

Description

i) Field of the Invention

This invention relates to finely powdered zinc salts of 2-mercaptopyridine-N-oxide and a method for producing same. It also relates to antibacterial compositions comprising such zinc salts.

ii) Description of the Prior Art

Polyvalent metal salts of 2-mercaptopyridine-N-oxide (which may be hereinafter referred to simply as polyvalent metal salts) are known to be effective as antibacterial agents and are widely used not only as ordinary bactericides, but also as dandruff removers being added to shampoo or rinse. The polyvalent metals of the salts are, for example, calcium, magnesium, barium, strontium, zinc, cadmium, tin or zirconium, of which zinc is widely used.

EP—A—70 046 describes the preparation of zinc-2-mercaptopyridine-N-oxide in the form of fine crystals having an average size of 0.5 to 2 μm . This finely divided zinc compound is used in the preparation of anti-dandruff shampoos. Further, US—A—3 723 325 discloses the use of antibacterial zinc salt of 2-mercaptopyridine-N-oxide in particulate form with average particle sizes ranging from 0.2 to about 3 μm in shampoos.

However, these polyvalent metal salts, e.g. zinc salt has a solubility in water of 15 ppm at 25°C and is thus sparingly soluble in water with a high specific gravity, so that they are sold and supplied in the form of a powder or an aqueous dispersion. Because of the high specific gravity, the metal salts have the disadvantage that even when suspended or dispersed in solvent, they are liable to coagulate, settle and separate.

Several shampoos and rinses containing the polyvalent metal salts are put on the market. In order to stably incorporate the salts into shampoo or rinse compositions, it is unavoidable to make them highly viscous or to add specific types of polymers or clay minerals. This leads to the disadvantage that the compositions become poor in performance, e.g. with shampoos, the foaming ability becomes poor with objectionable feeling to the touch after washing of the hair.

Recently, several methods of stably keeping such metal salts in compositions have been proposed including a method using the salts in combination with hydroxyalkyl celluloses (Japanese laid-open Application No 57—80499), a method using the salts in combination with amphoteric polymer compounds (Japanese Laid-open Application No. 54—41909), a method in which HPC is used in combination (Japanese Laid-open Application No. 35—97010), and a method in which polyacrylic acid/polyacrylates are used in combination.

However, all these methods still make use of the specific types of polymers and thus problems on the rise of cost and the performance of the products are not solved. Moreover, these methods are all techniques of applications to shampoos. The possibility of applications to other types of products are not made clear.

Summary of the Invention

In view of the above, we made intensive studies in order to stably add the polyvalent metal salts serving as excellent antibacterial agents to ordinary shampoos or hair rinses. As a result, it was found that when the salts are finely divided so that the particles thereof are below a specific size, dispersion stability of the salts is remarkably improved with the adsorbability of the fine particles on the skin and hair being also improved. Accordingly, shampoos or hair rinses and cosmetics which comprise the polyvalent metal salts have improved antibacterial and dandruff-removing actions.

We also found that it was difficult or took a long time to obtain finely divided polyvalent metal salts through ordinary media with a size of 0.6 mm to 3 mm as used in sand mills, sand grinders or the like. However, fine particles could be obtained efficiently within a short time by agitating a dispersion of the salts along with media having a size ranging from 0.5 mm to 0.1 mm.

It was also found that agitation of a dispersion of the salts comprising a specific type of dispersant resulted in more finely divided particles.

According to the present invention a finely divided zinc salt of 2-mercaptopyridine-N-oxide is provided having a size distribution of particles, in which the particles having a size below 0.2 μm are contained in an amount of not less than 50 wt.-%, the particles having a size ranging from 0.5 to 1.0 μm are contained in an amount of not more than 15 wt.-% and the particles having a size exceeding 1.0 μm are contained in an amount of not more than 2 wt.-%, with an average particle size below 0.2 μm . Also, there are provided a method for producing the finely divided zinc salts and antibacterial compositions comprising such salts.

