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(54) Title: METHOD AND CONCENTRATE FOR ENHANCING THE EFFICACY OF ZINC PYRITHIONE IN PERSONAL CARE PRODUCTS

(57) Abstract: The present invention relates to a method for increasing the deposition of zinc pyrithione present in a personal care product without reducing its bioavailability and while maintaining the efficacy of the product. The method comprises, including with the zinc pyrithione, a polymer selected from a powder blend of an alkyl ester of poly (methyl vinyl ether maleic acid) partially neutralized and polyvinyl pyrrolidone; an aqueous suspension of a water insoluble alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; and a partially neutralized linseed oil-modified dicarboxylic acid half-ester of maleic acid. The present invention further relates to concentrates and personal care products featuring zinc pyrithione and at least one of the above-described polymers.



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METHOD AND CONCENTRATE FOR ENHANCING THE EFFICACY OF ZINC PYRITHIONE IN PERSONAL CARE PRODUCTS

FIELD OF THE INVENTION

[0001] The present invention relates to the fungicide zinc pyrithione (ZPT) and more particularly, to a method and composition for increasing dispersability and the deposition of particulate ZPT on the scalp for personal care products such as anti-dandruff shampoos, without adversely affecting its bioavailability, and while maintaining the cosmetic benefits of the shampoo application.

BACKGROUND OF THE INVENTION

[0002] Personal care products such as shampoos often contain a fungicide in small amounts to prevent dandruff from forming and to reduce or preclude the possibility of any fungus attack. A suitable material for this purpose is zinc pyrithione (ZPT) which is a chelate of zinc ions and pyrithione. However, ZPT particles tend to agglomerate in use which decreases their dispersability, i.e., reduces their deposition and/or retention on the scalp during showering.

[0003] Furthermore, it is desired that ZPT should deposit on the scalp itself to enhance its bioavailability rather than on the hair. These and other attributes of ZPT are known in the art and are the subject of considerable research and development to provide improved ZPT-containing cosmetic products.

[0004] Accordingly, it is an object of this invention to provide a new and improved zinc pyrithione composition for use as an additive in personal care products. A particular object is to provide such compositions which will improve the deposition/retention of zinc pyrithione from shampoo products on the scalp rather than the hair, without affecting its bioavailability and while maintaining the cosmetic benefits of the shampoo application.

SUMMARY OF THE INVENTION

[0005] We have discovered that the deposition of zinc pyrithione (ZPT) present in a personal care product on the scalp can be significantly enhanced without reducing its bioavailability and while maintaining the efficacy of the product by including in the product a polymer selected from a powder blend of the partially neutralized monobutyl ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone; an aqueous suspension of a water insoluble C₁₆ alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; and a linseed oil-modified dicarboxylic acid half-ester of maleic acid.

[0006] More specifically, in accordance with this invention, there is provided a method for increasing the deposition of zinc pyrithione (ZPT) present in a personal care product without reducing its bioavailability and while maintaining the efficacy of such product, which comprises including in said product a polymer selected from the group consisting of: a) a powder blend of the partially neutralized alkyl ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone; b) an aqueous suspension of a water insoluble alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; and c) a linseed oil-modified dicarboxylic acid half-ester of maleic acid.

[0007] In another aspect, this invention provides a concentrate comprising zinc pyrithione, at least one of the above-described polymers and a carrier.

[0008] In a further embodiment, there is provided a personal care product comprising zinc pyrithione, at least one of the above described polymers and optionally one or more personal care ingredients.

DETAILED DESCRIPTION OF THE INVENTION

[0009] While the invention is described hereinafter with respect to preferred embodiments thereof, e.g., the deposition of zinc pyrithione (ZPT) in combination with specific polymers, i.e., a polymer selected from a powder blend of the partially neutralized monobutyl ester of poly (methyl vinyl ether maleic acid) and polyvinyl

pyrrolidone; an aqueous suspension of a water insoluble C₁₆ alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; and a linseed oil-modified dicarboxylic acid half-ester of maleic acid, the invention can also be practiced in conjunction with other actives besides zinc pyrithione, such as, for example, zinc/magnesium, copper, cadmium, barium, bismuth and zirconium pyrithiones, coal tar, salicylic acid, selenium sulfide, sulfur, and with other polymers, such as, for example, film forming anionic polymeric dispersants containing a significant number of negative charges and at least one hydrophobic anchoring group for every ten repeat units, either as a single polymeric moiety or combinations of two or more polymers.

[0010] For personal care applications, e.g., anti-dandruff applications, the zinc pyrithione can be present in a particle size of about 0.5- 5 μ , preferably 0.8- 4 μ , and most preferably 1-3 μ .

[0011] A preferred polymer additive for ZPT dispersing is the sodium salt of alkylvinylether maleic acid half-ester copolymer (EasySpense[®]) (ISP) and polyvinyl pyrrolidone (PVP K-30), most preferably in a weight ratio of about 1:1 to 1:4, sold by ISP as EasySpense[®] P-20. EasySpense[®] is described in U.S. Patent No. 6,158,803, the disclosure of which is hereby incorporated by reference in its entirety. In a particularly preferred embodiment, a powder blend of the partially neutralized monobutyl ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone is employed.

