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POLYMERIC BIOCIDAL COMPOSITION AND METHOD FOR MAKING SAME

TECHNICAL FIELD OF THE INVENTION

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 a biocidal or insect repelling releasing agent and method for making same.

BACKGROUND OF THE INVENTION

Chlorine dioxide ("ClO_2") is a well known bleach, disinfectant, fumigant and deodorizer [W. J. Masschelin and Rip G. Rice, "Chlorine Dioxide, Chemistry and Environmental Impact of Oxychlorine Compounds", Ann Arbor Science, Ann Arbor, Mich.] The biocidal uses of chlorine dioxide in packaging alone is a market of several hundred million dollars a year. Especially sought after are coatings which can release chlorine dioxide at surface concentrations of parts per million ppm over several months.

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ClO_2 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 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)]. 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 reaction:

$$H^+ + NaClO_2 \rightarrow HClO_2 + Na^+$$

1)

$$5HClO_2 \rightarrow 4ClO_2 + HCl + 2H_2O$$

[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 involving sulfonic acids are also available [Europ. Pat. Appl. EP 287,074, Alcide Corp., 1987; CA 111 P45299f].

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

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apparent 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].

Recently, the U.S. Patent No. 4,585,482 ('482) has used 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 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.

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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 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

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, oligomer or polymer that can be coated onto surfaces as a film prior to conversion to a chlorite bearing substance. Also, the present invention provides a non-toxic oligomer or polymer that can be safely converted into a chlorite bearing film by exposure to chlorine dioxide, generated on site in gaseous form or in a non-aqueous solvent, eliminating the problem of storage of unstable chlorites. 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.

The present invention provides a long acting biocidal and insect repelling composition which employs a chlorine dioxide liberating polymer film which is converted to its stored chlorite form by exposure to chlorine dioxide in the presence of an acid precursor. In the presence of water the local pH in the polymer film is reduced, releasing the chlorine dioxide.

The present invention disclosed herein comprises a method for making a composition which liberates a biocidal and/or insect repellant agent which comprises the steps of synthesizing hydrogen 'bonded amines as a neat material and dissolving the amines into a hydrogen bonded

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matrix. Next, the amine is mixed with an incompatible phase containing a hydrolyzable phosphate ester or anhydride. By exposing the mixture to a gaseous chlorine dioxide, an ionomeric composition is created having an iminium chlorite salt-bound to the ionomeric composition such that said ionomeric polymer releases chlorine dioxide when exposed to water for acting as a biocidal agent.

As part of the invention, a composition is disclosed which liberates a biocidal and/or insect repelling agent which comprises a hydrogen bonded amine blended therein. The amine is grafted into hydrogen bonded matrices to create a mixture. An incompatible phase is mixed with the amine mixture. A gaseous chlorine dioxide exposed to said mixture creates an ionomeric composition such that the ionomeric composition releases chlorine dioxide when exposed to water for acting as a repelling agent or biocidal.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention can be more readily understood by referring to the following figures in conjunction with the detailed description:

FIG. 1a illustrates the preparation of an iminium chlorite film; and

FIG. 1b illustrates the release of chlorine dioxide from iminium chlorite film upon exposure of water.

DETAILED DESCRIPTION

Referring to FIGS. 1a and 1b, chlorine dioxide is a stable free radical that can undergo a redox reaction with organic amines to produce chlorite ion and an aminium radical cation. The radical cation quickly converts to an iminium cation by loss of a proton from the adjacent carbon atom and oxidation by another chlorine dioxide molecule [D.H. Rosenbatt et al., JACS, 89(5), 1158, 1163(1987); C.K. Chen, A.G. Hortmann and M.R. Marzabadi, JACS 110, 4829 (1988)]. The ionic species so created would

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phase separate into ionic microdomains which would provide humectant properties so that atmospheric moisture could be concentrated.

