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(54) **ENHANCED EFFICACY OF FUNGICIDES IN PAPER AND PAPERBOARD**

VERSTÄRKTE WIRKUNG VON FUNGIZIDEN IN PAPIER UND PAPPE

EFFICACITÉ ACCRUE DE FONGICIDES DANS LE PAPIER ET LE CARTON

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Description

[0001] This patent claims priority from U.S. Provisional Patent Application 60/641,618, filed 05 January 2005.

Background of the Invention

[0002] Fungal growth is a serious threat to human health, and the potential costs for remediation or replacement of contaminated building materials are astronomical. Fungal spores, released from surface growth, are well-recognized as allergens, and additional concerns have been raised due to toxic byproducts of at least one species. According to recent studies by Gorny et al., occupant exposure to various health problems, including those referred to as "sick building syndrome," is increasing. Further concern is being raised by human allergic responses, similar to that observed with fungal spores, to fungal fragments that can be released at much lower humidity levels (as low as 20%).

[0003] Paper and paperboard used in those building materials have been observed as the sites for such fungal growth. Typical moisture in paper, paperboard, and building materials is sufficient to maintain growth. The cellulose of the paper and paperboard, along with the residual contaminants within the fiber web, offer a sufficient food source that is enhanced by other building product components such as starch binders.

[0004] Since fungi can grow in temperatures from as low as 40°F to as high as 130°F, most indoor conditions, as well as a large segment of outdoor conditions, will easily allow their growth. Although efforts have been made to use careful construction practices and humidity control to limit fungal growth, fungi contamination problems have been observed in regions such as the Northeast U.S. where relative humidity rarely exceeds recommended maximums, and building materials were not exposed to the weather. Atmospheric fungal spores provide sufficient inoculation of fungi to the materials, and added moisture from condensation or water damage makes the threat of fungal contamination more likely.

[0005] Gypsum panels are used for drywall building products in heavy use for residential, educational, and commercial buildings. Gypsum panels are used primarily for interior wall and ceiling construction, and some specialty panels are used in exterior applications. Even though fungal contamination can come from the gypsum core, made of calcium sulfate hemihydrates, the primary location for fungal growth on gypsum panels is the facing and backing paper that covers each side of the gypsum core. Once installed, gypsum panels can make treatment and/or remediation extremely difficult and expensive, as fungal contamination may be enclosed and inaccessible.

[0006] Homeowners typically see fungal growth in closets, along baseboards and on bathroom walls; removal of installed panels may reveal hidden growth on the backside. Areas with even minor water damage or condensation are often heavily contaminated. Growth is visible as dark green or black spots that can grow to a complete covering of the affected area. Many after-market treatments, usually based on chlorine bleach, lighten the spots. Such treatments tend to damage the paint or coating after multiple treatments and do not prevent return of fungi.

[0007] Many efforts have been made to develop a method that controls fungal growth. The patent literature describes different methods of treatment to address this problem:

U.S. Pat. No. 6,705,939 teaches design of air dehumidification systems to control growth. However, as discussed above, regions of the U.S. where low humidity is the typical condition, such as the Northeast, have discovered serious problems with contamination. Additionally, new studies indicate that fungal fragments, which are potentially as allergenic as fungal spores, are more optimally released at humidity levels as low as 40%.

[0008] Other methods replace the cellulose paper facings with synthetic sheets, attempting to eliminate potential fungal growth sites. U.S. Pat. Nos. 3,993,822 and 6,770,354 address the problem by replacing the paper coverings of the gypsum board with glass fiber. U.S. patent application 2003/0037502 teaches use of nonwoven sheets and demands control of described fungal nutrients in the gypsum core to prevent growth. These coverings are generally more expensive than paper facings, installation costs are higher, and they are difficult to paint or wallpaper. Control of fungal nutrients within the gypsum core remains difficult because of inconsistent raw material sources and the extreme flexibility exhibited by many fungal organisms. Therefore, as a result, this approach has not generated commercially viable options.

[0009] U.S. Pat. No. 5,421,867, to Yeager et al. and assigned to CuCorp, Inc., suggests application of a fungicidal agent to cementitious-based products. U.S. Pat. Nos. 3,918,891 and 3,998,944, to Long and assigned to United States Gypsum Company, recommend application of fungicidal agent to the paper that covers the gypsum core to improve gypsum board. The fungicidal agents discussed therein are water-soluble metal quinolate salts, more specifically a copper quinolate. Such preservatives are undesirable from an environmental perspective. Furthermore, the antifungal compositions discussed are quite specific in their application and lack the flexibility needed to handle the array of applications for gypsum products.

[0010] U.S. Pat. No. 6,440,365 discusses usage of hydrochloric acid and heat to destroy growth after it occurs. This method may destroy the organisms, but it also damages cellulose fibers present in paper facings of gypsum board and installed wood components. Additionally, hydrochloric acid presents serious fume exposure concerns for users, and a

corrosion concern for surrounding materials. Complete removal from enclosed areas of existing buildings is difficult, causing ongoing health and corrosion concerns.

