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| (30)<br>(43)<br>(73)<br>(72) | Priority:07.08.1989 JP 204488/89Date of publication of application:13.02.1991 Bulletin 1991/07Proprietor:SHISEIDO COMPANY LIMITEDChuo-ku Tokyo 104-10 (JP)Inventor:Funatsu, Shinichiro,C/o Shiseido LaboratoriesYokohama-shi, Kanagawa (JP) | <ul> <li>(56) References cited:<br/>EP-A- 0 308 238 FR-A- 2 068 447<br/>GB-A- 2 004 182</li> <li>CHEMICAL ABSTRACTS, vol. 87, no. 16, 17<br/>October 1977, Columbus, Ohio, US; abstract no.<br/>122707C, D. RAMBHAU ET AL: 'Stability studies<br/>on lyophilized o/w emulsions'</li> </ul> |  |  |  |  |  |  |  |

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## Description

## BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to a solid cosmetic composition. More specifically, it relates to a solidified cosmetic composition having a good solubility in water, feeling during use, high humectant effect, and free from thermal degradation.

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2. Description of the Related Art

Heretofore, as solid cosmetics of the type used as a solution when applied, generally well known in the art are those prepared by formulating a chemical which provides an aesthetically pleasing depigmentation or a good skin activating effect, pulverizing the formulation by spray drying or pulverizing mixing, and further, granulating the composition. Nevertheless, many problems remained to be solved in the solid cosmetic prepared according to this method. For example,

- a problem arises in the solid cosmetic prepared by spray drying in that a thermal degradation of the chemical and the base occur due to heat applied during the spray drying, Also, when an excipient, a fluidizing agent and the like are added, to improve the miscibility and filling characteristics of the powder, the water solubility is lowered. Further, when a water-soluble polymer is formulated, to increase the humectant effect or improve the feeling when used as a cosmetic, i.e., for
- 20 soluble polymer is formulated, to increase the humectant effect or improve the feeling when used as a cosmetic, i.e., for improving the body and health, undissolved powder lumps are often formed during the dissolution in water, and a problem arises in that it can be uniformly redissolved only with difficulty.

GB-A-2 004 182 describes a method for preparing pharmaceutical, cosmetic or diagnostic formulations by freeze drying one or more substances in solution or in suspension in a solvent or a mixture of solvents. The solution or sus-

- 25 pension is locally and progressively cooled in a controlled manner while agitating so as to produce microcrystals of solvent which are put in suspension in the remainder of the liquid until there is obtained a high-viscosity microcrystalline complex system comprising essentially isolated microcrystals of solvent in intimate mixture with interstitial liquid phases having a high concentration of the initially present substances. The microcrystalline complex system is hardened by cooling and lyophilized.
- 30 FR-A-2 068 447 discloses the preparation of an emollient cream in a porous support obtained by preparing an oilin-water emulsion and suspension, and finally freeze-drying the same.

Chemical Abstracts, Vol. 57, No. 16, 1977, Abtr. No. 122707C discloses stability studies on lyophilized O/W emulsions of peanut oil made with mannitol, mannitol plus

## 35 SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of the prior art and to provide a solid cosmetic composition having an excellent solubility in water, a good feeling during use, with a good body and a good effect on the skin, a high humectancy, and free from thermal degradation.

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Other objects and advantages of the present invention will be apparent from the following description. In accordance with the present invention, there is provided a solid cosmetic composition comprising a freeze-dried

product of an aqueous solution containing (i) at least one water-soluble substance selected from the group consisting of polyethylene glycols having a molecular weight of 9,000 to 20,000 and (ii) as a thickener or a humectant at least one water-soluble polymer selected from the group consisting of vegetable natural polymers, microorganism natural polymers, polymers derived from animals, starch polymers, cellulose polymers, alginic acid polymers, polyvinyl polymers,

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- mers, polymers derived from animals, starch polymers, cellulose polymers, alginic acid polymers, polyvinyl polymers, acrylic polymers, polyethyleneimines and mucopoly-saccharides and inorganic clay minerals, said solid cosmetic composition being used after being dissolved in a solvent, the contents of the water-soluble substance and of the water-soluble polymer in the freeze-dried product being respectively 10 to 99% by weight and 90 to 1% by weight based upon the total weight of the freeze-dried product.
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## DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is described in more detail as follows.

