

NON-SPHERICAL AND NON-PLATELET
PYRITHIONE SALTS

The present invention relates generally to method
5 for preparing particles of pyrithione salts, and more
specifically to methods of preparing particles of
pyrithione salts having non-spherical or non-platelet
forms, particularly needle or rod forms. The present
invention also relates to products made with the non-
10 spherical or non-platelet particles of pyrithione
salts.

Polyvalent metal salts of pyrithione (also known
as 1-hydroxy-2-pyridinethione; 2-pyridinethiol-1-oxide;
2-pyridinethione; 2-mercaptopyridine-N-oxide;
15 pyridinethione; and pyridinethione-N-oxide) are known
to be effective biocidal agents, and are widely used as
fungicides and bactericides in paints and personal care
products such as anti-dandruff shampoos. The
polyvalent metal salts of pyrithione are only sparingly
20 soluble in water and include magnesium pyrithione,
barium pyrithione, bismuth pyrithione, strontium
pyrithione, copper pyrithione, zinc pyrithione, cadmium
pyrithione, and zirconium pyrithione. The most widely
used divalent pyrithione salts are zinc pyrithione and
25 copper pyrithione.

Zinc and copper pyrithione are useful as
antimicrobial agents active against gram-positive and
negative bacteria, fungi, and yeasts. Zinc pyrithione
is used as an antidandruff component in shampoos, while
30 technical suspensions of zinc pyrithione and/or copper
pyrithione are used as preservatives in paints and
polymers. Synthesis of polyvalent pyrithione salts are
described in U.S. Patent No. 2,809,971 to Bernstein et
al. Other patents disclosing similar compounds and

processes for making them include U.S. Patent Nos. 2,786,847; 3,589,999; 3,590,035; 3,773,770.

Known methods for producing insoluble polyvalent salts of pyrithione result in platelet-shaped large particles having an average size greater than 2 micrometers (μm). These particles are either used directly, or converted into smaller spherical particles. Such small spherical particles of pyrithione salts are usually generated by a separate mechanical manipulation step (e.g., grinding or crushing) on larger particles or crystals that are made by conventional processes. For example, European Patent No. 70046 describes preparation of zinc pyrithione using organic solvents. This process results in production of large crystals of zinc pyrithione. A separate, optional grinding step is used to grind the large crystals and produce zinc pyrithione particles of smaller size. Small spherical particles of zinc pyrithione more easily form suspensions and provide a larger surface area for enhanced biocidal activity. However, grinding larger particles to produce smaller particles, as described in the prior art, generally results in substantial loss of useful product and are costly in terms of equipment, time, and energy required. In addition, alternative forms of pyrithione particles, such as rods, needles, or other shapes, cannot be produced by grinding.

Alternative forms of insoluble polyvalent pyrithione particles are often desirable because they offer certain physical properties that are not inherent in platelet or spherical forms. Elongated particles of pyrithione salts, such as rods, needles, ellipsoids,

and the like offer advantages such as a large and/or flat surface area for use in shampoos, soaps and paints. In addition, elongated particles are more easily isolable by conventional filtration methods than the platelet particles of the prior art.

U.S. Patent No. 5,540,860 to Hosseini et al. discloses a general method for producing several forms of copper pyrithione particles, such as rods, spheres, needles, platelets, and combinations thereof at processing temperatures of about 70°C or greater by using a variety of surfactants including POLYTERGENT 2A-1L, POLYTERGENT SLF-18, and TRITON X-100 surfactants. However, a general method of producing non-platelet or non-spherical forms of pyrithione salts is not disclosed. The present inventors have found that such a general method requires the use of lower temperatures and/or dispersants such as salts of polymerized alkyl naphthalene sulfonic acids. Neither of these parameters are disclosed in the '860 patent to Hosseini.

Thus, what is needed in the art is a general method of generating non-spherical or non-platelet particles of pyrithione salts in a single step production process at low temperatures. The present invention is believed to be an answer to that need.

In one aspect, the invention relates to a method for producing non-spherical and non-platelet particles of pyrithione salts, comprising reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble polyvalent metal salt in a carrier and in the presence of a dispersant at a temperature from about 20°C to

about 60°C to produce non-spherical and non-platelet particles of pyrithione salts.

In another aspect, the invention relates to non-spherical and non-platelet particles of pyrithione salts made by reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble polyvalent metal salt in a carrier and in the presence of a dispersant comprising from about 0.05 to about 10% by weight, based on the total weight of the reaction mixture, at a temperature from about 20°C to about 60°C to produce non-spherical and non-platelet particles of pyrithione salts, the non-spherical and non-platelet particles of pyrithione salt having a configuration selected from rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, tetrahedrons, hexahedrons (cube), octahedrons, dodecahedrons, icosahedrons, and combinations thereof.