Detailed Description of the Invention and Preferred Embodiments

The finely divided zinc salts according to the invention have a size distribution in which not less than 50 wt% of the particles have a size below 0.2 μm . Specifically the finely divided zinc salts have such a size distribution of particles comprising not less than 50 wt% of the particles having a size below 0.2 μm , not more than 15 wt% of the particles having a size ranging from 0.5 to 1.0 μm , and not more than 2 wt% of the particles exceeding 1.0 μm , with an average size below 0.2 μm . More preferably, the particles have a size distribution comprising not less than 70 wt% of the particles having a size below 0.2 μm , not more than

10 wt% of the particles having a size ranging from 0.5 to 1 μm and substantially free of particles exceeding 1.0 μm , with an average size below 0.15 μm .

Most preferably, the finely divided zinc salt has a size distribution in which not less than 50 wt% of particles have a size below 0.1 μm . In this case, a preferable size distribution is such that not less than 50 wt% of the particles have a size below 0.1 micron, not more than 15 wt% of the particles have a size ranging from 0.2 to 0.5 μm and not more than 5 wt% of the particles having a size exceeding 0.5 μm , with an average size below 0.1 μm . Most preferably, the size distribution is such that not less than 70 wt% of the particles have a size below 0.1 μm , not more than 10 wt% of the particles have a size ranging from 0.2 to 0.5 μm , and particles having a size exceeding 0.5 μm are not substantially contained, with an average size below 0.08 μm .

The finely divided zinc salts of the invention may be prepared by agitating a dispersion of the salt, as it is or admixed with a salt of (meth)acrylic acid-styrenesulfonic acid copolymer having an average molecular weight of from 10,000 to 1,000,000, along with rigid media having a size below 0.5 mm, thereby finely dividing the salt by the shearing strength of the media into fine particles.

Starting zinc salts are favorably used in the form of an aqueous dispersion. Commercially sold dispersions, dispersions obtained by dispersing commercially sold powders of such salts, or suitably prepared dispersions may be used. The content of the salt in the dispersion is preferably in the range of from 5 to 70 wt%. In view of the production efficiency, higher concentrations are more preferable. It will be noted that commercially sold dispersants of the salts usually contain 50 wt% of the effective component.

The salts of (meth)acrylic acid-styrenesulfonic acid copolymer used as the dispersant are water-soluble salts of copolymer of acrylic acid and/or methacrylic acid and styrenesulfonic acid, and may be prepared by a known method. The molar ratio of (meth)acrylic acid and styrenesulfonic acid in the copolymer ranges from 1/10 to 10/1, preferably from 1/3 to 7/1. The molecular weight is from 10,000 to 1,000,000, preferably from 100,000 to 700,000. The molecular weight is important in the practice of the invention. If the molecular weight is smaller than 10,000, the zinc salts may not be finely divided, or once formed particles may be considerably coagulated. On the other hand, when the molecular weight is larger than 1,000,000, it becomes difficult to handle because the high viscosity of the water-soluble copolymer salt itself.

The salts of the copolymers include salts of sodium, potassium, ammonium, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine or 2-amino-2-methylpropane-1,3-diol. Non-neutralized carboxyl groups may be left to an extent of impeding the performance of the copolymer salts.

Moreover, the copolymers may comprise a third component in amounts not impeding the nature thereof. Examples of the third component include styrene, acrylamide, sulfonic acids such as methacrylsulfonic acid or vinylsulfonic acid, 2-hydroxyethyl acrylate, various acrylates, various methacrylates, N-methylolacrylamide, and other copolymerizable monomers.

The water-soluble copolymer salts are generally added in an amount not smaller than 0.1 wt%, preferably from 0.5 to 10 wt%.

The media have a size below 0.5 mm, preferably from 0.1 to 0.2 mm. Although fine division of the zinc salts is possible using media having a size smaller than 0.1 mm, the mixture of the media and the zinc salts is so high in viscosity that handling becomes difficult. The materials for the media are rigid materials such as, for example, Ottawa sand, glass, alumina or zircon, of which glasses are preferred.

The apparatus in which the zinc salts and the media are agitated for fine division of the salts may be sand mills or sand grinders. Any known types of sand mills and sand grinders including vertical and horizontal types may be used in the practice of the invention. Discs may be of any ordinarily used types.