In the presence of water, at a sufficiently low pH, the iminium ion will cleave to an amine and an aldehyde. Each aldehyde has the potential to convert three chlorite anions to two chlorine dioxide molecules and a chloride anion with oxidation of the aldehyde to a carboxylic acid. The production rate of chlorine dioxide is of course enhanced by low pH. These protons can be supplied by the hydrolytic conversion of the anhydride or other acid generating moities to carboxylic acid or inorganic acids. All reacted groups can remain grafted to the polymer backbone after chlorine dioxide evolution and thus would not be released into the environment.

The above mechanism presents an easy a direct way to convert chlorine dioxide to chlorite in a polymer film and release it by stored moisture.

Chlorine dioxide can be continuously produced in 0.5% solution in water on a commercial scale. A water solution of chlorine dioxide will preferentially partition into a carbon tetrachloride phase with an equilibrium constant of 1.6 at 25°C [Int.Crit.Tab., 3, 419 (1928)]. Thus an efficient system for continuously reacting chlorine dioxide with the initial copolymer involves exchanging the chlorine dioxide from the water phase into an unreactive, hydrophobic solvent and expose the copolymer film to the organic solution saturated with chlorine dioxide. Since the diffusion constant and solubility for chlorine dioxide in the hydrophobic phase of the polymer phase will be much faster than water, the small amounts of moisture in the organic phase will be inconsequential.

The long acting chlorine dioxide releasing film of the present invention employs a "chlorine dioxide liberating compound" which is defined as the monomeric, oligomeric or polymeric iminium chlorite described

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above. The precursor amine to the iminium chlorite salt is dissolved in a hydrogen bonded oligomeric or polymeric matrix or suspended or emulsified in an apolar oligomeric or polymeric matrix. Alternatively, the matrix or the amine itself may be in a monomeric form which may be polymerized with or without grafting subsequent to coating onto the desired substrate.

In order for the amine functionality to react with chlorine dioxide to produce an iminium chlorite salt which may ultimately evolve chlorine dioxide, the amine nitrogen must be enclosed in a hydrogen bonded matrix The matrix must contain a sufficient molecular density of hydroxylic, -OH, or amide, -NHC(O)-, $H_2NC(O)$- groups, or amine, H_xNR_{3-x}, x=1,2. Possible matrices include formamide, acrylamide-isopropylacrylamide mixtures, water, glycerin, ethylene glycol or other oligoalkanols or oligoamides or primary or secondary oligoamines with sufficiently short apolar sections. Amine precursors to iminium chlorite salts can be of the form $H_xN(R)_{3-x}$, x=0,1,2, where R may be alkyl, cycloalkyl, pyridyl, benzyl, which can be dispersed as a separate phase in an apolar or polar non-hydrogen bonded matrix, which may be a monomeric, oligomeric or polymeric hydrocarbon.

Chlorine dioxide will react with the amines when amines of this type are dissolved to make one phase solutions in aliphatic or aromatic hydrocarbons or even in very polar solvents, such as dimethylformamide, dimethylsulfoxide, organic esters or acetonitrile, but in most cases no chlorite is formed and no chlorine dioxide can be released by acidification.

Neat primary and secondary amines with short non-hydrogen bonding groups will produce iminium chlorite which can release chlorine dioxide. However, neat tertiary amines with non-hydrogen bonding groups will react with chlorine dioxide, but will not produce a salt from which chlorine dioxide can be evolved.

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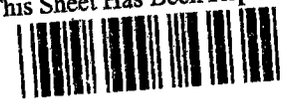

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An alternative strategy to assure reaction of the amine to form an iminium salt from which the chlorine dioxide can be released is to bond a hydrogen bonding group directly to the amine nitrogen. Thus, amines of the form $H_xN^1R_y{}^2R_{3-x-y}$ (x=0,1,2; R=CH_2CH_2OH, -$CH_2CH_2C(O)NH_2$) are especially preferred. Neat tertiary amines of this form will form chlorite salt from which chlorine dioxide can be released.

