

CHLORINE DIOXIDE GENERATING POLYMER PACKAGING FILMS

TECHNICAL FIELD OF THE INVENTION

5 The present invention relates generally to a composition for reducing bacterial and fungal growth and repelling insects, and more particularly to an ionomeric composition having biocidal or insect repelling releasing agent and method for making same.

BACKGROUND OF THE INVENTION

10 Chlorine Dioxide ("ClO₂") has been incorporated in polymer [JP 63,296,758, NOK Corp, 1988; CA 111 P120181s] and ceramic beads [JP 63,274,434, Enkler Busin.K.K., 1988; CA 111 P11975h], and in a calcium silicate wrapped in non-woven cloth [JP 57,168,977, Enkler Busin.K.K., 1982; CA 98 P77552] to be used as a deodorant. Food preservation is an application where a gel form is preferred [JP Patent, Diamaru Kogyo
15 Kaishi, Ltd., 1982; CA 97 22409]. Chlorine dioxide generating gels have also been used as topical applications for disinfection [A.J. Kenyon, S.G. Hamilton and D.M. Douglas, Am.J.Vet.Res., 45(5), 1101 (1986)].

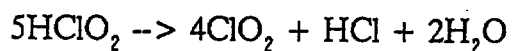
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Most attempts to generate chlorine dioxide involve acidification (and or chlorination) of an aqueous solution of chlorite, acidification (and/or reduction) of chlorates ["Comprehensive Inorganic Chemistry, The Halogens", Vol 3, R.C.Brasted, D. Van Nostrand Co., New York, 1954, 5 p134-142] or reduction of a chlorite solution with aldehydes [US 2,323,594, Mathieson Alkali Works, 1943]. Typically the preparation involves mixing component A (gel with suspended NaClO_2) with component B (gel with lactic acid) immediately prior to use. α -hydroxy carboxylic acids (citric, tartaric, malic, glycolic) are especially useful for generating ClO_2 by the 10 reaction:



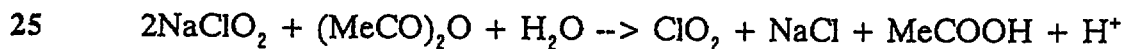
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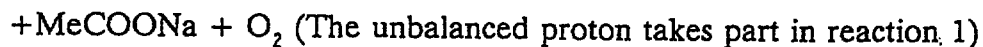
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[Ger.Offen. 2,817,942, H.Allinger, 1979; PCT Int. Appl. WO, J. Mason, 1988, CA 110 P98205h]. Alternatively, NaClO_2 and lactic acid have been separately encapsulated in polyvinyl alcohol and then mixed with water to generate ClO_2 [Can. 959,238, Chemical Generators, 1974]. Formulations 20 involving sulfonic acids are also available [Europ. Pat. Appl. EP 287,074, Alcide Corp., 1987; CA 111 P45299f].

Another method for the production of chlorine dioxide employs acetic anhydride in the reaction:



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Interestingly prehydrolysis of the anhydride to acetic acid prior to the addition of chlorite produces no chlorine dioxide. Direct reaction of chlorite with anhydride in the presence of water is obviously important in the reaction [W. Masschelein, I and EC Prod. Res. and Dev., 6(2), 137 (1967)].

This work suggests the possibility of storing chlorite in a complex with an acid anhydride in a stable form until reaction with moisture liberates the chlorine dioxide [US 2,482,134, R.Aston, 1949). Food packaging with the incorporated disinfectant, chlorine dioxide, brings up an important public health question pertinent to this practice: Does chronic ingestion of residual levels of disinfectants result in a significant genetic or carcinogenetic hazard to the human population? It is clear from published pharmacokinetic studies aided by incorporation of a chlorine radioisotope (^{36}Cl) that skin patch (Alcide gel) administration of chlorine dioxide and chlorite result in prolonged systemic residence of chlorine containing residues [J. Scatina, M. S. Abdel-Rahman, S.E. Gerges, Y. Khan and O. Gona, Fund.Appl.Tox., 4, 479 (1984)].