The water-soluble substance, which is solid at normal temperature, comprises polyethylene glycols such as PEG-20000, PEG-9000, PEG-6000, PEG-4000, and the like, polypropylene glycols and polyethylene glycol-polypropylene glycol block copolymers.

All of the water-soluble substances usable in the present invention preferably have a melting point of 40°C or more. The amount of the above-mentioned water soluble substance formulated is preferably 10 to 99% by weight of the solid cosmetic composition of the present invention. When the formulation amount is less, the amount of the above-

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mentioned water-soluble polymer formulated must be increased and the composition becomes sticky or slimy. Accordingly, the amount formulated is more preferably 70 to 99% by weight.

The water-soluble polymer usable as the thickening agent or the humectant in the present invention comprises at least one of vegetable natural polymers, microorganism natural polymers, polymers derived from animals, starch polymers, cellulose ploymers, alginic acid polymers, polyvinyl polymers, acrylic polymers, polyethyleneimines, mucopoly-saccharides, and inorganic clay minerals.

Examples of preferable vegetable natural polymers usable in the present invention include gum arabic, gum tragacanth, galactan, guar gum, carageenan, pectin, quince seed, algae colloid (algae extract), starch (rice, corn, potato, wheat), and glycyrrhizinic acid; examples of preferable microorganism natural polymers include xanthan gum, dextran,

- succinogulcan, and plullan; polymers of preferable polymers derived from animals include collagen or derivatives thereof, casein, albumin, and gelatin; examples of preferable starch polymers include carboxymethyl starch and methl-hydroxypropyl starch; examples of preferable cellulose polymers include methyl cellulose, ethyl cellulose, methyl-hydroxypropyl cellulose, hydroxyethyl cellulose, sodium cellulose sulfate, hydroxypropyl cellulose, and sodium carboxymethyl cellulose (CMC); examples of preferable aliginic acid polymers include sodium alginate, and alginic acid propylene glycol ester;
- 15 examples of preferably polyvinyl polymers include polyvinyl alcohol, polyvinyl methyl ether, polyvinyl pyrrolidone, and carboxyvinyl polymer (Carbopol); examples of preferable acrylic acid polymers include sodium polyacrylates; examples of preferable mucopolysacchrides include hyaluronic acid, sodium hyaluronate, chondroitin sulfuric acid, sodium chondroitin sulfate, dermatan sulfuric acid, sodium dermatan sulfate, heparan sulfuric acid, and sodium heparan sulfate; and examples of preferable clay minerals include bentonite, aluminum magnesium silicate Veegum, Laponite, hectorite, anhy-20 drous silic acid, and saponite.

The above-mentioned water-soluble polymer is preferably formulated in an amount of 1 to 90% by weight, in the solid cosmetic of the present invention. When the amount formulated is too large, the composition may be come sticky or slimy, and further the rate of dissolution in water become slower, and therefore, most preferably the amount of the above-mentioned water soluble polymer is 1 to 30% by weight.

- In the present invention, if necessary, additives which are solid at normal temperature may be also formulated within a range which does not interfere with the effect of the present invention, such as humectants, surfactants, antioxidants, preservatives, sterilizers, amino acids, sequestering agents, vitamins, plant extracts, animal extracts, dyes, and UV-ray absorbents and the like. These additives are useful as cosmetics, and are solid at normal temperature after freeze drying. The solid cosmetic composition of the present invention can be prepared by formulating the above-mentioned water-
- 30 soluble substance and the above-mentioned water-soluble polymer in preferable amounts, dissolving the formulation in, for example, deinoized water, filling a predetermined amount thereof in a vesel of glass or resin, freezing by cooling to 40 °C or lower, and subsequently, drying by sublimation under a reduced pressure in a vacuum of, for example, 0.5 Torr or lower. The concentration of the raw solution dissolved in deionized water is preferably 15% by weight of the solids, from the standpoint of the water solubility.
- 35 The resultant freeze-dried composition is dissolved in the solvent such as deionized water or any mixture of deionized water with one or more of lower aliphatic alcohols such as ethanol, propanol, i-propanol, butanol and the like. The preferable alcohol content in the mixture is 50% by weight or less, preferably 15% by weight or less, preferably in an amount of 0.5 to 10 parts by weight per 100 parts by weight of the solvent.

The solid cosmetic composition of the present invention is preferably formulated in, for example, a white powder, 40 humectant powder, pimple preventive, suntan preventive sunscreen, suntan, hair growth agent, and dandruff/itch preventive.

