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INDUSTRIA Y COMERCIO
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Dependencia: 0020 DIVISION DE NUEVAS CREACIONES

REF: Expediente No.:

[REDACTED] de Invención:

PROCESO PARA LA
PRODUCCIÓN DE
COMPOSICIONES DE
CUIDADO ORAL UTILIZANDO
POLIMEROS DISPERSABLES
AGLOMERADOS
HERCULES INCORPORATED

Titular:

***Publicada en la Gaceta de la Propiedad Industrial No. 503 de
27 de abril del 2.001***

SOLICITUD DE EXAMEN DE PATENTABILIDAD

HUMBERTO RUBIO CAMACHO, mayor de edad, domiciliado en Bogotá, D.C., identificado con la cédula de ciudadanía número 17.192.062 de Bogotá, abogado Titulado con Tarjeta Profesional No. 50.007 del Consejo Superior de la Judicatura, actuando en carácter de APODERADO de la Sociedad HERCULES INCORPORATED, domiciliada en AT 1313 N. Market Street, Hércules Plaza, Wilmington, Delaware, Estados Unidos de América; en forma respetuosa solicito se sirvan proceder a efectuar el examen de patentabilidad de la Invención de la referencia; de conformidad con lo establecido en el Artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina, precisando que me encuentro dentro del término legal de seis meses contados desde la publicación de la Solicitud en la Gaceta No. 503 de 27 de abril del 2.001.

Para que la presente petición sea viable estoy anexando recibo de pago No. 46.053 de 27 de julio del 2.001; por la suma de \$ 300.000,00, de acuerdo con la Resolución No. 701 de 30 de Enero de 2.001

Solicito se continúe con el trámite correspondiente.

Del Señor Superintendente,

[Firma]
HUMBERTO RUBIO CAMACHO
C.C. 17.192.062 de Bogotá
T.P. 50.007 Consejo Superior
de la Judicatura.
COD. 4134

PARA USO EXCLUSIVO DE
"HERBERTO RUBIO & CIA. LTDA

 6661
Industria y Comercio
SUPERINTENDENCIA

EXAMEN DE
PATENTABILIDAD
PATENTE DE INVENCION:
"PROCESO PARA LA PRODUCCION
DE COMPOSICIONES DE CUIDADO
ORAL UTILIZANDO POLIMEROS
DISPENSABLES AGLOMERADOS"

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FECHA : JULIO 27 DE 2001

***** CONSIGNACION *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	Nº. PAGO	FECHA PGO	Vr. PAGO
HERBERTO RUBIO CAMACHO	CONSIGNACION	BANCO POPULAR	050-00110-6	4030239	26/07/2001	1,500,000.00

***** CONCEPTO *****

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1 50005-01-01 SOLICITUDES	05 EXAMEN DE PATENTABILIDAD DE INVEN	300,000.00
	TOTAL :	300,000.00

SON: TRESCIENTOS MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No. _____

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United States Patent [19]

[11] Patent Number: 5,869,029

Graff-Andersen et al.

[45] Date of Patent: Feb. 9, 1999

[54] DISPERSIBLE WATER-SOLUBLE OR WATER-SWELLABLE POLYMERS AND PROCESS FOR MAKING TOOTHPASTES CONTAINING THEM

[75] Inventors: Arne Graff-Andersen, Knage, Denmark; Jashwant J. Modi, New Castle County, Del.

[73] Assignee: Hercules Incorporated, Wilmington, Del.

[21] Appl. No.: 668,181

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[51] Int. Cl.⁶ A61L 15/00; A61K 7/18; A61K 47/00

[52] U.S. Cl. 424/52; 514/777; 514/782; 514/781; 514/776; 252/175; 252/164; 252/315.3

[58] Field of Search 424/52; 514/777; 514/782; 781; 776; 252/175; 164; 315.3

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[57] ABSTRACT

This invention provides compositions comprising particulate water-soluble or water-swellaable polymer at least partially agglomerated by treatment with at least one polyol, wherein the polyol is present at a level greater than about 10 wt. % based on the total weight of the composition. The particulate water-soluble or water-swellaable polymer which has been at least partially agglomerated by treatment with polyol hydrates in water-containing solvents substantially faster than untreated water-soluble or water-swellaable polymer, without formation of polymer lumps. The invention further provides an improved process for preparing a toothpaste composition comprising at least one dry, water-soluble or water-swellaable polymer, the improvement comprising substituting for the dry, water-soluble or water-swellaable polymer, particulate water-soluble or water-swellaable polymer which has been at least partially agglomerated by treatment with polyol.

53 Claims, No Drawings

DISPERSIBLE WATER-SOLUBLE OR WATER-SWELLABLE POLYMERS AND PROCESS FOR MAKING TOOTHPASTES CONTAINING THEM

FIELD OF THE INVENTION

This invention relates to compositions comprising water-soluble or water-swella-ble polymers agglomerated by treat-ment with polyols, and to the use of the compositions in making toothpastes.

BACKGROUND OF THE INVENTION

Toothpaste formulations generally contain dentally acceptable abrasive, humectant, water, and water-soluble polymer which serves as a thickener and binder for the ingredients. A variety of other ingredients such as flavors, sweeteners, preservatives and fluoride are also utilized at low levels. Glycerol and sorbitol (usually as an aqueous solution) are the most commonly used humectants for toothpaste, and depending on the characteristics desired in the product, polyethylene glycol or propylene glycol may be incorporated as well. Two types of toothpaste are widely produced: 1) cream or opaque; and 2) transparent or translucent gel.

The most commonly used thickeners or binders for toothpaste are carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), silica and magnesium aluminum silicate. Carrageenan, xanthan and polyacrylates are also used, but much less widely.

In the manufacturing process for toothpastes, incorporation of the dry water-soluble binder polymer into the composition often presents difficulties because of the tendency for lump formation when the dry polymers are added to and dispersed in aqueous systems. This increases the time required to obtain uniform hydration or dispersion of the binder polymer. Consequently, there is a need in the industry for methods of incorporating water-soluble binder polymers which lead to lump-free products, rapid viscosity development and reduced batch preparation time, and which allow convenient handling of the binder.

Japanese Patent Application No. 73036167 II discloses a composition comprising (1) carboxymethyl cellulose, alginic acid, polyacrylic acid, or a salt thereof, treated by (a) coating with glycerol or alcohol, or (b) coating with starch paste, shellac, gelatin and agar, followed by treatment (a), or (c) coating with a mixture of substances in (a) and substances in (b); (2) alkali carbonate, bicarbonate, phosphate, polyphosphate or alkali salt of EDTA, optionally treated by the methods of (a), (b) and (c); and optionally (3) glucose, sugar, fructose, maltose, mannitol and common salt. When water is added to the composition, it is rapidly wetted and dispersed, and solutions of alginic acid, polyacrylic acid or carboxymethyl cellulose can be obtained rapidly.

Japanese Patent Application No. 72044335 B teaches improving the solubility of a water-soluble polymer by coating it with molten polyhydric alcohol, sugar or emulsion aid. The water-soluble polymers include methyl cellulose, CMC, polyvinyl alcohol, alginic acid salts, polyacrylic acid or its salts, and polyacrylamide. The polyhydric alcohols include sorbitol, mannitol, inositol, and sugars include glucose, sucrose and lactose. The coating substance is used in the amount of 0.5 to 10 wt. %, preferably 3 to 5 wt. % relative to the polymer.

U.S. Pat. No. 3,850,838 to Guckenberg et al. discloses methods for preparing alcohol insoluble hydrocolloids in

the form of readily dispersible and stable agglomerates, the process comprising intimately combining the hydrocolloid with a carbohydrate binder that is soluble in both water and alcohol and an aqueous alcoholic solvent for the carbohydrate, granulating the resulting mixture, and then drying the resulting agglomerated granules.

None of the above patents teach the use of polyol-agglomerated water-soluble or water-swella-ble polymer in toothpaste compositions.