Meier et.al. published a report on the effect of subchronic and acute oral administration of chlorine, chlorine dioxide, sodium chlorite, and sodium chlorate on the induction of chromosomal aberrations and sperm-head abnormalities in mice [J.R. Meier, R.J. Bull, J.A. Stober and M.C. Cimino, Environ. Mutagenesis, 7, 201 (1985)]. Only the highly reactive hypochlorite resulted in a weak positive effect for mutagenic potential. The disinfectants failed to induce any chromosomal aberrations or increased numbers of micronuclei in the bone marrow of mice. Other hazards which have been associated with chlorine dioxide but were not incorporated in the published study include hemolytic anemia and hypothyroidism. One of the reasons for the relatively innocuous effect of ClO_2 is its inability to produce

halomethanes, unlike hypochlorite and chlorine [R. Vilagines et al., Proc. AWWA Disinfect. Semin. 1977, paper 3, 24pp; CA 93 173513f].

U.S. Patent No. 4,585,482 describes the gradual hydrolysis of alternating poly (vinyl methyl ether-maleic anhydride) or poly (lactic-glycolic acid) to generate acid which can release chlorine dioxide from sodium chlorite. In the process a solution process is used to encapsulate a polyalcohol humectant and water with the polyanhydride or polyacid in a nylon coating. After sodium chlorite is permitted to diffuse into the capsule through the nylon wall, an impermeable polystyrene layer is
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coacervated around the nylon capsule. The capsules can be coated onto surfaces to release chlorine dioxide and provide biocidal action for several days to months.

Despite the many advantages of the '482 patent, there are some limitations. First, a large number of processing steps involving numerous chemical reactions and physical processes with disposal problems are
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required. Second, the chemistry is limited to batch processes. Third, a clear film cannot be produced. Finally, chlorine dioxide release starts immediately.

SUMMARY OF THE INVENTION

20 The object of the present invention is to improve over the prior art by a method which is continuous, safer and has minimal number of preparation steps.

The more specific objects of the invention are: to provide a low cost, chlorite containing oligomer or polymer that can be coated onto
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surfaces as a film prior to chlorine dioxide release. In addition, the invention provides a chlorite loaded film which will release chlorine dioxide over an extended period of time by exposure to moisture and both disinfect and repel insects from the surface onto which it is coated.

In the presence of water the local pH in the polymer film is reduced, releasing the chlorine dioxide.

5 The present invention disclosed herein comprises a method for making a composition which liberates a biocidal and/or insect repelling agent comprising the steps of dissolving a chlorite salt into a hydrogen bonded matrix to create a chlorite containing phase. The chlorite containing phase is then mixed with an incompatible phase having a hydrolyzable anhydride component therein to create a mixture having an ionomeric polymer. By exposing this mixture to the atmospheric moisture
10 the ionomeric polymer liberates a chlorine dioxide compound to in effect act as a biocidal agent or an insect repelling agent.

In addition, the present invention discloses a composition which liberates a biocidal and/or insect repelling agent when exposed to a water source in accordance with the method of making as described above.

15 DETAILED DESCRIPTION

The preferred constituents of the apolar phase are styrene - maleic anhydride copolymers and their grafts with olefins. The monomers are cheap, commercially available and will form charge transfer complex that will polymerize thermally in the presence of small amounts of oxygen.
20 Maleic anhydride contents between 0-50 mole % are available. At maleic anhydride concentrations below 33% the copolymers are soluble in apolar aromatic plasticizers.

In a preferred process an equimolar styrene-maleic anhydride monomer mix at 60°C is added to a melt of plasticized, low
25 molecular weight olefin such as, atactic polypropylene or other olefine in a Brabender Plasticorder equipped with a twin screw extruder. The styrene maleic-anhydride will spontaneously polymerize to a macroradical which will graft to the base polymer [N. Gaylord, ACS Adv.Chem.Ser., 129, 209

(1973); Z. Kopicova, J. Nemic and M. Protiva, Coll. Czechoslov.Chem. Commun. 41, 459 (1976)].

5 An alternative method to produce the desired anhydride substituted polymer is to copolymerize methacrylic anhydride with hydrophobic, aliphatic or aromatic vinyl monomers. Linear polymers that incorporate anhydride in the backbone generally require that the anhydride be included in mole percentages less than 6% [J.C.H. Hwa and L. Miller, J. Poly. Sci., 55, 197 (1961)].

10 The apolar phase may also contain components which may be induced to crosslink after film coating in order to stabilize the mechanical properties of the coating. These components include mixtures of hydrophobic epoxides and amines.

15 The gradual hydrolysis of the anhydride component in the presence of atmospheric moisture will generate acid functionality and ionomer formation. This will promote interphase compatibilization between the chlorite containing hydrogen bonded phase and the apolar phase containing the anhydride.