The temperature at which fine division is effected is preferably from 5 to 30°C. At temperatures exceeding 30°C, it takes a long time before completion of the fine division, making the fine division difficult.

The mixing ratio of the media and the dispersion of the zinc salt is from 40/60 to 80/20, preferably from 60/40 to 70/30, on the volume basis.

After finely divided, the zinc salt is filtered under pressure or centrifugally separated to separate the media and the salt dispersion from each other. If necessary, the media may be washed with water thereby obtaining a finely divided metal salt.

The thus obtained finely divided zinc salt comprises 50 wt% or more of particles having a size below 0.2 micron, preferably 0.1 micron (the size and its distribution are determined using a centrifugal automatic size distribution measuring instrument CAPA-500 (available from Horiba Seisakusho Co., Ltd.)). Because such fine particles have good dispersability, the dispersion obtained is stable over a long term. The finely divided metal salts are more stable and more adsorbable on the hair, skin, bark or building materials and are better in antibacterial effect than known counterparts. Accordingly, such finely divided salts can be utilized not only as dandruff in hair cosmetics, but also as ordinary aqueous bactericides using the salts as a dispersion which has never been used because of the problem of dispersion stability.

The present invention is described by way of examples.

Example 1

70 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 130 ml of glass beads (media) having a size of 0.1 to 0.2 mm or 0.6 to 0.8 mm were mixed (media/dispersion ratio by volume = 65/35) and placed

in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). Grinder discs were rotated for 3 hours at a peripheral speed of 6 m/s. The temperature within the grinder was 20 to 25°C. The resulting dispersion was filtered under pressure to obtain 35 ml of finely divided zinc salt. The media was washed twice each with 70 ml of water. As a result, 98 wt% of the zinc salt was recovered.

- 5 The finely divided zinc salt had, as shown in Table 1 below, a size distribution in which particles having a size below 0.2 μm were contained in an amount of 83 wt%.

TABLE 1

10	Size of Media		0.6—0.8 mm			0.1—0.2 mm		
	Treating Time		1 hour	3	8	1 hour	3	8
15	Zinc Salt Dispersion	over 1.0 (μm)	0%	0	0	0	0	0
20		1.0—0.8	13	12	10	1	0	0
		0.8—0.6	10	7	3	3	0	0
25		0.6—0.4	23	14	9	9	0	0
		0.4—0.2	38	40	29	32	17	14
		below 0.2	16	27	49	55	83	86
30	Average size (μm)		0.38	0.31	0.21	0.19	0.12	0.11

Example 2

- 35 70 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 130 ml of glass beads (media) having a size of 0.5 mm were mixed (media/dispersion ratio by volume = 65/35) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). Grinder discs were rotated for 8 hours at a peripheral speed of 6 m/s. The temperature within the grinder was 20 to 25°C. The resulting dispersion was filtered under pressure to obtain 32 ml of finely divided zinc salt.

- 40 The finely divided zinc salt had, as shown in Table 2, a size distribution in which particles having a size below 0.2 μm were contained in an amount of 54 wt%.

Example 3

- 45 70 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 130 ml of glass beads (media) having a size of 44 to 63 μm were mixed (media/dispersion ratio by volume = 65/35) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). Grinder discs were rotated for 3 hours at a peripheral speed of 5 m/s. The temperature within the grinder was 20 to 25°C. The resulting dispersion was filtered under pressure to obtain 31 ml of finely divided zinc salt.

- 50 The finely divided zinc salt had, as shown in Table 2, a size distribution in which particles having a size below 0.2 μm were contained in an amount of 88 wt%.

Example 4

- 55 80 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 120 ml of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 60/40) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). Grinder discs were rotated for 4 hours at a peripheral speed of 6 m/s. The temperature within the grinder was 20 to 25°C. The resulting dispersion was filtered under pressure to obtain 37 ml of finely divided zinc salt.

- 60 The finely divided zinc salt had, as shown in Table 2, a size distribution in which particles having a size below 0.2 μm were contained in an amount of 64 wt%.

