shear mixing as described above, the aqueous mixture is dried, preferably by spray drying, to form a particulate, co-dried clouding agent for a dry beverage mix. Other methods of drying, such as freeze drying, fluidized bed drying, vacuum drying, air drying, or drum drying may be used.

The amount of the key ingredients in the dried product will be the same as given above. Moisture content of the dried product is suitably less than 6% and preferably less than 5% by weight, based on the weight of the product.

A flow control agent is preferably included to enhance flow of the particulate product. A particulate flow control agent, such as tricalcium phosphate ("TCP"), is preferred. TCP is preferably included in a spray dried product by addition as a particulate powder to the spray drying tower. The amount of flow control agent is suitably from 0.1 to 5% and preferably 1 to 3% by weight based on the weight of the dried product The particulate clouding agent is intended to be utilized in dry beverage mixes such as those described in U.S. Pat. No. 4,187,326 and U.S. Pat. No. 4,529,613. Preferred dry beverage mixes are fruit-flavored and may include a natural and/or artificial sweetener. Typical ingredients of such dry beverage mixes include food grade acids, such as tartaric acid and citric acid, coloring, fruit or other flavors, and other ingredients such as vitamins. The amount of clouding agent included in a dry beverage mix is suitably from 0.1 to 10% and preferably from 0.5 to 5.0% by weight based on the weight of the sweetener-free dry beverage mix. The particle size of the particulate clouding agent is suitably 90% minimum through 140 mesh and 50% maximum through 325 mesh.

EXAMPLE 1

830 gallons of room temperature water is added to an agitated kettle equipped with a Greerco Corp. (Hudson, N.H.), in-line, 3-stage homogenizer. The agitator within the kettle was obtained from Chemineer, Inc. (Dayton, Ohio). The agitator and in-line homogenizer were started up at shear rates of about 34 rpms and 3430 rpms, respectively. 1000 pounds of TiO_2 (average particle size 0.3 microns) was added to the kettle and high shear mixing was continued for 30 minutes. 787.2 pounds of gum arabic was then fed into the circulating mixture and the high shear mixing is continued for an additional 30 minutes. 2,212.8 pounds of 15 D.E. maltodextrin (LoDex™ 15—Grain Processing Corp; Muscatine, Iowa) is added to the circulating mixture and high shear mixing is again continued for an additional 30 minutes.

The mixture is then heated to 150 to 160° F. The heated mixture is then transferred to a mixing tank and subjected to high shear mixing for at least 90 minutes while maintaining a temperature of 150 to 160° F. Mixing the heated mixture is continued until the mixture is fed to a spray-drying tower. The mixture, which contains 35% by weight solids, is then spray dried. During spray drying, 81.6 lbs. of particulate tricalcium phosphate is metered to the spray drying tower to provide a TCP content of 2% by weight in the spray dried product.

The empty mixing tank is observed to be clean, with little or no material stuck to the bottom or side walls. The particular spray-dried product has a moisture content of about 4.5% by weight and a particle size distribution of 100% through 60 mesh, at least 99% through 100 mesh, at least 90% through 140 mesh, and at most 50% through 325 mesh.

The solids content of the spray dried product, on a dry basis, is:

Ingredient	Amount (% by weight)
TiO_2	24.5
Maltodextrin-LoDex 15	54.2
Gum Arabic	19.3
TCP	2
Total	100

EXAMPLE 2

The procedure of Example 1 is followed except that the spacing agent (maltodextrin) is added prior to the suspending agent (gum arabic). After feeding the contents of the mixing tank to the spray drier, the mixing tank is observed to be clean, with little or no material stuck to the bottom of side wall of the tank.

COMPARISON EXAMPLE A

The procedure of Example 1 is followed except that the sequence of introduction of ingredients is changed. In Example 1, TiO_2 is added first, followed by the suspending agent and then the spacing agent. In Example 2, TiO_2 is added first, followed by the spacing agent and then the suspending agent. In this comparison example, the suspending agent (gum arabic) is added first followed by TiO_2 and then by the spacing agent (maltodextrin). The processing vessels are observed to have a sticky deposit of material, requiring cleaning. As compared to Examples 1 and 2, the throughput and yield are therefore lower and the measured opacity is lower while the measured sedimentation rate is higher.

COMPARISON EXAMPLE B

The procedure of Comparison Example A is followed, except that the sequence of addition of the ingredients is changed. In this example, the spacing agent is introduced first, followed by TiO_2 and then by the suspending agent. Again, a substantial amount of material remains adhered to the processing vessels. As compared to Examples 1 and 2, the throughput, yield, and opacity are lower and sedimentation rate is higher.

COMPARISON EXAMPLE C

The procedure of Comparison Example 1 is followed except that the sequence of the introduction of the ingredients is suspending agent first, then spacing agent, then TiO_2, the amount of TiO_2 is reduced, and the amount of spacing agent is increased by a corresponding amount. The composition of the spray dried clouding agent, on a dry basis, is:

Ingredient	Amount (% by weight)
TiO_2	19
Spacing Agent	60
Suspending Agent	19
TCP	2

Example C had the expected lower TiO_2 loading. There was again a coating of material in the empty tanks resulting in a reduced yield versus Example 1 and 2, and it was more difficult to pump the aqueous mixture to and through the nozzles of the spray drier resulting in a reduced throughput versus Examples 1 and 2. The sedimentation rate for Example C was equivalent to Examples 1 and 2. The opacity for Example C was equivalent to Examples 1 and 2 on an equal TiO_2 weight basis; but significantly lower than Examples 1 and 2 on an equal clouding agent basis.

