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(54) Title: DISCOLORATION PREVENTION IN PYRITHIONE-CONTAINING COATING COMPOSITIONS

## (57) Abstract

Disclosed is an aqueous coating composition comprising: (a) water, (b) a base medium, (c) a pyrithione salt, in an amount of from 0.01 % to 2.0 % based upon the weight of the composition, and (d) zinc oxide compound selected from the many grades suitable for paint manufacture at a concentration of from 0.001 % to 10 % based upon the weight of the coating composition. Also disclosed is an aqueous antimicrobial coating composition, characterized by antimildew efficacy and protected against discoloration attributable to the presence of pyrithione therein, said composition being selected from the group consisting of water-based paints, adhesives, caulk and sealants, and combinations thereof, said composition comprising water, a pyrithione salt or acid, an organic base medium and a zinc compound, said zinc ion being present in said composition in an amount of from 0.001 % to 10 % based upon the weight of the coating composition.

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DISCOLORATION PREVENTION IN  
PYRITHIONE-CONTAINING COATING COMPOSITIONS

This invention relates generally to coating compositions, and, more specifically, to such compositions that are characterized by enhanced antimicrobial efficacy and resistance to 5 discoloration, both in their wet state and, after drying, in the form of a dry film on a substrate.

Pyrithiones are well-known antimicrobial additives that are useful in a myriad of applications. Sodium pyrithione (also called the 10 sodium salt of 1-hydroxy-2-pyridinethione, sodium pyridine-2-thiol-N-oxide, or 2-pyridinethiol-1-oxide, Na salt) is one pyrithione salt having excellent antimicrobial properties, and is typically employed as a biocide and preservative in functional 15 fluids, such as metalworking fluids, lubricants, cosmetics and toiletries. Sodium pyrithione is a well-known commercial product commonly made by reacting 2-chloropyridine-N-oxide with NaSH and NaOH, as disclosed, for example, in U.S. Patent No. 20 3,159,640.

Likewise, zinc pyrithione [also known as zinc pyridine-2-thiol-N-oxide or bis [1-hydroxy-2(H) pyridinethionato]-zinc] is an excellent antimicrobial additive. Zinc pyrithione may be made 25 by reacting 1-hydroxy-2-pyridinethione or a soluble salt thereof with a zinc salt (e.g., ZnSO<sub>4</sub>) to form a zinc pyrithione precipitate, as disclosed, for example in U.S. Patent No. 2,809,971. Zinc pyrithione has been employed as a broad-spectrum 30 anti-microbial agent and preservative in metalworking fluids, plastics, paints, adhesives and cosmetics. Its principal uses are as an anti-

5 dandruff agent in hair products, as a preservative in various cosmetics, and as an antifoulant in marine paints. The commercial use of zinc pyrithione in paints, adhesives, caulk and sealants is growing.

10 In the presence of ferric ion, sodium or zinc pyrithione-containing compositions tend to turn blue, even when the ferric ion is present in mere trace amounts, much less when higher amounts of the ferric ion is present. Likewise, in the presence of ultraviolet radiation, which is a component of natural, outdoor light, photodegradation of the pyrithione moiety may occur. This blue or yellow discoloration is undesirable for aesthetic reasons, 15 as well as for functional reasons relating to unwanted color formulation.

20 Since the aesthetics of paints, adhesives, caulk and sealants normally require certain desirable colors after drying to form a dry coating on a substrate, and since the formulators of such products go to great lengths to achieve specific color effects, any ingredient which causes the formulation to vary much from a desired white or 25 color may make the colorant formulators' task very difficult. For example, when formulating water-based paints, paint bases (i.e., the partially formulated paint before pigment addition), adhesives, caulk and sealants, any unwanted color in an additive can adversely affect the color of the 30 formulated product. Such discoloration typically adversely affects the desired product color, producing an off-color product.

Likewise, yellowing of the dry coating film on a substrate, by virtue of ultraviolet ("uv") exposure as a component of natural outdoor light, adversely affects the paint in two respects. First, 5 the yellowing of the paint is an aesthetic problem since the paint changes color upon uv exposure. Second, photodegradation of pyrithione attributable to uv exposure diminishes the amount of pyrithione available to protect the paint film.

10 In the past, various solutions to the blue discoloration problem have been proposed. By way of illustration, U.S. Patents 4,957,658 and 4,818,436 disclose solutions to the above-discussed discoloration problem attributable to the presence 15 of ferric ion plus pyrithione, in paints and functional fluids (e.g., metalworking fluids) respectively, by adding to the paint or functional fluid an alkali metal or alkaline earth metal salt of 1-hydroxyethane-1,1-diphosphonic acid. Although 20 the '658 and '436 patents propose good solutions to the discoloration, these solutions are not always as cost effective or permanent as might be desired.

As another illustration, U.S. Patent 4,161,526 discloses a white to cream yellow pyrithione, 25 pyrithione salt or dipyrithione for application to skin or hair containing from about 0.01 percent to about 1 percent of the zinc salt of an organic carboxylic or inorganic acid, zinc hydroxide or zinc oxide, or a mixture thereof. The composition of the 30 '526 patent is said to be effective in preventing or removing discoloration caused by formation of a colored pyrithione, pyrithione salt, or dipyrithione contaminant (said to be iron pyrithione) in the

composition. The '526 patent does not teach a solution to the discoloration problem in compositions unrelated to skin or hair care, and not containing iron pyrithione.