Example 5

- 65 60 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 149 ml of glass beads (media) having

a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 70/30) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). Grinder discs were rotated for 4 hours at a peripheral speed of 6 m/s. The temperature within the grinder was 20 to 25°C. The resulting dispersion was filtered under pressure to obtain 29 ml of finely divided zinc salt.

The finely divided zinc salt had, as shown in Table 2, a size distribution in which particles having a size below 0.2 μ m were contained in an amount of 85 wt%.

Example 6

504 ml of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 896 ml of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 64/36) and placed in a 1400 ml horizontal sand grinder (Dyno Mill: Willy A. Bachofen, Engineering Works). Grinder discs were rotated for 2.5 hours at a peripheral speed of 10 m/s. The temperature within the grinder was 20 to 25°C.

The finely divided zinc salt had, as shown in Table 2, a size distribution in which particles having a size below 0.2 μ m were contained in an amount of 83 wt%.

Example 7

28 kg of a commercially available dispersion of zinc salt of 2-mercaptopyridine-N-oxide (commercial product A having a content of the effective ingredient of 50 wt%) and 58 kg of glass beads having a size of 0.1 to 0.2 mm were mixed in a mixing vessel. In a horizontal sand grinder (Pearl Mill 25 TEXH, by Serizawa Iron Works Co., Ltd.), grinder discs were rotated for 6 hours at a peripheral speed of 12 m/s. The mixture of the glass beads and the zinc salt dispersion was circulated to the mixing vessel at a rate of 8 liters/hour. The amounts of the mixture residing in the sand grinder and the mixing vessel were made equal.

The temperature in the sand grinder was maintained at 20 to 25°C because the mixture was cooled in the mixing vessel.

Thereafter, the mixture of the glass beads and the finely divided zinc salt was withdrawn and subjected to a centrifugal separator in which the glass beads and the finely divided salt were separated from each other. The separated glass beads were transferred to the mixing vessel for reuse.

As a result, 23.8 kg of the finely divided zinc salt was obtained. When the glass beads were washed with 28 kg of water, the starting zinc salt could be substantially recovered.

The finely divided zinc salt had, as shown in Table 2, a size distribution in which 88 wt% of the particles had a size below 0.2 μ m.

TABLE 2

Zinc Salt Dispersion	Commercial Product							
	Commercial Product A	Commercial Product B	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
Size Distribution (wt%)	over 1.0 (μm)	0	0	0	0	0	0	0
	1.0—0.8	7	16	2	0	2	0	0
	0.8—0.6	19	17	2	0	2	0	0
	0.6—0.4	29	34	8	5	7	2	2
	0.4—0.2	33	28	34	7	25	13	15
below 0.2	12	5	54	88	64	85	83	88
Average Size (μm)	0.45	0.50	0.19	0.13	0.16	0.11	0.12	0.13

Example 8

³⁵S-labelled zinc salt of 2-mercaptopyridine-N-oxide of the invention was dispersed in 500 ml of an aqueous solution of 1.0% sodium polyoxyethylene(2) lauryl sulfate. In the dispersion was placed 30 mg of a bundle of the hair, followed by immersing for 1 minute while agitating at 100 r.p.m. Thereafter, the hair bundle was rinsed twice with running water for 15 seconds and air-dried, after which 10 mg of the hair was exactly weighed and placed in a 20 ml vial. In the vial, it was dissolved in 1 ml of Soluen 350, to which was added 100 ml of a scintillator, followed by counting by a liquid scintillation counter to measure an amount of an adsorbed zinc salt. The results are shown in Table 3.

TABLE 3

Concentration of Zinc Salt Dispersion (%)	0.5	1.0	1.5	2.0
Product of Invention*	0.19	0.25	0.53	0.98
Comparative Product*	0.16	0.20	0.25	0.23

• µg/10 mg of hair

	Product of Invention	Comparative Product
Average size	0.11 µm	0.72 µm
<0.2 µm	78.0%	23%
0.5—1.0 µm	8.7%	53.2%
over 1.0 µm	0%	20.8%

Example 9

A commercially available zinc salt and a zinc salt obtained according to the invention were each dispersed in water in order to compare the resulting dispersions with respect to dispersion stability. The results are shown in Table 4.