In still another aspect, the present invention relates to a composition comprising non-spherical and/or non-platelet particles of pyrithione salt having a particle size of from about 0.1 to about 1 microns in width and from about 2 to about 50 microns in length. Advantageously, the particles are elongated and have an aspect ratio of from about 2 to about 500. Suitably, these particles have a shape or configuration selected from the group consisting of rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, tetrahedrons, hexahedrons (cube), octahedrons, dodecahedrons, icosahedrons, and combinations thereof. Alternatively, these particles can be employed in admixture with other pyrithione salts selected from the

group consisting of spheres, platelets, and combinations thereof.

In yet another aspect, the present invention relates to a shampoo or skin-care composition comprising a base fluid and non-spherical and/or non-platelet particles of pyrithione salt having a particle size of from about 0.1 to about 1 microns in width and from about 2 to about 50 microns in length. The base fluid is suitably a surfactant, a dispersant, or a combination thereof.

In still another aspect, the invention relates to a method for producing elongated particles of zinc pyrithione comprising reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble zinc salt selected from the group consisting essentially of zinc sulfate, zinc chloride, zinc acetate, and combinations thereof, in a carrier and in the presence of a dispersant comprising from about 0.05 and about 10% by weight, based on the total weight of the reaction mixture and selected from the group consisting essentially of salts of polymerized alkyl naphthalene sulfonic acid at a temperature from about 20°C to about 60°C to produce elongated particles of zinc pyrithione.

In yet another aspect, the invention relates to products made from the particles made from the method of the invention.

These and other aspects will become apparent upon reading the following detailed description of the invention.

The invention will be more fully understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a photomicrograph of rods and/or needles of zinc pyrithione prepared by the method of the invention viewed at 340X magnification; and

Fig. 2 is a photomicrograph of rods and/or needles
5 of zinc pyrithione prepared by the method of the invention viewed at 680X magnification.

It now has been surprisingly found, in accordance with the present invention, that a solution is provided to the problem of producing pyrithione salt particles
10 in forms other than platelet or spherical form, such as rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, cubes, and the like. The present inventors have solved this problem utilizing selected dispersants or a combination of dispersant and
15 surfactants, and a range of low processing temperatures which promote the formation of non-platelet forms of pyrithione salt particles. In one embodiment, pyrithione salt particles having an elongated form, such rods, needles may be produced in accordance with
20 the method of the present invention. The elongated pyrithione salt particles made by the method of the invention have excellent surface deposition properties due to the large surface area of the elongated particles. This large surface area results in improved
25 biocidal efficacy in shampoos, soaps and paints. In addition, the elongated particles made according to the method of the invention are more easily isolable by conventional filtration methods than the platelet or spherical particles of the prior art.

30 As used herein, the term "water-soluble salts of pyrithione" or "water-soluble pyrithione salts" include those salts of pyrithione in which the hydrogen atom of

the thiol group is substituted with a monovalent cation. The term "water-soluble polyvalent metal salt" refers to those water-soluble salts in which the cation has a charge of +2 or greater. The term "non-platelet" refers to any form other than platelet form. The term "elongated" is defined herein as any form having an aspect ratio greater than about 1.0, for example, rods, needles, or ellipsoids. As defined herein, the term "aspect ratio" means the ratio of length to width (L:W). The terms "particles of pyrithione salts" or "pyrithione salt particles" as used herein refer to those salts of pyrithione that form precipitates and are essentially insoluble or sparingly soluble in the surrounding medium. The term "induce" as used herein refers to any cause that results in morphological change of the non-spherical and non-platelet particles of the invention, for example, changes in temperature, pH, or pressure. The term "morphological transformation" is used herein to refer to the process of changing from one crystalline form to another crystalline form, for example, from elongated particles to small platelets. The term "more stable form" refers to a thermodynamically more stable form than non-spherical and non-platelet particles. The term "metastable" refers to a crystalline state that may be altered by application of external environmental factors. The term "dispersant" as used herein refers to a compound that promotes separation of solid particles, and that does not promote foaming.

30 In accordance with the process of the present invention, pyrithione or a water-soluble salt of pyrithione is reacted with a water-soluble salt of a

selected polyvalent metal in the presence of a dispersant to form elongated pyrithione salt particles as a precipitate. Pyrithione in its acid form, or a water-soluble salt of pyrithione may be used in the reaction. Useful water soluble salts of pyrithione preferably include an ammonium ion or an alkali metal ion such as sodium. Accordingly, exemplary water soluble salts of pyrithione include sodium pyrithione, potassium pyrithione, lithium pyrithione, ammonium pyrithione, and combinations of these. The most preferred water-soluble salt of pyrithione useful in the present invention is the sodium salt (i.e., sodium pyrithione). The amount of pyrithione or water-soluble salt of pyrithione can vary over a wide range and establishing a useful amount is within the capabilities of the ordinary skilled practitioner based on the stoichiometry of the reaction and the required amount of particles that must be generated. A preferred amount of pyrithione or water-soluble pyrithione salt is from about 3% to about 52% by weight of the total weight of the reaction mixture.