[0011] U.S. Pat. Nos. 5,338,345 and 5,882,731 teach the use of barrier coating to prevent atmospheric fungi from reaching the board. However, growth of fungi can proceed unhindered within the core or under the surface of the board, in areas where the coating is thinned or damaged from long-term exposure to cleaning or environmental stress.

[0012] U.S. Pat. Nos. 4,533,435 and 6,248,761 discuss using binders or microencapsulation to help control the preservative application. U.S. Pat. No. 6,767,647 involves the use of more than one fungicide in the wallboard manufacturing process and U.S. patent application 20040005484A1 teaches methods that rely on a high amount of a water-soluble fungicide in the core and migration of the preservative from the core to treat the facing paper. Whether the problem is inability to get sufficient treatment at the critical points or an inconsistent treatment throughout the sheet, none of these have been able to provide desired levels of antifungal protection for the sheet or the finished building products of which it is a component.

[0013] Current efforts to treat paper and paperboard with fungicide primarily involve coating operations with compositions that incorporate a preservative. Due to several challenges, coating application methods have had limited commercial success.. Some of the challenges to effective coating operations include:

- required decrease in machine production speed and its associated increase in costs or additional cost for off-machine coating
- increased cost for additional materials to serve as carriers and/or binders
- difficulty in maintaining an even dispersion in the coating solution and uniform application of the coating to the paper
- increased drying costs due to rewetting of the sheet
- increased complexity of paper manufacturing
- potential impact on other necessary machine additives or quality parameters
- loss of treatment through surface mechanical action (e.g. - sanding)

These challenges are especially difficult for fungicides with limited solubility in aqueous coating solutions.

[0014] A more desirable alternative to achieve an effective fungicidal preservative application would be to add the preservative to the pulp slurry, at a wet-end addition point. The current use of fungicides in the wet-end of paper processing, has generally been limited to slime (deposit) control, rather than incorporation into the finished paper product. Due to challenges associated with obtaining good distribution and cost-effective levels of preservative, wet-end addition of fungicides into paper products used in building materials has never achieved commercial success. Successful addition of a fungicide at the wet-end during paper processing would require a method of distributing a sufficient amount of the fungicide evenly in the pulp slurry. Having the fungicide distributed throughout the paper, preferably attached to the paper fibers, should offer enhanced protection of the finished paper or paperboard under typical use conditions.

[0015] Chemistries for improved fiber and fines retention and drainage are known to be useful additives to the wet-end of paper processing, and include flocculants. Polymer flocculants improve attachment of fibers and fines through their relatively high molecular weights to attract the cellulosic materials. In addition, such flocculants typically have limited charge density to reduce negative impact of charged contaminants and use, the complex mechanical and hydraulic action of the paper machine during processing to properly align the fibers to provide good formation. Fixatives, as compared to flocculants, are much more compact in size, have relatively high charge densities, are typically cationic, and are lower in molecular weight. A wide variety of both organic and inorganic molecules has been used to fix dye, pitch, size, stickies particles, and anionic trash. However, fixative use has not previously included the attachment of preservatives for enhancement of their application efficiency, proximity to the fiber and dispersion throughout the sheet, and finished goods effectiveness.

[0016] U.S. Pat. No. 4,443,222 teaches that a preservative can be permanently attached to a textile fiber through usage of a water-soluble compound, urea, and a non-reversible, heat-generated reaction. However, this type of permanent attachment reduces the effectiveness of many preservatives by binding up the active antimicrobial sites.

[0017] U.S. Pat. Nos. 6,680,127 and 6,773,822 and WO2004/076770A1 all deal with application to paper of a preservative that is cationic. Such preservatives have a natural affinity toward the anionic fibers and fines. The use of cationic preservatives, however, has not been a commercial success, due to either limited kill efficiency against fungi or the challenge of getting enough preservative into the sheet to be effective..

[0018] JP 2003/055117 describes the use of a combination of water-insoluble rot/fungus-proofing compound in combination with a quaternary ammonium salt as a cationic surfactant to ensure better dispersibility and longer stability of wet pulp, allowing long-term storage of wet pulp.

[0019] WO 01/36740 A2 deals with specific paper making processes where the pulp is treated with cellulytic enzymes and polymers. Optionally, conventional biocides can be added to the pulp.

[0020] US 2003/0031898 A1 teaches the production of gypsum boards with paper facings that have antifungal properties. An antifungal agent, preferably Cetylpyridinium Chloride (CPC), is added during manufacturing or sprayed onto

paper facings and can be retained by retention aids, allowing a release of the fungicide over time and/or upon exposure to moisture.

[0021] This invention is a method for making a fungal-resistant paper or paperboard sheet, particularly for use in building materials. The method includes adding a hydrophobic fungicide and a specific cationic fixative in a controlled manner to pulp slurry during manufacture of the paper or paperboard, as opposed to a surface coating, addition after sheet formation, or with an off-machine application. Addition to the pulp slurry is often referred to as addition to the wet end of a paper-making process. The method of this invention further includes processing the pulp slurry in a paper machine to create a finished sheet.