SUMMARY OF THE INVENTION

This invention relates to compositions comprising particulate water-soluble or water-swella-ble polymer at least partially agglomerated by treatment with at least one polyol, wherein the polyol is at a level greater than about 10 wt. % based on the total weight of the composition. The composition is dispersible in solvents substantially faster than the corresponding untreated water-soluble or water-swella-ble polymer, without formation of polymer lumps.

In another aspect the invention also relates to an improved process for preparing a toothpaste composition comprising at least one dry, water-soluble or water-swella-ble polymer, the improvement comprising substituting for the dry, water-soluble or water-swella-ble polymer, particulate water-soluble or water-swella-ble polymer which has been at least partially agglomerated by treatment with polyol. The particulate water-soluble or water-swella-ble polymer which has been at least partially agglomerated by treatment with polyol hydrates in water or water-containing solvents substantially faster than the corresponding untreated water-soluble or water-swella-ble polymer, without formation of polymer lumps.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of this invention comprise particulate water-soluble or water-swella-ble polymer at least partially agglomerated by treatment with at least one polyol, wherein the polyol is at a level greater than about 10 wt. % based on the total weight of the composition. Agglomeration is defined herein as the aggregation of individual particles resulting in an increase in the particle size of the particulate material.

Any natural or synthetic water-soluble or water-swella-ble polymer may be employed to prepare the compositions of this invention. Preferred water-soluble or water-swella-ble polymers are polysaccharides. Useful polysaccharides may include, but are not limited to, cellulose ethers, guar, guar derivatives, locust bean gum, psyllium, gums arabic, gum ghatti, gum karaya, gum tragacanth, carrageenan, agar, algin, xanthan, scleroglucan, dextran, pectin, starch, chitin and chitosan.

Preferred polysaccharides are cellulose ethers, carrageenan, guar, guar derivatives and pectin.

Cellulose ethers for use in the invention include hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), water soluble ethylhydroxyethyl cellulose (EHEC), carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), hydroxypropylhydroxyethyl cellulose (HPHEC), methyl cellulose (MC), methylhydroxypropyl cellulose (MHPC), methylhydroxyethyl cellulose (MHEC), carboxymethylmethyl cellulose (CMMC), hydrophobically modified carboxymethyl cellulose (HMC), hydrophobically modified hydroxyethyl cellulose (HHEC), hydrophobically modified hydroxypropyl cellulose (HHP),

hydrophobically modified ethylhydroxyethyl cellulose (HMEHEC), hydrophobically modified carboxymethylhydroxyethyl cellulose (HMCMEHC), hydrophobically modified hydroxypropylhydroxyethyl cellulose (HMHPHEC), hydrophobically modified methyl cellulose (HMMC), hydrophobically modified methylhydroxypropyl cellulose (HMHPC), hydrophobically modified methylhydroxyethyl cellulose (HMHEC), hydrophobically modified carboxymethylmethyl cellulose (HMCMMC), cationic hydroxyethyl cellulose (cationic HEC) and cationic hydrophobically modified hydroxyethyl cellulose (cationic HMEHC). Preferred cellulose ethers are carboxymethyl cellulose and hydroxyethyl cellulose.

Clear derivatives for use in the invention include carboxymethyl guar (CM guar), hydroxyethyl guar (HE guar), hydroxypropyl guar (HP guar), carboxymethylhydroxypropyl guar (CMHP guar), cationic guar, hydrophobically modified guar (HM guar), hydrophobically modified carboxymethyl guar (HMC guar), hydrophobically modified hydroxyethyl guar (HME guar), hydrophobically modified hydroxypropyl guar (HMHP guar), cationic hydrophobically modified hydroxypropyl guar (cationic HMHP guar), hydrophobically modified carboxymethylhydroxypropyl guar (HMCMP guar) and hydrophobically modified cationic guar (HM cationic guar).

More preferred polysaccharides for use in preparing the compositions of this invention are carboxymethyl cellulose, carrageenan and pectin, or mixtures thereof. Most preferred is carboxymethyl cellulose.

The polyols used for agglomerating the water-soluble or water-swellaible polymers include, but are not limited to, sugars, sugar alcohols, glycerol, polyethylene glycol, propylene glycol, and mixtures thereof.

Exemplary sugars are sucrose, glucose, lactose, fructose and xylose, or their mixtures. Exemplary sugar alcohols are sorbitol, inositol, mannitol, galactitol, arabitol, ribitol, xylitol and mixture thereof.

The preferred polyols for use in the invention are sorbitol and polyethylene glycol, or mixtures thereof. The molecular weight of the polyethylene glycols for use in the invention is not critical. Preferably the polyethylene glycols will have molecular weights of from about 200 to about 5,000,000, more preferably from about 600 to about 25,000, and most preferably from about 1,000 to about 10,000.

In the compositions of this invention the polyol used for agglomeration is at a level greater than about 10 wt. % based on the total weight of the composition. The maximum level of polyol is preferably about 90 wt. %, more preferably about 50 wt. %, and most preferably about 30 wt. %.

The agglomerated compositions may be prepared by spraying particulate polymer with polyol in liquid form. The polyol may be motion or in motion, preferably aqueous solution. In a preferred method the motion polyol or polyol solution is sprayed onto particles of water-soluble or water-swellaible polymer in a fluidized bed while, if the polyol is in solution, simultaneously drying the particles. Commercially available fluidized bed spray units may be employed for the operation.

The agglomerated compositions of this invention hydrate or dissolve in water or water-containing solvents substan-

tially faster without formation of polymer lumps than do the corresponding untreated water-soluble or water-swellaible polymers. This hydration or dissolving rate is measured using a Haake Viscometer 501, which measures the amount of torque (frees) needed to maintain the rotation of the sensor in the solution at a set speed (400 rpm) as the polymer hydrates and thickening occurs. Hydration time is considered to be the time in minutes it takes to achieve 95% of final viscosity, where the final viscosity is taken as the average of the last 20 minutes viscosity during a two-hour trial.

In this work, hydration in water was determined at 55° C. For example, under the above conditions, untreated carboxymethyl cellulose lumped immediately and then required about 15 minutes to reach 95% viscosity, while carboxymethyl cellulose agglomerated by treatment with 20 wt. % sorbitol or 20 wt. % polyethylene glycol gave some immediate lumping which quickly dispersed and dissolved in less than one minute. *dispersed*

An added advantage of these compositions is that the agglomeration serves to reduce the amount of dusting that occurs when the untreated polymers are handled. *no dust*

The toothpastes of this invention contain abrasives, humectants, and water-soluble polymer. Humectants are used to retain moisture in toothpaste, particularly at the nozzle end of the tube where the toothpaste can be in prolonged contact with air. The water-soluble polymers serve as thickeners and binders for the ingredients. A variety of other ingredients such as flavors, sweeteners, preservatives, detergents, tartar control agents, plaque control agents and fluoride may also be utilized at low levels.

The dental abrasives for use in the toothpastes of this invention are typically silicas and insoluble inorganic salts. Preferred inorganic salts are calcium carbonate, dibasic calcium phosphate, tribasic calcium phosphate, calcium sulfate, insoluble sodium metaphosphate, hydrated aluminum oxide, and magnesium carbonates and phosphates. Silicas and silica xerogels are particularly useful for translucent or transparent toothpastes.

Typical humectants for use in the toothpastes of this invention include glycerol, sorbitol, propylene glycol or mixtures thereof, which are mixed with a suitable humectant vehicle such as water.

In the toothpastes of this invention the agglomerated water-soluble or water-swellaible polymer may contain polyol at a level of from about 0.5 to about 90 wt. % based on the total weight of the agglomerated water-soluble or water-swellaible polymer. A preferred level is from about 2 to about 50 wt. %, and a more preferred level from about 10 to about 30 wt. %.

For preparation of the toothpastes of this invention, the water-soluble or water-swellaible polymer which has been agglomerated by treatment with polyol is stirred with: a) humectant or a mixture of humectants; b) humectant vehicle, most typically water; c) salts, flavors, colorants, surfactants; and d) abrasive to obtain a complete toothpaste formulation. In a preferred method of preparation, the agglomerated water-soluble polymer is added directly to the mixture of humectants and humectant vehicle and stirred until the polymer particles are fully dissolved or swollen; then any salts are added, followed by abrasive. The abrasive is added

after complete dissolution of the salts. The mixture is stirred until the particles of abrasive are worn out; then the flavors are added, followed by surfactant.

