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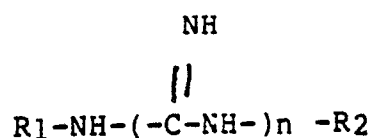
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(54) **Process for protecting articles from attack by bleaching solutions.**

(57) A process is disclosed for protecting articles, especially fibres, monofilaments and films, made from polymers against degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof. The process comprises coating the articles with a composition capable of protecting the articles from such solutions. The composition preferably comprises a reactive guanide compound. The guanide compound is cured in place on the article. The guanide compound is of the formula:



where n is from 2 to 10, R₁ has from 6 to 15 carbons and is either an alkyl, a cycloalkyl, a monocyclic aryl, or and alkyl-substituted monocyclic aryl, and R₂ has not more than 15 carbons and is either hydrogen, an alkyl, a cycloalkyl, or a monocyclic aryl or an alkyl-substituted monocyclic aryl.

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PROCESS FOR PROTECTING ARTICLES FROM ATTACK BY BLEACHING SOLUTIONS

The present invention relates to the use of compositions for the inhibition or prevention of oxidative degradation of articles formed from polymers in peroxide and hypochlorite bleaching solutions.

It is known from German Patentschrift 1 025 376 of Dithmar et al., granted on 1960 August 11, to incorporate N-phenylbiguanide into bleaching baths in order to protect polyamides against the effects of peroxide in bleaching baths. In U.S. Patent 3 628 906 of Dithmar et al., granted on 1971 December 21, it is disclosed that alkyl or cycloalkyl substituent groups on the first and fifth positions of biguanides reduce the tendency towards discolouration in the fibre when exposed to iron and manganese compounds in bleaching baths, compared to biguanides having aryl substituent groups. In both of the above-mentioned patent specifications, the biguanide material is employed in solution in a peroxide bleaching bath.

The use of guanide or guanidine materials (the two terms are used interchangeably) for a number of purposes is known. For example, in Chemical Abstracts Vol. 100(2), 15374g, a water-insoluble guanidine derivative is described in a paper coating composition over a barrier layer to improve storage stability. Guanidines have also been used as catalysts to reduce the curing time of polyureas (Chem. Absts., Vol. 96-(20), 164305m), and in curing epoxy resins (Chem. Absts., Vol. 87(10), 69185c).

The coating of fibres in general is also known in the art. Both dipping and spraying methods, among others, have been used. Many patent specifications disclose sizing compositions for coating on the surface of glass fibres, used to improve the adhesion of the glass to polymer matrixes. In U.S. Patent 4 263 082 to Temple, granted 1981 April 21, a sizing composition is disclosed that comprises a lubricant, a coupling agent, a stabilizer, a non-crosslinkable film-former, a softener, a surfactant and an aqueous carrier, which improves the adhesion of glass fibres to a polyolefin material. The stabilizer may act as a secondary coupler and assist in crosslinking of the coupling agent. In Chemical Abstracts, Vol. 103(10), 72549d, a wet-degradable fibre is disclosed, the fibre having a ethylene-vinyl acetate copolymer coating of low permeability.

In U.S. Patent 3 687 721 to Dardoufas, granted 1972 August 29, a lubricating protective film is disclosed which is applied to a multifilament polyester or polyamide yarn, and which gives the fibres greater elongation at break and greater resistance to aging. The liquid coating composition comprises a glycerol oleate, ethoxylated tall oil fatty acids, sulphated glycerol trioleate or ethoxylated alkylamine, and hexadecyl stearate.

U.S. Patent 4 325 857 to Champaneria et al., granted 1982 April 20, discloses an antisoiling coating for textile filaments comprising an aqueous dispersion of a perfluoroalkylester of a citric acid urethane and a fluorinated alcohol, the reaction product of an epoxy resin and a carboxyl-functional vinyl polymer and an aqueous solution of a tertiary amine. The treated filaments are heated to dry and cure the resins on the surface of the filaments.

Although the art has disclosed both protective coatings for fibres and other materials, and agents used in bleach baths to protect condensation polymer fibres from attack by peroxide, there remains a need for a method of protecting articles at the manufacturing stage in order to provide a product to be used in oxidative bleach environments that does not require the user to incorporate protective agents into the bleach baths. A method of protecting articles formed from polymers by coating the articles with a composition capable of protecting the articles from oxidative bleach environments has now been found.