20 The preferred constituents of the hydrogen bonded phase include sodium chlorites or other chlorites where the cation may be an alkali, alkaline earth metal or transition metal ion or a protonated primary, secondary, tertiary amine or quaternary amine. The hydrogen bonded phase which solubilizes the chlorite can be monomeric or polymeric amides (e.g. formamide, isopropylacrylamide-acrylamide mixture) or monomeric or polymeric alcohols (e.g. methanol, 2-(2-ethoxyethanol). The amides are
25 especially preferred since the amide functionality does not react with the anhydride below 150°C. In addition, chlorites, such as sodium chlorite remain stable in amides, such as formamide, up to 100°C.

 The hydrogen bonded phase may also contain components which may be induced to polymerize after film coating in order to stabilize the

mechanical properties of the coating. These components include hydrogen bonded epoxides and amines.

5 The final coating composition is made by mixing the hydrophobic and hydrogen bonded phases to the desired dispersion at temperatures below the decomposition temperature of the chlorite, preferably at temperatures less than 60°C. The coating is then applied as a hot melt to the substrate and then is induced to solidify by cooling to room temperature.

10 If both phases are mixed for short times at high viscosity little reaction of the anhydride with the chlorite occurs. However, if the dispersion is very fine, the phase compatibility very high (similar solubility parameters for the apolar phase and hydrogen bonded phase) and the viscosity of the phase is low extensive production of chlorine dioxide is observed even in dry films.

15 Exposure of the solid, unreacted film to water will hydrolyze the anhydride groups, compatibilize the phases and induce chlorine dioxide release. Thus chlorine dioxide release can be controlled by phase dispersion, phase viscosity, and exposure to atmospheric moisture.

20 The present invention is further illustrated by the following example.
A 7 wt% solution of sodium chlorite was made in 33wt% formamide:33wt% acrylamide:33wt% isopropylacrylamide (hydrogen bonded phase). Next a 40% solution of a 33mole% maleic anhydride:65%moles styrene copolymer solution in ethylbenzene plasticizer (apolar phase) was vortex mixed with the hydrogen bonded, chlorite containing phase. The resultant white blend of the two disperse phases
25 started a sustained release of chlorine dioxide in the absence of added water within five minutes at room temperature due to interphase diffusion and reaction.

The release rate could be slowed by cooling the mixture to 0°C or by increasing the viscosity of the phases. Water was observed to hydrolyze the maleic anhydride to maleic acid and increase the rate of chlorine dioxide release.

- 5 While the preferred embodiments of the invention and their advantages have been disclosed in the above detailed description, the invention is not limited thereto but only by the spirit and scope of the appended claims.

The following paragraphs summarise some important features of the invention:

5 The method for making the composition which liberates a repelling or biocidal agent comprises the steps of:

 dissolving a chlorite salt of a cation into hydrogen bonded matrices to create an amine containing phase; and

 mixing said amine containing phase with an incompatible phase
10 having a hydrolyzable anhydride component therein to create a mixture having an ionomeric polymer; and

 exposing said mixture to atmospheric moisture such that said ionomeric polymer releases chlorine dioxide when exposed to said moisture in order to liberate a repelling or biocidal agent.

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 The chlorite cation may comprise an alkali, alkaline earth, transition metal, protonated primary amine, protonated secondary amine, protonated secondary amine, protonated tertiary amine, quaternary monomeric amine, quaternary polymeric amine or a mixture thereof.

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 The method may further include the step of selectively forming a film of said composition on a substrate. This step may comprise the step of
 applying said ionomeric polymer as a tacky hot melt to the substrate;
 controlling the operating temperature to avoid the decomposition

temperature of any chlorite present; and

changing the viscosity and phase dispersion of the composition to control the reaction of the anhydride with the chlorite to release chlorine dioxide.

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The method may further comprise the step of lowering the pH of said ionomeric polymer to less than 8.0.

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The composition which liberates a repelling or biocidal agent when exposed to a water source may be said to comprise:

a cation;

a chlorite salt of said cation in a hydrogen bonded matrix; and

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an incompatible phase having a hydrolyzable acid anhydride component therein mixed with said hydrogen bonded matrices to form an ionomeric composition having a chlorite compound contained therein such that said ionomeric composition releases chlorine dioxide when exposed to the water source for acting as a repelling or biocidal agent.

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The chlorite salt may be derived of protonated primary amine, protonated secondary amine and protonated tertiary amine.

The cation may comprise an alkali, alkaline earth, transition metal, protonated primary amine, protonated secondary amine, protonated tertiary amine, quaternary monomeric amine, quaternary polymeric amine or

a mixture thereof.