COMPARISON EXAMPLE D

The procedure of Comparison Example C is followed except that the amount of TiO_2 is raised from 19 to 25%, and the amount of spacing agent is reduced by a corresponding amount. The composition of the spray dried clouding agent, on a dry basis, is:

Ingredient	Amount (% by weight)
TiO_2	25
Spacing Agent	54
Suspending Agent	19
TCP	2

As compared to Examples 1 and 2, Example D had a lower yield due to build-up on equipment surfaces, lower throughput due to a lower feed rate to spray tower. The resulting clouding agent had a lower opacity on an equal weight basis, and a higher sedimentation rate.

Evaluation of Cloud Compositions

The cloud compositions of Examples 1–2 and of Comparison Examples A–D are evaluated for opacity and sedimentation rate as determined by the procedures described below. Results are as follows:

Example	Average Opacity	Sedimentation Rate
1	45% transmission	0.25 cm after 1 week
2	45% transmission	0.25 cm after 1 week
A	60% transmission	2.5 cm after 1 week
B	60% transmission	2.5 cm after 1 week
C	70% transmission	0.25 cm after 1 week
D	60% transmission	2.5 cm after 1 week

Test Procedure

Opacity—a measurement of the % light transmission through a standardized aqueous medium containing equal weight levels of the clouding agent as measured by a Spectrometer™ 20 (Spectronic Instruments Co. Rochester, N.Y.) at a wavelength of 600 nm.

Sedimentation Rate—a standardized beverage from reconstituted powdered soft drink mix and containing equal amounts of TiO_2 is filled into an Imhoff™ cone (Fisher Scientific, Inc., Specialty Glass Division—Springfield, N.J.). The beverage is allowed to stand still for the test period after which the height of TiO_2 sediment residing at the bottom of the cone is measured.

Throughput—a measurement of production rate (pounds/hour of clouding agent) collected as product from the spray tower. Production rates 67% higher have been achieved through the use of this invention as compared to prior art procedures.

Yield—a measurement (expressed as a %) of the dry-weight of collected product from the spray tower versus the dry weight of starting materials. Yield increases of 3.5% have been achieved throughout the use of this invention as compared to prior art procedures.

Although not wishing to be limited to any specific theory, it is believed that when TiO_2 is mixed and subjected to high shear in the presence of water alone, the resulting TiO_2 particles have a preferred small size and/or physical structure that is not achieved when a spacing agent and/or suspending agent is also present. The preferred TiO_2 particles may be able to bind with the subsequently introduced spacing agent and/or suspending agent in a manner not heretofore obtained.

Although the invention has been described in considerable detail with respect to preferred embodiments thereof, variations and modifications will be apparent to those skilled in the art without departing from the spirit and scope of the invention set forth in the claims.

What is claimed is:

1. A method of making a particulate clouding agent for a dry beverage mix comprising:

(a.) subjecting particulate titanium dioxide and water to high shear mixing to form a first aqueous mixture;

(b.) adding a spacing agent and a suspending agent to said first aqueous mixture and subjecting the mixture to high shear mixing to form a further aqueous mixture; and

(c.) drying the further aqueous mixture to form a particulate clouding agent.

2. The method according to claim **1** wherein step (b.) comprises adding said spacing agent and said suspending agent sequentially and subjecting the mixture to said high shear mixing after addition of said spacing agent and after addition of said suspending agent.

3. The method according to claim **1** wherein said spacing agent and said suspending agent are added simultaneously.

4. The method according to claim **1** wherein the total amount of TiO_2, spacing agent, and suspending agent in said further aqueous mixture is from 20 to 45% by weight, based on the weight of said further aqueous mixture.

5. The method according to claim **4** wherein the total amount of TiO_2, spacing agent and suspending agent on a dry weight basis comprises:

from 21 to 30% by weight TiO_2,

from 50 to 60% by weight spacing agent, and

from 10 to 30% by weight suspending agent.

6. The methods according to claim **1** wherein the further aqueous mixture is spray-dried.

7. The method according to claim **1** further comprising incorporating a flow control agent in said particulate clouding agent.

8. The method according to claim **1** wherein each high shear mixing step is effected for a period of time of from 10 to 30 minutes.

9. The method according to claim **8** wherein said suspending agent is a hydrocolloid gum.

10. The method according to claim **1** wherein said spacing agent is at least one member selected from the group consisting of:

maltodextrin, starch hydrolyzates or sugars.

11. A particulate, co-dried clouding agent produced by the method of claim **1** wherein the dry clouding agent has a TiO_2 content of from 21 to 30% by weight based on the total dry weight of TiO_2, spacing agent and suspending agent.

12. A co-dried clouding agent according to claim **11**, wherein said spacing agent is present in an amount of from 50 to 60% by weight and said suspending agent is present in an amount of from 10 to 30% by weight based on the total weight of the TiO_2, spacing agent, and suspending agent, on a dry weight basis.

13. A co-dried clouding agent according to claim **11** further comprising from 1 to 3% by weight of a flow control agent based on the weight of the clouding agent.

14. A co-dried clouding agent according to claim **11** wherein said spacing agent is a maltodextrin and wherein said suspending agent is gum arabic.

15. A particulate, co-dried clouding agent according to claim **11** wherein the clouding agent is a spray dried material.

* * * * *