

Description

The present invention relates to processes and compositions for preserving aqueous systems against the deleterious action of bacteria, fungi and algae.

It is well known that various aqueous systems containing metabolizable components, either in trace or major quantities, are normally susceptible to attack and degradation by microorganisms. Examples of such compositions are cutting oils, cosmetics such as lotions and creams, fuel oil, textile emulsions, latex emulsions and paints, starch-base adhesives, industrial cooling water, emulsion waxes, water used in pulp and paper manufacture (so-called "process" water, e.g., "white water"), and flood water used in secondary oil recovery methods.

A number of problems and limitations have recently faced those in the art who seek to provide effective antimicrobial preservatives for such aqueous systems. These problems involve concerns about worker exposure and environmental impact. Many preservatives are effective because they are toxic to the microorganisms at low concentrations, i.e. concentrations in the order of about 100 parts per million. Human exposure to such preservatives in the part per million range does not normally pose a risk that raises concern. The pure product, however, may pose an unacceptable risk to workers who may be exposed to the pure concentrated material on a daily basis and who must protect themselves from accidental inhalation or accidental exposure to the skin. In the case where the substance is a liquid, its vapor pressure may be of concern, if concentrations in the air could reach levels which could be harmful to workers. If the material is a solid or a powder the inhalation of dust becomes a concern.

One way to keep the concentration of such antimicrobial agents to an acceptable handling level is to use diluents or inert carriers. Such diluents or carriers are also desirable in order to assist in delivering the antimicrobial agents to the medium to be preserved. These diluents must, of course, meet certain criteria. They must be compatible with a particular antimicrobial agent and with the medium in which the antimicrobial agent is to be used. They should not be highly flammable and should not be toxic. Very few diluents can satisfy these criteria at an acceptable price.

More recently, pressures concerning the toxicity of the diluent and its compatibility with the environment have served to restrict the number of diluents that are acceptable. It is expected that even fewer diluents or carriers will be acceptable in the future.

There is a need in the industry to find a diluent or a carrier system which meets the following criteria:

1) The diluent or carrier must be compatible with the antimicrobial agent and should not diminish or destroy the antimicrobial activity.

2) The final product must have a flash point of greater than 49°C (120 degrees Fahrenheit) in order to avoid dangers due to flammability; $x^{\circ}\text{F} = \frac{5}{9}(x-32)^{\circ}\text{C}$ or $y^{\circ}\text{C} = (\frac{5}{9}y + 32)^{\circ}\text{F}$.

3) The system must work in the medium for which it is intended.

4) It should not be on list 1 or list 2 of the Environmental Protection Agency's "Inert Ingredients in Pesticide Products; Policy Statement". (Federal Register, volume 52, number 77, dated April 22, 1987. Lists 1 and 2 cover inert ingredients of toxicological concern and potential toxicological concern, respectively.)

5) The system must be economically competitive, i.e., it must not be so expensive that the system cannot compete in the market place.

6) The diluent or carrier should be odorless, or at least have a pleasant odor.

The invention provides a novel means for the safe handling of β -bromo- β -nitrostyrene (BNS; see US-PS 3629465, 3871860) which meets the criteria set forth above, and which minimizes human exposure and environmental concerns. The present invention provides a product which comprises β -bromo- β -nitrostyrene absorbed on or encapsulated into a biodegradable and relatively inert, partially hydrolyzed starch such as a maltodextrin or corn syrup solid. Hydrolyzed starches are relatively inert to most antimicrobial agents and usually result in a product with a high flash point, in most cases greater than 93°C (200 degrees Fahrenheit). The hydrolyzed starch does not contribute any odor to the final product. It is water soluble and therefore releases the active ingredients in aqueous systems. It is biodegradable and a natural food material, which is not only compatible with eco-systems but actually contributes to them in a positive fashion. The fact that the final product is a solid and is in granular form minimizes worker and user exposure and environmental contamination from spills.

The product of the invention can be manufactured by the process described hereinafter. A suitable maltodextrin or corn syrup solid can be mixed with a solution of β -bromo- β -nitrostyrene in the desired proportions [for the properties of corn syrup see also Kirk-Othmer, Encyclopedia of Chemical Technology, Vol. 22, John Wiley and Sons, Inc. N.Y., 1983, Pages 510-3.] The solvent can then be removed, for example, by vacuum distillation.