Exemplary water-soluble polyvalent metal salts useful in accordance with the method of the invention include example zinc salts, tin salts, cadmium salts, copper salts, zirconium salts, magnesium salts, aluminum salts, and the like. Combinations of these salts may also be employed. Useful counterions for these metals include nitrates, acetates, sulfates, halides or combinations thereof. Preferred water-soluble polyvalent metal salts include zinc chloride (ZnCl_2), copper chloride (CuCl_2), zinc acetate ($\text{Zn}(\text{O}_2\text{CCH}_3)_2$) and zinc sulfate (ZnSO_4). The amount of

water-soluble polyvalent metal salt can vary depending on the amount of water-soluble salt of pyrithione. The molar ratio of pyrithione or water-soluble salt of pyrithione to the water-soluble polyvalent metal salt is generally in the range from about 1:2 to about 1:8. Preferably, a slight stoichiometric excess (e.g., 5% of water-soluble polyvalent metal salt by weight over pyrithione or water-soluble salt of pyrithione) is desirable to ensure a complete reaction.

Useful media or carriers for the reaction include aqueous media such as water, or water in combination with one or more organic solvent(s). Useful organic solvents include alcohols, such as methanol, ethanol, amines such as diethanolamine, ether, esters, and the like. Additional salts, such as potassium chloride, sodium chloride, magnesium chloride, and the like may also be added to the reaction medium to control particle length and shape. Addition of these salts result in elongated particles having a flatter appearance. Preferably, the additional salts are included in the reaction mixture in an amount of from 0.1% by weight to about 10% by weight, more preferably from about 1% by weight to about 8% by weight, and most preferably from about 3% by weight to about 6% by weight, all based on the total weight of the reaction mixture. A particularly useful amount of additional sodium chloride added to the reaction mixture to control particle size and shape is 5% by weight based on the total weight of the reaction mixture.

Pearlizing agents, such as TiO_2 -coated mica, may also be included to promote particle growth. Generally, these optional ingredients comprise from

about 0.1 to about 20% by weight, more preferably from about 1 to about 15% by weight, and most preferably from about 1 to about 6% by weight, all based on the total weight of the reaction mixture.

5 A dispersant is included in the reaction mixture to promote formation of elongated particles of pyrrithione salt. Preferably, the dispersant is a salt of polymerized alkyl naphthalene sulfonic acids, such as "DARVAN 1" (sodium naphthalene sulfonic acid
10 formaldehyde, a product of R.T. Vanderbilt Co. Inc.), "DEMOL N" (sodium salt of naphthalene sulfonic acid, a product of Kao Chemicals), "DAXAD 11" (sodium salt of polymerized alkyl naphthalene sulfonic acids, a product of W.R. Grace & Co.), "TAMOL N" (sodium salt of
15 condensed naphthalene sulfonic acid, a product of Rohm and Haas Co.), "HAROL KG" (potassium salts of polymerized alkyl naphthalene sulfonic acids, a product of Graden Chemical Co.), "HAROL RG-71" (sodium salts of polymerized alkyl naphthalene sulfonic acids, a product
20 of Graden Chemical Co.), "LOMAR LS" (sodium salt of condensed monomaphthalene sulfonic acid, a product of Henkel Corp.) and the like. Additional useful dispersants are disclosed in McCutcheons Handbook of Functional Materials (North American Volume I, 1992, pp
25 117-137). Combinations of two, three, four, or more dispersants as described herein may also be used according to the invention.

 The dispersants employed in the method of the present invention may suitably be combined with a
30 surfactant. Useful surfactants may be selected from the classes of surfactants known as nonionics, anionics, cationics, and amphoterics (the latter being

also commonly referred to as "zwitterionics"). The surfactants are suitably employed singly, or in combinations of two, three, or even four or more surfactants selected from the above-mentioned four
5 classes.

Useful nonionic surfactants include linear alcohol alkoxyates, such as the linear alcohol ethoxyates, ethoxyated/propoxyated block copolymers, ethoxyated/propoxyated fatty alcohols, and
10 polyoxyethylene cetyl ethers, and the like. Useful linear alcohol alkoxyates are commercially available, for example, under the registered trademark POLY-TERGENT SL-42, a product of Olin Corporation. If desired, the alcohol alkoxyate is suitably end-capped
15 with a lower alkyl group, and such a product is commercially available as POLY-TERGENT SLF-18, a propylene oxide-capped linear alcohol alkoxyate that is also a product of Olin Corporation, and these end-capped linear alcohol alkoxyates are notably low
20 foaming during use. Also advantageous for use in accordance with the present invention are surfactants within the group commercially available as POLY-TERGENT SLF-18B series surfactants, which are surfactants characterized by enhanced biodegradability (also
25 products of Olin Corporation), being alkene oxide-capped linear alcohol alkoxyates, containing ethylene oxide moieties in the backbone, and suitably also containing at least one propylene oxide moiety in the backbone, as disclosed, for example, in U.S. Patents
30 4,925,587 and 4,898,621.

