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3,060,079

GERMICIDAL PAPER AND METHOD

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This invention relates to germicidal paper and method of making same.

One object of the invention is the provision of paper having germicidal properties substantially permanently imparted thereto. Another object of the invention is the provision of methods of making germicidal papers. Other objects of the invention will be better understood by reference to the following detailed description of the invention.

Generally the objects of this invention are attained by conditioning the fibers of a paper pulp suspension and, by means of such conditioning, securing a germicide on the discrete fibers of the suspension, and thereafter forming paper from the thus treated fibers.

The advantages of the invention include, among others, complete distribution of the germicidal properties throughout a paper web, substantial permanence of the germicidal properties, ease of application, almost quantitative pick-up of both fiber conditioning chemical and germicide on the fibers with concomitant inexpensiveness, and an absence of interference with the web formation and other paper making steps.

To achieve the advantages of the invention requires the use of appropriate fiber conditioning chemicals and germicides. While there are many compounds which will condition fibers in aqueous suspension, the fiber conditioners most useful for purposes of this invention may be selected from either the polyalkylene imines or the water soluble polymers of amine-aldehyde condensation products. Illustrative examples of suitable fiber conditioning chemicals include polyethylene imine, polypropylene imine, polybutylene imine, water soluble condensation products of guanidine and formaldehyde, dicyandiamide formaldehyde, tetramethylol acetylene diurea, guanyl urea phosphate condensed with formaldehyde, guanidine phosphate condensed with formaldehyde, glyoxal condensed with ethylene diamine and alpha-hydroxyadipaldehyde condensed with diurea triamine.

Among the germicidal compounds which may be used in this invention are: alkyl-aryl polyether dimethylbenzylammonium chloride (Hyamine 1622—Rohm & Haas); o-phenylphenol (Dowicide No. I); 2,4,5-trichlorophenol (Dowicide No. II); 2-chloro-6-phenylphenol (Dowicide No. III); tetrachlorophenol (Dowicide No. VI); pentachlorophenol (Dowicide No. VII); phenyl mercury oleate in oil (sold as FD-2 in readily emulsifiable oil and FD-3 in oil); lauryl pyridinium chloride; a cationic dispersion of copper 8-quinolinolate (Marcocide C-8); an anionic dispersion of copper 8-quinolinolate (Marcocide CQ); alkyl dimethylethyl ammonium halide (Marcocide GF); coconut amine salt of tetrachlorophenol (Nuodex 72, covered by Patent Number 2,526,892); phenyl mercury lactate (Puratized SC); $C_{24}H_{33}N_2S_2Cl$ (Vancide 26EC); dodecylidimethyl benzylammonium cyclopentane salt (Nuodex 100, U.S. Patent Number 2,519,924); and a combination of hydroxy copper naphthenate and copper 8-quinolinolate (Nuodex Copper QN—18%, U.S. Patent Number 2,368,560).

The invention finds its primary utility in cellulose paper but it obviously may be used with other paper forming fibers such as asbestos, bagasse, etc., or in combinations thereof, or as one web layer of a laminated paper or

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paper board, depending, of course, on the end use to which the product will be put. It will also be understood that products other than a germicide may also be added to the fibers either before, simultaneously with, or after the addition of the germicide, provided, of course, that the other additaments do not destroy the effectiveness of the germicide used. Such other additaments include resins, pigments, sizes and other paper modifiers known to those skilled in the art.

In carrying out the procedure of the invention, both the fiber conditioning chemical and the germicide must be added to an aqueous suspension of fibers prior to web formation. The order of addition is critical, the fiber conditioning chemical being added to the fiber slurry prior to the addition of the germicide, and in sufficient time prior to the germicide addition to permit reaction of the fiber conditioning chemical with the fiber furnish, generally, however, from 20 minutes to one-half hour is sufficient reaction time. Thereafter, the germicide may be added in either soluble, dispersed or emulsified form, depending upon the nature of the germicide employed. The fiber conditioning chemical and the germicide employed may be added at any point in process flow, for example, in the beaters, hydropulpers or hydrofiners, beater chest, machine chests, and pipe lines provided that at the point of addition there is sufficient agitation of the fiber suspension to insure a completely uniform distribution of the added material, and provided also, that there is sufficient reaction time for the fiber conditioning chemical, and the subsequently added germicide, although in the instance of the germicide addition, reaction with the conditioned fibers is quite rapid. It is also preferred to add the fiber conditioning chemical after the greater part of the normal beating cycle has been completed, as it is well known that as beating continues, greater fiber surface is developed, and hence greater areas of reaction become available. Surprisingly, the fiber conditioners of this invention increase the freeness of a fiber suspension without reduction of the effectiveness of the increased surface of the fibers.

