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FIRE-PROOFING LIGNOCELLULOSIC STRUCTURES WITH BROMINE AND CHLORINE COMPOSITIONS

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This invention relates to the flameproofing of cellulosic compositions containing lignin and in particular to the production of lignocellulosic articles having some degree of resistance to burning. The expression "lignocellulosic articles" will be understood to mean lignin-containing cellulosic bodies or structures such as wooden beams, veneers or rods; paper sheets, rolls of newsprint; strawboard or chip board; yarns, webs, woven or knitted fabrics, ropes or belts made of lignocellulosic fibers such as, for example, jute, kenaf, sisal, hemp or the like; and such bodies or structures are distinguished from uniformed masses such as paper pulp.

Previous methods of rendering lignocellulosic articles flame-resistant have generally involved either the surface-coating or the impregnation of the articles with inorganic salts or organic compounds having a flame retarding effect. Coating or impregnating materials which have been used for this purpose include water-soluble silicates, phosphates and borates, tin, iron, antimony and chromium oxides, and chlorinated or brominated organic compounds. It is a disadvantage of these known methods that the flame retardant composition remains as a material extraneous to the lignocellulosic article and does not bond chemically thereto. As a result in many cases, the enhanced flame-resistance which is imparted to the article is gradually lost when the article is exposed to weathering or is soaked in water for any substantial length of time. In other cases relatively large amounts of the flame-retardant composition are necessary which adversely affect the material thus treated.

Wood is composed of three major ingredients, namely cellulose, hemicellulose and lignin. The first two are long chain carbohydrates whilst the lignin is a compound containing condensed phenyl-propane units. Most other plant materials contain these three major ingredients although the relative amounts vary widely. Although in some cases, for example in the case of cotton, a cellulosic material manufactured from the plant is lignin-free, there are many other products in which at least some lignin is retained. This applies in particular to groundwood which serves as the main ingredient in the manufacture of newsprint. Such groundwood flour may contain up to about 27% of lignin depending on the species of wood from which it has been prepared and also depending on the bleaching process employed. Semi-chemical pulps serving for the production of cardboard and of corrugated sheets for the manufacture of cardboard boxes contain varying amounts of lignin. Jute and sisal fibers contain substantial amounts, as do also bast and leaf fibers.

The lignin and hemicellulose form the so-called middle lamella which occurs between the fibrous cells of wood and many other plant tissues; the lignin also occurs in the lignocellulosic fibers such as those of jute, hemp and sisal. The middle lamella surrounds the fibrous cells, which themselves are composed mostly of cellulose, and cements the fibers together thereby serving to maintain the structure of the fiber bundle.

This invention consists in lignocellulosic articles in which the lignin component is halogenated.

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The halogenation may be effected at any desired stage of the manufacture of the lignocellulosic articles. For example, a fiber pulp may be so halogenated, or a semi-manufactured product such as groundwood which is used in the manufacture of newsprint, or a finished article may be subjected to the halogenation, e.g., a wood veneer, building timber or the like.

It is found that by the introduction of halogen into the lignin molecules the combustion resistance of the lignocellulose can be enhanced. This has the advantage that it is the inflammable material itself whose properties are modified, that is, the combustion resistance conferred in this way is not dependent upon the presence of an extraneous material which can be leached out. Since the lignin surrounds the fibrous cells, the present invention makes provision for a protective coating around each fiber. By comparison with the prior art processes, therefore, the combustion resistance imparted by the present invention is relatively stable and permanent, as the halogen is bound chemically to the lignin and constitutes an integral part of the lignocellulosic structure.

It is known to chlorinate wood pulp and subsequently to treat the chlorinated pulp with alkali for the purpose of removing the chlorinated lignin from the cellulose. The articles ultimately manufactured from such chlorinated pulp do thus not contain either chlorine or any substantial amount of lignin, nor are they flameproof.