[0022] Selection of feed points for the fungicide and cationic fixative need to be optimally chosen based upon individual paper machine system flow, available options for injection, potential for improved mechanical distribution and mixing, and locations of other potentially influencing additives. In one embodiment of this invention, the cationic fixative is added, either neat or diluted, directly to the higher concentration pulp slurry, often referred to as thick stock, in the machine chest, allowing distribution throughout the slurry and activation of the fiber before addition of the fungicide. The hydrophobic fungicide is then added into the main stock flow prior to the fan pump or pumps to allow for adequate distribution and mixing. In another embodiment, especially useful for some types of cylinder paper machines, the cationic fixative is added directly to the machine vats, while the hydrophobic fungicide is added indirectly to the stock return loop, which is then recycled back into the main pulp slurry flow. One skilled in the art may optimize the method of this invention for a particular paper machine system design. This invention allows for a pre-activation of the fiber by the fixative followed by a more even distribution of the fungicide.

[0023] Paper or paperboard made by the process of the invention exhibits the following benefits not presently found in fungicide-treated papers currently available in the marketplace:

- Reduced fungal growth because of an improved, even treatment.
- Reduced application requirements or increased application efficiency of fungicide due to the synergy exhibited.
- Better product control.
- Reduced waste of materials.
- Reduced cost of production.
- Reduced potential for human exposure to suspected triggers of respiratory illness and infection.

Detailed Description of the Invention

[0024] This invention is a method for making a fungal-resistant paper sheet for use in building materials. The method includes adding a hydrophobic fungicide and a cationic fixative to a paper slurry during manufacture of the paper or paperboard, and processing the paper slurry in a paper machine to create a sheet. Addition to the paper slurry is often referred to as addition to the wet end of a paper-making process.

[0025] The hydrophobic fungicide suitable for use in this invention must possess several qualities. It must have extremely limited water solubility to prevent its leaching after installation and reduce the threat of environmental or human exposure. A preferred water solubility is less than 0.3 g/L at 25 °C, and a more preferred water solubility is less 0.05 g/L at 25 °C. The preservative must be temperature-stable against both the conditions of the paper machine dryer section and the building product manufacturing process (such as the gypsum board kilns). The preservative must be considered safe for humans, especially due to the higher risk for exposure of children in homes and schools. The preservative application must be cost-effective enough to be practical. The preservative must provide a sufficient and consistent level of protection throughout the sheet to help prevent fungal growth. Examples of suitable fungicides include: diiodomethyl-p-tolylsulfone (DIMTS), zinc pyrithione, thiabendazole, 3-iodo-2-propynyl butylcarbamate, dichloro-octylisothiazolinone, o-phenylphenol, bromonitrostyrene, and 2-(thiocyanomethylthio) benzothiazole.

[0026] Table 1 gives approximate values of some low-solubility fungicides.

Table 1.

Fungicide	Water Solubility (g/L)
diiodomethyl-p-tolylsulfone (DIMTS)	0.0001 (25 °C)
zinc pyrithione	0.02 (20 °C)
Thiabendazole	0.03 (20 °C)
3-iodo-2-propynyl butylcarbamate (IPBC)	0.156 (20 °C)
Dichloro-octylisothiazolinone (DCOIT)	0.002

(continued)

Fungicide	Water Solubility (g/L)
o-phenviphenol (OPP)	0.20 (20 °C)
bromonitrostyrene (BNS)	0.128 (est.)
2-(thiocyanomethylthio) benzothiazole (TCMTB)	0.033

[0027] A preferred fungicide for use in the present invention is diiodomethyl-p-tolylsulfone, known by several names including P-Tolyl diiodomethyl sulfone and DIMTS (CAS Registry No. 020018-09-1). A preferred formulation of diiodomethyl-p-tolylsulfone for use in this invention is commercially available from The Dow Chemical Company of Midland, MI as FUNGI-BLOCK™ fungicidal agent, which contains approximately 40 wt. % DIMTS. The primary challenge to application of this material is to achieve a consistent and cost-efficient treatment. The haphazard entrapment of water-insoluble preservative particles in an application on its own leaves lower sheet concentrations and inconsistent results. The complex environment of paper manufacturing can lead to inefficient attachment of the preservative or uneven treatment of the whole sheet. Voids in the microenvironment of an inconsistently treated sheet allow fungi to "take root" at multiple points, allowing growth over the surface until it becomes completely covered.

[0028] Preferably, the active fungicide is added at amount equal to at least 0.02 pound active fungicide per ton dry fiber produced, more preferably, when the active fungicide is diiodomethyl-p-tolylsulfone, between about 2.0 pounds and 10.0 pounds DIMTS per ton dry fiber produced, most preferably between about 2.0 and 3.2 pounds DIMTS per ton dry fiber produced.