This invention is illustrated by the following examples, which are for illustration only, and are intended to be limiting. All percentages, parts, etc., are by weight unless otherwise indicated.

Examples 1-14 demonstrate the preparation and testing of carrageenan and carboxymethyl cellulose agglomerated by treatment with polyethylene glycol or sorbitol. The carrageenan was GENU[®] carrageenan (available from Hercules Incorporated, Wilmington, Del.). Carboxymethyl cellulose was either CMC 7MF or CMC 7MXIV (available from Hercules Incorporated, Wilmington, Del.).

The polymers were treated in a Glatt Fluid Bed Processor (Model GPCX-5) top spray unit with aqueous solutions (25, 33 and 50%) of polyethylene glycol, PEG 4600 and 1450 (Union Carbide, Carbowax[®] 4600 and 1450) to a final polymer level of approximately 20% by weight. They were also treated with sorbitol at the 10% and 20% level by application of a 70% aqueous solution of sorbitol.

In the operation, all aqueous polyol solutions were heated to 50° C. and metered in by calibrated pump and balance. The Glatt Fluid Bed Processor was preheated for all trials. A Schlick 945 nozzle was utilized with a filler stroke cycle of 24/3 seconds, switched to 2 minutes/3 seconds after

increase in particle size. The atomization air pressure was set at 2 bar. All products were dried to about 6-8% moisture and then cooled to 30°-34° C. The batch size was 3 kg.

The agglomerated samples and the untreated controls were evaluated for their dispersibility and hydration/dissolution characteristics in deionized water at 55° C. using a Haake VT501 viscometer equipped with an FI. 10 sensor. The instrument measures the amount of torque (force) needed to maintain the rotation of the sensor in the solution at the set speed (400 rpm) as the polymer hydrates and thickening occurs. The data are then mathematically converted by computer to viscosity (cps).

The hydration time reported in Table 1 is the time in minutes required to reach 95% viscosity when the viscosity of the last 20 minutes of a two hour run is taken as 100%. Each sample viscosity was run at 2% concentration based on total solution weight. No correction was made for the amount of polyol or moisture in the sample.

EXAMPLES 1-8 AND COMPARATIVE EXAMPLE A

These examples illustrate the agglomeration of carrageenan by treatment with sorbitol and with polyethylene glycol. The data are in Table 1. Comparative Example A is presented to show the hydration time for untreated carrageenan.

TABLE 1

Agglomeration Characteristics by Treatment with Sorbitol or Polyethylene Glycol

Example No.	Polyol	Agglomeration Process			
		Polyol Level, wt. %	Spraying Rate, g/min.	Product Temp., °C.	Time to 95% Viscosity, min.
1	sorbitol (70% aq. sol.)	20	34	50	3
2	sorbitol (70% aq. sol.)	10	33	48	2
3	PEG 4600 (50% aq. sol.)	20	35-36	43-44	9
4 ^a	PEG 4600 (50% aq. sol.)	20	16 ^b	38	48
5	PEG 4600 (50% aq. sol.)	20	9-20	38-43	11
6	sorbitol (70% aq. sol.)	10	12	54-55	30
7	sorbitol (70% aq. sol.)	20	8	60	22
8	sorbitol (70% aq. sol.)	20	9	43-42	23
A ^c	—	—	—	—	22

^a In this example the carrageenan was preagglomerated by spraying a 3 kg batch with 1200 g of water at 170 g/min prior to spraying with PEG.

^b Increased carrageenan

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EXAMPLES 9-14 AND COMPARATIVE EXAMPLES B AND C

These examples illustrate agglomeration of carboxymethyl cellulose by treatment with sorbitol and with polyethylene glycol. The data are in Table 2. Comparative Examples B and C are presented to show the hydration time for untreated carboxymethyl cellulose.

The data indicate that the hydration time of carboxymethyl cellulose is substantially reduced by agglomeration with sorbitol or polyethylene glycol at levels of 10% or above.

TABLE 2

Agglomeration of Carboxymethyl Cellulose with Sorbitol or Polyethylene Glycol

Sample No.	Polyol	Agglomeration Process				Time to 95% Viscosity, min
		Polyol Level, wt. %	Spraying Rate, g/min	Product Temp., °C.		
9 ^a	Sorbitol (70% aq. sol.)	20	44	52		<1
10 ^a	Sorbitol (70% aq. sol.)	20	8	41		6
11 ^b	PBG 1450 (50% aq. sol.)	20	150	38		<1
12 ^b	PBG 1450 (50% aq. sol.)	20	90-100	38		<1
13 ^b	PBG 1450 (50% aq. sol.)	20	165	36		<1
14 ^c	Sorbitol (70% aq. sol.)	16	9	42		15
15 ^d	—	—	—	—		15
16 ^d	—	—	—	—		10

^a Carboxymethyl cellulose is CMC 7MF (Farnco Incorporated).^b Carboxymethyl cellulose is CMC 7MCP (Farnco Incorporated).^c In this example the carboxymethyl cellulose was preagglomerated by spraying a 3 kg batch with 800 g of water at 120 g/min prior to spraying with PBG.^d In this example the carboxymethyl cellulose was preagglomerated by spraying a 3 kg batch with 1500 g of water at 70 g/min prior to spraying with PBG.

EXAMPLES 15 AND 16 AND COMPARATIVE EXAMPLES D AND E

These examples illustrate the formulation of toothpaste utilizing carboxymethyl cellulose agglomerated by treatment with sorbitol or polyethylene glycol. The comparative examples demonstrate formulation of control compositions where untreated carboxymethyl cellulose was used.

Examples 15 and 16 illustrate the preparation of toothpaste at room temperature using carboxymethyl cellulose CMC 7MF which was agglomerated by treatment with 9% sorbitol and 16% polyethylene glycol (PBG 1450) respectively. Comparative examples D and E demonstrate similar formulations where the CMC 7MF was untreated. The ingredients and ingredient levels for each formulation are listed in Table 3.

TABLE 3

Ingredient	Toothpaste Formulations, Wt. %			
	Example 15	Example 16	Comparative Example D	Comparative Example E
CMC 7MF agglomerated with 9% sorbitol	1.10			
CMC 7MF agglomerated with 16% PBG 1450		1.10		
CMC 7MF (Farnco)			1.10	1.10
Sorbitol (70% aq. sol.)	25.43	35.43	36.88	35.43
Distilled Water	8.70	8.79	34.36	8.79
Dicalcium Phosphate, anhydrous	45.0	45.0	45.0	45.0
Fluorocollum Pyrophosphate Sodium	0.42	0.42	0.42	0.42
Sodium Saccharin	0.20	0.20	0.20	0.20
Sodium	0.76	0.76	0.76	0.76

TABLE 3—continued

Ingredient	Toothpaste Formulations, Wt. %			
	Example 15	Example 16	Comparative Example D	Comparative Example E
Monofluorophosphate Sodium	0.50	0.50	0.50	0.50
Benzonate	6.25	6.25	6.25	6.25
Distilled Water	8.73	8.55	8.55	8.55
Sodium Lauryl sulfate	1.00	1.00	1.00	1.00

For the glycerol-free formulations (Examples 15, 16 and Comparative Example E), the following procedure was used:

1. Tetra sodium pyrophosphate (0.42 parts), sodium saccharin (0.20 parts), sodium monofluorophosphate (0.76 parts) and sodium benzoate (0.50 parts) were added to 6.25 parts of water with stirring, and heated to about 60° C. to dissolve.

2. The carboxymethyl cellulose (1.10 parts) was added to the sorbitol solution (35.43 parts) in a beaker and stirred for 15 minutes or until adequately dispersed. The 8.79 parts of water was then added and the resulting mixture was stirred for 15 to 30 minutes making sure the polymer was completely hydrated (no gels). Then the warm salt solution from step 1 was added with stirring, which was continued for 15 minutes or until homogeneity (no lumps or gels). The mixture was then transferred to a Ross double planetary mixer.