According to the present invention, chemicals unstable in heat or water can be maintained in a stable condition for a long time, to thereby provide a solid cosmetic composition having an excellent water solubility, good feeling during use, with a good body and good effect on the skin, a high humectancy, and free from thermal degradation.

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## EXAMPLES

The present invention will now be further illustrated by, but is by no means limited to, the following Examples.

#### 50 Example 1, Comparative Examples 1, 2

Water-soluble polymers and water-soluble substances were formulated as shown in Table 1, and dissolved in deionized water to prepare formulated raw solutions. The formulated raw solutions were freeze dried to - 40 °C, vacuum dried in a conventional manner to obtain solid cosmetic compositions, and the appearance, feeling during use, and water solubility thereof were evaluated. The water solubility was evaluated by dissolving 0.5 g of the solid cosmetic composition in 5 ml of deionized water. The evaluation standards were as follows:

good
 good

o normal

 $\triangle$  not good

x poor

| e                        | 80                                 |             | 0                            | •  | <b>R•</b> ••             |
|--------------------------|------------------------------------|-------------|------------------------------|--|--------------------------|
| icts and solutio         | Feeling durin<br>use<br>(solution) |             | With body,<br>smooth and wet | Slimy during<br>coating and<br>sticky after<br>coating               | Watery, withowi<br>body  |
| npo                      |                                    |             | 0                            |  | 0                        |
| eeze dried pr<br>thereof | Appearance                         |             | Crunchy<br>porous cake       | Fluffy<br>cotton   | Frmish<br>porous cake    |
| fr                       | ty                                 |             | 0                            | 4  | Ø                        |
| Evaluation of            | Water solubili                     |             | Quickly<br>dissolved         | Undissolved<br>powder lump of<br>water-soluble<br>polymer<br>remains | Quickly<br>dissolved     |
| freeze dried             | Deionized water                    |             | 90.0wt%                      | 98. Durt I   | 92.Owt <i>i</i>          |
| solution being           | Water-soluble<br>substance         | PEG 9000    | 8.0wt2                       | ·  | 8.0wtI                   |
| ion of aqueous           | Water-soluble polymer              | Xanthan gum | 1.0wt%                       | 1.0wtX   | 1                        |
| Compositi                |                                    | Quince seed | 1.04t <i>1</i>               | 1.0wt.Z  | 1                        |
|                          |                                    |             | Example 1                    | Comparative<br>Example 1   | Comparative<br>Example 2 |

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As apparent from Table 1, the water solubility of Example 1 was good, and the appearance was of a crunchy, porous cake, which was bulky and pleasing to the eye, and further, the feeling during use was excellent with an adequate body, smooth spreading, and wet feeling. In Comparative Example 1, the results of oil of the water solubility, appearance and feeling during use, were not satisfactory, and in Comparative Example 2 in which a water- soluble thickener was not formulated, the composition was watery without body, and the feeling during use was very bad.

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Accordingly the requirements for a good water solubility, appearance, and feeling during use were satisfied in the Examples, but were not all satisfied at the same time in the Comparative examples.

## Claims

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- 1. A solid cosmetic composition comprising a freeze-dried product of an aqueous solution containing (i) at least one water-soluble substance selected from the group consisting of polyethylene glycols having a molecular weight of 9,000 to 20,000 and (ii) as a thickener or a humectant at least one water-soluble polymer selected from the group consisting of vegetable natural polymers, microorganism natural polymers, polymers derived from animals, starch
- 15 polymers, cellulose polymers, alginic acid polymers, polyvinyl polymers, acrylic polymers, polyethyleneimines and mucopoly-saccharides and inorganic clay minerals, said solid cosmetic composition being used after being dissolved in a solvent, the contents of the water-soluble substance and of the water-soluble polymer in the freeze-dried product being respectively 10 to 99% by weight and 90 to 1% by weight based upon the total weight of the freeze-dried product.

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- 2. A solid cosmetic composition as claimed in claim 1, wherein the solvent is selected from the group consisting of deionized water and mixtures thereof with a lower aliphatic alcohol.
- 3. A solid cosmetic composition as claimed in claim 1, wherein the weight of the solid cosmetic composition to the solvent is 0.5 to 10 parts by weight per 100 parts by weight of the solvent.
- 4. A solid cosmetic composition as claimed in claim 1, further comprising at least one component selected from the group consisting of a humectant, surfactant, antioxidant, preservative, sterilizer, amino acid, sequestering agent, vitamin, plant extract, animal extract, dye, and UV-ray absorbents.