[0029] The cationic fixative is chosen to provide the optimum concentration of hydrophobic fungicide in the finished sheet and the best results with respect to antifungal treatment. The cationic fixative is chosen from the group consisting of cationic homopolymers and copolymers of polyacrylamides, polyamines, polyDADMACs, polyguanidines, polyethyleneamines, cellulosic ethers, starches, aluminum-based coagulants, iron-based coagulants, modified clays, modified talcs, silica microparticle systems, and combinations thereof, more preferably a polyamine. The fixative can be fed ahead of, together with, or after the addition of the diiodomethyl-p-tolylsulfone. However, we have found that the fixative works well when added before the fungicide. Dosage ratios of cationic fixative-to-fungicide can be from 1:35 to 15:1 parts by weight, more preferably 1:35 to 2.5:1. In particularly preferred embodiments, the cationic fixative is fed at a cationic fixative-to-fungicide ratio from about 1:3.5 to 1:0.8.

[0030] Some fixatives of the present invention may be selected from paper processing products referred to as coagulants. Even though coagulants are frequently used in paper manufacturing, their use has been completely unrelated to attachment of preservatives to fibers. Coagulants have been used exclusively to improve drainage, assist in fiber and fines retention, and to reduce problems with anionic trash (organic contaminants).

[0031] We have found that fixatives selected from polyamines work well in this invention. Polyamines have shorter chain lengths, especially in comparison with flocculants, and higher charge densities. Polyamines tightly bind any attracted particles to each other or to fiber. This tight binding provides polyamine with the lowest application dosage requirement to meet demand. Polyamines also provide a broader operating window in order to successfully make the mold-resistant material. Polyamines used in papermaking are generally obtained from condensation reactions between epichlorohydrin and dimethylamine (known commonly as EPI-DMA polyamines). With any overdose of polyamine, agglomeration of anionic particles can occur (instead of attachment to the fiber, particles attach to each other) and an uneven distribution can result. Also, with the tendency for overdose comes the possibility to convert the system from anionic to cationic, leading to a "reverse" dispersion. This is more likely to occur with an overdose of the larger molecular weight flocculants.

[0032] The selection of cationic fixative and levels that work best with a paper slurry can be optimized by one skilled in the art. Some of the application variables that will change the effectiveness of the fixative include, but are not limited to, system flows, raw materials (especially the fiber source), specific machine layout and components, percentage closure (percentage of excess water and stock not removed from the mill as waste), other additives present, feed location, feed method (e.g., continuous, slug), system temperatures, operating parameters (e.g., speed, drying capacity), and so forth.

[0033] Following the processing of the pulp slurry into a sheet of paper, the paper may be secondarily treated with a biocide to provide additional resistance to microbial growth. The paper sheet may be treated in any of the means known in the art, such as with a surface treatment or coating at the size press, calendar stack, water box, or off-machine. In addition, other treatments known in the art, such as treating the paper for moisture resistance and strength enhancement, may be done to improve the usefulness of the paper as a construction material.

Examples

[0034] TAPPI test (T-487) was used to evaluate fungal growth on paper made with fungicides and fixatives added to

the pulp. A 40% DIMTS formulation was used in the test. Values presented below are converted to an "as active" basis. Experiments were performed using six various cationic coagulants and two flocculants.

Example 1

[0035] The fixative was added to an aliquot of paper stock at variable doses. A 40% concentration of DIMTS was then added at a dose of 2 pounds per ton of active ingredient. The water was drained from the stock and the resulting paper mat was blotted, couched, and dried to form a paper sheet.

[0036] Paper without fixative retained about 400 ppm of DIMTS while paper with the fixative retained up to 750 ppm of DIMTS. Antifungal efficacy testing of the paper found that when the polyamine was dosed as a fixative at 1.2 pounds per ton or greater, the paper was mold-resistant, with a 2 pound per ton dose of DIMTS.

[0037] The cationic polyamine used was a medium molecular weight polyamine. Examples include Aquaserv AQ-294 from Aquaserv and Agefloc A50 from Ciba. The cationic flocculant used was a very high molecular weight cationic polyacrylamide with a charge density = 23% (w/w). Cationic polyacrylamides used in papermaking are typically copolymers of acrylamide and various cationic substituents. Examples include Aquaserv AQ-330 from Aquaserv and Drenafloc 402C from Europolimeri. When the flocculant was applied as a fixative with a 2 pound per ton dose of DIMTS, some of the paper samples supported mold growth while others were resistant.

[0038] Table 2 indicates fungal growth on paper, where "0" indicates no growth; "1" indicates 25% coverage of the surface with fungal growth; "2" indicates 50% coverage; "3" indicates 75% coverage; "4" indicates 100% coverage. Three sample results are presented for each mixture.