Partially hydrolyzed starches containing dextrose, maltose and higher molecular weight saccharides are available from corn starch. The hydrolyzed starch products are usually defined on the basis of their reducing sugar content referred to as the dextrose equivalency (DE). Solid, partially hydrolyzed starches with a dextrose equivalent (DE) of between 1 and 20 are preferred in the practice of the present invention. Partially hydrolyzed starches with a DE of less than 20 are generally classified as maltodextrins and are normally solid compositions of varying particle size and densities. Suitable solid hydrolyzed starches are available under such tradenames as Amaizo Fro-Dex® (American Maize-Products Co.), Maltrin® (Grain Processing Corporation) and Micropor Buds® (A.E. Staley Manufacturing Company; for details see also the promotional brochure dated 2/88). The source of the maltodextrin is not critical to the practice of the present invention. Micropor Buds® 1005, 1015 and 2010, with DE values of 10, 10 and 20, respectively, have been used for purposes of illustrating the present invention but any solid hydrolyzed starch with a DE of between 1-20 may be used. Maltodextrins with a DE value of 5-15 are preferred since they are more readily available and more economical to use.

In preparing the novel systems of the invention, it is preferred to first dissolve the β -bromo- β -nitrostyrene in a non-aqueous solvent. The nature of the solvent is not critical other than that it should be compatible with the antimicrobial agent, should be one which will dissolve the antimicrobial agent and should not react with the partially hydrolyzed starch. Suitable solvents for most applications would be, for example, hydrocarbon solvents such as toluene and the like.

The solution containing the antimicrobial agent and a suitable partially hydrolyzed starch are mixed together in the proper proportions to yield a final product with a correct level of antimicrobial agent. For example, if a final product is desired to have 50% partially hydrolyzed starch and 50% β -bromo- β -nitrostyrene, one could suitably add 100 parts of the partially hydrolyzed starch to 400 parts of a 25% solution of β -bromo- β -nitrostyrene and a suitable solvent, mix for a period of time and then remove the solvent under reduced pressure. The final product is a granular, free-flowing solid. Under most circumstances, one can vary the ratio of the antimicrobial agent to the partially hydrolyzed starch from as little as 0.5% antimicrobial agent and 99.5% partially hydrolyzed starch to as high as 90% antimicrobial agent to 10% partially hydrolyzed starch. It is preferred, however, to use a ratio of from 40-60% β -bromo- β -nitrostyrene to 60-40% partially hydrolyzed starch, since this provides the best free-flowing solid. The most preferred ratios will depend on a number of factors including the use to which the antimicrobial agent is to be applied.

Compositions prepared according to the present invention were found to be stable over time. Analysis of compositions containing 25% and 50% β -bromo- β -nitrostyrene on maltodextrin (DE =10), using standard ultraviolet spectroscopic methods, showed no deviation in the composition of the mixtures after 30 days of storage.

The compositions have also been shown to be effective, in general, against a broad spectrum of microorganisms which attack the aqueous systems described herein. Samples of 25% and 50% β -bromo- β -nitrostyrene on maltodextrin were evaluated in agar to obtain a minimum inhibitory concentration range of each sample against a series of bacteria, yeast, and molds. Pure β -bromo- β -nitrostyrene served as a control. The test was designed with small dilution increments so that relatively minor differences in antimicrobial activity could be detected. Results indicate that the activity of the two β -bromo- β -nitrostyrene/maltodextrin samples compared favorably with the control. No significant differences in antimicrobial activity were detected. In the ranges presented in the examples below, no growth occurred at the higher concentration while the lower concentration was non-inhibitory. (Maltodextrin was tested alone and was found to be non-inhibitory against all microorganisms at 100 mcg (micrograms)/ml, the highest concentration of carrier tested.)