Accordingly, the present invention provides a process for protecting an article made from a polymer against degradation through exposure to aqueous solutions containing peroxygen radicals, hypochlorite radicals or mixtures thereof. The process comprises coating the article with a composition capable of protecting the polymer against such degradation.

In another one of its aspects, the invention provides a process for protecting an article made from polymer against oxidative degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, comprising:

- (a) coating said article with a composition comprising a reactive guanide compound, and
- (b) curing the article coated with said composition, wherein the guanide compound is of the formula:



where n is from 2 to 10, R₁ has from 6 to about 15 carbons and is either an alkyl, a cycloalkyl, a

monocyclic aryl or an alkyl substituted monocyclic aryl and R_2 has not more than about 15 carbons and is either hydrogen, an alkyl, a cycloalkyl, an alky-substituted monocyclic aryl or a mono-cyclic aryl.

In a preferred embodiment of the process, the curing step comprises the application of heat to the articles, advantageously at a temperature of 50 to 120° C, preferably 80 to 120° C, for 2 to 30 minutes, and is followed by a step of cooling the articles.

The invention also provides articles protected against oxidative degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, said articles being coated with a reactive guanide compound having the above-noted formula cured on said coated articles.

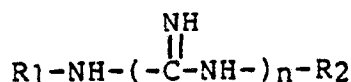
The invention further provides a composition for protecting articles made from polymers against oxidative degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, comprising a reactive guanide compound having the above-noted formula cured on the articles.

Preferably, the polymers are spandex polymers or are condensation polymers formed from monomers selected from the group consisting of dicarboxylic acids, diamines, aminoacids and diols, said monomers being aliphatic or monocyclic aromatic.

In another preferred embodiment of the process, the articles may be fibres, monofilament and blown or sheet-extruded film.

Any composition which is capable of being coated onto a polymer and which is capable of protecting the polymer from oxidative bleach baths may be used. Preferably, the composition is polymerizable on the surface of the polymer upon curing. Compositions containing guanide compounds are preferred.

Guanide compounds suitable for use in the invention have the formula:



where n is from 2 to 10, R_1 has from 6 to about 15 carbons and is either an alkyl, a cycloalkyl, a monocyclic aryl or an alkyl substituted monocyclic aryl and R_2 has not more than about 15 carbons and is either hydrogen, an alkyl, a cycloalkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl. The number of repeating units, expressed by " n " in the formula, and the size of the end group substituents is selected using the solubility and the necessary reactivity of the guanide compound. Thus guanides particularly useful in the process include biguanidines having phenyl groups substituted on the nitrogen atoms at the first and fifth positions. Especially preferred guanides having 2 repeating units ($n=2$) and an aryl or alkyl substituted aryl group are 1-(2-tolyl)-biguanide, in which R_2 is H and R_1 is 2-tolyl; 1-phenylbiguanide, in which R_2 is H and R_1 is phenyl; 1,5-diphenylbiguanide, in which R_1 and R_2 are phenyl; and salts thereof. Preferred guanides having 2 repeating units ($n=2$) and an alkyl or cycloalkyl group are 1-(N-hexyl)-biguanide, in which R_1 is N-hexyl and R_2 is H; 1,5 (N-hexyl) biguanide, in which R_1 is N-hexyl and R_2 is N-hexyl; 1-(cyclohexyl) biguanide in which R_1 is cyclohexyl and R_2 is H; and 1,5 -(cyclohexyl) biguanide in which R_1 and R_2 are both cyclohexyl.

The coating composition may be a sizing composition which may include conventional sizing components, for example if the articles are fibres, the coating composition may contain lubricants, surfactants, antistats, emulsifiers and dispersing agents. Advantageously, the coating composition containing the guanide is applied by spraying or dipping methods known in the art. Spraying is especially preferred as it is readily adaptable to existing equipment used for extrusion or spinning. For spray application the composition containing the guanide may be prepared by dissolving the guanide compound. The guanide compounds having 2 repeating units, i.e. $n=2$, tend to be soluble in warm water and in the lower alcohols and ketones; as the number of repeating units increases up to about 10, and as the length of the end-group substituents increases, the solubility decreases so that lower concentrations of guanide or stronger solvents are used. Conveniently, if the guanide has 2 to about 4 repeating units, it may be dissolved in water, preferably hot water, in a ratio of 1:20 to 1:50 by weight. Other ingredients as desired may be incorporated into the composition either in slurry or solution form, and the resulting solution or slurry may be sprayed onto the article downstream from the extrusion or spinning head after the point at which the polymer has solidified. A suitable coating may be obtained when the amount of guanide applied to the article is from 0.1 to 4.0 percent, preferably from 0.2 to 1.0 percent, by weight.