TABLE 2 DOSAGE SCREENING			
DIMTS (2 #/ton) with:	Week 1	Week 2	Week 3
Blank	4,4,4	4,4,4	4,4,4
No fixative	1,2,2	4,4,4	4,4,4
Polyamine (0.4#/ton)	0,0,0	1,1,0	3,3,2
Polyamine (0.8#/ton)	0,0,0	1,0,1	3,3,3
Polyamine (1.2#/ton)	0,0,0	0,0,0	0,0,0
Polyamine (1.6#/ton)	0,0,0	0,0,0	0,0,0
Polyamine (2.0#/ton)	0,0,0	0,0,0	0,0,0
Polyamine (3.0#/ton)	0,0,0	0,0,0	0,0,0
Polyamine (4.0#/ton)	0,0,0	0,0,0	0,0,0
Cationic flocculant (0.5#/ton)	0,0,0	0,0,0	0,0,0
Cationic flocculant (1.0#/ton)	0,0,0	0,1,1	2,3,3
Cationic flocculant (1.5#/ton)	0,0,0	0,0,0	3,4,3
Cationic flocculant (2.0#/ton)	0,0,0	0,0,0	0,0,0
Cationic flocculant (3.0#/ton)	0,0,0	0,0,0	1,0,1
Cationic flocculant (4.0#/ton)	0,0,0	1,1,0	4,4,2

Example 2

[0039] Paper samples were made to test the order of addition of DIMTS and polyamine, using similar conditions to Example 1. In Table 3, adding polyamine at 1# /ton ahead of the DIMTS addition prevented growth for all three weeks. However, adding 5#/ton of polyamine before adding the DIMTS resulted in microbial growth at 2 weeks. Using the reverse order, adding the DIMTS before adding polyamine at 5# per ton resulted in microbial growth in one sample at week 3.

[0040] Table 3 also shows the results of experiments conducted on other potential fixatives. These coagulants include

polyDADMAC (diallyldimethylammonium chloride) similar to Aquaserv AQ-299 (estimated MW = 150,000),

DADMAC-acrylamide copolymer similar to Aquaserv AQ-365 (estimated MW = 1,000,000),
 polyguanidine (branched) similar to Aquaserv AQ-651 (estimated MW = 25,000),
 polyguanidine (unbranched) similar to Aquaserv AQ-366 (estimated MW = 25,000),
 aluminum chlorohydrate (ACH) similar to Aquaserv AQ-292, and
 a very high molecular weight anionic polyacrylamide similar to Aquaserv AQ-367.

TABLE 3
FIXATIVE SCREENING

DIMTS (2 #/ton) with:	Week 1	Week 2	Week 3
Blank	4,4,4	4,4,4	4,4,4
No fixative	0,0,0	1,0,1	3,0,1
Polyamine (1#/ton)	0,0,0	0,0,0	0,0,0
Polyamine (5#/ton)	0,0,0	2,3,3	3,4,4
Polyamine (5#/ton) - reverse order	0,0,0	0,0,0	0,1,0
DADMAC-acrylamide copolymer	0,0,0	3,1,1	4,2,2
PolyDADMAC	0,0,0	0,3,0	1,4,0
ACH	0,0,0	1,3,3	1,4,4
Polyguanidine - branched	0,0,0	3,2,3	4,3,4
Polyguanidine - straight chain	0,0,0	0,2,0	0,3,0
Cationic flocculant	0,0,0	3,2,2	3,2,2
Anionic flocculant	0,0,0	2,0,2	2,0,3

[0041] Addition of a polyamine ahead of the DIMTS at reasonable levels (expectations of 0.5 - 1.5 #/ton) seems to enhance the antifungal benefits. However, a relatively high dose of polyamine, ahead of the DIMTS feed, does not lead to improved antifungal performance and can actually decrease the efficacy of the treatment when compared to paper made without any fixative.

Example 3

[0042] Similar experiments were conducted using a cationic and an anionic flocculant, typical of those used on recycle furnish paper machines. Using a dosage at the same level as the polyamine, the results for the cationic flocculant were less effective than those of the anionic flocculant. We infer that molecular weight is more of a factor for the flocculants than is charge density (the anionic performed better). The inconsistent results observed within each grouping of flocculants may be associated with a tendency of them to form three-dimensional, compact structures. These structures may serve to entrap the DIMTS particles, reducing the preservative's ability to interact with target organisms. Alternatively, the flocculants might simply agglomerate those DIMTS particles.

Claims

1. A method for making a fungal-resistant paper sheet for use in building materials comprising adding a hydrophobic fungicide with a solubility in water of less than 0.3 g/L at 25° C and a cationic fixative, selected from cationic homopolymers and copolymers of polyacrylamides, polyamines, polyDADMACs, polyguanidines, polyethyleneimines, cellulosic ethers, starches, aluminum-based coagulants, iron-based coagulants, microparticle silica systems, and combinations thereof, to a paper slurry during manufacture of the paper or paperboard, and processing the paper slurry in a paper machine to create a sheet.
2. The method of claim 1 wherein the hydrophobic fungicide is selected from the group consisting of diiodomethyl-p-tolylsulfone (DIMTS), zinc pyrithione, thiabendazole, 3-iodo-2-propynyl butylcarbamate, dichloro-octylisothiazolinone, o-phenylphenol, bromonitrostyrene, and 2-(thiocyanomethylthio) benzothiazole.