An effective chlorine dioxide introduction and reaction to chlorite occurs when the film is exposed above the T_g (glass transition temperature) of the microphase in which the amine is dissolved.

The iminium chlorite salts can be induced to release chlorine dioxide by exposure to a hydrolyzed "acid generating compound" which includes carboxylic acids, esters, anhydrides, acyl halides, phosphoric acid and its trimethylsilyl esters, dialkyl phosphate and phosphate trimethylsilyl esters and sulfonic acids and hydrolyzable sulfonic esters and chlorides.

The acid anhydride can be in the form of a random copolymer of maleic anhydride and styrene or numerous other alkenes. Trimethylsilane esters of phosphates of the form $Me_3SiOP(O)(OR)_2$ (R = non hydrogen bonding groups, alkyl, aryl) are especially useful. Comonomers and R groups are selected so that the acid generating compound will preferentially dissolve in the non-hydrogen bonded phase and will not react with the amine containing hydrogen bonded phase and will not exude or extract into the environment. This may be accomplished by grafting the R group to the apolar polymer phase or increasing the molecular weight of the R groups.

Upon exposure to moisture the anhydride will form a dicarboxylic acid and the trimethylsilyl phosphate ester will form hexamethyldisiloxane and phosphoric acid or phosphoric acid ester. These acid species will migrate, due to interphase dispersal and compatiblization, to the hydrogen bonded phase to release chlorine dioxide from the iminium chlorite salt. The apolar phases containing the acid generating compound include low

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melting polyethylene waxes or atactic polypropylene. The hydrogen bonded phase containing the iminium chlorite salt also acts as a humectant ensuring that a critical amount of water is absorbed for the hydrolysis of the "acid generating compound".

The chlorite containing film can be manufactured as a hot melt adhesive or coating composition and hermetically sealed until use. In applications involving the simple coating of boxes, the polymer can be a low molecular weight form, heavily plasticized (e.g. by waxes or chlorinated waxes) so that the film could be applied as a tacky hot melt to the surface of the dry cardboard at the end of the cardboard manufacturing line.

The present invention is further illustrated by the following Examples.

EXAMPLE 1

This example illustrates the utility of primary and secondary hydrogen bonding amines as precursors to iminium chlorite in hydrogen bonded matrices. Hydrogen bonded matrices include the neat amine or amide type solvents. Hydroxylic solvents such as water, ethylene glycol and glycerine were also useful but had the disadvantage of reacting with the acid generating compound. Chlorine dioxide is released by exposure to hydrolyzed phosphate acid precursors.

Convenient non-aqueous media for the chlorine dioxide in larger scale practice are chlorinated paraffins of 70% chlorine content and C_9-C_{15} fraction . These materials are non-toxic (suitable for food packaging), non-reactive with chlorine dioxide, and low viscosity, low vapor pressure liquids at room temperature. Their complete insolubility in water and high density of 1.30-1.36 g/cc would enable their easy separation from the chlorine dioxide saturated water phase. These compounds are also useful as fire retardant and plasticizer additives for hydrocarbon polymers.

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Their solubility parameter of 9.1 $(cal/cc)^{1/2}$ suggests that they would dissolve as much or more chlorine dioxide than carbon tetrachloride (8.6 $(cal/cc)^{1/2}$). The chlorinated paraffin is specially desirable because of its low fire danger. Its low vapor pressure would also permit it to be used in the vacuum loop of the chlorine dioxide generator in the place of water.

In smaller scale laboratory practice, volatile pentane was found to be more suitable. Thus $2.85X10^{-4}$ mole neat diethanolamine was exposed to $6X10^{-5}$ mole chlorine dioxide in pentane. The mixture remained two phase as the chlorine dioxide was completely absorbed in the amine to form a very viscous clear solution containing the iminium chlorite. Characteristic infrared absorbances for the chlorite anion were visible in the IR around 830 cm^{-1}. Absorbances for protonated amines were also visible. (Monoethanol and triethanol amines could both be converted to the iminium chlorite by a similar process).