The microbial activity of β -bromo- β -nitrostyrene diluted with maltodextrin is identical to an equivalent amount of the pure material, and would therefore be useful as a preservative of aqueous systems as described in U.S. Patent 3,629,465

Example 1: Preparation of Product

To 400 grams of a solution consisting of 100 grams of β -bromo- β -nitrostyrene and 300 grams of toluene, is added 100 grams of a hydrolyzed starch with a DE of 10 available under the tradename Micropor Buds® (grade 1015). The resulting mixture is heated to a temperature of 50°C. The toluene is then removed under reduced pressure (30 mm Hg) at 50°C to yield a granular solid. Analysis of the granular solid by ultraviolet spectroscopic analysis (UV) shows 48-52% β -bromo- β -nitrostyrene. (The range is due to deviations in the test procedure.)

Substitution of Micropor Buds® 1005 or 2010 for the Micropor Buds® 1015 in the above procedure yields the respective product containing 48-52% β -bromo- β -nitrostyrene.

Products containing 25% β -bromo- β -nitrostyrene are prepared using 350 grams of a solution of 50 grams of β -bromo- β -nitrostyrene in 300 grams of toluene in the above procedure. It is well within the skill of one in the

art to determine the proper proportions necessary to prepare a product with the desired level of β -bromo- β -nitrostyrene.

Example 2: Microbial Activity

Samples of 25% and 50% β -bromo- β -nitrostyrene on Micropor Buds® grade 1015 were evaluated in agar to obtain a minimum inhibitory concentration range based on BNS concentration of each sample against a series of bacteria, yeast, and molds. Pure β -bromo- β -nitrostyrene served as a control. The test was designed with small dilution increments so that relatively minor differences in antimicrobial activity could be detected.

Results listed in the following tables indicate that the activity of the two samples compared favorably with the control. No significant differences in antimicrobial activity were detected.

Sample Identification:

25BNS 25% β -bromo- β -nitrostyrene /75% Micropor Buds® #1015
50BNS 50% β -bromo- β -nitrostyrene /50% Micropor Buds® #1015
Control Pure β -bromo- β -nitrostyrene (m.p. 62°-63°C)

TABLE I - BACTERIA
Minimum Inhibitory Concentration Range in mcg/ml

Sample	Staphylococcus aureus	Escherichia coli	Pseudomonas aeruginosa	Proteus vulgaris	Bacillus subtilis
25BNS	>25	17.5-20.0	12.5-15.0	17.5-20.0	22.5-25.0
50BNS	>25	15.0-17.5	10.0-12.5	15.0-17.5	20.0-22.5
Pure BNS	>25	15.0-17.5	10.0-12.5	15.0-17.5	20.0-22.5

TABLE II - YEAST, MOLDS
Minimum Inhibitory Concentration Range in mcg/ml

Sample	Candida albicans	Aspergillus niger	Aspergillus oryzae	Penicillium piscarium	Aureobasidium pullulans
25BNS	15.0-17.5	7.5-10.0	17.5-20.0	7.5-10.0	2.5-5.0
50BNS	12.5-15.0	7.5-10.0	15.0-17.5	7.5-10.0	2.5-5.0
Pure BNS	12.5-15.0	10.0-12.5	17.5-20.0	7.5-10.0	2.5-5.0

In the ranges presented, no growth occurred at the higher BNS concentration while the lower BNS concentration was non-inhibitory. Micropor Buds® alone was non-inhibitory against all microorganisms at 100

mcg/ml, the highest concentration of carrier tested.

Example 3: Stability and Compatability

Samples of 25% and 50% β -bromo- β -nitrostyrene on Micropor Buds® grade 1015 were placed in brown sealed bottles and assayed for β -bromo- β -nitrostyrene by standard Ultraviolet Spectroscopic methods over 30 days period.