The amount of fiber conditioning chemical and the amount of germicide may be varied considerably, depending upon the choice of materials and the amount of materials other than germicide which may be added at the same time. Ordinarily the amount of fiber conditioning chemical will be from about 0.1% to 1% and even up to 4%, especially when other materials are added also, and the amount of germicide will be from about 0.25% to 1.5% on a solids basis on the dry weight of the fibers. The preferred amount of fiber conditioning chemical is about 0.25% and the preferred amount of germicide is about 0.5%.

The invention is illustrated by the following typical examples.

Example 1

A bacteriostatic, wet strength, creped toweling paper was made in a machine production run using a Yankee Fourdrinier paper machine, trimming 90 inches, and the machine unit was completely equipped with the Hydropulper and the Jordan engines for stock processing. In addition to the Yankee drier, there were also two sections of conventional drum driers.

Three Hydropulper units were furnished for the machine run, each Hydropulper being loaded with 500 pounds of unbleached kraft pulp and 500 pounds of mechanical pulp, and the stock reduced to about 450 Canadian standard freeness, after which the stock of each Hydropulper was pumped to each of three Holland type beaters, which were subsequently treated in an identical manner. The stock of each beater was reduced to about 350 Canadian standard freeness at which point exactly

1/4 of 1%, on a solids basis, of a dicyandiamide formaldehyde condensation product was added to the stock of each beater, and reacted therewith for 20 minutes. Then there was added exactly 1/2 of 1% on a solids basis of alkylaryl polyether dimethylbenzylammonium chloride (Hyamine 1622 from Rohm & Haas) in the form of a 5% solids solution. Reaction with the conditioned fiber was continued for 10 minutes. Then, 12 pounds on a solids basis of a cationic urea formaldehyde wet strength resin was added to each beater as a 10% solids dispersion, and after a 15 minute reaction time, the suspension of each beater was adjusted to pH 5 by the addition of approximately 1% of papermaker's alum, and the processed stock of each beater dropped to the common beater chest in process flow to the paper machine where the paper was formed by conventional processing.

The freeness in the machine head box was 300 Canadian standard freeness, the pH was 5.0. The machine speed was 290 f.p.m.

An excellent wet strength, bacteriostatic, creped toweling paper was produced having the following physical properties:

Basis weight 24 x 36—500	lbs.	26.5
Average caliper	inches	.006
Average bursting strength, lbs.		12.0
Average dry tear, grams, CD		50
Average wet tear, grams, CD		46
Percentage wet tearing strength, CD		92
Average dry tear, grams, MD		40
Average wet tear, grams, MD		32
Percentage wet tearing strength, MD		80
Average dry tensile strength, MD, lb./in.		4.4
Average dry tensile strength, CD, lb./in.		2.5
Percentage stretch		3.8

The wet strength toweling produced was classified as bacteriostatic showing no growth of the organisms, *micrococcus pyogenes* var. *aureus* (*Staphylococcus aureus*) on standard F.D.A. agar, incubated at 37° C. for 24 hours.

The dicyandiamide formaldehyde condensation product used is a polyfunctional cationically active, chemically reactive, nonresinous condensation product of dicyandiamide and formaldehyde which is readily dilutable in water. It is prepared by reacting dicyandiamide with formaldehyde under acid conditions in the presence of ammonium chloride. The product is a colorless, slightly hazy, viscous liquid with a mild odor of formaldehyde, having a viscosity of between 8 and 14 seconds at 25° C. as determined by the Stormer viscosimeter.

The above example was repeated using a polyethylene imine of 30,000 molecular weight in place of the dicyandiamide formaldehyde condensation product. The results were substantially the same but the relative cost of the polyethylene imine was quite high.

Example 2

A bacteriostatic, wet strength, creped napkin paper was made in a machine run using a high speed Fourdrinier machine equipped with a Yankee drier with creping doctor, the machine trimming 100 inches. For the purpose of this production run, three Hydropulper units were used, each unit being furnished with 350 pounds of bleached Cellate pulp and 650 pounds of a bleached sulfite pulp, and the stock reduced to about 550 Canadian standard freeness. At a Canadian standard freeness of 550, the Hydropulper stock was pumped to standard Holland type beaters, three such beaters being used, and each beater then treated individually as hereafter described.