For the purposes of the present invention the use of bromine has been found to be particularly useful. The proportion of halogen used for the treatment of the lignocellulosic material depends on many factors, e.g., the halogen used, the nature of the material to be flame-proofed, the degree of flame-resistance which is required. For a given degree of halogenation, the time required to effect the halogenation will in general be less where the lignocellulose to be treated is finely comminuted. This applies for example in the case of groundwood or wood pulp, and in other cases where a large specific surface is available for example in the case of yarn and rope, as contrasted with chips for the fabrication of chip board, or with wooden veneers or structural wood.

For example, groundwood treated with 4 to 8% by weight of bromine will produce a paper which does not burn when ignited with a match. Smaller additions of bromine will confer a smaller degree of non-inflammability whilst nevertheless representing a considerable improvement as compared with paper produced from untreated groundwood. The general properties of the materials treated in this way are not substantially changed, especially if care is taken to avoid degradation of the cellulose by the acid formed as a by-product of the halogenation process, which can be done, for example, by neutralization of the reaction mixture or by the use of buffers, as will be described below.

The halogenation can be carried out in various ways. For example, the lignocellulosic material to be treated may be brought into contact with gaseous halogen in a closed vessel at room temperature or any other temperature below the inflammation point of the material. The residence time may be from a few seconds to several hours, depending on the nature of the materials being treated, the degree of halogenation required and the conditions of halogenation such as the pressure of the halogen gas, temperature and illumination.

Or the material to be treated may be immersed in an aqueous halogen solution for a time ranging from several seconds to several hours. The aqueous solution may contain the predetermined amount of halogen required for the production of the desired degree of halogenation, and the process is terminated when the halogen content of the solution has been exhausted. The liquor containing the solution of the hydrogen halide formed during the halo-

genation is then decanted or filtered off, and the halogenated lignocellulosic material can be neutralized with a dilute solution of ammonia or another alkalifying agent such as sodium carbonate or milk of lime whereby the desired pH of the halogenated material is obtained.

The aqueous halogen solution may also contain buffers, e.g., mixtures of borax and boric acid, or of alkali metal or ammonium phosphate of the desired pH, in order to prevent the acid formed in the course of the halogenation from attacking the cellulose. These buffers are absorbed by the material to be treated in amounts which may range from, for example, 0.01 to 16%. In addition to their buffering action they may also enhance the flameproofing of the material.

Other alkaline flameproofing agents such as sodium silicate can also be incorporated into the aqueous solution.

Such buffers and alkaline flameproofing agents can also be used where the halogenation is effected by means of gaseous halogen. In this case the lignocellulosic material may be impregnated, before or after the halogenation, with the buffer or alkaline fireproofing material which latter can be employed either as a solution or as a fine powder.

Where bromine is the halogenating agent it may be used in the form of an aqueous alkali metal hypobromite solution, which has the advantage of immediately neutralizing the acid forming in the course of the bromination.

It may be desirable to keep the free-halogen concentration of the aqueous halogen solution low in order to minimize oxidation of the lignocellulosic material by the action of the halogen.

For this purpose, the halogen may gradually be introduced into an aqueous bath in which the lignocellulosic material is immersed or suspended. Or, in the case of bromine being the halogenating agent, the bromine may be used in the form of an aqueous solution of a mixture of equivalent amounts of bromide and bromate, e.g., those of an alkali metal or an alkaline-earth metal, which solution is gradually acidulated whereby elementary bromine is liberated at the desired rate.

Where, in the case of bromine being used for the halogenation, the spent halogenating aqueous liquor separated from the halogenated lignocellulosic material contains hydrobromic acid or bromides formed in the course of the halogenation, elementary bromine may be recovered by the introduction into the liquor of an equivalent amount of chlorine in gaseous form or as an aqueous solution, and the aqueous bromine-chloride solution thereby formed, which may in addition contain elementary chlorine, can be used as a brominating solution for the treatment of lignocellulosic material.

Instead of in aqueous solution the halogen, e.g., bromine, may be used in solution in an organic solvent such as, for example, chloroform or carbon tetrachloride.