The above process, utilizing the neat amines, was successful for virtually any primary or secondary amine which could be reacted as a phase separate from the chlorine dioxide solution.

This iminium chlorite solution was stable for at least one week at room temperature and exhibited a pH of 9. Up to one mole of chlorine dioxide per three moles of diethanol amine could be absorbed before the pH approached neutrality, precluding any more chlorine dioxide absorption. Long term stability of the solution was assured provided that the pH remained above 7-8, otherwise a slow decomposition of the iminium chlorite with a sustained release of chlorine dioxide would occur. Water appeared to enhance the release rate.

Bis (2-ethyl hexyl) phosphate (BCHP) is very soluble in pentane and other apolar media but is quite insoluble in highly hydrogen bonded solvents or ionomeric solutions such as formamide or the iminium chlorite. Thus, $3.0X10^{-4}$ mole BCHP solution in 1 ml pentane was added to the

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iminium chlorite with vortex mixing and the pentane pumped off under vacuum until a two phase dispersion resulted.

The interphase transfer of the BCHP was sufficient to induce a slow release of chlorine dioxide in the absence of water. However, the addition of 0.05 ml water accelerated the release rate. The initial release in the absence of water could be eliminated by dissolving the BCHP in mineral oil or other higher molecular weight hydrocarbon to minimize the interfacial acid concentration and decrease the diffusion rate through a viscosity increase.

Further improvements in the dry chemical stability of the two phase solution was achieved by dissolving the same amount of diethanol amine in formamide or a mixture of polymerizable acrylamide-isopropylacrylamide prior to chlorine dioxide exposure. Interestingly, the double bond in the acrylamides were stable to oxidation by chlorine dioxide. In these cases the phase segregation of the BCHP was complete enough that the BCHP could be added to the pentane solution of chlorine dioxide during the conversion to chlorite.

The acrylamide-isopropylacrylamide melt could be preoligomerized in the presence of the amine by means of heating to 60-70°C in the presence of ca. 0.01% azobisisobutyronitrile initiator. Provided that the film was sufficiently plasticized by the amine, formation of the iminium chlorite upon exposure of the film to the pentane-chlorine dioxide solution was still possible.

Other secondary, hydrogen bonded amines could be easily formed by the acetic acid catalyzed, addition of primary amines to Michael type substrates such as acrylamide and N,N methylene bisacrylamide. The secondary amines that could be converted to iminium chlorite in formamide or monomeric or oligomerized acrylamide-isopropylacrylamide mixtures include N,N methylene bis-[1-(N-cyclohexylamino) 2-carboxyamido] ethane

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and 1-(N-benzylamino) 2-carboxyamido ethane. Linear polymers formed by the coupling bifunctional primary amines such as 1,3 diamino propane and 1,2 diamino ethane to N,N methylene bisacrylamide could also be converted to iminium chlorite species in the same hydrogen bonded matrices.

Glassy polymer amine films which reacted only slowly with the chlorine dioxide could be induced to react to iminium chlorite in under 2 minutes provided that they were plasticized with at least 10 wt% low molecular weight amides.

EXAMPLE 2

This example illustrates the use of tertiary, hydrogen bonding amines as chlorite storage media in hydrogen bonded matrices in the presence of hydrolyzable trimethyl silylphosphate esters.

Unlike primary and secondary amines which possess active hydrogens, tertiary amines will not react with anhydrides or trimethylsilyl phosphate esters. This permits the tertiary amines to be rather more intimately mixed with the "acid generating compound" providing for some processing advantages.

1-(N-dipropylamino), 2-carboxyamido ethane (DPACAE) was made by reacting 0.2 mole di(n-propyl)amine with 0.1 mole acrylamide in the presence of a small amount of acetic acid in 10 wt% solution methanol. The reaction was carried out for 3 hours at 70°C. After vacuum evaporation of the excess amine and crystallization in the presence of pentane, a white low melting solid was obtained (T_m =60°C) which tended to lose amine and form acrylamide upon prolonged heating above the melting point.