Other useful nonionic surfactants include one commercially available as NEODOL 91-6, a registered

trademark surfactant product of Shell Chemical. This surfactant is a detergent range mixture of C₉-C₁₁ linear primary alcohol ethoxylates having an average of six moles of ethylene oxide per mole of alcohol. Other
5 useful nonionic surfactants include those containing a linear C₉-C₁₁ carbon chain and five or six ethylene oxide or propylene oxide groups per molecule.

Useful anionic surfactants include alkyl diphenylether disulfonates, alkyl phenyl ethoxylated
10 phosphate esters, carboxylated linear alcohol alkoxyates, linear alkyl benzene sulfonic acid, diisobutyl sulfosuccinate, and alkyl sulfonates. Useful anionics also include the alkylated diphenyl oxide sulfonates, and their methods of preparation are
15 well-known, as illustrated by the disclosures of U.S. Patents 3,264,242; 3,634,272; and 3,945,437. Commercial methods of preparation of the alkylated diphenyl oxide sulfonates generally do not produce species which are monoalkylated, monosulfonated,
20 dialkylated or disulfonated. The commercially available species typically are predominately (greater than 90 percent) disulfonated and are a mixture of mono- and di- alkylated with the percentage of dialkylation being about 15 to about 25 percent, and
25 the percentage of monoalkylation being about 75 to 85 percent. Most typically, the commercially available species are about 80 percent monoalkylated and 20 percent dialkylated.

Two illustrative commercially available solutions
30 containing alkylated diphenyl oxide sulfonate surfactants are DOWFAX 8390 and DOWFAX 8390A surfactants, trademarked products of The Dow Chemical

Company. In each, the alkyl group is predominantly a hexadecyl C₁₆ group. These products are suitably employed in a solution fully or partially neutralized with ammonium hydroxide if desired.

5 An advantageous anionic surfactant is also provided by reacting the above-described alkylated diphenyl oxide sulfonates with a piperazine compound to produce a molar ratio of sulfonate compound to piperazine compound of between about 10:1 and about
10 1:10, preferably between about 2:1 and about 1:2. Although any piperazine compound can be used for such reaction, preferred compounds include those selected from the group consisting of 1,2-aminoethyl piperazine, 1,4-piperazinediethane sulfonic acid, anhydrous
15 piperazine, hydrated piperazine, and combinations thereof.

Other useful anionics are polycarboxylated alcohol alkoxylates, preferably those selected from acids or organic or inorganic salts of the following:
20 polycarboxylated linear alcohol alkoxylates, polycarboxylated branched alcohol alkoxylates, polycarboxylated cyclic alcohol alkoxylates, and combinations thereof. These polycarboxylated alcohol alkoxylates typically contain at least two succinic
25 acid radicals per molecule. Preferred polycarboxylated alcohol alkoxylates are those having a backbone containing both poly(propylene oxide) and poly(ethylene oxide) blocks, and such preferred polycarboxylated alcohol alkoxylates are readily commercially available,
30 for example, as POLY-TERGENT CS-1, a trademarked surfactant of Olin Corporation. If desired, at least a portion of the acid groups on the polycarboxylated

alcohol alkoxylate are neutralized with a base to provide the corresponding salt. Suitable bases include alkali metal hydroxides, alkaline earth metal hydroxides, and metal-free hydroxides, including
5 potassium hydroxide, ammonium hydroxide, calcium hydroxide, magnesium hydroxide, ammonia, mono-, di- and tri-ethanol amines, and combinations thereof. Sodium hydroxide is preferred, and although potassium hydroxide can be employed, it is not
10 preferred. The organic or inorganic base is preferably employed in at least an equimolar amount relative to the number of moles of polycarboxylated alcohol alkoxylated used. The polycarboxylated alcohol may also contain a polycarboxylic acid, for example,
15 polyacrylic acid, along with the starting alcohol alkoxylate and esters of the alkoxylate of the polycarboxylic acid.

Although individually the cationic and the amphoteric surfactants are acceptable for use in the
20 process of the present invention, they may also be used in combination with at least one surfactant from one of the other classes. Illustrative cationics include alkyl triammonium halide, non-linear alkyl dimethyl halide and alkyl dimethyl benzyl ammonium halide-
25 containing surfactants. Illustrative amphoteric surfactants include polyglycol ether derivatives, ethoxylate oxazoline derivatives, lauramidopropyl betaine, and lecithin.

Suitable blends can be employed in the process of
30 the present invention based on various combinations of the above-described surfactants. Such a blend can be any combination of two or more surfactants, between or

within the above-described four broad classes of surfactants. Combinations can include blends of: anionic with anionic, anionic with nonionic, anionic with cationic, anionic with amphoteric, cationic with cationic, cationic with amphoteric, nonionic with nonionic, nonionic with amphoteric, and amphoteric with amphoteric. Likewise, ternary and quaternary blends of surfactants by selecting three or four surfactants, respectively, from within or among the above-described classes.