The ionomer composition may be meltable to create a film on a substrate.

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In the above method and composition, the matrices may comprise aliphates amides, aromatic amides, aliphatic alcohol, aromatic alcohol or a mixture thereof and may be selected from formamide, acrylamide-isopropylacrylamide mixtures or their polymerized products, neat primary or secondary amines and
10 their polymerization products with acrylamide, isopropylacrylamide and N,N methylene bisacrylamide, and glycerine, ethylene glycol, or poly hydroxylic alcohols or mixtures of the above.

The incompatible phase with the hydrogen bonded phases may
15 consist of grafted anhydride styrene copolymer of a concentration between approximately 5 weight percent and approximately 50 weight percent blended with or grafted to hydrocarbons such as polypropylenes, polyethylenes, or polystyrenes.



CLAIMS

- 5 1. A method for making a composition which liberates a repelling
 or biocidal agent comprising chlorine dioxide and which comprises
 mixing (a) the product of dissolving a chlorite salt into hydrogen
 bonded matrix with (b) an incompatible phase comprising a polymer
 containing hydrolyzable anhydride component.
- 10 2. A method as claimed in Claim 1, wherein said chlorite salt
 comprises a salt of an alkali metal, alkaline earth metal, transition metal,
 protonated primary amine, protonated secondary amine, protonated tertiary
 amine, quaternary monomeric amine, quaternary polymeric amine or a mixture
 thereof.
- 15 3. A method as claimed in Claim 1 or Claim 2, wherein said
 matrix comprises aliphatic amide, aromatic amide, aliphatic alcohol, aromatic
 alcohol or a mixture thereof.
- 20 4. A method as claimed in Claim 1 or Claim 2, wherein said
 hydrogen bonded matrix comprises formamide, acrylamide-
 isopropylacrylamide mixtures or their polymerized products, neat primary or
 secondary amines or their polymerization products with acrylamide,
 isopropylacrylamide and N,N methylene bisacrylamide, glycerine, ethylene



glycol, poly hydroxylic alcohol or a mixture of the above.

5. A method as claimed in any one of Claims 1 to 4, further comprising the step of lowering the pH of said polymer to less than 8.0.

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6. A method as claimed in any one of Claims 1 to 5, further comprising the step of selectively forming a film of said composition on a substrate.

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7. The method as recited in Claim 6, wherein said step of forming a film comprises the steps of:

applying said polymer as a tacky hot melt to the substrate;

controlling the operating temperature to avoid the decomposition temperature of any chlorite present; and

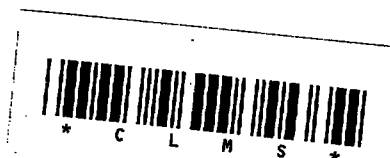
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changing the viscosity and phase dispersion of the composition to control the reaction of the anhydride with the chlorite to release chlorine dioxide.

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8. A composition which liberates a repelling or biocidal agent comprising chlorine dioxide when exposed to a water source, said composition comprising

a chlorite salt in a hydrogen bonded matrix and, mixed therewith, an incompatible phase, preferably comprising polymeric material, and having a hydrolyzable acid anhydride component therein.



9. The composition as claimed in Claim 8, wherein said salt is a salt of an alkali metal, alkaline earth metal, transition metal, protonated primary amine, protonated secondary amine, protonated tertiary amine, quaternary monomeric amine, quaternary polymeric amine or a mixture thereof.

10. A composition as claimed in Claim 8 or Claim 9, wherein said composition is meltable to create a film on a substrate.

11. A composition as claimed in any one of Claims 8 to 10, wherein said hydrogen bonded matrix comprises formamide; an acrylamide-isopropylacrylamide mixture or polymerized product thereof; neat primary or secondary amine or a polymerization product thereof with acrylamide, isopropylacrylamide and N,N methylene bisacrylamide; glycerine; ethylene glycol; polyhydroxylic alcohol or mixture thereof.

12. A composition as claimed in any one of Claims 8 to 12 where said incompatible phase comprises a polymeric material, for example grafted anhydride styrene copolymer of a concentration between approximately 5 weight percent and approximately 50 weight percent blended with or grafted to a hydrocarbon such as polypropylene, polyethylene or polystyrene.

13. A method for the release of a repelling or biocidal agent comprising chlorine dioxide, over an extended period of time, said method

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comprising exposing a composition as claimed in any one of Claims 8 to 12
or obtained by the method of any one of Claims 1 to 7 to atmospheric
moisture.