The beater stock was reduced to 350 Canadian standard freeness. Thereafter, exactly 1/4 of 1%, on a solids basis, of the dicyandiamide formaldehyde condensation product previously described was added to the stock in each beater in the form of a 5% solids colloidal suspension, and reacted with the fibers for 30 minutes. Then

exactly 1/4 of 1%, on a solids basis, of an alkyl-aryl dimethylbenzylammonium chloride, the alkyl-aryl group ranging from 8 to 18 carbon atoms, was added. The solids content of this sanitizing agent was approximately 20%, was added in a 5% solids solution, and reacted with the conditioned fibers for about 15 minutes. Thereafter, exactly 1/2 of 1% on a solids basis of a standard rosin sizing agent was added to each beater of stock, specifically, a rosin size mixture consisting of about 75 parts by weight of a conventional sodium rosin soap and 25 parts by weight of a maleic anhydride adduct of rosin. The sizing agent was added as about a 5% solids dispersion. After a 5 minute reaction with the same processed stock, exactly 1 pound on a solids basis, of sodium silicate solution was added, and finally an alum solution was added to adjust the pH to 4.7 to 4.8, and the finished stock of each beater dropped to the beater chest in process flow to the paper machine.

The finished stock was passed through the Jordan engine, operating with a 50 ampere loading, and the stock freeness reduced to 173 Canadian standard freeness. The consistency at the machine head box was 0.20% and the pH value 4.7.

The machine wire was a standard 70 mesh wire. Machine speed was 540 f.p.m. The slice was 2 1/2", the head in back of the slice 15". The first suction box operated at 10" vacuum, the second suction box at 5" vacuum, and the suction couch roll at 4" vacuum.

The first press loading was 150 pounds front and back, the second press loading 180 pounds front and back, and the pressure roll 190 pounds front and back. The Yankee drier operated 15 pounds' steam pressure.

No difficulty was experienced in the operation of the machine and an excellent appearing creped napkin was produced having the following physical properties:

Basis weight 24 x 36—500	lbs.	15.5
Average caliper	inches	0.0011
Average bursting strength		8.5
Average dry tear, grams, MD		20
Average dry tear, grams, CD		24
Average dry tensile, lb./in., MD		1.00
Average dry tensile, lb./in., CD		.60
Average percentage stretch		21
Average bulk		35

The material produced was classified as bacteriostatic, showing no growth of the organisms, *Micrococcus pyogenes* var. *aureus* (*Staphylococcus aureus*) on standard F.D.A. agar, incubated at 37° C. for 24 hours.

This example was repeated, using a colloidal, sub-resinous, chemically reactive, cationactive condensation product of acetylene diurea and formaldehyde (with slightly more than 1 mol of formaldehyde for each mol of acetylene diurea) in double the amount of the dicyandiamide formaldehyde condensation product and in lieu thereof. The results of this example were substantially duplicated.

The term "germicide" has been used throughout the specification as a term of convenience to mean those chemical materials which kill, inhibit the growth of, or otherwise destroy the dangerous properties of bacteria and fungus.

While the invention has been described in terms of the preferred methods of application of the principles disclosed, it will be obvious to those skilled in the art that detailed procedures may be widely varied without departing from the scope of the invention as defined in the claims.

I claim:

1. Germicidal paper comprising water laid cellulose fibers carrying 0.1 to 4% of a fiber conditioning chemical selected from the group consisting of a polyalkylene imine and a water soluble polymeric amine aldehyde condensation product, and 0.25 to 1.5% of an alkyl-aryl dimethylbenzylammonium chloride having 8 to 18 car-

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bon atoms in the alkyl-aryl group thereof, said percentages being based on the dry weight of said fibers.

2. Germicidal paper as set forth in claim 1 wherein said fiber conditioning chemical is polyethylene imine.

3. Germicidal paper as set forth in claim 1 wherein said fiber conditioning chemical is a condensation product of dicyanamide and formaldehyde.

4. The process of making germicidal paper which comprises severely agitating fibers suspended in water, adding to the agitated fiber suspension 0.1 to 4% of a fiber conditioning chemical selected from the group consisting of a polyalkylene imine and a water soluble polymeric amine aldehyde condensation product, adding 0.25 to 1.5% of an alkyl-aryl dimethylbenzylammonium chloride having 8 to 18 carbon atoms in the alkyl-aryl group thereof, to the agitated fiber suspension and thereafter forming a paper web from the suspended fibers, said percentages being based on the dry weight of said fibers.

5. The process as set forth in claim 3 wherein said

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fiber conditioning chemical is added first and said alkyl-aryl dimethylbenzylammonium chloride is added later.

6. The process set forth in claim 4 wherein said fibers are cellulose fibers.

7. The process as set forth in claim 5 wherein said fiber conditioning chemical is polyethylene imine.

8. The process as set forth in claim 5 wherein said fiber conditioning chemical is a dicyanamide-formaldehyde condensation product.

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