It has been found that lignocellulosic articles according to the invention acquire resistance not only to combustion but also to biological deterioration, such as the action of fungi. It is known that halogen-containing compounds can serve for the protection of lignocellulosic materials against biological deterioration; for example, pentachlorophenol has been used for this purpose on wood. These chlorinated compounds are, however, extraneous additions to the lignocellulosic material to be protected, and they are not stable on leaching, storage and weathering. In the lignocellulosic articles according to the present invention the halogen enters into the composition of the lignocellulosic material.

The invention is illustrated by the following examples to which it is not limited:

Example 1

80.4 grams of air-dry beech veneer sheets of 1 mm. thickness were placed in a closed desiccator-like vessel

of 6 liters' capacity. The air was evacuated from the vessel, then 12.9 grams of gaseous bromine were introduced from an ampoule into the evacuated vessel. After 30 minutes the bromination was completed and the vessel was flushed with air. The veneer sheets were rinsed in cold water until neutral, and dried in air. The veneers were then analyzed by the Carius method for bromine and were found to contain 8% by weight of bromine.

Specimens of the brominated beech veneer of a size of 20 by 20 cm. were tested in the Inclined-Panel Inflammability tester according to British Standard 476/1932—Fire Resistance, Incombustibility and Non-Inflammability of Building Materials and Structures. The veneers did not inflame and were classified as "not inflammable." While no fire appeared or spread on the sample, only an area of about 10 cm.² which was in contact with the ethanol flame used in the test became charred and underwent dry distillation without flame. A similar sample of not-brominated beech veneer burnt completely when tested under the same conditions.

19 specimens of the brominated beech veneer of 5 by 5 cm. size and 19 specimens of the not-brominated beech veneer were tested for biological stability according to the T.A.P.P.I. (Technical Association of the Pulp and Paper Industry, U.S.A.) Specification T 487M55 against *Aspergillus niger*, *Chaetomium globosum* and *Aspergillus terreus*. The micro-organisms did not develop after 2 weeks on the brominated beech veneer specimens but covered completely the not-brominated specimens. This test showed that the brominated specimens were completely resistant to the attack of micro-organisms according to the specification aforesaid.

Example 2

24 grams of Okumè wood veneers of 1.5 mm. thickness were brominated with 2.35 grams of gaseous bromine for 15 minutes similarly as in Example 1. After the bromination the sample contained 4.1% of bromine. The sample was rinsed in water and immersed for 3 minutes in 300 mls. of a solution containing per liter 18 grams of borax and 1 gram of boric acid, and air-dried.

Specimens of the brominated Okumè veneers were then tested in the Inclined-Panel Inflammability tester in the manner described in Example 1. The specimens were classified as non-inflammable. Not-brominated specimens of the same Okumè veneer burnt out completely when tested under the same conditions.

Example 3

520 grams of commercial spruce groundwood were suspended in 4.0 liters of water at room temperature. A solution of 40 grams of bromine in 4.0 liters of water was added to the suspension with vigorous stirring in the course of 3 minutes, then the stirring was continued for another 2 minutes. Thereafter the mixture was filtered and the amount of hydrobromic acid, determined in the filtrate by potentiometric titration with 0.1 N sodium hydroxide, corresponded to 20 grams of bromine, i.e., half of the bromine originally added to the suspension was recovered as hydrobromic acid. The other half had reacted with the lignin of the ground-wood structure. The filtered mass was returned to the vessel and neutralized with a dilute ammonia solution so as to adjust the pH of the suspension to 7 as measured with a Beckmann model pH meter. The pulp was then filtered again. The lignocellulosic material contained 4% of bromine calculated on the oven-dry weight of the groundwood, as determined by Carius determination. A part of the pulp was made into standard sheets of a basic weight of 250 g./m.² in the Standard T.A.P.P.I. Sheetmaking Apparatus. The sheets were tested by the Inclined-Panel Test as described in Example 1. The sheets did not inflame and were classified as non-inflammable. Several sheets were stored for 210 days at 21°

C. and 70% relative humidity. After that time the sheets were analyzed for bromine by the Carius determination and were found to contain 4%. The stored sheets were tested by the Inclined-Panel Test and were non-inflammable.