3. The dicalcium phosphate dihydrate (DCP) (45.00 parts) was added to the mixer and mixing was continued for 10 minutes to completely wet the DCP. The mixer was then opened and the bottom and bowl sides were scraped down. The mixer was then closed; vacuum was applied; and mixing was continued at high speed for 20 minutes or until the mix was smooth.

4. The sodium lauryl sulfate (1.00 parts) was then added and mixing was continued for 5 minutes at low speed

without vacuum. Then the flavor (0.55 parts) was added followed by mixing for 2 minutes at low speed. The mixer was then opened and the beaters and bowl sides were scraped down. The mixer was then closed; vacuum was applied; and mixing was continued at medium speed for 15 minutes. The mixer was then shut off; vacuum was broken; and toothpaste was packed out.

In Comparative Example D, where glycerol was utilized, the procedure was essentially the same as the above, with the exception that in step 2 the carboxymethyl cellulose was dispersed in the glycerol with stirring. Stirring was continued for 5 minutes or until the carboxymethyl cellulose was adequately dispersed. The sorbitol solution was then added and stirring was continued for another 10 minutes. The water (14.36 parts) was added and stirring was continued for 15 to 30 minutes making sure that the polymer was completely hydrated (no lumps). The warm salt solution was added and stirring was continued for 15 minutes or until homogeneity (no lumps or gels). Then the mixture was transferred to the Run mixer for the remaining steps.

In Examples 15 and 16 it was observed that the agglutinated carboxymethyl cellulose dispersed very easily in the aqueous sorbitol solution. Hydration of the polymer appeared to begin in about 3 to 4 minutes and proceeded slowly until addition of the water and salts solution. No lumping of the carboxymethyl cellulose was observed.

In comparative Example D, the untreated carboxymethyl cellulose dispersed easily in the anhydrous glycerol with no lumping. However, in comparative Example E, the untreated carboxymethyl cellulose dispersed in the sorbitol solution only with a very high rate of agitation. Hydration of the polymer appeared to begin in 1 to 2 minutes. Some lumping of the carboxymethyl cellulose was observed in the sorbitol/salt solution.

EXAMPLES 17 AND 18 AND COMPARATIVE EXAMPLES F AND G

These examples illustrate the formulation of toothpastes utilizing carboxymethyl cellulose agglomerated by treatment with sorbitol or with polyethylene glycol at 55° C. The comparative examples demonstrate formulation of control compositions where untreated carboxymethyl cellulose was used.

Examples 17 and 18 illustrate the preparation of toothpastes at room temperature using carboxymethyl cellulose CMC 7M¹ agglomerated by treatment with 9% sorbitol and with 16% polyethylene glycol (PEG 1450) respectively. Comparative examples F and G demonstrate similar formulations where the CMC 7M¹ was untreated. The ingredients and ingredient levels for each formulation are listed in Table 4.

TABLE 4

Toothpaste Formulations, Wt. %				
Ingredient	Example 17	Example 18	Comparative Example F	Comparative Example G
CMC 7M ¹ agglomerated with 9% sorbitol	1.00			
CMC 7M ¹ agglomerated with 16% PEG 1450		1.00		

TABLE 4-continued

Toothpaste Formulations, Wt. %				
Ingredient	Example 17	Example 18	Comparative Example F	Comparative Example G
CMC 7M ¹			1.00	1.00
Glycerol			13.00	
Sorbitol (70% aq. sol.)	35.43	35.43	16.26	35.43
Distilled Water	4.89	4.89	14.46	8.89
Dicalcium Phosphate Dihydrate	43.00	43.00	43.00	43.00
Pyrrophosphate Sodium	0.42	0.42	0.42	0.42
Sodium Saccharin	0.20	0.20	0.20	0.20
Sodium Benzoate	0.76	0.76	0.76	0.76
Monocalcium phosphate heptahydrate	0.50	0.50	0.50	0.50
Urea				
Distilled Water	6.25	6.25	6.25	6.25
Flavor	0.55	0.55	0.55	0.55
Sodium Lauryl Sulfate	1.00	1.00	1.00	1.00

For the glycerol-free formulations (Examples 17 and 18 and Comparative Example G), the following procedure was used:

1. Tetra sodium pyrophosphate (0.42 parts), sodium saccharin (0.20 parts) sodium monobutylphosphate (0.76 parts) and sodium benzoate (0.50 parts) were added to 6.25 parts of water with stirring, and heated to about 60° C. to dissolve.

2. The sorbitol solution (35.43 parts) was heated to 55° C. and then the carboxymethyl cellulose (1.00 parts) was added with stirring which was continued for 15 minutes or until adequate dispersion was achieved. The water (8.89 parts), heated to 55° C., was then added, and stirring was continued for 15 to 30 minutes to ensure complete hydration of the polymer (no gels). Then the warm salt solution from step 1 was added with stirring, which was continued for 15 minutes or until homogeneity (no lumps or gels). The mixture was then transferred in a Run double planetary mixer.

3. The dicalcium phosphate dihydrate (DCP) (43.00 parts) was added to the mixer and mixing was continued for 10 minutes to completely wet the DCP. The mixer was then opened and the beaters and bowl sides were scraped down. The mixer was then closed; vacuum was applied; and mixing was continued at high speed for 20 minutes or until the mix was smooth.

4. The sodium lauryl sulfate (1.00 parts) was then added and mixing was continued for 5 minutes at low speed without vacuum. Then the flavor (0.55 parts) was added followed by mixing for 2 minutes at low speed. The mixer was then opened and the beaters and bowl sides were scraped down. The mixer was then closed; vacuum was applied; and mixing was continued at medium speed for 15 minutes. The mixer was then shut off; vacuum was broken; and toothpaste was packed out.

The procedure for Comparative Example F¹ differed from the above only in the second step. The carboxymethyl cellulose was dispersed in glycerol at 55° C. with stirring, which was continued for 5 minutes, or until adequate dispersion was achieved. Then the sorbitol solution was added and stirring continued for an additional 10 minutes. The water at 55° C. was then added with stirring for 15 to

30 minutes to ensure complete hydration (no gels), and then the warm salt solution from step 1 was added with stirring, which was continued for 15 minutes or until homogeneity (no lumps or gels). The mixture was then transferred to a Ross double planetary mixer.

In Examples 17 and 18 and in Comparative Example F, it was found that the carboxymethyl cellulose materials dispersed easily and evenly in hot sorbitol without lumping. Hydration of the polymer began after 1-2 minutes and proceeded rapidly after addition of water and salt solution. The resulting gel phases were very smooth and the resulting pastes were smooth creams. In contrast, in Comparative Example G, it was not possible to achieve a smooth dispersion of the untreated carboxymethyl cellulose. Even with a high rate of agitation severe lumping of the polymer could not be avoided.

EXAMPLE 19

This example illustrates preparation of toothpaste containing carrageenan agglomerated by treatment with 20% sorbitol.

Ingredients	
glycerol	22 parts
carra-genan (agglomerated by treatment with 20% sorbitol)	0.86
sodium benzoate	0.50
sodium saccharin	0.2
tetrasodium pyrophosphate	0.25
sodium monofluorophosphate	0.76
deionized water	21.28
dicalcium phosphate	51.75
sodium lauryl sulfate	1.50
peppermint oil	0.08

Procedure:

A dry blend of the sodium saccharin, sodium benzoate, agglomerated carrageenan, sodium monofluorophosphate, tetrasodium pyrophosphate was mixed with the glycerol and stirred for 5 minutes. Then the water was added, and the resulting mixture was heated at 66°-71° C. for 15 minutes. The weight was then adjusted back to original weight by addition of distilled water. The mixture was transferred to a Hobart mixer, the dicalcium phosphate was added, and the resulting mixture was stirred at mixer speed 1 for 2 minutes. The mixer was stopped; the bowl and blade were scraped down, and then mixing was resumed at speed 2 for 10 minutes.