5        In addition to the discoloration problem, unwanted ions, such as ferric ion, can cause a functional problem with respect to the antimicrobial performance of pyrithione. It is believed by the present inventors that this performance problem  
10      results from the fact that the pyrithione tends to form a blue precipitate in the presence of ferric ion, and precipitation of pyrithione reduces the amount of available pyrithione throughout the composition, thereby diminishing the biocidal  
15      protection thereof.

Moreover, the present inventors have found that the presence of a large amount of zinc oxide in a pyrithione-containing paint can suppress the short-term (or initial stage) of antimicrobial efficacy  
20      imparted by the pyrithione to the paint when dried to form a dry film on a substrate. This diminished short term efficacy adversely affects the performance of the paint, particularly in regard to resistance of the paint film to mildew growth.

25      New solutions to the yellow, blue and green discoloration problem in various pyrithione-containing aqueous coating compositions, particularly paints, adhesives, caulk and sealants would be highly desired. Preferred solutions would  
30      include those that enable pyrithione to be utilized in coating compositions containing iron or copper, without encountering any resulting discoloration of the composition, and that is cheaper, longer

lasting, and/or uses lower levels of additives than required by the above-discussed prior art. A particularly preferred solution, namely one providing improved short-term and long-term 5 antimicrobial resistance of the coating composition and resulting coating against microbial attack, would be highly desired by the paint, adhesives, caulks and sealants manufacturing community. The present invention provides one such solution.

10 In one aspect, the present invention relates to an aqueous coating composition comprising:

a) water,  
b) a base medium,  
c) a pyrithione salt, in an amount of  
15 from 0.01% to 2.0% based upon the weight  
of the composition, and  
d) zinc oxide compound selected from  
the many grades suitable for paint  
manufacture at a concentration of from  
20 0.001% to 10% based upon the weight of the  
composition. Typical coating compositions  
include aqueous compositions of a paint,  
adhesive, caulk, sealant, latex emulsion,  
pigment slurry, patching compound, joint  
25 compound, or concrete admixture.

In another aspect, the present invention  
relates to a process for inhibiting dry film-  
discoloration of a pyrithione-containing coating  
composition, attributable to ultraviolet light  
30 degradation of said pyrithione, which comprises  
incorporating into said coating composition an  
effective amount of a zinc compound selected from  
the group consisting of zinc salts of organic acids,

zinc salts of inorganic acids, zinc hydroxide, zinc oxide, and combinations thereof.

In yet another aspect, the present invention relates to a process for removing an undesirable 5 discoloration in an aqueous antimicrobial composition containing a dissolved metal ion selected from the group consisting of ferric ion, cupric ion, and combinations thereof, and containing pyrithione, which comprises contacting said 10 composition with a zinc ion in a molar amount at least equal to the amount of said dissolved metal ion in said composition.

In still another aspect, the present invention relates to an aqueous antimicrobial coating 15 composition, characterized by antimildew efficacy and protected against discoloration attributable to the presence of pyrithione therein, said composition being selected from the group consisting of water-based paints, adhesives, caulks and sealants, and 20 combinations thereof, said composition comprising water, a pyrithione salt or acid, an organic base medium and a zinc compound, said zinc ion being present in said composition in an amount of from 0.001% to 10% based upon the weight of the coating 25 composition.

In yet another aspect, the present invention relates to a coated substrate comprising a substrate selected from the group consisting of wood, metal, 30 plastic substrates, and combinations thereof, and a coating on said substrate, said coating comprising pyrithione and a zinc compound selected from the group consisting of zinc salts of organic acids,

zinc salts of inorganic acids, zinc hydroxide, zinc oxide, and combinations thereof

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

It has now been surprisingly found in accordance with the present invention that the combination of a zinc compound (such as a zinc salt, zinc oxide or zinc hydroxide) together with a  
10 pyrithione compound (preferably zinc pyrithione) in a coating composition provides an advantageous combination of antimicrobial (particularly anti-mildew) efficacy and resistance to UV attack with respect to the dry coating made by applying the  
15 coating composition to a substrate.

It has also been surprisingly found in accordance with the present invention that the addition of zinc to a composition containing pyrithione and ferric or cupric ion reduces or  
20 avoids a discoloration problem otherwise attributable to such composition. Without wishing to be bound by any particular theory, there are multiple potential causes of the discoloration problem. For example, the presence of undesirable  
25 ions in tap water and "filler" components of the coating composition, such as iron ion, causes the formation of an insoluble iron pyrithione precipitate that not only discolors the composition, but also depletes the available pyrithione in sodium  
30 pyrithione-containing compositions, thereby diminishing the antimicrobial efficacy of the composition.

Additionally, ultraviolet radiation, a component of natural, outdoor light, tends to cause yellow discoloration of dry-film coatings containing pyrithione. It has now been found that the presence 5 of zinc oxide within the preferred range of from 0.02% to 0.5% by weight, based upon the weight of the coating composition, in a pyrithione-containing coating composition contributes both to antimicrobial efficacy and avoidance of undesirable 10 blueing or other discoloration of the coating composition, as well as avoidance of undesirable yellowing or other discoloration of the dry film resulting from the coating of a substrate with the coating composition.