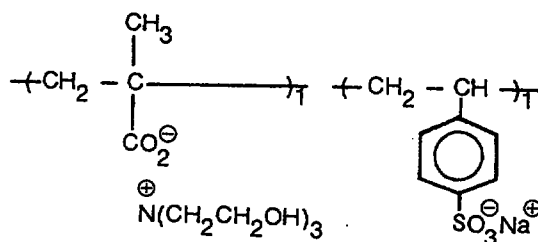
TABLE 4

	Product of Invention (Example 3)	Commercial Product	Commercial Product
Average size	0.13 µm	0.45 µm	1.0 µm
Dispersion stability	stable	precipitated	precipitated

Dispersion stability test: each zinc salt was dispersed in water in a concentration of 1%, which was placed in a test tube and allowed to stand for 10 days. After 10 days, the state of the dispersion was visually judged.

Example 10

23 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 680,000;

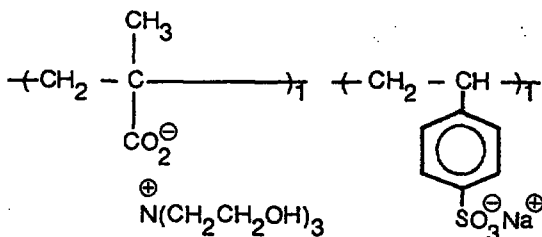


63 g of water, and 187 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 63/37) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 12 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 40 g of a finely divided zinc salt dispersion. When the media were washed twice each with 70 g of water, 98% of the zinc salt could be recovered.

The finely divided zinc salt had, as shown in Table 5, a size distribution in which 91 wt% of the particles had a size below 0.1 μm .

Example 11

14 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 320,000;

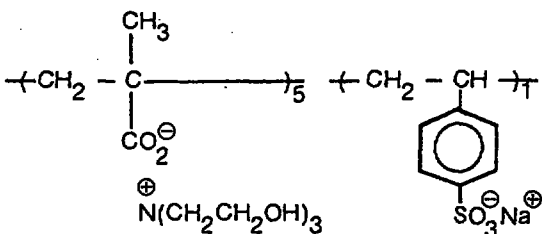


72 g of water, and 187 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 63/37) and placed in a 400-ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 12 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 35 g of a finely divided zinc salt dispersion.

The finely divided zinc salt had, as shown in Table 5, a size distribution in which 77 wt% of the particles had a size below 0.1 μm .

Example 12

14 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 100,000;



72 g of water, and 203 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 65/35) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 3 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 38 g of a finely divided zinc salt dispersion.

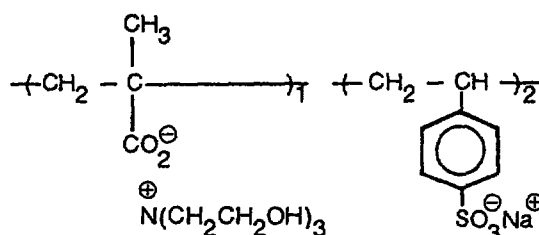
The finely divided zinc salt had, as shown in Table 5, a size distribution in which 50 wt% of the particles had a size below 0.1 μm .

TABLE 5

Zinc Salt Dispersion	Treating Time (hours.)	Example 1			Example 2		Example 3
		3	5	12	6	12	3
Size Distribution (wt%)	over 0.5 (μm)	3%	0	0	0	0	1
	0.5—0.2	12	1	2	2	3	12
	0.2—0.1	25	7	8	16	15	37
	0.1—0.05	46	70	35	62	37	36
	below 0.05	14	22	55	20	45	14
Average Size (μm)		0.09	0.07	0.05	0.07	0.06	0.10

Example 13

23 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 260,000;

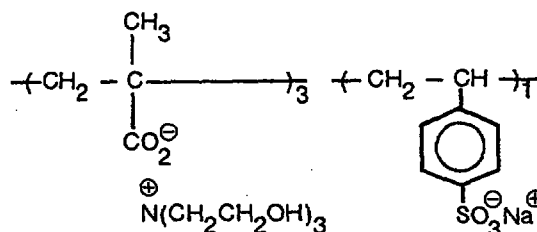


63 g of water, and 187 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 63/37) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 8 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 50 g of a finely divided zinc salt dispersion.