The guanide may be cured on the article by exposure to a temperature of about 50 to 120° C, preferably 80 to 120° C, most preferably 100 to 120° C, for a period of about 2 to 30 minutes, preferably from about 3 to 10 minutes. As described in more detail hereinafter, the curing reaction appears to be a

condensation both between the reactive groups on the polymer and the biguanide and within the biguanide itself involving evolution of ammonia, and consequently no oxygen need be present during curing. The cured coated article may then be cooled to an appropriate temperature readily selectable by the person skilled in the art. Finally, the article may be prepared for shipment; for example if the article is a fibre, the fibre may be wound onto a suitable package.

Articles that may be treated by the process include fibres, monofilament, blown and extruded film, moulded articles and extruded shapes. Especially preferred are articles having a high surface-to-volume ratio, for example fibres, monofilament and blown and extruded film, which tend to be more affected by bleaching treatment than articles of a low surface-to-volume ratio.

The present invention is illustrated by the following examples.

Example 1

In a spinning run, a hexamethylene diamine-adipic acid polymer having a relative viscosity of 51 (in 90 wt.% formic acid) was melt-spun into filaments having a mass of 15 denier (17 dtex). A 2.5 % aqueous solution of a guanide having the parameters $n=2$, R_1 being 2-tolyl and R_2 being hydrogen, which is 1-(2-tolyl)-biguanide (Proventine 7, Henkel Chemicals (Canada) Ltd., Montreal, Quebec) was prepared at 68 °C and sprayed onto the fibre, the fibre being at about 40 °C, through pre-warmed transfer lines and conventional spraynozzles. The fibre was heated in a conventional drier at a temperature of 110 °C with a residence time of 3 minutes. The moisture content of the coated polymer in staple form was 21.99 % before the heating step and 2.45 % after the heating step, compared to 4.19 % before the heating step and 2.31 % after, respectively, for an uncoated control sample produced under the same conditions. The moisture content in the bale was 5.73 % and 3.77 % respectively for coated and uncoated fibre. The level of biguanide coating on the fibre was measured by trichloroethane extraction, both before and after heating, and was determined to be 0.2 % by weight prior to the heating step, indicating a high degree of curing onto the polyamide fibre under the coating conditions. The coating was unextractable after the heating step, suggesting that the curing was complete thereafter.

Both coated and control samples of fibre were bleached in either 1.5 wt.% hydrogen peroxide solution at pH 4 at 90 °C for 120 minutes and in 1.5 wt.% sodium hypochlorite bleach solution at pH 10 at 90 °C for 120 minutes. Table 1 illustrates the performance of the coated and uncoated fibres compared to that of uncoated fibres treated in a similar bleaching bath according to the prior art process.

In peroxide bleach and especially in hypochlorite bleach, the fibres coated according to the invention retain more of their original properties than untreated fibres or fibres bleached in the presence of the biguanide in the bleach solution according to the prior art.

Table 1

Percentage Change in Fibre Properties After Bleaching			
Property	Spray Coated	Untreated Fibre	Biguanide in Bleach
	Hydrogen Peroxide Bleach		
Breaking Strength	-11.9	-37.4	-23.7
Elongation at Break	-30.6	-50.2	-27.3
Tenacity	-11.5	-39.7	-22.3
	Sodium Hypochlorite Bleach		
Breaking Strength	-29.7	-33.9	-42.4
Elongation at Break	-36.9	-44.8	-40.3
Tenacity	-30.0	-32.2	-41.0

Example 2

A mass of hexamethylene diamine-adipic acid polymer fibres similar to those of Example 1 was taken from a normal industrial spinning operation. The mass was divided into several samples comprising smaller masses, some of which were coated with the biguanide composition of Example 1 by dipping each fibre mass into a 2.5 wt.% aqueous solution of the biguanide of Example 1 for one hour at 55 °C. The fibre masses were removed from the hot biguanide solutions and remained hot for about ten minutes. Each mass was dried overnight at room temperature (23 °C). The level of coating on the fibre was measured by a method of completely hydrolyzing the coated biguanide in an acidic aqueous solution followed by high performance liquid chromatography analysis, and was determined to be 1.0 wt.%. Both coated and control samples of the fibre were bleached with hydrogen peroxide and sodium hypochlorite bleach solutions under conditions as outlined in Example 1. It is believed that during the period when the fibre is immersed in the coating bath at 55 °C, the guanide migrates to the fibre surface, and both in the coating bath and after removal from the bath when the hot fibre mass is exposed to air in the laboratory, the guanide reacts with reactive groups on the fibre surface, and thus the guanide cures in-place on the fibres. The results shown in Table 2 illustrate the performance of dip-coated fibres compared to uncoated fibres bleached in the bleaching bath containing the biguanide according to the prior art process. The process of the invention is thus shown to be more useful in preventing degradation of the polyamide fibres than the prior art, particularly in hypochlorite bleach environments.