Suitably, any single or combination of two, three or four surfactants from the following illustrative list are suitably employed: (a) nonionics, including alkoxyated linear alcohols (such as POLY-TERGENT SLF-18 surfactant, a product of Olin Corporation), linear alcohol ethoxylates (such as NEODOL 91-8 surfactant, a product of the Shell Corporation), ethoxylated linear alkyl benzene (such as TRITON X-100 surfactant, a product of Union Carbide Corporation), and EO/PO block copolymers (such as POLY-TERGENT E-17A surfactant, a product of Olin Corporation); (b) anionics, including alkyl diphenyl ether disulfonates (such as POLY-TERGENT 2A1 surfactant, a product of Olin Corporation), alkyl phenyl ethoxylated phosphate esters (such as Wayfos M-60 surfactant, a product of Olin Corporation), carboxylated linear alcohol alkoxyates (such as POLY-TERGENT CS-1 surfactant, a product of Olin Corporation), linear alkyl benzene sulfonic acid (such as BIOSOFT S-130 surfactant, a product of Stepan Company), alpha-olefin sulfonates (such as BIO TERG AS-40 surfactant, a product of Stepan Company), dialkylsulfosuccinates (such as AROWET SC-75

surfactant, a product of Arol Chemical Products), and alkyl sulfates (such as STEPANOL SLS surfactant, a product of Stepan Company); (c) cationics including alkyl triammonium halides (such as CTAB surfactant, a product of VWR Scientific Inc.), polyoxyethylene cocoamine (such as MAZEEN surfactant, a product of PPG Industries), primary alkyl amines (such as ARMEEN surfactant, a product of Akzo Chemical Co.), dicoco dimethyl ammonium halide (such as JET QUAT surfactant, a product of Jetco Chemical Inc.), di-isodecyl dimethyl ammonium halides (such as AMMONYX K9 surfactant, a product of Stepan Company), and diethyl aminoethyl stearate (such as CERASYNT 303 surfactant, a product of ISP Van Dyke); and, (d) amphoterics, including polyglycol ether derivatives (such as ALBEGAL A surfactant, a product of Ciba-Geigy), ethoxylated oxazolin derivatives (such as ALKATERG T-IV surfactant, a product of Angus Chemicals), lauramide propyl betain (such as LEXAINE C surfactant, a product of Inolex Chemicals), lecithin (such as CANASPERSE surfactant, a product of Can Amoral), disodium cocoamphodiacetate (such as MONATERICS surfactant, a product of Mona Industries), complex fatty amine salt (such as MAFO 13 surfactant, a product of PPG Industries), and cocoamine oxide (such as MACKAMINE CO surfactant, a product of the McIntyre Group Ltd.).

The dispersant or disperant/surfactant combination is preferably employed in a total amount of between about 0.05 and 10%, more preferably between about 0.1 and 5%, most preferably between about 0.5 and about 1.5% by weight, based on the total weight of the reaction mixture.

The temperature of the reaction may be any temperature which permits precipitation of elongated particles of pyrithione salt. Preferable temperatures for the reaction are in the range of from between about 5 20°C and about 60°C, and more preferably between about 30°C and about 55°C. In addition, the reaction may be gently agitated to promote formation of elongated particles. Stirring at high rpm of greater than 150 rpm tends to produce metastable particles that can be 10 induced to undergo a morphological transformation to more stable small particles having sizes about 1 μ m or less by perturbing the environment of the particles. Generally, gently stirring the reaction at 150 rpm or less, and preferably about 100 rpm, most preferably 15 from 50 to 100 rpm, is sufficient to promote formation of elongated particles that are physically stable against thermal degradation up to 60°C.

In order to produce the elongated particles of the invention, pyrithione or a selected water-soluble salt 20 of pyrithione and a selected water-soluble polyvalent metal salt are reacted in the presence of a surfactant or combination of surfactants in any suitable reaction vessel at a temperature below 70°C, and preferably between about 20°C and 60°C. The particles formed by 25 the method of the invention can take any nonspherical or non-platelet form, such as rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, and the like. The particles formed by the present invention may also take the form of tetrahedrons, 30 hexahedrons (cube), octahedrons, dodecahedrons, icosahedrons, and the like.

In a preferred embodiment, sodium pyrithione is reacted with zinc chloride or zinc sulfate in the presence of salt (e.g., sodium chloride) and a selected dispersant or combination of dispersant and surfactant at about 35°C to form zinc pyrithione having rod and/or needles shapes, along with aqueous sodium chloride or aqueous sodium sulfate as by-products. The method of the invention may also be utilized in a "continuous" process in which the zinc pyrithione particles are collected, and the mother liquor containing aqueous sodium chloride or sodium sulfate is recycled back to the reaction vessel to provide a source of additional salt. An optional filter (e.g., carbon or charcoal filter) may be employed to remove impurities such as colored organic compounds from the mother liquor. Particles of zinc pyrithione so formed have a "needle" and/or "rod" appearance as shown in Figs. 1 and 2. Generally, the rods or needles of zinc pyrithione salt produced in accordance with the present invention are between about 0.1 and about 1 μm in width and between about 2 and about 50 μm in length. Accordingly, the aspect ratio of the elongated particles is greater than about 1, and more preferably from about 2 to about 500.