The finely divided zinc salt had, as shown in Table 6, a size distribution in which 100 wt% of the particles had a size below 0.1 μm.

Example 14

23 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 380,000;

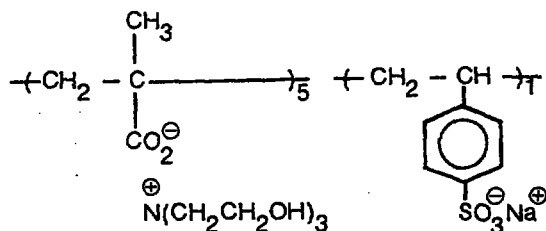


63 g of water, and 187 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 63/37) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 8 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 45 g of a finely divided zinc salt dispersion.

The finely divided zinc salt had, as shown in Table 6, a size distribution in which 100 wt% of the particles had a size below 0.1 μm.

Example 15

23 g of a commercially available powder of zinc salt of 2-mercaptopyridine-N-oxide, 4.5 g of a water-soluble copolymer salt of the formula having a molecular weight of 350,000;



63 g of water, and 187 g of glass beads (media) having a size of 0.1 to 0.2 mm were mixed (media/dispersion ratio by volume = 63/37) and placed in a 400 ml sand grinder (made by Igarashi Machine Manufacturing Co., Ltd.). In the grinder, discs were rotated for 8 hours at a peripheral speed of 6 m/s. The temperature in the sand grinder was found to be 20 to 25°C. The content was filtered under pressure to obtain 40 g of a finely divided zinc salt dispersion.

The finely divided zinc salt had, as shown in Table 6, a size distribution in which 100 wt% of the particles had a size below 0.1 µm.

TABLE 6

Zinc Salt Dispersion		Example 4	Example 5	Example 6
Size Distribution (wt%)	over 0.5 (µm)	0	0	0
	0.5—0.2	0	0	0
	0.2—0.1	0	0	0
	0.1—0.05	68	55	25
	below 0.05	32	45	75
Average Size (µm)		0.06	0.05	0.03

Example 16

Zinc salts of 2-mercaptopyridine-N-oxide, one being a product of the invention (average size of 0.08 µm) and the other being a commercial product (average size of 0.72 µm), were labelled with ³⁵S. The labelled zinc salts were each dispersed in 500 ml of an aqueous solution of 1% sodium polyoxyethylene(2) laurylsulfate. In the dispersion was placed 30 mg of a hair bundle, followed by immersing for 1 minute under agitation at 100 r.p.m. Subsequently, the hair bundle was rinsed twice each with running water for 15 seconds and air-dried, after which 10 mg of the hair was exactly weighed and placed in a 20 ml of vial. In the vial, it was dissolved in 1 ml of Soluen 350. To the solution was added 10 ml of a scintillator, followed by counting with a liquid scintillation counter to determine an amount of adsorbed and remaining zinc salt. The results are shown in Table 7.

TABLE 7

Concentration of Zinc Salt Dispersion (%)	0.5	1.0	1.5	2.0
Product of Invention	0.23	0.32	0.76	1.34
Commercial Product	0.16	0.20	0.25	0.23

µg/10 mg of hair

Example 17

Dandruff Remover:

5	Zinc salt (obtained in Example 7)	2.0%
	Propylene glycol	5.0%
10	Ethanol	10.0
	Perfume	very small amount
	Water	balance

15 The dandruff remover had a remarkable dandruff-removing effect and was stable over 3 months or more at room temperature. In contrast, with the remover using a commercial zinc salt product, the zinc salt was precipitated in 3 days.