Example 4

1800 grams of wet insulation-board-grade pulp, containing 500 g. of oven-dry material consisting to 80% of *Eucalyptus rostrata* wood and to 20% of Okumè wood, was suspended in 8.0 liters of water at room temperature. 27.0 grams of bromine dissolved in 3 liters of water were added to the suspension under vigorous stirring in the course of 10 seconds, then the stirring continued for another 110 seconds. Then the supernatant liquid was decanted and the residual pulp was neutralized with ammonium carbonate and filtered. The pulp contained 2.7% of bromine, calculated on the oven-dry weight as determined by the Carius method.

The pulp was made up by a suitable board making apparatus into insulation boards of 32 by 32 cm. and a thickness of 5 mm. The specific gravity of the insulation boards was 0.4 g./cm.³. The insulation boards made from the brominated pulp, and those made in the same manner from the not-brominated pulp, were tested by the Fire Testing Apparatus and method according to the French Standard Method, based on the Decree of the Minister of Interior, No. 57-1161 of 17.10.1957 and published in the Journal Officiel de la République Française of January 16, 1958, pp. 611-618.

The insulation boards made from the brominated material were classified as non-inflammable since the Index of Inflammability ("i"), the Index of Flame Spreading ("S") and the Index of the Maximum Height of Flame ("h") were 0.0. and the Index of Combustibility ("C") was 0.8, i.e., smaller than 1.0. According to the French Standard these results show that the sample is not-inflammable.

The insulation boards prepared from the not-brominated pulp, tested in the same manner, gave the following results: "i"=0.39; "S"=2.1; "h"=2.2 and "C"=10.3, showing the boards to be easily inflammable according to the French Standard.

I claim:

1. The process of forming fire resistant lignocellulose articles comprising: applying a nondestructive liquid reaction medium to a material naturally containing lignin and cellulose, said liquid reaction medium comprising a solution of a metal bromide and wherein bromine is liberated from said bromide to provide essentially elementary bromine in an amount insufficient to destroy the lignin; brominating said lignin component in situ up to a bromine content of 2.7 to 8% by weight of the lignocellulose by the introduction of elementary chlorine into said reaction medium to liberate said bromine from said bromide in the course of the brominating treatment, and separating the lignocellulose material comprising brominated lignin from the reaction medium.

2. A process in accordance with claim 1 wherein said liquid reaction medium is selected from the group consisting of an aqueous solution of elementary bromine, and an organic solution of elementary bromine.

3. A process in accordance with claim 1 wherein a pre-bromination is applied which utilizes substantially half

the bromine contained in the reaction solution while the other half of the bromine in solution is converted into bromide to form said reaction medium, comprising the said step of introducing elementary chlorine into the previously utilized reaction medium to reconvert said bromide ion into elementary bromine.

4. A process in accordance with claim 1 further comprising gradually adding bromine to the reaction medium during the bromination.

5. A process in accordance with claim 1 wherein said liquid reaction medium also comprises dissolved buffer flameproofing agents.

6. A process in accordance with claim 5 wherein said buffer flameproofing agents are selected from the group consisting of alkali metal phosphates, ammonium phosphates, sodium silicate, and mixtures of borax and boric acid.

7. A process in accordance with claim 6 wherein said material absorbs said buffer flameproofing agents in an amount of from 0.01 to 16%.

8. A process in accordance with claim 1 wherein said material is immersed in said liquid reaction medium.

9. Fire resistant material produced according to the process of claim 1.

10. Fire resistant material in accordance with claim 1 wherein the material is in the form of wooden structures.

11. Fire resistant material in accordance with claim 1 wherein the material is in the form of ground wood pulp.

12. Fire resistant material in accordance with claim 1 wherein the material is in the form of particle boards.

13. Fire resistant material in accordance with claim 1 wherein the material is in the form of laminated boards.

14. Fire resistant material in accordance with claim 1 wherein the material is in the form of paper articles.

15. Fire resistant material in accordance with claim 1 wherein the material is in the form of fiber products.

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