15 The term "discoloration" as employed herein with respect to pyrithione-containing coating compositions is intended to describe any unacceptable gray, blue, black, purple, green, or color other than the natural color or desired 20 artificial color of the paint or paint base formulation. The term "discoloration" is also intended to describe any yellow or brown discoloration of the dry film resulting from coating a substrate with the coating composition. Such 25 yellow or brown discoloration is typically caused by photodegradation of pyrithione in the coating.

Discoloration of the coating composition can be attributable to unwanted metal ions (such as iron or copper) entering the coating composition from the 30 starting materials employed in the preparation of the coating composition. Typical starting materials include tap water, and fillers (such as calcium carbonate) used to prepare coating compositions, as

well as a source of pyrithione in the form of sodium pyrithione, zinc pyrithione, and combinations thereof. It is noted, for example, that the natural color of sodium pyrithione itself is a clear yellow.

5 It is quite common, however, for iron and/or copper contaminants to be introduced into the aqueous composition from the tap water or fillers used in preparing the coating compositions, causing discoloration of the composition. One way of  
10 quantifying the extent of discoloration is by measuring the reflectance color parameters, and calculating a whiteness value from them. Another method is to visually inspect the composition for any signs of off-whiteness, as compared to the  
15 desired or white color.

In water-based paints, adhesives, caulk and sealants, significant levels of ferric or copper ion impurities in an amount of 250 ppm or higher are not uncommon. By incorporating an effective amount of  
20 the zinc salt of an organic acid or inorganic acid, zinc hydroxide or zinc oxide or a mixture thereof into the composition, the blue discoloration typically attributable to the presence of ferric ion bound with pyrithione is suitably reduced,  
25 eliminated or avoided, as is the green discoloration attributable to the presence of copper ion.

The amount of the above described zinc salt of an organic acid or inorganic acid, zinc hydroxide or zinc oxide, or combination thereof, needed to  
30 prevent discoloration in the coating composition in which it is employed, and the resulting dry film made by coating a substrate with the coating composition, can vary over a wide range of from

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0.001% or lower to 10% or greater (advantageously from 0.001% to 3%, more advantageously from 0.02% to 0.5%), based upon the weight of the coating composition in which it is employed.

5        In order to provide an advantageous combination of short term and longer term antimicrobial efficacy in the dry film when using zinc oxide, it has now been found that the amount of zinc oxide preferably should not exceed 0.5% by weight (advantageously from 0.002% to 0.2%) based upon the weight of the coating composition. Above 0.5%, there is a risk that the zinc oxide will inhibit the short term efficacy of the zinc pyrithione in the dry film due to the well-known "common ion effect" attributable 10      to the zinc present in both of these components. This "common ion effect" forces an equilibrium toward unionized zinc pyrithione where zinc ion, pyrithione ion, and unionized zinc pyrithione are 15      all present in the composition, and the antimicrobial efficacy of zinc pyrithione is suppressed as long as this component remains in 20      unionized form.

25        The pyrithione used in the process and composition of this invention is preferably a pyrithione salt, such as sodium pyrithione, zinc pyrithione, chitosan pyrithione, magnesium disulfide pyrithione, and the like, although pyrithione acid can be used if desired. More preferable pyrithione salts include sodium pyrithione, and zinc 30      pyrithione, most preferably zinc pyrithione.

      The sodium pyrithione useful in the present invention is a well-known commercial product that is commonly made by reacting 2-chloropyridine-N-oxide

with NaSH and NaOH, as illustrated by the disclosures of U.S. Pat. No. 3,159,640.

5 Zinc pyrithione may be made by reacting 1-hydroxy-2-pyridinethione (i.e., pyrithione acid) or a soluble salt thereof with a zinc salt (e.g., ZnSO<sub>4</sub>) to form a zinc pyrithione precipitate, as illustrated by the disclosures of U.S. Pat. No. 2,809,971.

10 The aqueous compositions of the present invention are suitable for a variety of uses, such as, for example as soap, shampoo, skin care medicaments, paint, or incorporated into or onto plastic or a woven or non-woven fibers, when formulated to contain the requisite components in 15 addition to the antimicrobial component.

20 The antimicrobial compositions of the present invention are particularly useful in the form of paints, including indoor and outdoor household paints, industrial and commercial paints. In addition, the antimicrobial compositions provide desirable results when the antimicrobial component is incorporated into exterior paints of the latex types.

25 The coating compositions of the present invention are suitably applied to a substrate, such as a wood, plastic or metal substrate, and allowed to dry to form a dry coating.

30 The dry film formed by coating and drying the coating composition of the present invention onto a substrate exhibits excellent resistance to the growth of fungus and algae, as shown by outdoor exposure tests using boards painted with the coating composition. However, it can be envisioned that

certain paint formulations, namely those that are rich in hydrophilic components, might provide an environment that is more favorable to the growth of both mildew and algae, as compared to the coatings tested. Mildew needs moisture to survive. Hydrophilic materials in a paint film will keep the moisture level of the film higher. This provides a better environment for mildew and also may contribute to accelerated leaching out of hydrophilic materials. The hydrophilic components in these formulations tend to cause relatively soluble antimicrobial additives to leach out of the formulation, thus providing good short-term antimicrobial protection at the expense of longer-term antimicrobial protection due to this leaching effect. Under these circumstances, it is envisioned, in accordance with the present invention, that the use of zinc pyrithione, a relatively water-insoluble antimicrobial additive, in combination with a relatively water-soluble antimicrobial additive provides an excellent combination of desired short-term and long-term antimicrobial protection in dry paint films made using paint formulations containing high levels of hydrophilic components. Relatively water-soluble antimicrobials that are useful as co-biocides for dry-film efficacy when used in combination with zinc pyrithione in accordance with the present invention include iodopropynyl butylcarbamate ("IPBC"), n-octyl isothiazolin-one ("OIT"), methylene thiocyanate ("MTC"), thiocyanomethylthio benzothiazole ("TCMTB"), thiazolyl benzimidazole ("TBZ"), benzimidazolyl carbamic acid methylester