TABLE III

β -bromo- β -nitrostyrene (BNS)/Micropor Buds® Stability

Sample	Percent Initial	β -bromo- β -nitrostyrene 14 days	30 days
25% BNS	24.7	24.1	24.5
50% BNS	51.2	51.2	50.6

Claims

1. An antimicrobial composition which comprises β -bromo- β -nitrostyrene absorbed on or encapsulated into a partially hydrolyzed starch with a DE value of 20 or less and which composition is in granular solid form.
2. A composition according to claim 1 consisting essentially of 90-10% β -bromo- β -nitrostyrene and 10-90% of partially hydrolyzed starch.
3. A composition according to claim 1 or 2 consisting essentially of 50-25% β -bromo- β -nitrostyrene and 50-75% partially hydrolyzed starch.
4. A composition according to any one of claims 1 to 3 wherein the DE value is from 5 to 15.
5. A process for combatting spoilage caused by the action of microorganisms in aqueous compositions normally subject to such spoilage, which comprises inhibiting said organism in such compositions with an effective inhibiting amount of a composition which comprises β -bromo- β -nitrosytrene absorbed on or encapsulated into a partially hydrolyzed starch with a DE value of 20 or less in granular solid form.
6. A process according to claim 5 for combatting spoilage by the action of slime-forming algae, bacteria and fungi microorganisms in industrial cooling water and water used in pulp and paper manufacturing, which comprises inhibiting said slime-forming organism in such waters with an effective inhibiting amount of a composition which comprises β -bromo- β -nitrosytrene absorbed on or encapsulated into a partially hydrolyzed starch with a DE value of 20 or less in granular solid form.

Patentansprüche

1. Eine antimikrobiell wirksame Komposition, gekennzeichnet durch einen Gehalt an β -Brom- β -nitrostyrol, auf partiell hydrolysierter Stärke mit einem DE-Wert von 20 oder weniger absorbiert, oder in partiell hydrolysierter Stärke mit einem DE-Wert von 20 oder weniger verkapselt, und in granulierter, fester Form vorliegend.
2. Komposition gemäss Anspruch 1, gekennzeichnet durch einen Gehalt an 90-10% β -Brom- β -nitrostyrol und 10-90% partiell hydrolysierter Stärke.
3. Komposition gemäss Anspruch 1 oder 2, gekennzeichnet durch einen Gehalt an 50-25% β -Brom- β -nitrostyrol und 50-75% partiell hydrolysierter Stärke.
4. Komposition gemäss einem der Ansprüche 1 bis 3, worin der DE-Wert 5 bis 15 beträgt.
5. Verfahren zur Bekämpfung des durch Mikroorganismen verursachten Verderb wässriger Kompositio-



mcg/ml, the highest concentration of carrier tested.

Example 3: Stability and Compatability

Samples of 25% and 50% β -bromo- β -nitrostyrene on Micropor Buds® grade 1015 were placed in brown sealed bottles and assayed for β -bromo- β -nitrostyrene by standard Ultraviolet Spectroscopic methods over 30 days period.

TABLE III

β -bromo- β -nitrostyrene (BNS)/Micropor Buds® Stability

Sample	Percent Initial	β -bromo- β -nitrostyrene 14 days	30 days
25% BNS	24.7	24.1	24.5
50% BNS	51.2	51.2	50.6

Claims

1. An antimicrobial composition which comprises β -bromo- β -nitrostyrene absorbed on or encapsulated into a partially hydrolized starch with a DE value of 20 or less and which composition is in granular solid form.

2. A composition according to claim 1 consisting essentially of 90-10% β -bromo- β -nitrostyrene and 10-90% of partially hydrolyzed starch.

3. A composition according to claim 1 or 2 consisting essentially of 50-25% β -bromo- β -nitrostyrene and 50-75% partially hydrolyzed starch.

4. A composition according to any one of claims 1 to 3 wherein the DE value is from 5 to 15.

5. A process for combatting spoilage caused by the action of microorganisms in aqueous compositions normally subject to such spoilage, which comprises inhibiting said organism in such compositions with an effective inhibiting amount of a composition which comprises β -bromo- β -nitrostyrene absorbed on or encapsulated into a partially hydrolyzed starch with a DE value of 20 or less in granular solid form.

6. A process according to claim 5 for combatting spoilage by the action of slime-forming algae, bacteria and fungi microorganisms in industrial cooling water and water used in pulp and paper manufacturing, which comprises inhibiting said slime-forming organism in such waters with an effective inhibiting amount of a composition which comprises β -bromo- β -nitrostyrene absorbed on or encapsulated into a partially hydrolyzed starch with a DE value of 20 or less in granular solid form.