3. The method of claim 1 wherein the hydrophobic fungicide is diiodomethyl-p- tolylsulfone.
4. The method of making fungal-resistant paper sheet according to claim 1, further comprising processing the sheet into pressed paper.
- 5 5. The method of making fungal-resistant paper sheet according to claim 1, further comprising processing the sheet into multi-ply paperboard.
- 10 6. The method of making fungal-resistant paper sheet according to claim 1 wherein the hydrophobic fungicide is added by wet end application to the pulp slurry before the cationic fixative is added to the pulp slurry.
7. The method of making fungal-resistant paper sheet according to claim 1 wherein the hydrophobic fungicide is added by wet end application to the pulp slurry after the cationic fixative is added to the pulp slurry.
- 15 8. The method of making fungal-resistant paper sheet according to claim 1 the hydrophobic fungicide is added by wet end application to the pulp slurry at the same time that the cationic fixative is added to the pulp slurry.
9. The method of claim 7 where the hydrophobic fungicide and the cationic fixative are mixed together to form a pre-mix and the pre-mix is added by wet end application to the pulp slurry.
- 20 10. The method of making fungal-resistant paper sheet according to claims 1 to 3, wherein the cationic fixative is a polyamine.
11. The method of making fungal-resistant paper sheet according to claim 1 to 3, wherein the weight ratio of cationic fixative to fungicide is from 1:35 to 15:1.
- 25 12. The method of making fungal-resistant paper sheet according to claims 1 to 3, wherein the weight ratio of cationic fixative to fungicide is from 1:35 to 2.5:1.
13. The method of making fungal-resistant paper sheet according to claims 1 to 3, further comprising treating the sheet to provide moisture resistance and/or strength enhancement.
14. The method of making a fungal resistant paper sheet of claims 1 to 3, further comprising adding a second antifungal material either to the paper slurry or to the finished sheet, by coating as neat product, or a formulation.
- 35 15. A fungal-resistant sheet of paper or paperboard made according to the method of claims 1 to 3, where the hydrophobic fungicide is present in an amount equal to at least 0.02 pounds per ton of dry fiber present in the sheet.
16. A fungal-resistant sheet of paper or paperboard made according to the method of claim 3, where the diiodomethyl-p-tolylsulfone is present in an amount between about 2.0 and 10.0 pounds per ton of dry fiber present in the sheet.
- 40 17. A fungal-resistant sheet of paper or paperboard made according to the method of claim 3, where the diiodomethyl-p-tolylsulfone is present in an amount between about 2.0 and 3.2 pounds per ton of dry fiber present in the sheet.
18. A fungal-resistant sheet made by the method of claim 1 that has 30% or less fungal growth after 7 days of testing under the conditions of ASTM method G-21.
- 45 19. A fungal-resistant sheet made by the method of claim 1 that has 30% or less fungal growth after 4 weeks of testing under the conditions of ASTM method G-21.
- 50 20. A fungal-resistant sheet made by the method of claim 1 that receives a rating of 7 to 10 in ASTM D 3273.
21. A fungal-resistant sheet made by the method of claims 1 to 3 further comprising an antifungal surface treatment.
- 55 22. A finished gypsum board comprising a fungal-resistant sheet made by the method of claim 1 to 3 wherein the gypsum board passes ASTM D3273 with a rating of 7 to 10 inclusive.