("BCM"), triazoles, such as chlorophenylethyl dimethylethyl triazole ethanol ("Tebuconazole", commercially available from Bayer), substituted triazines such as tert-butylamino cyclopropylamino 5 methylthio-s-triazine, and dichlorophenyl dimethylurea ("Diuron", commercially available from Bayer), as well as combinations thereof. These cobiocides are suitably added either alone, or in admixture with zinc pyrithione, to the desired 10 paint, to provide a paint containing a molar ratio of zinc pyrithione to co-biocide of from 1:10 to 10:1.

Typically a paint composition will contain, in addition to the antimicrobial component, a resin, a 15 pigment, and various optional additives such as thickening agent(s), wetting agents and the like, as is well known in the art. The resin is preferably selected from the group consisting of vinyl, alkyd, epoxy, acrylic, polyurethane and polyester resins, 20 and combinations of thereof. The resin is preferably employed in an amount of between about 20% and about 80% based upon the weight of the paint or paint base.

In addition, the paint composition of the 25 present invention optionally additionally contains optional additives which have a favorable influence on the viscosity, the wetting power and the dispersibility, as well as on the stability to freezing and electrolytes and on the foaming 30 properties. If a marine paint is being fabricated, the paint preferably contains a swelling agent to cause the paint to gradually "slough off" in its marine environment, thereby causing renewed biocidal

efficacy of newly exposed biocide at the surface of the paint in contact with the water medium of the marine environment. Illustrative swelling agents are naturally occurring or synthetic clays, such as 5 kaolin, montmorillonite, and bentonite), clay mica (muscovite), and chlorite (hectonite), and the like. In addition to clays other swelling agents, including natural or synthetic polymers, such as that commercially available as POLYMERGEL, have been 10 found to be useful in the compositions of the present invention to provide the desired "sloughing off" effect. Swelling agents can be used singly or in combination. The total amount of optional additives is preferably no greater than 20% by 15 weight, more preferably between about 1% and about 5% by weight, based upon the total weight of the paint composition.

Illustrative, thickening agents include cellulose 30 derivatives, for example methyl, 20 hydroxyethyl, hydroxypropyl and carboxymethyl cellulose, poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethyleneglycol), salts of poly(acrylic acid) and salts of acrylic acid/acrylamide copolymers.

25 Suitable wetting and dispersing agents include sodium polyphosphate, salts of low molecular weight poly(acrylic acid), salts of poly(ethane sulfonic acid), salts of poly(vinyl phosphonic acid), salts of poly(maleic acid) and salts of copolymers of 30 maleic acid with ethylene, 1 olefins 3 to 18 carbon atoms and/or styrene.

In order to increase the stability to freezing and electrolytes there may be added to the paint

composition various monomer 1,2-diols for example glycol, propylene glycol (1,2) and butylene glycol 1,2) or polymers thereof, or ethoxylated compounds. For example reaction products of ethylene oxide with 5 long-chain alkanols, amines, alkyd phenols, poly(propylene glycol), or poly(butylene glycol), or a combination thereof, or the like.

The minimum temperature of film formation of the paint composition may be reduced by adding 10 solvents, such as ethylene glycol, butyl glycol, ethyl glycol acetate, ethyl diglycol acetate, butyl diglycol acetate, or alkylated aromatic hydrocarbons. As defoaming agents there are suitable for example poly(propylene glycol) and 15 polysiloxanes. Optionally other biocides can additionally be incorporated into the paint formulations of the present invention.

The paint composition of the present invention may be used as a paint for natural or synthetic 20 materials, for example wood, paper, metals, textiles and plastics. It is particularly suitable as an outdoor paint, and is excellent for use as a marine paint.

Another significant use for the aqueous 25 composition of the present invention is as a latex tile adhesive typically containing, for example, in addition to the antimicrobial component, a latex emulsion, an optional rosin emulsion, an optional plasticizer, an optional antioxidant, and an 30 optional pigment or filler (such as calcium carbonate). Yet another significant use for the aqueous composition of the present invention is as a latex caulk, typically containing, in addition to

the antimicrobial component, an acrylic latex, a nonionic surfactant, a dispersant, an optional plasticizer, and an optional pigment or filler (such as calcium carbonate).

5        The aqueous antimicrobial compositions of the present invention are useful, in any of the variety of applications described herein, as disinfectants and preservatives, in a liquid or spreadable solid form, alone or in combination with an inert carrier  
10      such as water, liquid hydrocarbons, ethanol, isopropanol, or the like. They can be employed using conventional procedures to control bacteria and fungi on various substrates, and can be applied to bacterial or fungal organisms or on substrates in  
15      an antimicrobial amount by conventional procedures such as spraying, dipping, drenching impregnation, and the like.

20      The invention is further illustrated by the following Examples. Unless otherwise stated, the "parts" and "%" are "parts by weight" and "percent by weight", respectively.