The paste was transferred in a vacuum deaerating paddle; the sodium lauryl sulfate and flavor oil were added with mixing, and then the mixture was deaerated for 5 minutes at 0.94 bar. The resulting toothpaste was then packed into tubes for storage.

During this preparation, dispersion of the agglomerated carrageenan occurred rapidly without lump formation.

It is not intended that the examples presented here should be construed to limit the invention, but rather they are submitted to illustrate some of the specific embodiments of the invention. Various modifications and variations of the present invention can be made without departing from the scope of the appended claims.

What is claimed is:

1. A composition comprising particulate water-soluble or water-swella-ble polymer at least partially agglomerated by treatment with at least one polyol selected from the group consisting of sugar alcohols, glycerol, polyethylene glycol, propylene glycol, and mixtures thereof, wherein the polyol

is at a level greater than about 10 wt. % based on the total weight of the composition, and wherein the composition is substantially dry.

2. The composition of claim 1 wherein the composition is dispersible in solvents substantially faster than untreated water-soluble or water-swella-ble polymer, without formation of polymer lumps.

3. The composition of claim 1 wherein the treatment comprises spraying the at least one polyol in liquid form onto particles of water-soluble or water-swella-ble polymer in a fluidized bed while simultaneously drying the particles.

4. The composition of claim 1 wherein the water-soluble or water-swella-ble polymer is at least one polysaccharide.

5. The composition of claim 4 wherein the polysaccharide is at least one member selected from the group consisting of cellulose ethers, guar, guar derivatives, locust bean gum, psyllium, gum arabic, gum ghatti, gum karaya, gum tragacanth, carrageenan, agar, algin, xanthan, scleroglucan, dextran, pectin, starch, chitin and chitosan.

6. The composition of claim 4 wherein the polysaccharide is at least one cellulose ether selected from the group consisting of hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), water soluble ethylhydroxyethyl cellulose (EHEC), carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), hydroxypropylhydroxyethyl cellulose (HPHEC), methyl cellulose (MC), methylhydroxypropyl cellulose (MHPC), methylhydroxyethyl cellulose (MHEC), carboxymethylmethyl cellulose (CMMC), hydrophobically modified carboxymethyl cellulose (HMC), hydrophobically modified hydroxyethyl cellulose (HMHEC), hydrophobically modified hydroxypropyl cellulose (HMHPC), hydrophobically modified ethylhydroxyethyl cellulose (EHHEC), hydrophobically modified carboxymethylhydroxyethyl cellulose (HMCHEC), hydrophobically modified hydroxypropylhydroxyethyl cellulose (HMHPEEC), hydrophobically modified methyl cellulose (HMMC), hydrophobically modified methylhydroxypropyl cellulose (HMHPC), hydrophobically modified methylhydroxyethyl cellulose (HMHHEC), hydrophobically modified carboxymethylmethyl cellulose (HMCMMC), cationic hydroxyethyl cellulose (cationic HEC) and cationic hydrophobically modified hydroxyethyl cellulose (cationic HMHEC).

7. The composition of claim 4 wherein the polysaccharide is at least one guar derivative selected from the group consisting of carboxymethyl guar (CM guar), hydroxyethyl guar (HE guar), hydroxypropyl guar (HP guar), carboxymethylhydroxypropyl guar (CMHP guar), cationic guar, hydrophobically modified guar (HM guar), hydrophobically modified carboxymethyl guar (HMC guar), hydrophobically modified hydroxyethyl guar (HME guar), hydrophobically modified hydroxypropyl guar (HMP guar), cationic hydrophobically modified hydroxypropyl guar (cationic HMP guar), hydrophobically modified carboxymethylhydroxypropyl guar (HMCMP guar) and hydrophobically modified cationic guar (HM cationic guar).

8. The composition of claim 4 wherein the polysaccharide is carboxymethyl cellulose.

9. The composition of claim 4 wherein the polysaccharide is carrageenan.

10. The composition of claim 4 wherein the polysaccharide is a mixture of carboxymethyl cellulose and carrageenan.

11. The composition of claim 1 wherein the polyol is selected from the group consisting of sorbitol, mannitol, galactitol, arabitol, ribitol, xylitol, glycerol, polyethylene glycol, propylene glycol, and mixtures thereof.

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12. The composition of claim 1 wherein the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

13. The composition of claim 8 wherein the polyol is selected from the group consisting of sorbitol and polyethylene glycol, or mixtures thereof.

14. The composition of claim 9 wherein the polyol is selected from the group consisting of sorbitol and polyethylene glycol, or mixtures thereof.

15. The composition of claim 10 wherein the polyol is selected from the group consisting of sorbitol and polyethylene glycol, or mixtures thereof.

16. The composition of claim 1 wherein the maximum level of polyol is about 90 wt. % based on the total weight of the composition.

17. The composition of claim 16 wherein the maximum level of polyol is about 50 wt. % based on the total weight of the composition.

18. The composition of claim 17 wherein the maximum level of polyol is about 30 wt. % based on the total weight of the composition.

19. The composition of claim 1 wherein the water-soluble or water-swellaible polymer is at least one member selected from the group consisting of carrageenan, carboxymethyl cellulose and mixtures thereof, and the polyol is at least one member selected from the group consisting of sorbitol, polyethylene glycol and mixtures thereof, wherein the maximum level of polyol is about 50 wt. % based on the total weight of the composition.

20. In a process for preparing a toothpaste composition comprising at least one dry, water-soluble or water-swellaible polymer, the improvement comprising substituting for the dry, water-soluble or water-swellaible polymer the composition of claim 1.

21. The process of claim 20 wherein the agglomerated water-soluble or water-swellaible polymer hydrates in water or water-containing solvents substantially faster than untreated water-soluble or water-swellaible polymer, without formation of polymer lumps.

22. The process of claim 20 wherein the water-soluble or water-swellaible polymer is polysaccharide.

23. The process of claim 22 wherein the polysaccharide is at least one member selected from the group consisting of cellulose ethers, guar, guar derivatives, locust bean gum, psyllium, gum arabic, gum ghatti, gum karaya, gum tragacanth, carrageenan, agar, algin, xanthan, scleroglucan, dextran, pectin, starch, chitin and chitosan.

24. The process of claim 22 wherein the polysaccharide is at least one cellulose ether selected from the group consisting of hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC), water soluble ethylhydroxyethyl cellulose (EHEC), carboxymethyl cellulose (CMC), carboxymethylhydroxyethyl cellulose (CMHEC), hydroxypropylhydroxyethyl cellulose (HPHEC), methyl cellulose (MC), methylhydroxypropyl cellulose (MHPC), methylhydroxyethyl cellulose (MHEC), carboxymethylmethyl cellulose (CMMC), hydrophobically modified carboxymethyl cellulose (HMC MC), hydrophobically modified hydroxyethyl cellulose (HMEHC), hydrophobically modified hydroxypropyl cellulose (HMHPC), hydrophobically modified ethylhydroxyethyl cellulose (HMEHEC), hydrophobically modified carboxymethylhydroxyethyl cellulose (HMCMEHC), hydrophobically modified hydroxypropylhydroxyethyl cellulose (HMHPHEC), hydrophobically modified methyl cellulose (HMMC), hydrophobically modified methylhydroxypropyl cellulose (HMHMPC), hydrophobically modified methylhydroxyethyl cellulose (HMHMEC), hydrophobi-

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cally modified carboxymethylmethyl cellulose (HMCMMC), cationic hydroxyethyl cellulose (cationic HEC) and cationic hydrophobically modified hydroxyethyl cellulose (cationic HMHEC).

25. The process of claim 22 wherein the polysaccharide is at least one guar derivative selected from the group consisting of carboxymethyl guar (CM guar), hydroxyethyl guar (HE guar), hydroxypropyl guar (HP guar), carboxymethylhydroxypropyl guar (CMHP guar), cationic guar, hydrophobically modified guar (HM guar), hydrophobically modified carboxymethyl guar (HMC MC guar), hydrophobically modified hydroxyethyl guar (HMEHC guar), hydrophobically modified hydroxypropyl guar (HMHPC guar), cationic hydrophobically modified hydroxypropyl guar (cationic HMHP guar), hydrophobically modified carboxymethylhydroxypropyl guar (HMCMHPC guar) and hydrophobically modified cationic guar (HM cationic guar).