Patentansprüche

- 5 1. Ein Verfahren zum Herstellen eines pilzresistenten Papierbogens zur Verwendung bei Baumaterialien, beinhaltend das Zugabe eines hydrophoben Fungizids mit einer Löslichkeit in Wasser von weniger als 0,3 g/l bei 25 °C und eines kationischen Fixiermittels, ausgewählt aus kationischen Homopolymeren und Copolymeren aus Polyacrylamiden, Polyaminen, PolyDADMAC, Polyguanidinen, Polyethylenimin, Celluloseethern, Stärken, auf Aluminium basierenden Koagulationsmitteln, auf Eisen basierenden Koagulationsmitteln, Siliciumdioxidmikroteilchensystemen und Kombinationen davon, zu einer Stoffsuspension während der Produktion des Papiers oder der Pappe und Verarbeiten der Stoffsuspension in einer Papiermaschine, um einen Bogen zu erzeugen.
- 10 2. Verfahren gemäß Anspruch 1, wobei das hydrophobe Fungizid ausgewählt ist aus der Gruppe, bestehend aus Diiodmethyl-p-tolylsulfon (DIMITS), Zink-Pyrithion, Thiabendazol, 3-Iod-2-propinylbutylcarbammat, Dichloroctylisothiazolinon, o-Phenylphenol, Bromnitrostyren und 2-(Thiocyanomethylthio)benzothiazol.
- 15 3. Verfahren gemäß Anspruch 1, wobei das hydrophobe Fungizid Diiodmethyl-p-tolylsulfon ist.
4. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß Anspruch 1, ferner beinhaltend das Verarbeiten des Bogens zu gepresstem Papier.
- 20 5. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß Anspruch 1, ferner beinhaltend das Verarbeiten des Bogens zu mehrlagiger Pappe.
- 25 6. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß Anspruch 1, wobei der Stoffsuspension das hydrophobe Fungizid mittels Nasspartieanwendung zugegeben wird, bevor der Stoffsuspension das kationische Fixiermittel zugegeben wird.
- 30 7. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß Anspruch 1, wobei der Stoffsuspension das hydrophobe Fungizid mittels Nasspartieanwendung zugegeben wird, nachdem der Stoffsuspension das kationische Fixiermittel zugegeben wird.
- 35 8. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß Anspruch 1, der Stoffsuspension wird das hydrophobe Fungizid mittels Nasspartieanwendung zur gleichen Zeit zugegeben, wie der Stoffsuspension das kationische Fixiermittel zugegeben wird.
- 40 9. Verfahren gemäß Anspruch 7, wobei das hydrophobe Fungizid und das kationische Fixiermittel miteinander gemischt werden, um eine Vormischung zu bilden, und der Stoffsuspension die Vormischung mittels Nasspartieanwendung zugegeben wird.
10. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß den Ansprüchen 1 bis 3, wobei das kationische Fixiermittel ein Polyamin ist.
- 45 11. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß den Ansprüchen 1 bis 3, wobei das Gewichtsverhältnis von dem kationischen Fixiermittel zu dem Fungizid von 1 : 35 bis 15 : 1 beträgt.
12. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß den Ansprüchen 1 bis 3, wobei das Gewichtsverhältnis von dem kationischen Fixiermittel zu dem Fungizid von 1 : 35 bis 2,5 : 1 beträgt.
- 50 13. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß den Ansprüchen 1 bis 3, ferner beinhaltend das Behandeln des Bogens, um Feuchtigkeitsbeständigkeit und/oder Stärkeverbesserung bereitzustellen.
14. Verfahren zum Herstellen eines pilzresistenten Papierbogens gemäß den Ansprüchen 1 bis 3, ferner beinhaltend das Zugabe eines zweiten antifungialen Materials entweder zu der Stoffsuspension oder zu dem fertigen Bogen, mittels Beschichtung als unverdünntes Produkt oder eine Formulierung.
- 55 15. Ein pilzresistenter Bogen aus Papier oder Pappe, hergestellt gemäß dem Verfahren aus den Ansprüchen 1 bis 3, wobei das hydrophobe Fungizid in einer Menge vorhanden ist, die gleich mindestens 0,02 Pfund pro Tonne an in dem Bogen vorhandener Trockenfaser ist.

16. Pilzresistenter Bogen aus Papier oder Pappe, hergestellt gemäß dem Verfahren aus Anspruch 3, wobei das Diiod-methyl-p-tolylsulfon in einer Menge von zwischen etwa 2,0 und 10,0 Pfund pro Tonne an in dem Bogen vorhandener Trockenfaser vorhanden ist.

17. Pilzresistenter Bogen aus Papier oder Pappe, hergestellt gemäß dem Verfahren aus Anspruch 3, wobei das Diiod-methyl-p-tolylsulfon in einer Menge von zwischen etwa 2,0 und 3,2 Pfund pro Tonne an in dem Bogen vorhandener Trockenfaser vorhanden ist.

18. Pilzresistenter Bogen, hergestellt gemäß dem Verfahren aus Anspruch 1, der nach 7 Tagen Testen unter den Bedingungen des ASTM-Verfahrens G-21 30 % oder weniger Pilzwachstum aufweist.

19. Pilzresistenter Bogen, hergestellt gemäß dem Verfahren aus Anspruch 1, der nach 4 Wochen Testen unter den Bedingungen des ASTM-Verfahrens G-21 30 % oder weniger Pilzwachstum aufweist.

20. Pilzresistenter Bogen, hergestellt gemäß dem Verfahren aus Anspruch 1, der in ASTM D 3273 eine Bewertung von 7 bis 10 erhält.

21. Pilzresistenter Bogen, hergestellt gemäß dem Verfahren aus den Ansprüchen 1 bis 3, der ferner eine antifungielle Oberflächenbehandlung beinhaltet.

22. Eine fertige Gipsplatte, beinhaltend einen pilzresistenten Bogen, hergestellt gemäß dem Verfahren aus den Ansprüchen 1 bis 3, wobei die Gipsplatte ASTM D3273 mit einer Bewertung von 7 bis einschließlich 10 besteht.

Revendications

1. Une méthode pour la réalisation d'une feuille de papier à résistance fongique destinée à être utilisée dans des matériaux de construction comprenant le fait d'ajouter un fongicide hydrophobe avec une solubilité dans l'eau inférieure à 0,3 g/L à 25 °C et un fixateur cationique, sélectionné parmi des homopolymères et copolymères cationiques de polyacrylamides, polyamines, polyDADMAC, polyguanidines, polyéthylèneimines, éthers celluloses, amidons, coagulants à base d'aluminium, coagulants à base de fer, systèmes de silice microparticulaire, et des combinaisons de ceux-ci, à une suspension épaisse à papier au cours de la fabrication du papier ou carton, et le fait de transformer la suspension épaisse à papier dans une machine à papier afin de créer une feuille.