Example 18

20 An aqueous bactericidal composition of the following formulation using a zinc salt of 2-mercaptopyridine-N-oxide according to the invention was prepared.

	Zinc salt (average size 0.1 μ)	0.1 wt%
25	Spreader	0.01
	Water	suitable amount
30	Total	100.00

This aqueous bactericide was stable over 1 month or more and exhibited a good bactericidal effect when applied to trees.

Example 19

Dandruff Remover:

35	Zinc salt (obtained in Example 11)	2.0%
40	Propylene glycol	5.0%
	Ethanol	30%
45	Perfume	very small amount
	Water	balance
	Total	100%

50 This dandruff remover had a remarkable dandruff-removing effect and was stable over 3 months or more at room temperature. In contrast, with the remover using a commercial zinc salt product, the zinc salt was found to settle in 1 day.

55 **Claims**

1. A finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size distribution of particles, in which the particles having a size below 0.2 μ m are contained in an amount of not less than 50 wt.-%, the particles having a size ranging from 0.5 to 1.0 μ m are contained in an amount of not more than 15 wt.-% and the particles having a size exceeding 1.0 μ m are contained in an amount of not more than 2 wt.-%, with an average particle size below 0.2 μ m.

2. A method for producing a finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size distribution as defined in claim 1, the method comprising agitating a dispersion of a zinc salt of 2-mercaptopyridine-N-oxide along with rigid media having a size below 0.5 mm.

65 3. A method for producing a finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size



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Example 17

Dandruff Remover:

5	Zinc salt (obtained in Example 7)	2.0%
	Propylene glycol	5.0%
	Ethanol	10.0
10	Perfume	very small amount
	Water	balance

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	Propylene glycol	5.0%
40	Ethanol	30%
	Perfume	very small amount
45	Water	balance
	Total	100%

50 This dandruff remover had a remarkable dandruff-removing effect and was stable over 3 months or more at room temperature. In contrast, with the remover using a commercial zinc salt product, the zinc salt was found to settle in 1 day.

55 **Claims**

1. A finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size distribution of particles, in which the particles having a size below 0.2 μ m are contained in an amount of not less than 50 wt.-%, the particles having a size ranging from 0.5 to 1.0 μ m are contained in an amount of not more than 15 wt.-% and the particles having a size exceeding 1.0 μ m are contained in an amount of not more than 2 wt.-%, with an average particle size below 0.2 μ m.

2. A method for producing a finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size distribution as defined in claim 1, the method comprising agitating a dispersion of a zinc salt of 2-mercaptopyridine-N-oxide along with rigid media having a size below 0.5 mm.

65 3. A method for producing a finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size



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distribution as defined in claim 1 in which particles having a size below 0.1 μm are contained in amounts not smaller than 50 wt.-%, the method comprising agitating a dispersion of a zinc salt of 2-mercaptopyridine-N-oxide in the coexistence of a salt of a (meth)acrylic-styrenesulfonic acid copolymer along with rigid media having a size below 0.2 mm.

5 4. The method according to claim 2 or 3, wherein said rigid media are made of a material selected from the group consisting of Ottawa sand, glass, alumina and zircon.

5. An antibacterial composition comprising an effective amount of a finely divided zinc salt of 2-mercaptopyridine-N-oxide having a size distribution as defined in claim 1.

10 6. The antibacterial composition according to claim 6, wherein the size distribution is such that particles having a size below 0.1 μm are contained in amounts not smaller than 50 wt.-%.

Patentansprüche

15 1. Fein zerteiltes Zinksalz von 2-Mercaptopyridin-N-oxid mit einer Größenverteilung der Teilchen, bei der die Teilchen mit einer Größe unter 0,2 μm in einer Menge von nicht weniger als 50 Gew.-% enthalten sind, die Teilchen mit einer Größe im Bereich von 0,5 bis 1,0 μm in einer Menge von nicht mehr als 15 Gew.-% enthalten sind und die Teilchen mit einer Größe über 1,0 μm in einer Menge von nicht mehr als 2 Gew.-% enthalten sind, wobei eine durchschnittliche Teilchengröße von unter 0,2 μm vorliegt.