26. The process of claim 22 wherein the polysaccharide is selected from the group consisting of carboxymethyl cellulose, carrageenan, pectin, and mixtures thereof.

27. The process of claim 22 wherein the polysaccharide is carboxymethyl cellulose.

28. The process of claim 22 wherein the polysaccharide is carrageenan.

29. The process of claim 22 wherein the polysaccharide is a mixture of carboxymethyl cellulose and carrageenan.

30. The process of claim 20 wherein the polyol is selected from the group consisting of sorbitol, mannitol, galactitol, sorbitol, ribitol, xylitol, glycerol, polyethylene glycol, propylene glycol, and mixtures thereof.

31. The process of claim 20 wherein the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

32. The process of claim 27 wherein the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

33. The process of claim 29 wherein the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

34. The process of claim 28 wherein the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

35. The process of claim 20 wherein the toothpaste composition further comprises dental abrasive and humectant.

36. The process of claim 35 wherein the humectant is selected from the group consisting of glycerol, sorbitol, polyethylene glycol, propylene glycol, and mixtures thereof.

37. The process of claim 36 wherein the water-soluble or water-swellaible polymer is carboxymethyl cellulose and the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

38. The process of claim 36 wherein the water-soluble or water-swellaible polymer is carrageenan and the polyol is selected from the group consisting of sorbitol, polyethylene glycol, and mixtures thereof.

39. The process of claim 20 wherein the at least partially agglomerated particulate water-soluble or water-swellaible polymer is prepared by spraying at least one polyol in liquid form onto particles of water-soluble or water-swellaible polymer in a fluidized bed while simultaneously drying the particles.

40. The process of claim 39 wherein the polyol is in aqueous solution.

41. The process of claim 39 wherein the water-soluble or water-swellaible polymer is at least one member selected from the group consisting of cellulose ethers, guar, guar derivatives and carrageenan.

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42. The process of claim 39 wherein the water-soluble or water-swellaible polymer is carboxymethyl cellulose.

43. The process of claim 39 wherein the water-soluble or water-swellaible polymer is carrageenan.

44. The process of claim 39 wherein the water-soluble or water-swellaible polymer is a mixture of carboxymethyl cellulose and carrageenan.

45. The process of claim 20 wherein the toothpaste composition further comprises ingredients selected from the group consisting of flavors, sweeteners, preservatives, surfactants, antibacterials, coloring agents, tartar control agents and fluoride.

46. The process of claim 20 wherein the polyol in the agglomerated water-soluble or water-swellaible polymer is at a level of from about 11.5 to about 50 wt. % based on the total weight of the agglomerated water-soluble or water-swellaible polymer.

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47. The process of claim 46 wherein the polyol in the agglomerated water-soluble or water-swellaible polymer is at a level of from about 2 to about 50 wt. % based on the total weight of the agglomerated water-soluble or water-swellaible polymer.

48. The process of claim 47 wherein the polyol in the agglomerated water-soluble or water-swellaible polymer is at a level of from about 10 to about 30 wt. % based on the total weight of the agglomerated water-soluble or water-swellaible polymer.

49. Toothpaste made by the process of claim 20.

50. Toothpaste made by the process of claim 39.

51. Toothpaste made by the process of claim 31.

52. Toothpaste made by the process of claim 32.

53. Toothpaste made by the process of claim 33.

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United States Patent (19)

(11)

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Jones

[43]

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[54] AGGLOMERATION OF
STARCH-HYDROLYZED
POLYACRYLONITRILE GRAFT
COPOLYMER

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[52] U.S. Cl. 280/174 GC; 47/DIG. 10;
128/294; 128/285; 128/290 R; 128/296

[53] Field of Search 280/174 ST, 174 GC

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[57] ABSTRACT

A method of agglomerating and desolventizing starch-
hydrolyzed polyacrylonitrile graft copolymer using
steam, liquid water.

3 Claims, No Drawings

AGGLOMERATION OF STARCH-HYDROLYZED POLYACRYLONITRILE GRAFT COPOLYMER

This invention relates to a process for agglomerating and desolventizing particles of starch-hydrolyzed polyacrylonitrile graft copolymer. More especially, this invention relates to a process of agglomerating and desolventizing particles of starch-hydrolyzed polyacrylonitrile graft copolymer which does not reduce its fluid absorbency.

SUMMARY OF INVENTION

The process of this invention comprises wetting particles of starch-hydrolyzed polyacrylonitrile graft copolymer during mixing with atomized, liquid water until a moisture content of the particles reaches about 17 to 22% by weight based upon the weight of the total composition and subsequently drying the particles at a temperature of about 25° C. to 100° C. to a moisture content of about 3% to 12.5% by weight of the total composition and preferably about 7.5% to 12.5% by weight of the total composition for optimum dispersibility. Agglomeration by this method does not decrease the fluid absorbency of the copolymer. In addition, alcohol solvents containing one to three carbon atoms commonly used in purifying the copolymer are released during the process without adversely affecting the copolymer's fluid absorbency.

BACKGROUND OF INVENTION

Starch-hydrolyzed polyacrylonitrile graft copolymers exhibiting the capacity to absorb from about 300 to 1,000 times their weight of deionized water are known at this time. The development of these compositions was carried out by the Northern Regional Research Laboratory, Peoria, Illinois. The starch-hydrolyzed polyacrylonitrile graft copolymer is produced by exposure of starch, either gelatinized or ungelatinized, to cerium salt, such as cerium ammonium nitrate, which acts as a catalyst to generate free radicals. Polyacrylonitrile chains form at the site of these free radicals. The resulting material is then saponified in sodium hydroxide to hydrolyze the polyacrylonitrile chains to carboxamide and alkali metal carboxylate groups mixed with metal salts. After drying, the material can absorb about 300 to 400 times its weight. Drying can be accomplished by drum, tumble air or vacuum drying. Extraction of the copolymer dispersion with alcohol before drying provides a material with fluid absorbency of 800 to 1,000 times its weight. The fluid absorbency is determined by suspending a weighed amount of dry copolymer in an excess of testing fluid and filtering to recover unabsorbed fluid.

The copolymer can be made as film, flakes, powder or mat. These forms take up water, swelling but not dissolving, and hold it in expanded duplications of their own dry shapes. Films extend and thicken to sheets. Powders become piles of water textured like crushed ice. A flake expands to a clear, angular piece of water. The swollen forms shrink in dilute acid and expand again in dilute alkali solution. They also shrink as they dry and expand again with water.

The copolymer, with these properties, can be mixed with or coated on a wide variety of materials including, for example, sand, straw, sawdust, seeds and roots, natural or synthetic fibers, and flour, gelatin and starch. It can hold water in soils, animal bedding and kitty litter,

loweling and diapers, bandages, surgical pads and dental absorbents.

The copolymer, as commercially produced, is a granular powder. The powder varies in granulation, typically from 30 mesh to 400 mesh U.S. Standard Sieve. Fine powders such as those having granulation of 200 mesh to 325 mesh U.S. Standard Sieve, and especially those having a granulation of less than 325 mesh U.S. Standard Sieve, are not as generally useful as coarser granulations because they are harder to apply, harder to contain and, in some instances, they do not disperse or wet-out as well as the coarser particles. Finer granulations can be mechanically separated from the coarser. With respect to economics and material conservation, however, the finer material must be used in some manner.

A further disadvantage of the commercial product is the solvent content. Some alcohol residues are normally retained in the product upon drying. It is known that alcohol solvents used in purification of starch alone can be removed by passing gaseous water or humidified air through particles of the starch and, thereafter, drying the particles. Unfortunately, the fluid absorbency of the copolymer of this invention is adversely affected by these processes. The results of desolventizing with gaseous water or humidified air are shown in Examples I and II. In the past, therefore, there has been a problem in producing low alcohol content, high fluid absorbent copolymers suitable for uses in which alcohols could not be tolerated.