2. La méthode de la revendication 1 dans laquelle le fongicide hydrophobe est sélectionné dans le groupe constitué de la diiodométhyl-p-tolylsulfone (DIMTS), de la pyriothione de zinc, du thiabendazole, du butylcarbamate de 3-iodo-2-propynyle, de la dichlorooctylisothiazolinone, de l'o-phénylphénol, du bromonitrostyrène, et du 2-(thiocyanométhylthio)benzothiazole.

3. La méthode de la revendication 1 dans laquelle le fongicide hydrophobe est la diiodométhyl-p-tolylsulfone.

4. La méthode de réalisation de feuille de papier à résistance fongique selon la revendication 1, comprenant en sus le fait de transformer la feuille en papier apprêté.

5. La méthode de réalisation de feuille de papier à résistance fongique selon la revendication 1, comprenant en sus le fait de transformer la feuille en carton multijet.

6. La méthode de réalisation de feuille de papier à résistance fongique selon la revendication 1 dans laquelle le fongicide hydrophobe est ajouté par application en partie humide à la suspension épaisse de pâte avant que le fixateur cationique ne soit ajouté à la suspension épaisse de pâte.

7. La méthode de réalisation de feuille de papier à résistance fongique selon la revendication 1 dans laquelle le fongicide hydrophobe est ajouté par application en partie humide à la suspension épaisse de pâte après que le fixateur cationique a été ajouté à la suspension épaisse de pâte.

8. La méthode de réalisation de feuille de papier à résistance fongique selon la revendication 1 le fongicide hydrophobe est ajouté par application en partie humide à la suspension épaisse de pâte simultanément au moment où le fixateur cationique est ajouté à la suspension épaisse de pâte.

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9. La méthode de la revendication 7 où le fongicide hydrophobe et le fixateur cationique sont mélangés ensemble afin de former un pré-mélange et le pré-mélange est ajouté par application en partie humide à la suspension épaisse de pâte.
- 5 10. La méthode de réalisation de feuille de papier à résistance fongique selon les revendications 1 à 3, dans laquelle le fixateur cationique est une polyamine.
11. La méthode de réalisation de feuille de papier à résistance fongique selon les revendications 1 à 3, dans laquelle le rapport en poids du fixateur cationique au fongicide va de 1/35 à 15/1.
- 10 12. La méthode de réalisation de feuille de papier à résistance fongique selon les revendications 1 à 3, dans laquelle le rapport en poids du fixateur cationique au fongicide va de 1/35 à 2,5/1.
13. La méthode de réalisation de feuille de papier à résistance fongique selon les revendications 1 à 3, comprenant en sus le fait de traiter la feuille afin de fournir une résistance à l'humidité et/ou un accroissement de la robustesse.
- 15 14. La méthode de réalisation d'une feuille de papier à résistance fongique des revendications 1 à 3, comprenant en sus le fait d'ajouter une deuxième matière antifongique soit à la suspension épaisse à papier, soit à la feuille finie, par enduction sous forme de produit pur, ou de formulation.
- 20 15. Une feuille de papier ou carton à résistance fongique réalisée selon la méthode des revendications 1 à 3, où le fongicide hydrophobe est présent dans une quantité égale à au moins 0,02 livre par tonne de fibre sèche présente dans la feuille.
- 25 16. Une feuille de papier ou carton à résistance fongique réalisée selon la méthode de la revendication 3, où la diiodo-méthyl-p-tolylsulfone est présente dans une quantité comprise entre environ 2,0 et 10,0 livres par tonne de fibre sèche présente dans la feuille.
- 30 17. Une feuille de papier ou carton à résistance fongique réalisée selon la méthode de la revendication 3, où la diiodo-méthyl-p-tolylsulfone est présente dans une quantité comprise entre environ 2,0 et 3,2 livres par tonne de fibre sèche présente dans la feuille.
- 35 18. Une feuille à résistance fongique réalisée par la méthode de la revendication 1 qui présente une croissance fongique de 30 % ou moins après 7 jours d'essais dans les conditions de la méthode ASTM G-21.
19. Une feuille à résistance fongique réalisée par la méthode de la revendication 1 qui présente une croissance fongique de 30 % ou moins après 4 semaines d'essais dans les conditions de la méthode ASTM G-21.
- 40 20. Une feuille à résistance fongique réalisée par la méthode de la revendication 1 qui reçoit une notation allant de 7 à 10 dans l'ASTM D 3273.
21. Une feuille à résistance fongique réalisée par la méthode des revendications 1 à 3 comprenant en sus un traitement de surface antifongique.
- 45 22. Une plaque de plâtre finie comprenant une feuille à résistance fongique réalisée par la méthode des revendications 1 à 3, la plaque de plâtre passant avec succès l'ASTM D3273 avec une notation allant de 7 à 10 inclus.

REFERENCES CITED IN THE DESCRIPTION

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