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1-(N-Dimethylamino), 2-carboxyamido ethane (DMACAE) was made by reacting 0.2 mole dimethylamine (as 40 wt% solution in water) with 0.1 mole acrylamide in 10 wt % solution in methanol. The reaction was carried out for 1 hour at room temperature. After vacuum evaporation of excess amine, methanol and water, the DMACAE was taken up in methylene chloride, dried with magnesium sulfate and isolated as a low melting (T_m = 45°C) hydroscopic solid.

Both DPACAE and DMACAE crystallized only slowly and thus could be studied in the liquid state at room temperature. However, neither neat liquid formed iminium chlorite. 10-30% wt% solutions in formamide or acrylamide-isopropyl acrylamide readily formed iminium chlorite when exposed to chlorine dioxide.

Since the amide functionality is unreactive to anhydrides (acetic, propionic or succinic anhydride or anhydride containing polymers) or trimethylsilyl phosphate esters (tris-trimethylsilyl phosphate; O-trimethylsilyl bis-(2-ethyl hexyl) phosphate) at room temperature, DMACAE and DPACAE in formamide or acrylamides can be mixed with these acid generating compounds without reaction.

4-dimethylamino pyridine, tetramethylene ethylene diamine, and N,N dimethylamino cyclohexane also would form stable iminium chlorites in hydrogen bonding amide solvents. However, since both of these tertiary amines had considerable solubility in pentane, extraction of the amines into the apolar phase was avoided by layering the chlorine dioxide solution on the amide solution. None of these tertiary amines would form iminium chlorite when reacted in the pentane phase. However, they would react with the chlorine dioxide.

In practice it is still desirable to dissolve the silyl esters or anhydrides in an apolar hydrocarbon oligomer and disperse the apolar phase in the polar matrix containing either the amine or the imine chlorite. Even

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though the silyl esters and anhydrides do not react with tertiary amine they will react with the iminium chlorite reducing the ultimate yield of regenerated chlorine dioxide.

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.

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Some important features of the invention are summarised in the following paragraphs.

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

synthesizing hydrogen bonded amines as a neat material;

dissolving said amines into hydrogen bonded matrices;

mixing the amine with an incompatible phase; and

exposing said mixture to gaseous chlorine dioxide to create an ionomeric composition having an iminium chlorite salt-bound to said ionomeric composition such that ionomeric polymer releases chlorine dioxide when exposed to water for acting as a biocidal agent.

The method may further comprise the step of creating said chlorine dioxide gas by dissolving chlorine dioxide in an organic solvent. The chlorine dioxide may be incorporated into n-pentane or other hydrocarbons or low melting chlorowaxes as a vehicle for reaction of the amine containing films to the iminium chlorite containing films.

The method may further comprise the step of selectively forming a film of ionomeric composition on a substrate.

The step of forming a film may comprise the steps of:

applying said ionomeric composition as a tacky hot melt to the

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substrate; and

controlling the operating temperature to avoid the decomposition temperature of any chlorite present.

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

The composition which liberates a repelling or biocidal agent may comprise:

a hydrogen bonded amine grafted or mixed into hydrogen bonded matrices to create a mixture;

an incompatible phase mixed with the amine mixture; and

a gaseous chlorine dioxide exposed to said mixture to create an ionomeric composition such that said ionomeric composition releases chlorine dioxide when exposed to water for acting as a repelling or biocidal agent.

The hydrogen bonded amine may comprise a primary, secondary or tertiary hydrogen bonded amine and may be a monomeric amine, a polymeric amine or a mixture thereof.

The matrices may comprise aliphatic amides, aromatic amides, aromatic alcohols, aliphatic alcohols and mixtures thereof and may be selected from formamide, acrylamide–isopropylacrylamide mixtures or their polymerized products, neat primary or secondary amines and their polymerization products

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with acrylamide, isopropylacrylamide and N,N methylene bisacrylamide, and glycerine, ethylene glycol, or polyhydroxylic alcohols or mixtures of the above.