DETAILS OF THE INVENTION

It has now been found that particles of starch-hydrolyzed polyacrylonitrile graft copolymer can be agglomerated by adding atomized, liquid water, mixing and, thereafter, drying. One unexpected result of this process is that trace levels of the process solvents, namely alcohols, remaining in the product after manufacture, typically in an amount of from about 0.5% to 2.5% by weight of the total composition, were significantly reduced during the process to levels of about 0.10% by weight or less without adversely affecting the fluid absorbency of the material.

The process of the present invention is useful in converting fine particles to useful material. It is also useful in producing high fluid absorbent copolymer for applications in which alcohol in significant levels can not be tolerated.

The atomized, liquid water spray or stream can be supplied through an aspirator or atomizer. It is essentially a fine spray of liquid water.

Preferably the mixing of the copolymer particles during the process is carried out by tumbling the particles. This permits the particles to be exposed to the atomized, liquid water spray or stream as well as with each other. Alternatively, the particles could be mixed in a fluid bed or some other mixing arrangement which permits uniform distribution of the water and contact with other copolymer particles.

Drying of the wetted or dampened particles can be carried out at a temperature between about 25° C. and 100° C. Best results were obtained at temperatures of about 40° C. to 80° C. Drying can be carried out in forced-air drying ovens or in vacuum ovens. It was found that a product which contained about 17% by weight water dried at a temperature of about 40° C. in a period of about 16 hours.

Set out below are specific examples illustrating the invention and comparing the results obtained from the practice of the invention with the results obtained from other possible methods of agglomeration investigated. These specific examples are presented for purposes of illustration and not as limiting the scope of the invention.

EFFECT OF HUMIDIFIED AIR UPON COPOLYMER

Example I

A series of samples of copolymer were exposed to humidified air at different temperatures to determine if the copolymer could be agglomerated and/or desolvated by that method. The samples initially contained 3.3% by weight methanol and 3.7% by weight water and exhibited a fluid absorbency of 83.0-85.0 grams of 1% by weight sodium chloride solution per gram of copolymer. It was found that, in order to effect desolvation, a relative humidity of 37% or greater was necessary. The results of the above series of tests are shown in Table 1. These results show that the samples which exhibited desolvation exhibited reduced fluid absorbency in 1% by weight sodium chloride solution.

Table 1

RELATIVE HUMIDITY %	TEMP. °C.	% METHANOL (GLC)	% MOISTURE (Calc.)	ABSORBENCY 1% NaCl g/g
38.3	21	<0.1	32.7	43.6
	40	<0.1	32.9	41.9
	51	<0.1	32.3	39.6
47.2	21	<0.1	21.6	61.0
	40	<0.1	21.8	60.0
	51	<0.1	21.2	62.3
37.1	21	<0.1	17.6	77.8
	40	<0.1	17.6	77.8
	51	<0.1	14.9	80.6
18.3	21	1.9	10.6	82.5
	40	0.9	10.3	76.6
	51	0.3	10.0	86.4
1.5	21	2.9	6.3	81.8
	40	2.6	6.2	80.3
	51	2.6	5.8	83.6
1.2	21	2.8	4.9	80.6
	40	2.7	3.9	76.2
	51	2.8	1.5	86.6
Control	—	—	—	83.0-85.0

Exposure time 16 hours

^aAfter drying at 45° C. under vacuum for 16 hours

Example II

Using the procedure set out in Example I, a series of copolymer samples containing 33% by weight methanol and 6.4% by weight water were exposed to air streams having relative humidities of 38% or 48% and a temperature of 40° C. The results are shown in Table 2.

Table 2

Exposed to Humidified Air Time/Hours	38% Relative Humidity		
	% Methanol (GLC)	% Moist. ¹	Absorbency 1% NaCl g/g ²
1	7.3	14.7	48.3
1	1.4	16.0	43.6
2	0.80	14.6	30.4
3	0.38	13.3	48.6
4	0.34	12.3	47.1
8	0.17	12.1	—
16	0.16	12.1	—
Oven Dried Control	1.1	3.7	31.0-33.4
Exposed to Humidified Air	48% Relative Humidity		
	% Methanol		Absorbency

Table 2-continued

Time/Hours	(GLC)	Moist. ¹	1% NaCl g/g ²
1	1.3	16.9	49.2
2	0.54	15.1	49.6
3	0.13	15.1	44.8
4	0.12	17.9	44.8
8	0.08	16.4	44.8
16	—	—	—
Oven Dried Control	1.3	3.7	31.0-33.4

¹Analyzed by Karl Fisher procedure

²After drying at 45° C. for 16 hours

AGGLOMERATION WITH ATOMIZED LIQUID WATER

Example III

Dry copolymer powder having the following analysis and granulations

Moisture: 1.2%

Methanol: 1.2%

Granulations

30-100 mesh: 37.0%

100-200 mesh: 23.0%

200-325 mesh: 14.0%

—325 mesh: 25.0%

was agglomerated with 10%, 15% and 20% added water, based on total weight of the wetted copolymer, in the following manner: the powder charge was placed in an inclined cylinder, closed at the bottom, which could be rotated like a cement mixer. While revolving, water was added slowly in the form of a mist using a pressure aspirator to atomize the water. Rate of addition was controlled so as to prevent build-up of large agglomerates. After addition of water was complete, agglomerated products were transferred to trays and dried in a forced air oven at a temperature of 40°-45° C. for 16 hours. Dried product was then classified to determine agglomeration efficiency and GLC analyzed to determine methanol remaining in the product after water agglomeration and redrying. Results, tabulated in Table 3, show that about 17% water must be added, based the wet agglomerated product, to reduce methanol level of final product to 0.10% methanol or below. At 20% water addition, the fine fraction (-100 mesh) of the product was halved, i.e. decreased from 73% to 37%.

Table 3

AGGLOMERATION OF POWDERED COPOLYMER WITH VARYING AMOUNTS OF WATER				
Sample	% by weight H ₂ O added	Product Granulation, %		% Methanol Content
		+100 mesh	-100 mesh	
1	None (Control)	37	73	1.2
2	10	55	—	0.75
		—	45	0.16
3	15	64	—	0.36
		—	36	0.16
4	20	73	—	0.10
		—	27	0.23
5	25	— ^a	— ^a	— ^a

^aWater addition level was too high. Product became doughy in rotary mixer and produced a non-granular, glossy solid on drying.

Example IV

Dry copolymer having the following analysis and granulations

Moisture: 6.3% by weight

Methanol: 1.2% by weight

Fluid Absorbency: 87 ml/g (1.0% NaCl solution)

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Granulation

- 30 - 100 mesh: 19.0%
- 100 - 200 mesh: 34.0%
- 200 - 325 mesh: 22.0%
- 325 mesh: 26.0%

was sieve-classified to separate into the following portions: +100 mesh, 100-140 mesh, 140-200 mesh and -200 mesh. Portions of the last three portions were agglomerated as described in Example 3 using 20% by weight water (based the wet weight of agglomerate) and dried in the same manner. Dried products were declassified to determine agglomeration efficiency, analyzed for methanol to determine degree of desolventization and evaluated for fluid absorbency to determine effect of agglomeration on product performance. Results, tabulated in Table 4, show that agglomeration of product powders ranging from fine (100-140 mesh) to very fine (-200 mesh) in the manner described here significantly increased product granulation, reduced product methanol content and did so without adversely affecting the fluid absorbency of the product.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

- 1. A process of agglomerating and desolventizing starch-hydrolyzed polyacrylonitrile graft copolymer wherein said acrylonitrile is hydrolyzed to carbonamide and alkali metal carboxylate groups, comprising wetting particles of starch-hydrolyzed polyacrylonitrile copolymer during mixing with atomized, liquid water until the moisture content of the particles reaches about 17% to 22% by weight based upon the weight of the total composition and subsequently drying the particles at a temperature between about 25° C. to 100° C. to a moisture content of about 3% to 12.5% by weight of the total composition.
- 2. The process of claim 1 wherein the drying temperature is between about 40° C. and 80° C.
- 3. The process of claim 1 wherein the final moisture content of the copolymer is between about 7.5% to 12.5% by weight of the total composition.