[0012] Another suitable polymer to disperse or retain ZPT is milk of Ganex (ISP), which is an aqueous suspension of Ganex[®] 216 (ISP), a water-insoluble alkyl grafted polyvinyl pyrrolidone graft copolymer having a particle size at the submicron level. Milk of Ganex is described in U.S. Patent No. 6,624,242, the disclosure of which is hereby incorporated by reference in its entirety. In a preferred embodiment, an aqueous suspension of a water-insoluble C₁₆ alkyl grafted polyvinyl pyrrolidone graft copolymer having a particle size at the submicron level.

[0013] Still another useful polymer herein is a partially netralized linseed oil-modified dicarboxylic acid half-ester of maleic acid. This material is commercially

available as a liquid from Ashland Chemical under the tradename Bomol 4N. This product is neutralized with 2-aminopropanol to a neutral pH.

[0014] Mixtures of the above polymers also may be used. The concentrate according to this invention includes ZPT, at least one of the above-described polymers and a suitable carrier. A preferred suitable carrier is water. The ZPT can be present in the concentrate in an amount of 1-55, preferably 5-50 and most preferably 10-40% by weight. The concentrate can contain conventional adjuvants, e.g., suspending agents, defoamers and thickening agents, known in the art in amounts up to about 10% by weight.

[0015] The polymer can be present in the concentrate generally in an amount of 0.1 to about 15% by weight. In the case of polymer a) the polymer preferably can be present in an amount of about 0.1-10, more preferably 0.5-5, and most preferably 1-4% by weight. In the case of polymer b) the polymer preferably can be present in an amount of about 2-15, more preferably 3-12, and most preferably 4-10% by weight. In the case of polymer c) the polymer preferably can be present in an amount of about 0.1-15, more preferably 0.5-12, and most preferably 1-10% by weight. The optimum amount of polymer present depends on, e.g., the polymer and active selected, the ZPT particle size, etc. and can readily be determined by one of ordinary skill in the art.

[0016] Personal care products according to this invention feature ZPT and at least one of the above-described polymers. In the end use personal care product, the ZPT can be present in an amount of 0.001-10, preferably 0.01-5 and more preferably 0.1-2% by weight. For anti-dandruff applications, e.g., anti-dandruff shampoos, it is preferred that the ZPT be present in an amount of 0.1-2% by weight.

[0017] The polymer can be added to the personal care product by known techniques. For example, the polymer can be added directly to the ZPT containing personal care product. In a preferred embodiment, the concentrate of this invention is incorporated into the process for manufacturing the personal care product. The following examples further illustrate the invention.

EXAMPLES

[0018] Described below is a test shampoo matrix used to incorporate the various polymeric dispersants with ZPT. A second test shampoo matrix evaluated was a commercial shampoo matrix. However, these formulations are merely representative and it is understood that the invention can be practiced, e.g., with other shampoos and personal care compositions containing various surfactants, blends of surfactants and adjuvants known in the art. See, for example, U. S. Patent No. 7,026,308, the disclosure of which is hereby incorporated by reference in its entirety.

Test Shampoo Matrix

Order of addition	Ingredient	Wt in 90 parts
1	Deionized water	43.61
2	Cocamidopropyl Betaine (Miratene CB)	8.00
3	Sodium Laureth Sulfate (Rodapex ES-2)	17.50
4	Ammonium Lauryl Sulfate (Rodapon L-22)	17.50
5	Ceraphyl 41	1.00
6	Liquid Germall Plus	0.30
7	Citric Acid (25% aq. sol'n)	0.09
8	Sodium Chloride (25% aq. sol'n)	2.00
	Sodium Hydroxide (50% aq. sol'n)	To pH 5.91
	Total	90.00

Procedure:

1. Weigh water into a suitable container, start mixing.
2. Add ingredients one at a time in order indicated above.
3. Mix well in between each addition.

[0019] Shampoo matrices containing bio-active materials and polymeric additives were prepared. Polymeric additives were first incorporated into commercial ZPT dispersions. The fortified commercial ZPT dispersions were then added and homogenized with the shampoo matrices.

1.83% Zinc pyrithione and 0.19% Ganex 216 fine suspension in water (10% solid) in shampoo base

[0020] 1.83% Zinc Pyrithione, 0.19% Ganex emulsion and 89.83% shampoo base was formulated as follows: a premix oil was prepared by mixing 6.08 g zinc pyrithione (Arch 30% suspension concentrate) with 0.34% Ganex 216 fine suspension in water (pre-dispersed with EasySpense (ISP) in water) in a 10 ml vial. The pre-mixed sample was shaken vigorously and it was allowed to mix in a rotary wheel for four hours. 3.5 g of a shampoo matrix was weighed and added to a 50 ml container. 3.38 g of water and 45.03 g of a shampoo base were added to the container. This formulated sample was shaken vigorously and it was allowed to mix in a rotary wheel overnight. A homogeneous cloudy suspension was formed that separated over a weekend but was re-dispersible with moderate shaking.

