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(54) **DISCOLORATION PREVENTION IN PYRITHIONE-CONTAINING COATING COMPOSITIONS**  
**VERFAHREN ZUR VERHINDERUNG DER ENTFÄRBUNG VON PYRITHION ENTHALTENDEN BESCHICHTUNGSZUSAMMENSETZUNGEN**  
**PREVENTION DE LA DECOLORATION DANS DES COMPOSITIONS DE REVETEMENT CONTENANT DE LA PYRITHIONE**

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**EP 0 963 291 B1**

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## Description

- 5 [0001] This invention relates generally to coating compositions, and, more specifically, to such compositions that are characterized by enhanced antimicrobial efficacy and resistance to discoloration, both in their wet state and, after drying, in the form of a dry film on a substrate.
- 10 [0002] Pyrithiones are well-known antimicrobial additives that are useful in a myriad of applications. Sodium pyrithione (also called the 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 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. 3,159,840.
- 15 [0003] 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 by reacting 1-hydroxy-2-pyridinethione or a soluble salt thereof with a zinc salt (e.g.,  $ZnSO_4$ ) 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 anti-microbial agent and preservative in metalworking fluids, plastics, paints, adhesives and cosmetics. Its principal uses are as an antidandruff 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, caulks and sealants is growing.
- 20 [0004] 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, as well as for functional reasons relating to unwanted color formulation.
- 25 [0005] Since the aesthetics of paints, adhesives, caulks 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 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, caulks and sealants, any unwanted color in an additive can adversely affect the color of the formulated product. Such discoloration typically adversely affects the desired product color, producing an off-color product.
- 30 [0006] 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, 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.
- 35 [0007] 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 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 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.
- 40 [0008] As another illustration, U.S. Patent 4,161,526 discloses a white to cream yellow pyrithione, 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 '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.
- 45 [0009] 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 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 protection thereof.
- 50 [0010] 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 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.
- 55 [0011] New solutions to the yellow, blue and green discoloration problem in various pyrithione-containing aqueous coating compositions, particularly paints, adhesives, caulks and sealants would be highly desired. Preferred solutions

would include those that enable pyrrhione 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 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.

**[0012]** The present invention relates to an aqueous coating composition being a paint containing a single pyrrhione salt, that being zinc pyrrhione, wherein the paint is characterized by:

- a) water;
- b) a base medium being a resin selected from vinyl, alkyd, epoxy, acrylic, polyurethane and polyester resins, and combinations thereof.
- c) zinc pyrrhione, in an amount of from 0.01% to 2.0% based upon the weight of the composition, and
- d) a zinc oxide compound selected from the many grades suitable for paint manufacture at a concentration of from 0.02% to 0.5% based upon the weight of the coating composition.

**[0013]** The coating composition of the present invention 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 coating composition to a substrate.

**[0014]** The addition of zinc oxide to a composition containing pyrrhione and ferric or cupric ion reduces or 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 ions in tap water and "filler" components of the coating composition, such as iron ion, causes the formation of an insoluble iron pyrrhione precipitate that not only discolors the composition, but also depletes the available pyrrhione in sodium pyrrhione-containing compositions, thereby diminishing the antimicrobial efficacy of the composition.

**[0015]** Additionally, ultraviolet radiation, a component of natural, outdoor light, tends to cause yellow discoloration of dry-film coatings containing pyrrhione. It has now been found that the presence 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 pyrrhione-containing coating composition contributes both to antimicrobial efficacy and avoidance of undesirable 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.

**[0016]** The term "discoloration" as employed herein with respect to pyrrhione-containing coating compositions is intended to describe any unacceptable gray, blue, black, purple, green, or color other than the natural color or desired 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 yellow or brown discoloration is typically caused by photodegradation of pyrrhione in the coating.

**[0017]** Discoloration of the coating composition can be attributable to unwanted metal ions (such as iron or copper) entering the coating composition from the 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 pyrrhione in the form of sodium pyrrhione, zinc pyrrhione, and combinations thereof. It is noted, for example, that the natural color of sodium pyrrhione itself is a clear yellow. 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 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 desired or white color.

**[0018]** In water-based paints, 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 zinc oxide into the composition, the blue discoloration typically attributable to the presence of ferric ion bound with pyrrhione is suitably reduced, eliminated or avoided, as is the green discoloration attributable to the presence of copper ion.