The incompatible phase may comprise hydrolyzable phosphate ester or anhydrides and may consist of grafted anhydride or phosphate ester phases blended with or grafted to hydrocarbons such as polypropylenes, polyethylenes, or polystyrenes.

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

The chlorine dioxide is incorporated into n-pentane or other hydrocarbons or low melting chlorowaxes as a vehicle for reaction of the amine containing films to the iminium chlorite containing films.

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CLAIMS

1. A method for making a composition which liberates a repelling or biocidal agent when exposed to water and which comprises the steps of:

forming a mixture of (a) a solution of a hydrogen bonded amine in a hydrogen bonded matrix and (b) an incompatible phase containing groups which are hydrolyzable to acid groups on exposure to water; and

exposing said mixture to gaseous chlorine dioxide to form iminium chlorite in the composition.

2. A method as claimed in Claim 1, further comprising the step of creating said chlorine dioxide gas by dissolving chlorine dioxide in an organic solvent.

3. A method as claimed in Claim 1 or Claim 2, further comprising the step of lowering the pH of said ionomeric polymer to less than 8.0.

4. A method as claimed in any one of Claims 1 to 3, wherein said chlorine dioxide is incorporated into n-pentane or other hydrocarbon or low melting chlorowaxes as a vehicle for the reaction to form the iminium chlorite containing product.

5. A method as claimed in any one of Claims 1 to 4, further

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comprising the step of selectively forming a film of the composition on a substrate.

6. A method as claimed in Claim 5, wherein said step of forming a film comprises the steps of:

applying said composition as a tacky hot melt to the substrate; and

controlling the operating temperature to avoid the decomposition temperature of any chlorite present.

7. A composition adapted to liberate a repelling or biocidal agent comprising chlorine dioxide, said composition comprising a mixture of two substantially incompatible phases wherein:

the first phase comprises an admixture of an iminium chlorite and a hydrogen-bonded matrix and

the second phase comprises groups which are hydrolyzable by atmospheric moisture to acid groups.

8. A composition as claimed in Claim 7, wherein the first phase includes an oligomeric or polymeric component.

9. A composition as claimed in Claim 8 or Claim 9, wherein the second phase comprises a polymer containing said hydrolyzable groups.

10. A composition as claimed in any one of Claims 7 to 9 which is

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meltable to create a film on a substrate.

11. A composition as claimed in any one of Claims 7 to 10, wherein the iminium chlorite is derived from a hydrogen bonded amine.

12. A method as claimed in Claim 1 or a composition as claimed in Claim 11, wherein said hydrogen bonded amine is selected from primary, secondary and tertiary hydrogen bonded amines.

13. A method or composition as claimed in Claim 12, wherein said amine is selected from monomeric amines, polymeric amines and mixtures thereof.

14. A method or composition as claimed in any one of Claims 1 to 13, wherein said matrix is selected from aliphatic amides, aromatic amides, aromatic alcohols, aliphatic alcohols and mixtures thereof.

15. A method or composition as claimed in Claim 14, wherein said hydrogen bonded matrix comprises formamide, an acrylamide–isopropylacrylamide mixture or polymerized product; a neat primary or secondary amine or polymerization product thereof with acrylamide, isopropylacrylamide or N,N methylene bisacrylamide; glycerine, ethylene glycol, a polyhydroxylic alcohol or a mixture of the above.

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16. A method or composition as claimed in any one of Claims 1 to 14, wherein said hydrolyzable groups are selected from hydrolyzable phosphate ester and anhydride groups.

17. A method or composition as claimed in Claim 16, wherein said incompatible phase comprises a grafted anhydride or phosphate ester component blended with or grafted to a hydrocarbon such as a polypropylene, polyethylene or polystyrene.

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