Table 4

AGGLOMERATION OF POWDERED COPOLYMER OF VARYING GRANULATIONS USING 20% BY WEIGHT WATER ADDED					
Agglomerated Product					
Sample	Powdered Granulation Before Agglomeration	Granulation (mesh)		Methanol Content (%)	1% NaCl Solution Absorbency
		40-60	- 80		
1	100-140	70	30	0.05	—
2	140-200	73	37	0.01	96
3	-200 mesh	60	40	0.01	97
Control	unclassified	—	—	1.30	86

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

DIVISION DE NUEVAS CREACIONES

2020

Bogotá, D.C., Marzo 9 de 2008

Doctor

HUMBERTO RUBIO CAMACHO

ASUNTO	Radicación No.	00 083 905
	Trámite	002
	Evento	001
	Actuación	430
	Oficio No.	31.7
	Folios	0

Como resultado del examen de patentabilidad de la solicitud de patente de invención, realizado según lo establece el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se notifica el siguiente concepto técnico:

1. Documentos estudiados

Para el presente estudio se tuvieron en cuenta el capítulo descriptivo comprendido en los folios 37 - 52 y el capítulo reivindicatorio de los folios 53 - 56 de la solicitud en estudio.

2. Objeto de la invención

El objeto de la presente solicitud de patente de invención consiste en:

Las reivindicaciones 1 - 21, 23 - 28 se refieren a un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua (excepto MHPC) se aglomera parcialmente por tratamiento con agua o una solución acuosa del polímero y posterior secado.

La reivindicación 22 se refiere a una composición para cuidado oral preparada por el proceso de la reivindicación 1.

El problema planteado en esta solicitud es la necesidad de proporcionar un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua tenga mayor dispersabilidad, no produzca polvo y no forme terrones.

Para resolver este problema técnico la solicitud en estudio proporciona un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua (excepto MHPC) se aglomera parcialmente por tratamiento con agua o una solución acuosa del polímero y posterior secado.

El objeto de la invención definido anteriormente se clasificó de acuerdo con la IPC: A 61 K 7/16.

También se reivindica prioridad de la Solicitud de Patente de los Estados Unidos USSN 09/432 542 de noviembre 03 de 1999, con respecto a la cual la fecha de presentación de la actual solicitud cumple el plazo máximo permitido.

3. Determinación del Estado de la Técnica

El artículo 16 de la decisión 486 de la comisión de la Comunidad Andina que establece que *"El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida.*

Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ésta se publique o hubiese transcurrido el plazo previsto en el artículo 40".

Considerando que la fecha de presentación de la primera solicitud de patente de la cual se reivindica prioridad es noviembre 03 de 1999, se consultaron las bases de datos y los archivos con que cuenta la entidad con fecha de publicación anterior y se encontraron los siguientes documentos que anticipan el objeto de esta solicitud:

No.	Documento	Título	Fecha de Publicación
D1	US 5 869 029	Polímeros solubles-dispersables ó hinchables en agua y proceso para hacer pasta de dientes que los contienen	Feb 9, 1999
D2	US 4 123 397	Aglomeración de copolímeros injerto almidón-poliacrilonitrilo hidrolizado	Oct 31, 1978

4. Evaluación de los requisitos de Patentabilidad

El artículo 14 de la Decisión 486 de la Comisión de la Comunidad Andina establece que *"Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento, en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial".*

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar el cumplimiento de los requisitos de novedad, nivel inventivo y aplicación industrial, con el fin de establecer la patentabilidad de la invención reivindicada en la solicitud en estudio.

Evaluación de la Novedad

El Art. 16 de la Decisión 486 de la Comisión de la Comunidad Andina establece: *"Una invención se considerará nueva cuando no está comprendida en el estado de la técnica. El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente, o, en su caso, de la prioridad reconocida.*

Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica, el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el Art 40°.

Las reivindicaciones 1 – 21, 23 - 28 se refieren a un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua (excepto MHPC) se aglomera parcialmente por tratamiento con agua o una solución acuosa del polímero y posterior secado.

La reivindicación 22 se refiere a una composición para cuidado oral preparada por el proceso de la reivindicación 1.

D1 enseña un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua se aglomera por tratamiento con agua y posterior secado. Menciona que las ventajas de este polímero son: mayor dispersabilidad (ver columna 4), no produce polvo (ver columna 4) y no forma terrones (ver columna 13, reivindicación 21).

D2 enseña un proceso para aglomerar un polímero soluble o hinchable en agua por tratamiento con agua y posterior secado (ver columnas 1, 2, 4)

Se observa que:

- (a) Los pasos del proceso de las reivindicaciones 1 – 21, 23 - 28 para aglomerar el polímero que consisten en tratamiento con agua y posterior secado ya se habían mencionado en D1 y en D2. De manera que este proceso no es nuevo.
- (b) La composición para cuidado oral preparada por el proceso de la reivindicación 1 que consiste en tratamiento con agua y posterior secado ya se había mencionado en D1. De manera que esta composición no es nueva.

Evaluación del Nivel Inventivo

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina establece que Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica.

Las reivindicaciones 1 – 21, 23 - 28 se refieren a un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua (excepto MHPC) se aglomera parcialmente por tratamiento con agua o una solución acuosa del polímero y posterior secado.

La reivindicación 22 se refiere a una composición para cuidado oral preparada por el proceso de la reivindicación 1.

D1 enseña un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua se aglomera por tratamiento con agua y posterior secado. Menciona que las ventajas de este polímero son: mayor dispersabilidad (ver columna 4), no produce polvo (ver columna 4) y no forma terrones (ver columna 13, reivindicación 21).

D2 enseña un proceso para aglomerar un polímero soluble o hinchable en agua por tratamiento con agua y posterior secado (ver columnas 1, 2, 4)

Se observa que:

- (a) los pasos del proceso de las reivindicaciones 1 – 21, 23 - 28 para aglomerar el polímero que consisten en tratamiento con agua y posterior secado ya se habían mencionado en D1 y en D2, y los polímeros que caracterizan a las composiciones también eran conocidos en las anterioridades; así que para una persona conocedora de la materia era evidente el elaborar las composiciones de manera similar, teniendo en cuenta estos pasos y estos polímeros aglomerados;
 - (b) las reivindicaciones de esta solicitud no mencionan una característica que conceda un efecto diferente o especial al proceso, a los polímeros, ni a las composiciones, que pueda considerarse como un aporte a la técnica, así que son obvias para una persona versada en la materia;
 - (c) el problema planteado en esta solicitud que era la necesidad de proporcionar un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua tenga mayor dispersabilidad, no produzca polvo y no forme terrones, se resuelve proporcionando un proceso para preparar una composición de cuidado oral donde el polímero soluble o hinchable en agua (excepto MHPC) se aglomera parcialmente por tratamiento con agua o una solución acuosa del polímero y posterior secado, es decir de manera similar a como se resolvía en las anterioridades; las reivindicaciones son obvias y evidentes para una persona versada en la materia.
 - (d) el resultado obtenido: que los polímeros tengan mayor dispersabilidad, no produzca polvo y no forme terrones no es inesperado, sino que ya se había logrado en el arte.
 - (e) no parece haberse superado un prejuicio técnico anterior, ni con el proceso, ni con las composiciones propuestas.
- Así que de acuerdo con lo anterior, ni con el proceso, ni con las composiciones reivindicadas tienen nivel inventivo.

5. Conclusión

En conclusión, los requisitos de patentabilidad de la presente solicitud están afectados así:

Item	Documento	Reivindicaciones afectadas	Requisito que afecta
D1	US 5 869 029	1 – 28	Novedad y Nivel inventivo
D2	US 4 123 397	1 – 28	Novedad y Nivel inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal

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e), del capítulo quinto del título primero de la Circular Unica No. 10 de 2001.



ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones.

El anterior requerimiento fue notificado por fijación en lista, de fecha
16 MAR 2006

CONCEPTO TÉCNICO No. 379	EXAMINADOR TÉCNICO Código 202007
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