25      While the invention has been described above with references to specific embodiments thereof, it is apparent that many changes, modifications and variations can be made without departing from the inventive concept disclosed herein. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and broad scope of the appended claims.

30      The following examples are intended to illustrate, but in no way limit the scope of, the present invention.

COMPARATIVE EXAMPLE AEfficacy of Zinc Oxide as an Antimicrobial  
Against Mildew in an Acrylic Latex House Paint

5 In order to test the effectiveness of zinc oxide as an anti-mildew additive in a latex house paint, the following experiment was conducted. A paint was prepared having the following composition:

**Latex Paint Formulation Containing Zinc Oxide:**

	<u>Ingredient</u>	<u>Grams</u>
10	Water	240.0
	Hydroxyethyl Cellulose	6.0
	Tamol 960 1	6.2
	Ethylene Glycol	50.0
	Colloid 643 2	2.0
15	Triton® CF-103	5.0
	Potassium Tripolyphosphate	3.0
	<b>Pigment grind:</b>	
	Titanium Dioxide (Rutile)	500.0
	Aluminum Magnesium Silicate	335.0
20	Attapulgite Clay	6.0
	Zinc Oxide	12.0
	Aluminum Silicate	47.0
	Propylene Glycol	68.0
	<b>Let Down:</b>	
25	Water	201.0
	Acrylic Latex Emulsion 60.0% solids	760.0
	Colloid 643	6.0
	Texanol® 4	22.0
	Hydroxyethyl Cellulose 2.5% in water	80.0
30	Ammonia	0.5
	Total Mass in Grams	2349.7

The paint was applied by brush in two coats to an unprimed white pine substrate to determine whether the coating supported the growth of mildew on the coating. After four months of outdoor aging, 5 the growth was rated in accordance with the procedure of ASTM D 3274-82 to a rating of 6 (moderate growth).

COMPARATIVE EXAMPLE B

10 Efficacy of Zinc Pyrithione in an Acrylic Latex House Paint

As another test of the effectiveness of zinc oxide as an anti-mildew additive in a latex house paint, the following experiment was conducted. A paint was prepared having the following composition:

15 **Latex Paint Formulation Containing Zinc Pyrithione and No Zinc Oxide:**

	<u>Ingredient</u>	<u>Grams</u>
	Water	240.0
	Hydroxyethyl Cellulose	6.0
20	Tamol 960 1	6.2
	Ethylene Glycol	50.0
	Colloid 643 2	2.0
	Triton® CF-10 3	5.0
	Potassium Tripolyphosphate	3.0
25	<b>Pigment Grind:</b>	
	Titanium Dioxide (Rutile)	500.0
	Aluminum Magnesium Silicate	335.0
	Attapulgite Clay	6.0
	Zinc Pyrithione 48% Dispersion	24.0
30	Aluminum Silicate	47.0

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Propylene Glycol	68.0
<b>Let Down:</b>	
Water	201.0
Acrylic Latex Emulsion 60.0% solids	760.0
5 Colloid 643	6.0
Texanol® 4	22.0
Hydroxyethyl Cellulose 2.5% in water	80.0
Ammonia	0.5
Total Mass in Grams 2361.7	

10        The paint was applied by brush in two coats to an unprimed white pine substrate to determine whether the coating supported the growth of mildew on the coating. After four months of outdoor aging, the growth was rated in accordance with the 15 procedure of ASTM D 3274-82 to a rating of 8 (light growth).

EXAMPLE 1

Efficacy of Zinc Pyrithione and Zinc Oxide  
in a Acrylic Latex House Paint

20        In order to test the effectiveness of the combination of zinc oxide and zinc pyrithione as a combination of anti-mildew additives in a latex house paint, the following experiment was conducted. A paint was prepared having the following 25 composition:

**Latex Paint Formulation Containing Zinc Pyrithione and Zinc Oxide:**

<u>Ingredient</u>	<u>Grams</u>
Water	240.0

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	Hydroxyethyl Cellulose	6.0
	Tamol 960 1	6.2
	Ethylene Glycol	50.0
	Colloid 643 2	2.0
5	Triton® CF-10 3	5.0
	Potassium Tripolyphosphate	3.0
	<b>Pigment Grind:</b>	
	Titanium Dioxide (Rutile)	500.0
	Aluminum Magnesium Silicate	335.0
10	Attapulgite Clay	6.0
	Zinc Pyrithione 48% Dispersion	18.0
	Zinc Oxide	3.0
	Aluminum Silicate	47.0
	Propylene Glycol	68.0
15	<b>Let Down:</b>	
	Water	201.0
	Acrylic Latex Emulsion 60.0% solids	760.0
	Colloid 643	6.0
	Texanol® 4	22.0
20	Hydroxyethyl Cellulose 2.5% in water	80.0
	Ammonia	0.5
	Total Mass in Grams	2361.7

**Footnotes**

25 1 An anionic dispersant, a product of Rohm and Haas Company.  
 2 A defoamer, a product of Rhone-Poulenc Corp.  
 3 A nonionic surfactant, a product of Union Carbide Corp.  
 4 A coalescent, a product of Eastman Kodak Company.

30 The paint was applied by brush in two coats to an unprimed white pine substrate to determine whether the coating supported the growth of mildew on the coating. After four months of outdoor aging, the growth was rated in accordance with the procedure of ASTM D 3274-82 to provide a rating of 10 (no growth).