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## Patentansprüche

- 1. Feste kosmetische Zubereitung, umfassend ein gefriergetrocknetes Produkt aus einer wäßrigen Lösung enthaltend (i) mindestens eine wasserlösliche Substanz, ausgewählt aus der Gruppe bestehend aus Polyethylenglykolen mit
- einem Molekulargewicht von 9 000 bis 20 000 und (ii) als ein Dickungsmittel oder Feuchthaltemittel mindestens ein wasserlösliches Polymer, ausgewählt aus der Gruppe bestehend aus vegetabilischen natürlichen Polymeren, natürlichen Mikroorganismus-Polymeren, Polymeren, die sich von Tieren ableiten, Stärkepolymeren, Cellulosepolymeren, Alginsäurepolymeren, Polyvinylpolymeren, Acrylpolymeren, Polyethyleniminen und Mucopolysacchariden sowie anorganischen Tonmaterialien, wobei die feste kosmetische Zubereitung verwendet
   wird, nachdem sie in einem Lösungsmittel gelöst worden ist, wobei die Bestandteile aus wasserlöslicher Substanz
- und dem wasserlöslichen Polymer in dem gefriergetrockneten Produkt bei 10 bis 99 Gew.-% bzw. 90 bis 1 Gew.-%, bezogen auf das Gesamtgewicht des gefriergetrockneten Produktes, liegen.
- **2.** Feste kosmetische Zusammensetzung nach Anspruch 1, in der das Lösungsmittel ausgewählt ist aus der Gruppe bestehend aus deionisiertem Wasser und Mischungen hiervon mit einem kurzkettigen aliphatischen Alkohol.
  - 3. Feste kosmetische Zubereitung nach Anspruch 1, in der das Gewicht der festen kosmetischen Zusammensetzung im Verhältnis zum Lösungsmittel bei 0,5 bis 10 Gew.-Teilen pro 100 Gew.-Teile Lösungsmittel liegt.
- 50 4. Feste kosmetische Zubereitung nach Anspruch 1, die weiterhin enthält mindestens eine Komponente, ausgewählt aus der Gruppe bestehend aus einem Feuchthaltemittel, einem oberflächenaktiven Mittel, einem Antioxidationsmittel, einem Schutzmittel, einem Sterilisator, einer Aminosäure, einem Sequestriermittel, Vitamin, Pflanzenextrakt, tierischem Extrakt, Farbstoff und UV-Strahlen-Absorber.

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## Revendications

- 1. Une composition cosmétique solide comprenant un produit lyophilisé d'une solution aqueuse contenant:
- (i) au moins une substance hydrosoluble choisie dans le groupe consistant en polyéthylèneglycol présentant un poids moléculaire de 9000 à 20 000; et

(ii) en tant qu'épaississant ou humectant, au moins un polymère hydrosoluble choisi dans le groupe consistant en polymères naturels végétaux, polymères naturels de micro-organismes, polymères dérivés d'animaux, polymère amylacés, polymères de cellulose, polymères d'acide alginique, polymères polyvinyliques, polymères acryliques, polyéthylèneimines et mucopolysaccharides et argiles minérales inorganiques, ladite composition cosmétique solide étant utilisée après avoir été dissoute dans un solvant, la teneur en substance hydrosoluble et en polymère hydrosoluble dans le produit lyophilisé étant respectivement de 10 à 99% en poids et de 90 à 1% en poids, exprimés par rapport au poids total du produit lyophilisé.

- **2.** Une composition cosmétique solide selon la revendication 1, dans laquelle le solvant est choisi dans le groupe consistant en eau déminéralisée et ses mélanges avec de l'alcool aliphatique inférieur.
  - 3. Une composition cosmétique solide selon la revendication 1, dans laquelle le rapport du poids de la composition cosmétique solide au solvant est de 0,5 à 10 parties en poids pour 100 parties en poids de solvant.
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4. Une composition cosmétique solide selon la revendication 1, comprenant en outre un composant choisi dans le groupe consistant en humidifiant, agent tensioactif, anti-oxydant, conservateur, antiseptique, acide aminé, agent séquestrant, vitamine, extrait de plante, extrait d'origine animale, colorant et absorbants de rayonnement ultra-violet.

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