The non-spherical and/or non-platelet pyrithione salt particles produced by the method of the invention at a mixing speed of greater than 150 rpm have been observed to undergo a morphological transformation to small particles when the particles are subjected to certain external environmental factors. While not wishing to be bound by any particular theory, the applicants postulate that the non-spherical and/or non-platelet particles produced by the method of the

invention at rpm greater than 150 rpm are in a metastable state and can be induced to undergo a morphological transformation to more stable small particles having sizes about 1 μm or less by perturbing the environment of the particles. Accordingly, it is the applicants' intention to cover all those more stable crystalline forms that result from morphological transformation of the metastable particles in accordance with the present invention.

10 The particles produced according to the method of the invention are useful in a variety of items such as personal care products (soaps, shampoos, and the like), paints, coatings, fertilizers, and foodstuffs. For example, zinc pyrithione particles made according to the method of the invention are a useful antidandruff additive to antidandruff shampoos.

 Alternatively, the mixture of particles and by-products may be added to commercial products directly without further purification. Illustratively, the by-products (e.g., aqueous sodium chloride or aqueous sodium sulfate) are useful in shampoo or soap formulations as thickeners. An additional benefit derived from the needle/rod shape is the ease of separation of these particles from the reaction medium.

25 The following examples are intended to illustrate, but in no way limit the scope of the present invention. All parts and percentages are by weight and all temperatures are in degrees Celsius unless explicitly stated otherwise. In the following Examples "q.s." means quantity sufficient.

EXAMPLES

EXAMPLE 1: Production of Needles of Zinc Pyrithione

To a 1200 g of 6% sodium pyrithione solution is added 6.0 g of dispersant (sodium salt of polymerized alkyl naphthalene sulfonic acid sold under the tradename DARVAN 1 available from R.T. Vanderbilt & Company) in a 3000 ml jacketed cylindrical pyrex reactor. The temperature is raised to 35°C and maintained throughout the reaction sequence. The agitation speed is set at about 100 rpm 437 g of a 10% aqueous zinc sulfate monohydrate solution was pumped into the reactor over 50 to 60 minutes using a peristaltic pump. The product slurry is isolated by filtration with a Buchner funnel and washed with water.

Upon analysis, the isolated reaction product was about 19.6% zinc pyrithione by weight. Under microscopic examination, the isolated product was found to consist of particles of zinc pyrithione having rod and/or needle shape.

20

EXAMPLE 2: Production of Needles of Zinc Pyrithione

A solution of 355 g of 16.9% by weight sodium pyrithione, 845 ml water, and 2.4 g of DARVAN 1 (as described in Example 1) was placed in a 2000 ml jacketed reaction vessel and warmed to 39°C. A solution of 198.5 g of 20% by weight zinc sulfate monohydrate and 595.4 ml water was added over about 68 minutes at a stirring speed of 400 rpm. Following addition of the zinc sulfate solution, the mixture was stirred for 20 minutes and the product is isolated by filtration and washed. The isolated precipitate is

30

assayed and found to contain about 33.6% by weight zinc pyrithione.

The zinc pyrithione particles were resuspended in an aqueous solution of water and DARVAN 1 (sodium naphthalene sulfonic acid formaldehyde) to form
5 solution containing 25% by weight zinc pyrithione and 0.1% by weight DARVAN 1. Photomicrographs showed that the particles had an elongated form and appeared as rods or needles (See Figs. 1 and 2). The width of the
10 rods and needles varied from about 0.1 to about 1 μ m, and the length of the rods and needles varied from about 2 to about 10 μ m. In addition, small platelets having a diameter of 0.1 to 1 micron were also present.

15 EXAMPLE 3: (Proposed Example) Antidandruff Shampoo Formulation I

An antidandruff shampoo composition is made using needle and rod forms of zinc pyrithione made as described in Examples 1 and 2 in combination with the
20 following ingredients:

Component A:

Water	41.0%
Magnesium aluminum silicate	1.0%
Hydroxypropyl methylcellulose	0.8%

25

Component B:

Zinc Pyrithione (needles/rods, 25% aqueous dispersion)	4.0%
---	------

Component C:

30 Cocamide DEA	1.0%
-----------------	------

Component D:

	Triethanolamine lauryl sulfate, 40%	40.0%
	Triethanolamine, 99%	3.2%
	FD&C Blue No. 1 (0.2%)	1.5%
5	FD&C Yellow No. 5 (0.1%)	0.5%
	Fragrance	q.s.

The antidandruff shampoo composition is made as follows:

- 10 Component A is prepared by heating water to 70°C and dissolving the other two components with stirring (about 1500 rpm). The temperature of the mixture is lowered to 50°C, and component B is added, and stirring continued for 5 minutes. Stirring speed is reduce
- 15 stirring to ~300 rpm. Component C is melted in a separate container, and added to the A/B mixture. The heat is removed and component D is added while the mixture cooled.