1.83% Zinc pyrithione in shampoo base

[0021] 1.8% Zinc pyrithione in 89.73% shampoo base (containing water) made up to 100% with water was formulated as follows: 3.35 g of ~ 55% zinc pyrithione concentrate (Arch chemicals), was weighed and added to a 50 ml container. 3.47 g of water and 45.01 g of shampoo base were also added to the container. This formulated sample was shaken vigorously and it was allowed to mix in a rotary wheel overnight. A homogeneous cloudy suspension was formed that separated over the weekend but was re-dispersible with moderate shaking.

[0022] Table 1 summarizes compositions prepared for evaluating dispersion stability and effects of improvement in accordance with this invention.

Table 1 - Addition of polymers to ZPT concentrate

	Polymer	ZPT Concentrate (30% a.i.)
No Polymer (control)	0%	100%
Milk of Ganex	5%	95%
Milk of Ganex	10%	90%
Bomol 4N	5%	95%
Bomol 4N	10%	90%
EasySpense P20	2%	98%

[0023] Six samples containing 12 g of the mixed polymer/ZPT concentrate were prepared by mixing polymers and ZPT concentrate in the above percentage in a 4 dram vial. Each sample was initially shaken manually and left in a rotary wheel overnight. Samples were tested for phase stability.

[0024] In vitro simulated test using animal skin substrate was used to evaluate deposited ZPT from ZPT polymer concentrates and the various shampoos evaluated in accordance with this invention. Concentrates and shampoos were applied to the skin which is loaded with hair bundle, lathered and washed. The deposited active ZPT was extracted and determined analytically by techniques known in the art.

[0025] It was found that the addition of polymers a, b and c to the shampoo matrices evaluated resulted in an increase in dispersability and a considerable reduction in agglomeration of ZPT particles. Polymers a and b were found to provide enhanced deposition amounts, i.e., increased deposited zinc concentration on skin, compared to the control. In the case of polymers a and b in the commercial shampoo matrix, enhanced deposition amounts, i.e., from about 50 to greater than a 100% increased deposited zinc concentration on skin, were measured compared to the control. Moreover, the addition of polymers a, b and c into the shampoo matrices did not adversely affect important hair attributes such as wet combability, wet feel, dry combability, dry feel, shine or static of the shampoo compositions.

[0026] While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art.

CLAIMS

What is claimed:

1. A method for increasing the deposition of zinc pyrithione (ZPT) present in a personal care product without reducing its bioavailability and while maintaining the efficacy of said product, which comprises including in said product a polymer selected from the group consisting of:

- a) a powder blend of the partially neutralized alkyl ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone;
- b) an aqueous suspension of a water insoluble alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; and
- c) a partially neutralized linseed oil-modified dicarboxylic acid half-ester of maleic acid.

2. The method of claim 1 wherein said ZPT has a particle size of 0.5-5 μ .

3. The method of claim 1 wherein said ZPT has a particle size of 0.8-4 μ .

4. A concentrate comprising zinc pyrithione, a polymer selected from the group consisting of:

- a) a powder blend of the partially neutralized ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone; or
- b) an aqueous suspension of a water insoluble alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; or
- c) a partially neutralized linseed oil-modified dicarboxylic acid half-ester of maleic acid; and
- d) a carrier.

5. The concentrate of claim 4 wherein said carrier is water.
6. The concentrate of claim 4 wherein said ZPT has a particle size of 0.5-5 μ .
7. The concentrate of claim 4 wherein said polymer is present in an amount of 0.1-15% by weight.
8. A personal care product comprising ZPT and a polymer selected from the group consisting of:
 - a) a powder blend of the partially neutralized ester of poly (methyl vinyl ether maleic acid) and polyvinyl pyrrolidone; or
 - b) an aqueous suspension of a water insoluble alkylated grafted vinyl pyrrolidone graft copolymer having a submicron particle size; or
 - c) a partially neutralized linseed oil-modified dicarboxylic acid half-ester of maleic acid.
9. The personal care product of claim 8 wherein said ZPT has a particle size of 0.5-5 μ .
10. The personal care product of claim 8 wherein said ZPT is present in an amount of 0.001-10% by weight.
11. The personal care product of claim 9 that is an anti-dandruff shampoo.
12. The personal care product of claim 11 wherein said ZPT is present in an amount of 0.01-2% by weight.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 08/78665

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - A61Q 5/02 (2008.04)

USPC - 510/119

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
USPC: 510/119

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Electronic Databases Searched: USPTO WEST (PGPUB, EPAB, JPAB, USPT), Google Patent, Google Scholar. Search Terms Used: ZPT or zinc pyrithione, increas\$ adj deposi\$, vinyl pyrrolidone, water adj insoluble, dicarboxylic acid, maleic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,335,312 B1 (Coffindaffer et al.) 01 January 2002 (01.01.2002) entire document especially col 2, ln 63-67; col 56, ln 15-25; col 67, ln 54 to col 68, ln 18; col 31, ln 10-16; col 64, ln 42-47	1-12
Y	US 2002/0011584 A1 (Uchiyama et al.) 31 January 2002 (31.01.2002) especially para [0247]-[0248]	1-12

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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