Table 2

Percentage Retention of Original Fibre Properties After Bleaching - Second Sample			
Property	Dip Coated	Untreated Fibre	Biguanide in Bleach
	Hydrogen Peroxide Bleach		
Breaking Strength	+ 4	-30	-8
Elongation at Break	0	-57	-34
Tenacity	+ 4	-30	-1
	Sodium Hypochlorite Bleach		
Breaking Strength	+ 2	-25	-25
Elongation at Break	+ 1	-45	-45
Tenacity	+ 2	-25	-28

Example 3

Several sample masses of hexamethylene diamine-adipic acid fibres similar to those of Example 1 were coated with the biguanide composition of Example 1 under the conditions outlined in Example 2. The samples were subjected to hydrogen peroxide bleaching treatment as outlined in Example 1, for 2 hours. One-half of the bleached samples, after being dried, were subjected to a second bleaching treatment under the same conditions. Table 3 illustrates the performance of the coated fibres compared to that of the uncoated fibres treated repeatedly in the hydrogen peroxide bleaching bath. Table 4 illustrates the effect of the bleaching on polyhexamethylene adipamide fibre molecular weight and carboxyl ends. It is believed that when chemical degradation of the polyamide occurs, the polymer chain scission results in a reduction of the molecular weight of the polymer (as indicated by its relative viscosity) and an increase of carboxyl end groups. There is also a concomitant deterioration of physical properties of the fibre, reflected in a reduction of its breaking strength, elongation at break and tenacity, as well as other properties. It is seen from the good performance of the coated fibres that the biguanide coating remains on the fibre after the first bleaching cycle. It is thought that the cured coating will remain on the fibre through many bleaching cycles. This conclusion is supported by the low change of relative viscosity and carboxyl end groups count.

Table 3

Percentage Change in Properties After Repeated Bleaching in Hydrogen Peroxide				
Property	Untreated Fibre		Dip Coated	
	2 h	2 + 2 h	2 h	2 + 2 h
Breaking Strength	-30	-35	+ 4	-6
Elongation At Break	-57	-58	+ 0	+ 14
Tenacity	-30	-43	+ 4	-16.5

Table 4

Effect of Repeated Bleaching on Molecular Weight and Carboxyl Ends of Polyhexamethylene Adipamide with Biguanide Coating					
Property	Unbleached	Bleached in Hydrogen Peroxide			
		Untreated Fibre		Dip Coated	
		2 h	2 + 2 h	2 h	2 + 2 h
Relative Viscosity	50.6	44.2	41.0	48.5	48.9
Carboxyl End Groups	83.9	97.9	104.6	79.3	84.5

Example 4

The samples with biguanide coating mentioned in Example 3 were subjected to a hydrogen peroxide bleaching under the same conditions as Example 2 except that the pH of the bleach bath was adjusted to 10. The results are illustrated in Table 5 below.

Table 5

Percent Change in Fibre Properties After Bleaching in Hydrogen Peroxide at pH 10		
Property	Dip Coated	Untreated Fibre
Breaking Strength	-13	-41
Elongation at Break	+ 12	-45
Tenacity	-22	-45

These results illustrate that the guanide coating is effective in both acidic and basic hydrogen peroxide bleaching conditions.

Example 5

The samples with biguanide coating mentioned in Example 1 were subjected to a test in which the samples were exposed to chlorine at a concentration of 1000 ppm at pH 4.5 and 75 °C for four hours. For the polyamide staple coated with 0.2 wt.% of the biguanide composition, the average loss in tenacity after exposure is 48 percent loss as compared to 82.5 percent loss for the untreated fibre.