20 2. Verfahren zur Herstellung eines fein zerteilten Zinksalzes von 2-Mercaptopyridin-N-oxid mit einer Teilchengrößenverteilung, wie sie in Anspruch 1 definiert ist, wobei man eine Dispersion eines Zinksalzes von 2-Mercaptopyridin-N-oxid gemeinsam mit festen Medien mit einer Größe unter 0,5 mm agitiert.

3. Verfahren zur Herstellung eines fein zerteilten Zinksalzes mit einer Größenverteilung, wie sie in Anspruch 1 definiert ist, wobei Teilchen mit einer Größe von unter 0,1 μm in einer Menge enthalten sind, die nicht kleiner ist als 50 Gew.-%, wobei man eine Dispersion eines Zinksalzes von 2-Mercaptopyridin-N-oxid in der Coexistenz von einem Salz eines (Meth)acrylsäure-Styrolsulfonsäure-Copolymeren gemeinsam mit festen Medien mit einer Größe unter 0,2 mm agitiert.

4. Verfahren gemäß Anspruch 2 oder 3, wobei die erwähnten festen Medien aus einem Material bestehen, ausgewählt aus der Gruppe Ottawasand, Glas, Aluminiumoxid und Zirkon.

30 5. Antibakterielles Mittel, umfassend eine wirksame Menge eines fein zerteilten Zinksalzes von 2-Mercaptopyridin-N-oxid mit einer Größenverteilung, wie sie in Anspruch 1 definiert ist.

6. Antibakterielles Mittel gemäß Anspruch 6, wobei die Größenverteilung derart ist, daß Teilchen mit einer Größe unter 0,1 μm in einer Menge enthalten sind, die nicht kleiner ist als 50 Gew.-%.

Revendications

35 1. Sel de zinc de mercapto-2-pyridine-N-oxyde, finement divisé, présentant une distribution granulométrique des particules suivant laquelle les particules ayant une dimension qui se situe au-dessous de 0,2 μm sont contenues en une quantité non inférieure à 50% en poids, les particules ayant une dimension se situant dans la plage de 0,5 à 1,0 μm sont contenues en une quantité non supérieure à 15% en poids, et les particules ayant une dimension qui dépasse 1,0 μm , sont contenues en une quantité non supérieure à 2% en poids, avec une dimension moyenne de particule au-dessous de 0,2 mm.

40 2. Procédé de fabrication d'un sel de zinc de mercapto-2 pyridine-N-oxyde, finement divisé, ayant une distribution granulométrique telle que définie à la revendication 1, ce procédé consistant à agiter une dispersion d'un sel de zinc de mercapto-2 pyridine-N-oxyde conjointement avec des véhicules rigides présentant une dimension qui se situe au-dessous de 0,5 mm.

45 3. Procédé de fabrication d'un sel de zinc de mercapto-2 pyridine-N-oxyde, finement divisé, présentant une distribution granulométrique telle que définie à la revendication 1, suivant laquelle les particules ayant une dimension qui se situe au-dessous de 0,1 μm sont contenues en quantités non inférieures à 50% en poids, le procédé consistant à agiter une dispersion d'un sel de zinc de mercapto-2 pyridine-N-oxyde en présence d'un sel d'un copolymère acide (méth)acrylique-styrènesulfonique, conjointement avec des véhicules rigides présentant une dimension qui se situe au-dessous de 0,2 mm.

50 4. Procédé selon la revendication 2 ou 3, dans lequel lesdits véhicules rigides sont faits d'une matière choisie dans le groupe constitué par le sable d'Ottawa, le verre, l'alumine et le zircon.

55 5. Composition antibactérienne comprenant une quantité efficace d'un sel de zinc de mercapto-2 pyridine-N-oxyde, finement divisé, présentant une distribution granulométrique telle que définie à la revendication 1.

60 6. Composition antibactérienne selon la revendication 5, dans laquelle la distribution granulométrique est telle que des particules ayant une dimension qui se situe au-dessous de 0,1 μm sont contenues en quantités non inférieures à 50% en poids.