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(54) Title: LOW WATER PAPER

(57) Abstract: Provided is a low water paper product comprised of wood pulp having at least some of the water present in the amorphous regions of the cellulosic pulp fiber structure replaced with a polyhydroxy polymer. The preferred polyhydroxy polymer used to replace the water is polyvinyl alcohol. The resulting paper product exhibits improved dimensional stability, particularly when exposed to water or water vapor. Characteristics of the paper product make it quite suitable for use in transformers.



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LOW WATER PAPER

BACKGROUND OF THE INVENTIONField of the Invention

5 The present invention relates to a low water paper product. More specifically, the paper product of the present invention is comprised of wood pulp having at least some of the water present in the amorphous regions replaced with polyhydroxy polymer. The resulting paper
10 product is more rigid and dimensionally stable, and has a lower equilibrium moisture content.

Description of the Related Art

 Cellulose is a rigid polymer which is composed of linear chains of polymerized glucose units. In living
15 wood and in cellulose isolated at low temperature from wood, there is a low degree of lateral order. When heated during the pulping process, for example, the cellulose chains become more ordered or crystalline. Even in air dried fibers made from southern pine Kraft
20 pulp, there exists regions of low lateral order. These areas are easily penetrated by water. It has been found that the water is present as a liquid in the non-crystalline regions. The presence of the water in the non-crystalline regions satisfies the need in the
25 structure for hydrogen bonding. However, the presence

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of the water also makes the fibers more plastic and swellable when exposed to water vapor or liquid water. Thus, the presence of the water adversely affects the dimensional stability of the paper.

5 It is known that many paper products exhibit failures in the presence of water. This is of particular relevance when a cellulose or paper-based product is used as insulation in a transformer. The weakest link of any transformer insulation system is the
10 cellulose. In the majority of cases, the failure of a transformer is related to insulation breakdown. Practically speaking, the lifespan of the transformer is really the lifespan of the cellulose insulation.

 The Achilles' heel of cellulose used in the oil
15 filled electrical transformer is thermal degradation. The combination of water, oxygen, and heat break down the physical strength of the cellulose fiber. When these elements are present at the same time, the aging process is accelerated. For example, a one percent
20 water content will age the cellulose ten times faster than if the water content was 0.1 percent. If the effects of oxygen and the presence of water are combined, aging can increase by an order of 25 times. This is the reason transformer manufacturers have begun
25 making sealed transformers and transformers with expansion reservoirs equipped with a bladder. These technologies are aimed at countering the migration of water and oxygen towards the main tank.

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It is understood in the prior art that water in paper may generally be found in four external states. The water can be absorbed to the surface, the water can be present as a vapor (a high humidity environment), as
5 free water in capillaries, and as embibed free water.

Practical recommendations have been made to counter the presence of such exterior water in the transformer industry. These recommendations include reducing the temperature of the transformer either by leaving the
10 cooling system running or by reducing the cooling set point. Also, it has been recommended to regularly conduct a comparative evaluation of the cooling capability of the radiators with the help of infrared camera. It is also recommended to reduce the water
15 content in the windings by drying under vacuum, as well as to specify the maximum water content in the purchase specifications of the transformers. Thus, being able to reduce the amount of external water has been recognized as important in the prior art for applications such as
20 transformer insulation.

The incorporation of sugars into the cellulose structure has been described in the prior art for purposes of increasing tear strength, among other purposes. Such work has been primarily reported by Dr.
25 Graham Allan of the University of Washington. For example, in the TAPPI Journal, Vol. 82, No. 3, March 1999, Dr. Allan describes that the placement of simple sachrides within the micropores of the cell wall of never dried pulp fibers creates a cellulose substitute

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so as to reduce the fiber content and hence the cost of the paper. In the article "Sugar Cellulose Composites V. The Mechanism of Fiber Strengthening by Cell Wall Incorporations of Sugars", Cellulose, Vol. 8, pages 127-
5 138, 2001, Dr. Allan describes the incorporation of sucrose or some other disachrides into the cell wall of pulp fibers in order to increase the tearing strength of the resulting sugar containing paper relative to that of its sugar-free counterpart, but only when the fiber is
10 well refined. In the article "The Microporosity of Pulp", TAPPI Journal, January 1991, page 83, Dr. Allan further describes the pore structure of cellulose, which contains voids in the polymer structure. It is suggested that various liquid and solid chemicals can be
15 inserted into the void volumes as a general micropackaging or encapsulation system. See also U.S. Patent Nos. 5,096,539, and 5,725,699 wherein the cell wall loading of never dried pulp fibers is disclosed by Dr. Graham Allan.