20 EXAMPLE 4: (Proposed Example) Another antidandruff Shampoo

- Another antidandruff shampoo composition is made using needle and rod forms of zinc pyrithione made as described in Examples 1 and 2 in combination with the
- 25 following ingredients:

Component A:

	Deionized water	76.0%
	Ammonium lauryl sulfate	15.0%
30	Cocamide DEA	2.0%

Component B:

	Di(hydrogenated) tallow phthalic	
	acid amide	5.0%
5	Zinc Pyrithione (needles/rods,	
	25% aqueous dispersion)	4.0%

Component C:

	Preservative	q.s.
--	--------------	------

Component D:

	Citric Acid, 50% aq. Solution, OR	
10	Sodium hydroxide, 50% aqueous solution	q.s.

Component E:

	Ammonium chloride	q.s.
--	-------------------	------

15 The antidandruff shampoo composition is made as follows:

In separate containers, components A and B are each mixed well. Component A is heated to 60°C and component B is added. The mixture is stirred for 30 minutes. The mixture is then cooled to 50°C, and
20 component C is added. The pH of the resulting mixture is adjusted to 5.0-6.2 with component D, and the viscosity is adjusted with component E.

25 EXAMPLE 5: (Proposed Example) Conditioning
antidandruff Shampoo

An antidandruff shampoo and conditioner composition is made using needle and rod forms of zinc pyrithione made as described in Examples 1 and 2 in combination with the following ingredients:

Component A:

Deionized Water	77.0%
Ammonium lauryl sulfate	20.0%
Cocamide DEA	2.0%

5 Component B:

Di(hydrogenated) tallow phthalic acid amide	4.0%
Zinc Pyrithione (needles/rods, 25% aqueous dispersion)	4.0%

10 Dimethicone, 12,000 cps	0.5%
----------------------------	------

Component C:

Preservative	q.s.
--------------	------

Component D:

Citric acid, 50% aqueous solution, OR	
15 Sodium hydroxide, 50% aqueous solution	q.s.

Component E:

Ammonium chloride	q.s.
-------------------	------

20 The antidandruff shampoo and conditioner composition is made as follows:

In separate containers, components A and B were each mixed well. Component A is heated to 60°C and component B is added. The mixture is stirred for 30 minutes. The mixture is then cooled to 50°C, and
25 component C is added. The pH of the resulting mixture is adjusted to 5.0-6.2 with component D, and the viscosity is adjusted with component E.

EXAMPLE 6: (Proposed Example) Another antidandruff
30 Shampoo Another antidandruff shampoo and conditioner composition is made using needle and rod forms of zinc

pyrithione made as described in Examples 1 and 2 in combination with the following ingredients:

Component A:

5	Deionized water	21.75%
	Guar hydroxypropyl trimonium chloride	0.30%
	Magnesium Aluminum Silicate	0.70%
	Zinc Pyrithione (needles/rods, 25% aqueous dispersion)	4.0%

10 Component B:

	Sodium laureth sulfate	30.0%
	Ammonium xylene sulfonate, 40% aq.	02.0%

Component C:

	Tricetylammonium chloride	0.50%
15	Cetyl alcohol NF	0.40%
	Stearyl alcohol	0.40%
	Glycol distearate	2.00%

Component D:

	Cocamide MEA	1.70%
20	Ammonium lauryl sulfate	36.00%

Component E:

	Preservative	0.05%
	Fragrance and dye	q.s.

Component F

25	Citric acid, 25% aqueous solution	q.s.
----	-----------------------------------	------

The antidandruff shampoo and conditioner composition is made as follows:

30 Component A is prepared by heating water to 50°C and dispersing the guar hydroxypropyl trimonium chloride and the magnesium aluminum silicate with rapid agitation. The zinc pyrithione dispersion is added to

this combination with stirring. The pH of component A is adjusted to 4.5-5.0 with component F. Both components of B were slowly added to component A, mixing well. The pH of the mixture is adjusted to 5.7-6.3 with component F. In a separate container, component C is heated to 70-75°C. The A/B mixture is heated to 60°C and blend with component C, mixing well. Both components of D were added to the hot mixture, and stirred well. The pH of the mixture is adjusted to 5.7-6.3 with component F. The mixture is cooled to 40-45°C, and component E is added with stirring. If desired, the viscosity of the product can be increased by adding 0.05-1% sodium chloride.