Example 6

A finish free 1880 dtex LYCRA spandex fibre mass was dipped into a 1.5 wt.% aqueous solution of the guanide for one hour at 55 °C. The fibre masses were removed from the hot guanide solution and remained hot for about ten minutes. Each mass was dried overnight at room temperature (23 °C). The level of coating on the spandex fibre was measured by the method described in Example 2. As discussed in Example 2, it is believed that during the period when the fibre is immersed in the coating bath at 55 °C, the guanide migrates to the fibre surface, and both in the coating bath and after removal from the bath when the hot fibre mass is exposed to air in the laboratory, the guanide reacts with reactive groups on the fibre surface, and thus the guanide cures in place on the fibre.

The coated sample and an uncoated control sample were each bleached in hot aqueous sodium hypochlorite solution (90 °C, pH = 10, NaOCl = 0.45%) for two hours. The coated sample showed a complete retention of physical strength whereas the control sample showed a loss of 30% of physical strength. The test to determine strength is a standard Instron elastomer test. The method characterizes the tensile properties of spandex fibre under conditions simulated to garment preparation and wear. A yarn sample is stretched to various extension lengths and the stretch loads are measured at these various fixed extension lengths to determine the "physical strength" of the fibre under the specific conditions. The break strength is the load required to break the fibre after the fibre had been stretched to 300% of its original length for five times.

The bleached coated and control samples were air dried and subjected to a second bleach in sodium hypochlorite solution under the same conditions for an additional 2.5 hours. After the second chlorine bleaching, the coated sample showed a complete retention in break strength whereas the control sample showed a 50% loss in strength. The coated sample also showed a 60% improvement in load at 300% elongation compared to the control sample.

Example 7

A finish free 1880 dtex LYCRA spandex fibre mass was dipped into a 1.5 wt.% aqueous solution of the guanide for one hour at 55 °C. The fibre masses were removed from the hot guanide solution and remained hot for about ten minutes. Each mass was dried overnight at room temperature (23 °C). The level of coating on the spandex fibre was measured by the method described in Example 2. As discussed in Example 2, it is believed that during the period when the fibre is immersed in the coating bath at 55 °C, the guanide migrates to the fibre surface, and both in the coating bath and after removal from the bath when the hot fibre mass is exposed to air in the laboratory, the guanide reacts with reactive groups on the fibre surface, and thus the guanide cures in place on the fibres.

The coated sample and an uncoated control sample were each bleached in hot aqueous sodium hypochlorite solution (90 °C, pH = 10, NaOCl = 0.45%) for two hours. The physical strength of the fibres was determined by measuring the load at 300% elongation at the first and fifth cycles of elongation. The coated sample showed a complete retention of physical strength whereas the control sample showed a loss of more than 40% of physical strength. The coated sample showed an 88% retention in break strength whereas the control showed only a 45% retention.

The bleached coated and control samples were air dried and subjected to a second bleach in sodium hypochlorite solution under the same conditions for an additional 2.5 hours. After the second chlorine bleaching, the coated sample showed a 70% retention in physical strength whereas the control sample showed only a 30% retention in strength. In addition, the coated sample showed an 85% retention of its original break strength whereas the control sample showed a 36% retention of break strength.

Without wishing to be bound by a technical explanation of the protection process, compositions and products disclosed herein, it is believed that upon heating, the guanide compound bonds with reactive groups on the polymer article, and itself polymerises to change from a substance soluble in water, alcohol

and acetone, melting at about -144 to 147 °C in the case of N-(2-methylphenyl)imidocarbonimidic diamide, to an insoluble substance that does not melt at temperatures up to 200 °C. The polymer formed by polymerization of the guanide has a glass transition temperature between 45 and 90 °C. The longer the guanide is subjected to heat and the higher the temperature, the higher is the glass transition temperature, suggesting that a cross-linking reaction is occurring. When heated as a coating on polymers, the guanide is believed to cross-link with itself as well as to react with the reactive groups of the polymers and thus to form a very adherent coating. Further, in combining with the reactive groups of the polymers, the coating not only acts as a barrier but also effectively makes unavailable those reactive groups, and thus prevents by two means the cracking and embrittlement of the polymer that would otherwise occur.

In a proton NMR spectrum of the guanide described in Example 1 which has been heated mildly and remains slightly soluble, the patterns in the aromatic and methyl regions are very different as compared to the unheated guanide, leading to the conclusion that not all of the tolyl rings are the same. This difference could be due either to stereochemical differences, for example tacticity, or to changes in the substitution pattern from ortho to meta and/or para. The aromatic to aliphatic hydrogen ratio is nevertheless about 4:3, indicating that the tolyl ring is not involved in the thermally induced reaction of the guanide.