20 Nevertheless, real problems still exist due to paper products and their failures in the presence of water. It would therefore be highly desirable and of great value to the industry to provide a cellulosic structure which can help to overcome the foregoing
25 problems and exhibit better dimensional stability in the presence of humidity or water.

It is therefore an object of the present invention to provide such a paper product.

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Yet another object is to provide such a paper product which exhibits improved dimensional stability.

Another object of the present invention is to provide a paper product with improved stiffness.

5 Still another object of the present invention is to provide a paper product having excellent dielectric properties.

Yet another object of the present invention is to provide a novel paper product useful as a heat
10 transformer paper, or circuit board paper, or in graphic arts.

Another object of the present invention is to provide a process for preparing such paper products.

15 These and other objects of the present invention will become apparent to the skilled artisan upon a review of the following description and the claims appended thereto.

SUMMARY OF THE INVENTION

20 In accordance with the foregoing objectives, there is provided a low water paper product comprised of cellulosic pulp, with the cellulosic (wood) pulp having at least some of the water present in the amorphous regions of the fiber structure replaced with a polyhydroxy polymer, preferably polyvinyl alcohol.
25 Preferably, sufficient water in the structure is replaced with the polyvinyl alcohol such that the treated pulp contains at least 0.70 wt.%, and more preferably at least 1.0 wt.% of the polyvinyl alcohol.

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The resulting paper product made from the pulp is more rigid and dimensionally stable. When dried it reaches a lower water content. This is particularly useful for paper used in the manufacture of transformers. In use, transformers generate heat. Water in the cellulose paper used to separate the coils in a transformer causes hydrolytic damage to the paper thus weakening the paper. Thus, the lower water content is a significant advantage in transformer paper.

10 In another embodiment, the present invention provides a process for preparing such a low water paper product. Wood pulp is exposed to a solution of polyhydroxy polymer until at least some of the water present in the amorphous regions of the wood pulp fiber structure are replaced with the polyhydroxy polymer. 15 The exposure generally employs soaking the wood pulp in a solution of the polyhydroxy polymer, preferably polyvinyl alcohol. The soaking of the wood pulp generally occurs such that the treated wood pulp, and hence the final paper product made therefrom, will 20 contain from 0.5 wt % to 3.0 wt % of the polyvinyl alcohol, and preferably at least 1.0 wt.%.

Among other factors, the present invention is based upon the discovery that the water contained in the non-crystalline regions of a cellulose fiber structure can 25 in fact be replaced with a polyhydroxy polymer, such as polyvinyl alcohol, and provide a useful cellulosic product. The water is generally present to satisfy the need in the structure for hydrogen bonding, and it is

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believed that the polyhydroxy polymer somehow replaces the water, thereby removing the water from the structure and creating a low water paper product. As a result of the lowering of the water content of the paper product, a more dimensionally stable paper product is achieved, particularly when that paper product is exposed to water vapor or water. The paper product also has a lower equilibrium moisture content, reducing the chance of hydrolysis. The reduced water content paper would also exhibit excellent dielectric properties. Also, paper with lower moisture content would pick up less water during an aqueous saturation since the fibers will swell less, which would be useful in many different types of paper products.

15 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

Cellulose is a polymer made of beta linked glucose units. The polymer is linear and ordered. The degree of lateral order is commonly referred to as crystallinity. The wood fiber used in the paper made for transformer wire coil insulation is less crystalline than the fiber of cotton. The crystallinity of wood fiber is approximately 45-65% while the crystallinity of cotton fiber is up to 90%. (Wood Chemistry, Vol. 1, Louis E. Wise and Edwin C. Jahn, Reinhold Publishing, 1952, p. 157.) It is the amorphous portion of the cellulose that is penetrated by water.

In the present invention, a lower water paper product is provided, as compared to one which has not

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been treated with a polyhydroxy polymer in accordance with the present invention. As noted above, cellulose is composed of crystalline and amorphous areas, and liquid water exists in the amorphous areas, even in air
5 dried pulp. Generally, a cellulose structure will contain at least 3 wt % by water. It has been found that by removing at least some of the water, or in effect replacing it in the cellulose structure, that an improved paper product with regard to rigidity and
10 dimensional stability, particularly when exposed to water vapor or water in its final form, can be obtained.