EXAMPLE 7: (Proposed Example) "Extra Body"
Antidandruff Shampoo

An "extra body" antidandruff shampoo and conditioner composition is made using needle and rod forms of zinc pyrithione made as described in Examples 1 and 2 in combination with the following ingredients:

Component A:

	Deionized Water	62.6%
25	Zinc Pyrithione (needles/rods, 25% aqueous dispersion)	4.0%

Component B:

	Methyl Paraben	0.30%
	Propyl Paraben	0.10%
	Propylene Glycol	0.50%
30	Sodium Chloride	0.50%

Component C:

Triethanolamine lauryl sulfate

20.0%

Cocamide MEA

4.0%

5 Ethylene glycol distearate

7.0%

Component D:

Cocodimonium hydrolyzed animal protein 1.00%

Component E:

FD&C Blue No. 1

q.s.

10 Component F:

Citric Acid, 50% aqueous solution

q.s.

The antidandruff shampoo and conditioner composition is made as follows:

15 Component A is heated to 60°C. The ingredients of component B were added with good stirring until dissolved. The ingredients of component C were added to the mixture sequentially, and heated with mixing at 60°C. The mixture is cooled with stirring to 40°C, and
20 components D and E were added with stirring. The pH of the final composition is adjusted to 4.7 with component F.

Although the invention has been shown and
25 described with respect to illustrative embodiments thereof, it should be appreciated that the foregoing and various other changes, omissions and additions in the form and detail thereof may be made without departing from the spirit and scope of the invention as
30 delineated in the claims.

WHAT IS CLAIMED IS:

1. A method for producing non-spherical and/or non-platelet particles of pyrithione salts characterized by
5 reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble polyvalent metal salt in a carrier and in the presence of a dispersant, optionally in the presence of a surfactant, at a temperature from about 20°C to about 60°C to produce
10 non-spherical and non-platelet particles of pyrithione salts.
2. The method of claim 1 characterized in that said water-soluble salt of pyrithione is selected from the
15 group consisting of sodium pyrithione, potassium pyrithione, lithium pyrithione, ammonium pyrithione, and combinations thereof.
3. The method of claim 1 characterized in that said
20 water-soluble polyvalent metal salt is a divalent salt selected from the group consisting essentially of zinc salts, tin salts, cadmium salts, bismuth salts, copper salts, zirconium salts, magnesium salts, aluminum salts, nitrate salts, acetate salts, sulfate salts,
25 halide salts, and combinations thereof, and wherein said divalent salt is selected from the group consisting of zinc sulfate, zinc chloride, zinc acetate, copper chloride, bismuth acetate, and combinations thereof.



4. The method of claim 1 characterized in that the ratio of said pyrithione or water-soluble salt of pyrithione to said water-soluble polyvalent metal salt is in the range from about 1:2 to about 1:8.

5

5. The method of claim 1 characterized in that said dispersant is selected from the group consisting of sodium salts of polymerized alkyl naphthalene sulfonic acids and combinations thereof.

10

6. A composition characterized by containing non-spherical and/or non-platelet particles of pyrithione salt having a particle size of from about 0.1 to about 1 microns in width and from about 2 to about 50 microns in length.

15

7. The composition of claim 6 characterized in that said particles of pyrithione salt are selected from the group consisting of rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, tetrahedrons, hexahedrons (cube), octahedrons, dodecahedrons, icosahedrons, and combinations thereof.

20

8. A shampoo or skin-care composition comprising a base fluid and non-spherical and/or non-platelet particles of pyrithione salt having a particle size of from about 0.1 to about 1 microns in width and from about 2 to about 50 microns in length.

25



9. Non-spherical and/or non-platelet particles of pyrithione salts characterized by reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble polyvalent metal salt in a carrier and in the presence of a dispersant comprising from about 0.1 to about 10% by weight, based on the total weight of the reaction mixture, optionally in the presence of a surfactant, at a temperature from about 20°C to about 60°C to produce non-spherical and/or non-platelet particles of pyrithione salts, said non-spherical and/or non-platelet particles of pyrithione salt having a configuration selected from rods, needles, cylinders, cones, ellipsoids, prisms, parallelepipeds, pyramids, tetrahedrons, hexahedrons (cube), octahedrons, dodecahedrons, icosahedrons, and combinations thereof.

10. A method for producing elongated particles of zinc pyrithione characterized by reacting pyrithione or a water-soluble salt of pyrithione and a water-soluble zinc salt selected from the group consisting essentially of zinc sulfate, zinc chloride, zinc acetate, and combinations thereof, in an aqueous medium and in the presence of a dispersant comprising from about 0.05 and about 10% by weight, based on the total weight of the reaction mixture and selected from the group consisting of salts of polymerized alkyl naphthalene sulfonic acid at a temperature from about 20°C to about 60°C to produce elongated particles of zinc pyrithione having an aspect ratio of from about 2 to about 500.



11. Stable non-spherical and/or non-platelet particles of pyrithione salts characterized by being physically stable against thermal degradation up to a temperature of 60°C, said particles being made by reacting a
5 reaction mixture comprising pyrithione or a water-soluble salt of pyrithione and a water-soluble polyvalent metal salt in a carrier and in the presence of a dispersant comprising from about 0.1 to about 10% by weight, based on the total weight of the reaction
10 mixture, while stirring said reaction mixture at a mixing speed of less than 150 rpms.