All three of the paints from the above three examples (Comparative Examples A and B and Example 1) were painted on three different sections of the same pine board to minimize the effect of using 5 different pieces of wood. Example 1 demonstrates that the combination of zinc pyrithione and zinc oxide suitably provides total resistance to the growth of mildew on painted wood substrates, whereas zinc oxide or zinc pyrithione alone (Comparative 10 Examples A and B) does not provide such resistance.

#### EXAMPLE 2

Efficacy of Zinc Oxide in Avoiding  
Yellow Discoloration Caused by  
Exposure to Ultraviolet Light in  
15 Pyrithione Containing Paint Bases

In order to test the effectiveness of zinc oxide in avoiding, eliminating or reducing yellow discoloration caused by ultraviolet in a pyrithione-containing paint, the following experiment was 20 conducted.

Two samples of an aqueous latex paint formulation (below) containing zinc pyrithione and one not containing zinc pyrithione were applied to a panel and exposed in a QUV weatherometer for 500 25 hours. The yellowness index ("YI") was measured at time zero and after 500 hours of exposure. The difference in YI for the paint without zinc pyrithione after 500 hours of exposure was an increase in yellowness of 1.34. The difference in 30 YI for the paint with 0.3% by weight of active zinc pyrithione was an increase of 3.68, indicating an

increase in yellowing on exposure to UV with the paint containing zinc pyrithione.

To samples of each of these paints, 0.5% of zinc oxide was added. The difference in YI for the 5 paint without zinc pyrithione was an increase 0.37 after 500 hours of exposure in a QUV weatherometer. The difference in YI for the paint that contained zinc pyrithione was 0.19 after 500 hours of exposure. This result demonstrates that zinc oxide 10 will prevent the development of yellow color in a paint that contains zinc pyrithione when the paint is exposed to ultraviolet light.

#### **Latex Paint Formulation with and without pyrithione**

	<u>Ingredient</u>	<u>A</u>	<u>B</u>
15	Water	103.0 grams	103.0
	Hydroxyethyl Cellulose	2.5 grams	2.5
	Tamol 9601	12.90	12.9
	Ethylene Glycol	18.00	18.0
	Colloids 643 2	2.0	2.0
20	Nuosept 95	3.00	3.0
	Potassium Tripolyphosphate	2.0	2.0
	<b>Pigment Grind:</b>		
	Titanium Dioxide (Rutile)	200.0	200.0
	Sodium Potassium Aluminum Silicate	225.0	225.0
25	Attapulgite Clay	4.0	4.0
	<b>Let Down:</b>		
	Water	50.0	50.0
	Acrylic Latex Emulsion 63.0% solids	260.0	260.0
	Colloids 643	4.0	4.0
30	Texanol® 3	12.0	12.0
	Hydroxyethyl Cellulose 2.5% in water	132.0	132.0

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Ammonia	1.0	1.0
<b>Zinc Pyrithione 48% Dispersion</b>		
Total Mass in Grams	1031.4	1037.4

5 To 200 grams of both A and B, 2.00 grams of a 50% zinc oxide dispersion was added for comparing the yellowing of paints with and without zinc pyrithione as summarized on page 23 lines 3-10.

EXAMPLE 3

10 Efficacy of Reduced Amounts Zinc Oxide in  
Avoiding Yellow Discoloration Caused by  
Exposure to Ultraviolet Light in  
Pyrithione Containing Paint Bases

15 To determine if a lower concentration of zinc oxide could be used to provide effectiveness in avoiding, eliminating or reducing yellow discoloration caused by ultraviolet in a pyrithione-containing paint, the following experiment was conducted. Following the procedure of Example 2, two paints were prepared as follows: to Example 2  
20 were prepared as follows:

<u>Ingredient</u>	<u>A</u>	<u>B</u>
Water	103.0 grams	103.0
Hydroxyethyl Cellulose	2.5 grams	2.5
Tamol 9601	12.90	12.9
25 Ethylene Glycol	18.00	18.0
Colloids 643 2	2.0	2.0
Nuosept 95	3.00	3.0
Potassium Tripolyphosphate	2.0	2.0

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**Pigment Grind:**

Titanium Dioxide (Rutile)	200.0	200.0
Sodium Potassium Aluminum Silicate	225.0	225.0
Attapulgite Clay	4.0	4.0
5 Zinc Oxide	2.0	6.0

**Let Down:**

Water	50.0	50.0
Acrylic Latex Emulsion 63.0% solids	260.0	260.0
Colloids 643	4.0	4.0
10 Texanol® 3	12.0	12.0
Hydroxyethyl Cellulose 2.5% in water	132.0	132.0
Ammonia	1.0	1.0
<b>Zinc Pyrithione 48% Dispersion</b>	<b>6.0</b>	<b>6.0</b>
Total Mass in Grams	1045.4	1049.4

**15 Footnotes**

1 An anionic dispersant, a product of Rohm and Haas Company

2 A defoamer, a product of Rhone-Poulenc Corp.

3 A coalescent, a product of Eastman Kodak Company

Films from these paints were exposed in a QUV

20 weatherometer for 72 hours of continuous light with UVA 340 bulbs. The YI index was measured at that time and the difference from the YI at time zero was as follows:

	<u>YI</u>
25 Paint Sample A	1.35
Paint Sample B	0.76

The results provided in this example demonstrate that less than 0.2% of zinc oxide in the formulation will result in a reduction in yellowing 30 caused by UV exposure. Adding an additional 0.4% zinc oxide for a total of 0.6% by weight resulted in an even greater reduction of UV induced yellowing.