**[0019]** The amount of zinc oxide incorporated into the coating composition of the present invention is in the range of from 0.02% to 0.5%, based upon the weight of the coating composition in which it is employed.

**[0020]** In order to provide an advantageous combination of short term and longer term antimicrobial efficacy in the dry film when using zinc oxide, it is necessary that the amount of zinc oxide 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 pyrrhione in the dry film due to the well-known "common ion effect" attributable to the zinc present in both of these components. This "common ion effect" forces an equilibrium toward unionized zinc pyrrhione where zinc ion, pyrrhione ion, and unionized zinc pyrrhione are all present in the composition, and the antimicrobial efficacy of zinc pyrrhione is suppressed as long as this component remains in

unionized form.

**[0021]** The pyrrithione used in the composition of this invention is zinc pyrithione.

**[0022]** Zinc pyrithione may be made by reacting 1-hydroxy-2-pyridinethione (i.e., pyrrithione acid) or a soluble salt thereof with a zinc salt (e.g.,  $ZnSO_4$ ) to form a zinc pyrithione precipitate, as illustrated by the disclosures of U.S. Pat. No. 2,809,971.

**[0023]** The antimicrobial compositions of the present invention are useful as 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.

**[0024]** 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.

**[0025]** 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 ("Tabuconazole", commercially available from Bayer), substituted triazines such as tert-butylamino cyclopropylamino methylthio-s-triazine, and dichlorophenyl dimethylurea ("Diuron", commercially available from Bayer), as well as combinations thereof. These biocides are suitably added either alone, or in admixture with zinc pyrithione, to the desired paint, to provide a paint containing a molar ratio of zinc pyrithione to co-biocide of from 1:10 to 10:1.

**[0026]** Typically a paint composition will contain, in addition to the antimicrobial component, a resin, a 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 selected, in accordance with the present invention, from the group consisting of vinyl, alkyd, epoxy, acrylic, polyurethane and polyester resins, 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.

**[0027]** In addition, the paint composition of the 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 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 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 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 weight, more preferably between about 1% and about 5% by weight, based upon the total weight of the paint composition.

**[0028]** Illustrative, thickening agents include cellulose 30 derivatives, for example methyl, hydroxyethyl, hydroxypropyl and carboxymethyl cellulose, poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethyleneglycol), salts of poly(acrylic acid) and salts of acrylic acid/acrylamide copolymers.

**[0029]** 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 maleic acid with ethylene, 1 olefins 3 to 18 carbon atoms and/or styrene.

**[0030]** 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 long-chain alkanols, amines, alkyd phenols, poly(propyleneglycol), or poly(butylene glycol), or a combination thereof, or the like.

**[0031]** The minimum temperature of film formation of the paint composition may be reduced by adding 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 polysiloxanes. Optionally other biocides can additionally be incorporated into the paint formulations of the present invention.

[0032] The paint composition of the present invention may be used as a paint for natural or synthetic 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.

[0033] 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 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 an antimicrobial amount by conventional procedures such as spraying, dipping, drenching impregnation, and the like.

[0034] The invention is further illustrated by the following Examples. Unless otherwise stated, the "parts" and "%" are "parts by weight" and "percent by weight", respectively.

[0035] 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 scope of the appended claims.

[0036] The following examples are intended to illustrate, but in no way limit the scope of, the present invention.

#### COMPARATIVE EXAMPLE A

##### Efficacy of Zinc Oxide as an Antimicrobial Against Mildew in an Acrylic Latex House Paint

[0037] 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:	
Ingredient	Grams
Water	240.0
Hydroxyethyl Cellulose	6.0
Tamol 960 1	6.2
Ethylene Glycol	50.0
Colloid 643 2	2.0
Triton® CF-103	5.0
Potassium Tripolyphosphate	3.0
<b>Pigment grind:</b>	
Titanium Dioxide (Rutile)	500.0
Aluminum Magnesium Silicate	335.0
Attapulgite Clay	6.0
Zinc Oxide	12.0
Aluminum Silicate	47.0
Propylene Glycol	68.0
<b>Let Down:</b>	
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
Ammonia	0.5
Total Mass in Grams	2349.7

[0038] 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 a rating of 6 (moderate growth).