The type of pulp to which the present invention relates can be any wood pulp. Particularly good results have been achieved with northern pine Kraft pulp. The
15 water in the structure of the wood pulp is replaced at least partially with a polyhydroxy polymer. The preferred polyhydroxy polymer is that of polyvinyl alcohol. Any commercially available polyvinyl alcohol can generally be used, and many appropriate polyvinyl
20 alcohols are available from Celanese of New Jersey. For example, their Celvol 165, Celvol 203 and Celvol 205 SF polyvinyl alcohol has been found to be suitable in connection with the present invention.

It is preferred that the polyvinyl alcohol be water
25 soluble, which will enhance the amount of polymer that replaces water in the cellulosic structure. Thus, the polyvinyl alcohol can be hydrolyzed (e.g., about 89%), but is preferably not super-hydrolyzed (e.g., at least 98%). Super-hydrolyzed polyvinyl alcohol can also be

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used, but due to its limited solubility in water, less polymer is available for replacing water in the cellulosic structure.

By using simply hydrolyzed polyvinyl alcohol, which is water soluble, replacement of water in the structure can amount to more than 0.70 wt.% of the treated pulp (when dried), and more preferably at least 1.0 wt.%. Replacement of greater than 1.5 or 2.0 wt.%, up to 3.0 wt.%, can therefore be achieved. The more water replaced, the greater the advantages realized by the ultimate paper product made from the pulp in terms of rigidity and dimensional stability.

The low water paper product of the present invention comprises a wood pulp having at least some of the water present in the amorphous regions of the wood pulp fiber structure replaced with a polyhydroxy polymer. The polyhydroxy polymer is preferably polyvinyl alcohol. The resulting paper product prepared from such wood pulp is more rigid and dimensionally stable when exposed to water.

The water in the structure is replaced by the polyhydroxy polymer upon exposing the wood pulp to a solution of the polyhydroxy polymer until at least some of the water present in the amorphous regions of the wood pulp fiber structure are replaced. The wood pulp is generally exposed to the solution of the polyhydroxy polymer for a period of time ranging from 1 to 120 minutes, more preferably from 5 to 60 minutes, and most preferably from about 10 to 30 minutes. It is preferred

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that the wood pulp is simply soaked in a solution, i.e., aqueous solution, of the polyhydroxy polymer, as this is the easiest and most efficient way in order to effect the replacement of the water with the polyvinyl alcohol.

5 The treatment generally continues until the amount of polyvinyl alcohol contained in the cellulosic product ranges from 0.5 wt % to 3.0 wt %, more preferably from about 1.0 to 3.0 wt %, and most preferably from about 1.5 to 2.5 wt %. The exact amount of polyhydroxy

10 polymer of course will depend on the amount of water in the wood pulp, e.g., how many amorphous sites and regions there are. The wood pulp used or treated can be dried or not dried. The process of the present invention works equally well with any pulp, in any state

15 of refinement.

While the present invention can be used on an actual finished paper product, it is preferred for purposes of convenience and efficiency that the wood pulp itself is exposed to the polyhydroxy polymer

20 solution. In fact, the wood chips used to make the pulp can also be treated to effect the polymer exchange in the cellulosic structure. Once the water has been replaced by the polyhydroxy polymer in the wood pulp, the wood pulp can then subsequently be refined and

25 formed into a paper product using conventional methods.

The resulting paper product prepared from the treated wood pulp as discussed above, exhibits improved rigidity and dimensional stability, particularly when exposed to water or water vapor, and a lower equilibrium

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moisture content. Because of the reduced water content, the paper of the present invention would suffer less hydrolytic degradation during heat aging (needed for heat resistant transformer paper), would exhibit
5 excellent dielectric properties (needed in circuit board paper), respond less to changes in humidity levels in air (improved dimensional stability for printed and graphic art papers), and exhibit superior stiffness. In particular, the paper product of the present invention
10 finds great applicability as dried E-board in transformers since the lower equilibrium moisture content minimizes the water available for any hydrolysis in the heated environment of a transformer. This will extend the useful life of the paper insulation, and
15 hence, the transformer itself. In a specific embodiment of the present invention, therefore, a transformer comprised of the paper product of the present invention is provided.

The following example is provided to further
20 illustrate the present invention, but is not meant to be limiting.

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EXAMPLE

A three ply paper structure employing a layer comprised of a wood pulp in accordance with the present invention was prepared. A cylinder machine was used
5 where separate stock was employed for the outside layers and the inside layer.