EXAMPLE 4Elimination of Blue Discoloration Caused by the  
Presence of Pyrithione and Ferric Ion In a  
Paint Base

5       Efficacy of zinc oxide in eliminating blue  
coloration caused by the presence of ferric ion in  
sodium pyrithione containing paint bases.

10      In order to test the effectiveness of zinc  
oxide in eliminating or reducing blue color caused  
by ferric ion in a pyrithione-containing paint, the  
following experiment was conducted.

15      Two samples weighing 150 grams each of below  
aqueous (latex) paint formulation containing sodium  
pyrithione and zinc oxide were placed in plastic  
cups. A wooden tongue depressor was then dipped  
into each sample and then allowed to dry to provide  
a control or "blank" comparison. Ferric chloride  
was then added to each sample to provide a  
concentration of 64 ppm of ferric ion in each  
20      sample. Tongue depressor coatings were taken to  
provide a basis for comparison. No discoloration  
formed in the paints themselves or the dry films of  
the painted tongue depressor.

Latex Paint Formulation Containing Sodium Pyrithione and Zinc Oxide:		
	Ingredient	Grams
	water	240.00
	hydroxyethyl cellulose	6.0
5	Tamol 850 <sup>1</sup>	14.2
	Ethylene Glycol	50.0
	Colloid 643 <sup>2</sup>	2.0
	Triton® CF-10 <sup>3</sup>	5.0
	sodium pyrithione 40% active	3.0
10	potassium tripolyphosphate	3.0
	<b>Pigment grind:</b>	
	titanium dioxide (Rutile)	424.0
	aluminum magnesium silicate	228.0
	attapulgite clay	3.0
15	zinc oxide	50.0
	aluminum silicate	100.0
	propylene glycol	68.0
	<b>Let Down:</b>	
	water	84.0
20	acrylic latex emulsion 58.0% solids	700.0
	Colloid 643	6.0
	Texanol® <sup>4</sup>	18.6
	hydroxyethyl cellulose 2.5% in water	236.4
	Total Mass in Grams	2241.2

<sup>1</sup>An anionic dispersant, a product of Rohm and Haas Company

<sup>2</sup>A defoamer, a product of Rhone-Poulence Corp.

<sup>3</sup>A nonionic surfactant, a product of Union Carbide Corp.

<sup>4</sup>A coalescent, a product of Eastman Kodak Company

Next, as a comparison, two samples weighing 150 grams each of below aqueous (latex) paint formulation containing sodium Pyrithione and no zinc oxide were placed in paper cups. A wooden tongue 5 depressor was then dipped into each sample and then allowed to dry to provide a control or "blank" comparison. Ferric chloride was then added to each sample to provide a concentration of 64 ppm of ferric ion in each sample. The comparison coatings 10 on the tongue depressor were visually observed to provide a basis for the comparison. After 30 minutes a bluish gray discoloration formed in the paints themselves and the dry films of the painted tongue depressor.

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Latex Paint Formulation Containing Sodium Pyrithione and Zinc Oxide:		
	Ingredient	Grams
5	water	240.00
	hydroxyethyl cellulose	6.0
	Tamol 850 <sup>5</sup>	14.2
	Ethylene Glycol	50.0
	Colloid 643 <sup>6</sup>	2.0
	Triton® CF-10 <sup>7</sup>	5.0
10	sodium pyrithione 40% active	3.0
	potassium tripolyphosphate	3.0
	<b>Pigment grind:</b>	
	titanium dioxide (Rutile)	424.0
	aluminum magnesium silicate	228.0
	attapulgite clay	3.0
15	aluminum silicate	100.0
	propylene glycol	68.0
	<b>Let Down:</b>	
	water	84.0
	acrylic latex emulsion 58.0% solids	700.0
20	Colloid 643	6.0
	Texanol® <sup>8</sup>	18.6
	hydroxyethyl cellulose 2.5% in water	236.4
	Total Mass in Grams	2191.2

<sup>5</sup>An anionic dispersant, a product of Rohm and Haas Company

<sup>6</sup>A defoamer, a product of Rhone-Poulence Corp.

<sup>7</sup>A nonionic surfactant, a product of Union Carbide Corp.

<sup>8</sup>A coalescent, a product of Eastman Kodak Company

EXAMPLE 5Elimination of Blue Discoloration Caused by the Presence of Pyrithione and Ferric Ion In a Paint

5 Efficacy of zinc oxide in eliminating blue coloration caused by the presence of ferric ion in zinc pyrithione containing paint.

10 In the presence of ferric ion, zinc pyrithione-containing paint compositions also tended to turn blue to gray, although at a much slower rate than did the sodium pyrithione-containing paints.

15 48 percent aqueous zinc pyrithione was added to a white paint which contained 1.0 percent zinc oxide to provide a level of 3000 ppm of zinc pyrithione in the sample. Ferric chloride was then added to provide a concentration of 64 ppm of ferric ion in the sample. Upon standing for a month, the paint was found to have no discoloration.

20 When this composition is painted over bare steel or copper, no discoloration is detected. This result is surprising, since the copper would have been expected to turn the paint a greenish color, and the steel would have been expected to turn the paint a bluish color.