From the results shown above it is clear that the guanide coating is effective to provide chemical resistance to the fibre in both acidic and alkaline hypochlorite environments, as well as acidic and alkaline peroxide environments.

An advantage to the process of the invention is that it provides a treated polymer article which is resistant to oxidative degradation of its surface in aqueous peroxide and hypochlorite bleaching environments without further necessity for incorporating treating agents into the bleaching solution. Another advantage is that the article appears to have greater abrasion resistance after exposure to bleaching solutions.

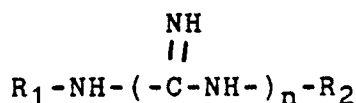
Claims

1. A process for protecting an article made from a polymer against degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, said process comprising coating said article with a composition capable of protecting said polymer against degradation.

2. The process of claim 1 wherein said composition is capable of undergoing polymerization and wherein said process further comprises the step of curing the coated article.

3. A process for protecting an article made from a polymer against degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, said process comprising:

- (a) coating said article with a composition comprising a reactive guanide compound, and
 - (b) curing said coated article,
- wherein the guanide compound is of the formula:



wherein n is from 2 to 10, R₁ has from 6 to about 15 carbons and is either an alkyl, a cycloalkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl and R₂ has not more than 15 carbons and is either hydrogen, an alkyl, a cycloalkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl.

4. The process of claim 3 wherein said polymer is selected from (i) spandex and (ii) condensation polymers formed from monomers selected from the group consisting of dicarboxylic acids, diamines aminoacids and diols, said monomers being aliphatic or monocyclic aromatic.

5. A process according to claim 3 or claim 4 wherein said guanide compound is selected from 1-phenylbiguanide; 1-(2-tolyl)biguanide; 1,5-diphenylbiguanide; and salts thereof.

6. A process according to claim 3 or claim 4 wherein said guanide compound is selected from 1-(N-hexyl)biguanide; 1,5-(N-hexyl)-biguanide; 1-(cyclohexyl)biguanide and 1,5-(cyclohexyl)-biguanide.

7. A process according to any one of the preceding claims, wherein said article is selected from the group consisting of fibres, monofilament and film.

8. A process according to any one of the preceding claims wherein said articles are made of polymers selected from the group consisting of polyamides and polyesters.

9. A process according to any one of the preceding claims wherein said coating step is accomplished by either spraying or dipping.

10. A process according to any one of claims 2 to 9 wherein said curing step is accomplished by heating the coating on said article to a temperature of from 100 C to 120 C for from 3 to 10 minutes.

5 11. A process according to any one of claims 3 to 10 wherein said composition comprising a reactive guanide compound is an aqueous sizing composition.

12. An article selected from fibres, film and monofilament, said article being obtainable by coating a polymer with a composition comprising a reactive guanide compound of the formula:



15 where n is from 2 to 10, R₁ has from 6 to about 15 carbons and is either an alkyl, a cycloalkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl, and R₂ has not more than 15 carbons and is either hydrogen, an alkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl, and curing said article after coating with said composition.

20 13. An article according to claim 12 wherein said polymer is selected from spandex and a condensation polymer formed from monomers selected from the group consisting of dicarboxylic acids, diamines, aminoacids and diols, said monomers being aliphatic or monocyclic aromatic.

14. An article according to claim 12 or claim 13 said article being obtainable by curing at a temperature from 100 to 120 °C for from 3 to 10 minutes.

25 15. A composition for protecting articles made from a polymer against degradation through exposure to aqueous solutions containing peroxygen groups, hypochlorite groups or mixtures thereof, said coating being obtainable by curing a composition comprising a reactive guanide compound of the formula:



35 where n is from 2 to 10, R₁ has from 6 to about 15 carbons and is either an alkyl, a cycloalkyl, or a monocyclic aryl, or an alkyl-substituted monocyclic aryl, and R₂ has not more than 15 carbons and is either hydrogen, an alkyl, a cycloalkyl, a monocyclic aryl, or an alkyl-substituted monocyclic aryl, on the surface of said polymer.

16. The coating of claim 15 wherein said polymer is selected from (i) spandex and (ii) condensation polymers formed from monomers selected from the group consisting of dicarboxylic acids diamines, aminoacids and diols, said monomers being aliphatic or monocyclic aromatic.

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