#### COMPARATIVE EXAMPLE B

##### Efficacy of Zinc Pyrithione In an Acrylic Latex House Paint

[0039] 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:

<b>Latex Paint Formulation Containing Zinc Pyrithione and No Zinc Oxide:</b>	
<b>Ingredient</b>	<b>Grams</b>
Water	240.0
Hydroxyethyl Cellulose	6.0
Tamol 960 1	6.2
Ethylene Glycol	50.0
Colloid 643 2	2.0
Triton® CF-10 3	5.0
Potassium Tripolyphosphate	3.0
<b>Pigment Grind:</b>	
Titanium Dioxide (Rutile)	500.0
Aluminum Magnesium Sillicate	335.0
Attapulgite Clay	6.0
Zinc Pyrithione 48% Dispersion	24.0
Aluminum Sillicate	47.0
Propylene Glycol	68.0
<b>Let Down:</b>	
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
Ammonia	0.5
<b>Total Mass In Grams</b>	<b>2361.7</b>

[0040] 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 a rating of 8 (light growth).

#### EXAMPLE 1

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

[0041] 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 composition:

<b>Latex Paint Formulation Containing Zinc Pyrithione and Zinc Oxide:</b>	
<b>Ingredient</b>	<b>Grams</b>
Water	240.0
Hydroxyethyl Cellulose	6.0

(continued)

Latex Paint Formulation Containing Zinc Pyrithione and Zinc Oxide:	
Ingredient	Grams
Tamol 960 1	6.2
Ethylene Glycol	50.0
Colloid 643 2	2.0
Triton® CF-10 3	5.0
Potassium Tripolyphosphate	3.0
<b>Pigment Grind:</b>	
Titanium Dioxide (Rutile)	500.0
Aluminum Magnesium Silicate	335.0
Attapulgite Clay	6.0
Zinc Pyrithione 48% Dispersion	18.0
Zinc Oxide	3.0
Aluminum Silicate	47.0
Propylene Glycol	68.0
<b>Let Down:</b>	
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
Ammonia	0.5
Total Mass in Grams	2361.7

**Footnotes**

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

[0042] 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).

[0043] 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 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 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 Pyrithione Containing Paint Bases**

[0044] 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 conducted.

[0045] 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 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 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.

5 [0046] To samples of each of these paints, 0.5% of zinc oxide was added. The difference in YI for the 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 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		
Ingredient	A	B
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
Nuosept 95	3.00	3.0
Potassium Triphosphate	2.0	2.0
<b>Pigment Grind:</b>		
Titanium Dioxide (Rutile)	200.0	200.0
Sodium Potassium Aluminum Silicate	225.0	225.0
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
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>		
Total Mass in Grams	1031.4	1037.4

35 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**

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

45 [0047] 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 were prepared as follows:

Ingredient	A	B
Water	103.0 grams	103.0
Hydroxyethyl Cellulose	2.5 grams	2.5
Tamol 960 1	12.90	12.9
Ethylene Glycol	18.00	18.0
Colloids 643 2	2.0	2.0

**Footnotes**

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

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

(continued)

Ingredient	A	B
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
Attapulgitte Clay	4.0	4.0
Zinc Oxide	2.0	6.0
<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
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>	6.0	6.0
Total Mass in Grams	1045.4	1049.4

3 A coalescent, a product of Eastman Kodak Company

Films from these paints were exposed in a QUV 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:

	YI
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 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 4

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

**[0049]** Efficacy of zinc oxide in eliminating blue coloration caused by the presence of ferric ion in sodium pyrithione containing paint bases.

**[0050]** 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.

**[0051]** 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 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

(continued)

Latex Paint Formulation Containing Sodium Pyrithione and Zinc Oxide:	
Ingredient	Grams
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
potassium tripolyphosphate	3.0
Pigment grind:	
titanium dioxide (Rutile)	424.0
aluminum magnesium silicate	228.0
attapulgate clay	3.0
zinc oxide	50.0
aluminum silicate	100.0
propylene glycol	68.0
Let Down:	
water	84.0
acrylic latex emulsion 58.0% solids	700.0
Colloid 643	6.0
Texanok® <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

[0052] 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 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 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.

Latex Paint Formulation Containing Sodium Pyrithione and Zinc Oxide:	
Ingredient	Grams
water	240.00
hydroxyethyl cellulose	6.0
Tamol 850 <sup>5</sup>	14.2
Ethylene Glycol	50.0

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