25 As a comparison, 48 percent aqueous zinc pyrithione is added to a white paint containing no zinc oxide to provide a level of 3000 ppm of zinc pyrithione in the sample. Ferric chloride is then added to provide a concentration of 64 ppm of ferric ion in the sample. Upon standing for a week, the 30 paint is found to turn bluish in color.

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EXAMPLE 6

Process for the Removal of Discoloration Caused  
by the Presence of Pyrithione and Ferric Ion  
in Water-based Coatings

5        48 percent aqueous zinc pyrithione was added to  
a white paint sample to provide a level of 3000 ppm  
of zinc pyrithione in the sample. Ferric chloride  
was then added to provide a concentration of 25 ppm  
of ferric ion in the sample. Upon standing for two  
10 days, the paint was found to turn bluish in color.  
To this point 0.007 percent (70 ppm) of zinc sulfate  
was added and the paint was mixed for 5 minutes.  
After sitting for an additional 5 minutes it was  
observed that the paint had whitened and the bluish  
15 color was no longer noticeable. The addition of the  
zinc sulfate to this paint had removed the blue  
color which was formed from the addition of zinc  
pyrithione and ferric chloride.

WHAT IS CLAIMED IS:

1. An aqueous coating composition characterized by containing:

- a) water,
- 5 b) a base medium,
- c) a pyrithione salt, in an amount of from 0.01% to 2.0% based upon the weight of the composition, and
- d) zinc oxide at a concentration of from 0.001%
- 10 to 10% based upon the weight of the coating composition.

2. The coating composition of claim 1 characterized in that said zinc oxide is present in an amount of from 0.001% to 3%, based upon the 15 weight of the coating composition.

3. The coating composition of claim 1 characterized in that said zinc oxide is present in an amount of from 0.02% to 0.5%, based upon the weight of the coating composition.

20 4. The coating composition of claim 1 characterized in that said zinc oxide is present in an amount of from 0.002% to 0.2%, based upon the weight of the coating composition.

25 5. The coating composition of claim 1 characterized in that said base medium is a polymer latex.

6. The coating composition of claim 1 characterized in that said composition additionally contains a co-biocide selected from the group consisting of iodopropynyl butylcarbamate ("IPBC"), 5 n-octyl isothiazolin-one ("OIT"), methylene thiocyanate ("MTC"), thiocyanomethylthio benzothiazole ("TCMTB"), thiazolyl benzimidazole ("TBZ"), benzimidazolyl carbamic acid methylester ("BCM"), triazoles, such as chlorophenylethyl 10 dimethylethyl triazole ethanol, substituted triazines such as tert-butylamino cyclopropylamino methylthio-s-triazine, and dichlorophenyl dimethylurea, and combinations thereof.

7. A process for inhibiting dry film-discoloration of a pyrithione-containing coating composition, attributable to ultraviolet light degradation of said pyrithione, which is characterized by incorporating into said coating composition an effective amount of a zinc compound 15 selected from the group consisting of zinc salts of organic acids, zinc salts of inorganic acids, zinc 20 hydroxide, zinc oxide, and combinations thereof.

8. The process of claim 7 characterized in that said zinc compound is selected from the group 25 consisting of zinc oxide, zinc hydroxide, zinc acetate, zinc sulfate, zinc chloride, and combinations thereof.

9. A process for removing an undesirable discoloration in an aqueous antimicrobial composition containing a dissolved metal ion selected from the group consisting of ferric ion, 5 cupric ion, and combinations thereof, and containing pyrithione, which is characterized by contacting said composition with a zinc ion in a molar amount at least equal to the amount of said dissolved metal ion in said composition.

10 10. The process of claim 9 characterized in that said amount of said zinc ion is between 100 ppm and 10,000 ppm in said composition.

11. The process of claim 9 characterized in that said zinc ion provided by incorporating into 15 said composition a zinc compound selected from the group consisting of zinc salts of organic acids, zinc salts of inorganic acids, zinc hydroxide, zinc oxide, and combinations thereof.

12. An aqueous antimicrobial coating 20 composition, characterized by antimildew efficacy and protected against discoloration attributable to the presence of pyrithione therein, said composition being selected from the group consisting of water-based paints, adhesives, caulk and sealants, and 25 combinations thereof, said composition characterized by containing water, a pyrithione salt or acid, an organic base medium and a zinc compound, said zinc ion being present in said composition in an amount of from 0.001% to 10% based upon the weight of the 30 coating composition.

13. A coated substrate comprising a substrate selected from the group consisting of wood, metal, plastic substrates, and combinations thereof, and a coating on said substrate, said coating  
5 characterized by containing pyrithione and a zinc compound selected from the group consisting of zinc salts of organic acids, zinc salts of inorganic acids, zinc hydroxide, zinc oxide, and combinations thereof.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/01935

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 27/18

US CL :106/18.27; 428/469

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)

U.S. : 106/18.27; 428/469

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)

CAS ONLINE, APS

search terms: pyrithione, zinc

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 4,161,526 (GORMAN) 17 July 1979, claim 4; col. 1, lines 49-55.	1-4, 7-11 -----
Y		5, 6, 12, 13
Y	US 4,565,856 (TROTZ et al) 21 January 1986, col. 2, lines 19-35; Example 25; col. 28, lines 58-64.	1-13

Further documents are listed in the continuation of Box C.  See patent family annex.

* Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
26 MARCH 1998	23 JUN 1998

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer MARY E. CEPERLEY Telephone No. (703) 308-0196
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