Patentansprüche

1. Eine antimikrobiell wirksame Komposition, gekennzeichnet durch einen Gehalt an β -Brom- β -nitrostyrol, auf partiell hydrolysierter Stärke mit einem DE-Wert von 20 oder weniger absorbiert, oder in partiell hydrolysierter Stärke mit einem DE-Wert von 20 oder weniger verkapselt, und in granulierter, fester Form vorliegend.

2. Komposition gemäss Anspruch 1, gekennzeichnet durch einen Gehalt an 90-10% β -Brom- β -nitrostyrol und 10-90% partiell hydrolysierter Stärke.

3. Komposition gemäss Anspruch 1 oder 2, gekennzeichnet durch einen Gehalt an 50-25% β -Brom- β -nitrostyrol und 50-75% partiell hydrolysierter Stärke.

4. Komposition gemäss einem der Ansprüche 1 bis 3, worin der DE-Wert 5 bis 15 beträgt.

5. Verfahren zur Bekämpfung des durch Mikroorganismen verursachten Verderb wässriger Kompositio-



nen, die einem solchen Verderb normalerweise ausgesetzt sind, dadurch gekennzeichnet, dass man solche Mikroorganismen mit einer wirksamen Menge einer Komposition hemmt, welche Komposition durch einen Gehalt an β -Brom- β -nitrostyrol, absorbiert auf partiell hydrolysierte Stärke mit einem DE-Wert von 20 oder weniger, oder verkapselt in partiell hydrolysierte Stärke mit einem DE-Wert von 20 oder weniger, gekennzeichnet ist, und welche Kompositionen in granulierter, fester Form vorliegen.

6. Verfahren gemäss Anspruch 5 zur Bekämpfung des durch Schleim bildende Algen, Bakterien und Fungi in Industriekühlwasser und in von der Papierherstellung benötigtem Wasser verursachten Verderb, dadurch gekennzeichnet, dass man diese Mikroorganismen im Wasser mit einer wirksamen Menge einer Komposition hemmt, welche Komposition durch einen Gehalt an β -Brom- β -nitrostyrol, absorbiert auf partiell hydrolysierte Stärke mit einem DE-Wert von 20 oder weniger, oder verkapselt in partiell hydrolysierte Stärke mit einem DE-Wert von 20 oder weniger, und welche Kompositionen in granulierter, fester Form vorliegen.

Revendications

1. Une composition antimicrobienne qui comprend du β -bromo- β -nitrostyrène absorbé sur ou encapsulé dans un amidon partiellement hydrolysé avec une valeur de DE de 20 ou moins, et laquelle composition est sous forme granulaire solide.

2. Une composition selon la revendication 1 consistant essentiellement en 90-10% de β -bromo- β -nitrostyrène et 10-90% d'amidon partiellement hydrolysé.

3. Une composition selon la revendication 1 ou 2 consistant essentiellement en 50-25% de β -bromo- β -nitrostyrène et 50-75% d'amidon partiellement hydrolysé.

4. Une composition selon l'une quelconque des revendications 1 à 3 dans laquelle la valeur de DE va de 5 à 15.

5. Un procédé pour combattre les dommages causés par l'action des microorganismes dans des compositions aqueuses normalement soumises à de tels dommages, qui comprend l'inhibition dudit organisme dans de telles compositions avec une quantité inhibitrice efficace d'une composition qui comprend du β -bromo- β -nitrostyrène absorbé sur ou encapsulé dans un amidon partiellement hydrolysé avec une valeur de DE de 20 ou moins sous forme d'un solide granulaire.

6. Un procédé selon la revendication 5 pour combattre les dommages causés par l'action des microorganismes formateurs de mucus, algues, bactéries et champignons dans l'eau de refroidissement industriel et l'eau utilisé dans la manufacture de la pulpe et du papier, qui comprend d'inhiber ledit organisme formateur de mucus dans ces eaux avec une quantité inhibitrice efficace d'une composition qui comprend du β -bromo- β -nitrostyrène absorbé sur ou encapsulé dans un amidon partiellement hydrolysé avec une valeur de DE de 20 ou moins sous forme d'un solide granulaire.