The outside layers were fed a furnish of cellulosic pulp. The furnish for the inside layer comprised 70% by weight of a cellulosic pulp, 20% by weight of a
10 polymeric binder, i.e., polyvinyl alcohol, and 10% by weight of a polyaramide fiber. The polymeric binder was comprised of Celvol 165 SF polyvinyl alcohol, and the high temperature fiber was NOMEX[®] fiber, one-quarter
15 inch length and 2.0 denier. The polyvinyl alcohol, wood pulp and high temperature fiber were blended in a pulper for 15 minutes. Thus, the cellulosic pulp was exposed to the polyvinyl alcohol (polyhydroxy polymer) for a
20 significant amount of time to have at least some of the water present in the amorphous regions of the cellulosic pulp fiber structure be replaced with the polyhydroxy polymer.

Once the furnish for the outside layers and the inside layer had been provided to each of the respective cylinders, a three ply paper structure was prepared.
25 The outer layers were comprised of solely cellulosic pulp, and the inside layer was comprised of the cellulosic pulp in combination with the high temperature

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fiber and the polymeric binder. The resulting paper structure was then pressed, dried and calendared in conventional fashion. The drying was conducted at a temperature sufficient to activate the polyvinyl alcohol
5 polymeric binder.

The resulting paper structure exhibited good strength properties, and is believed useful as electrical insulation in transformer coils.

Having now fully described the invention, it will
10 be apparent to one of ordinary skill in the art of any changes and modifications that can be made thereto without departing from the spirit and the scope of the invention as set forth therein.

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What is Claimed is:

1. A low water paper product comprised of wood pulp having at least some of the water present in the amorphous regions of the cellulosic pulp fiber structure replaced with a polyhydroxy polymer, such that the paper product is more rigid and dimensionally stable when exposed to water.
2. The paper product of claim 1, wherein the polyhydroxy polymer is polyvinyl alcohol.
3. The paper product of claim 1, wherein the wood pulp fiber is comprised of a Kraft pulp.
4. The paper product of claim 1, wherein the amount of polyhydroxy polymer contained in the product ranges from 0.5 weight percent to 3.0 weight percent.
5. The paper product of claim 4, wherein the amount of polyhydroxy polymer is at least 1.0 weight percent.
6. A process for preparing the low water paper product of claim 1, which comprises exposing cellulosic pulp to a solution of the polyhydroxy polymer until at least some of the water present in the amorphous regions of the cellulosic pulp fiber structure are replaced with the polyhydroxy polymer.

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7. The process of claim 6, wherein the wood pulp is exposed to the solution of the polyhydroxy polymer for a period of time ranging from 1 to 120 minutes.

8. The process of claim 6, wherein the wood pulp
5 is soaked in a solution of the polyhydroxy polymer.

9. The process of claim 6, wherein subsequent refining and formation of the paper product takes place once the exposure to the solution of the polyhydroxy polymer is complete.

10 10. A transformer comprised of the paper product of claim 1.

11. A transformer comprised of the paper product of claim 2.

12. A transformer comprised of the paper product
15 of claim 4.

13. A transformer comprised of the paper product of claim 5.

14. The process of claim 6, wherein the cellulosic pulp is first refined before exposure to the solution of
20 the polyhydroxy polymer.

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15. A wood pulp having at least some of the water present in the amorphous regions of the cellulosic fiber structure replaced with a polyhydroxy polymer.

5 16. The wood pulp of claim 15, wherein the pulp is comprised of northern pine Kraft pulp.

17. The wood pulp of claim 15, wherein the amount of polyhydroxy polymer contained in the wood pulp is at least 1.0 weight percent.

10 18. The wood pulp of claim 15, wherein the amount of polyhydroxy polymer contained in the wood pulp ranges from 1.0 to 3.0 weight percent.

19. The wood pulp of claim 15, wherein the amount of polyhydroxy polymer contained in the wood pulp ranges from 1.5 to 2.5 weight percent.

15 20. The wood pulp of claim 15, wherein the polymer is polyvinyl alcohol.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

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B. FIELDS SEARCHED

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 U.S. : 162/164.1,138,168.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2,330,314 A (SCHWARTZ) 28 September 1943 (28.09.1943), see the entire document.	1-6,10-13,15-20
Y	US 3,674,632 A (Wennergren et al) 04 July 1972 (04.07.1972), see entire document.	1,3,4,6-8,10-19
Y	US 3,736,178 A (Sadler et al) 29 May 1973 (29.05.1973), see entire document.	1,3-8,10-19
Y	US 5,391,473 A (Lacz et al) 21 February 1995, see entire document.	1-8,9-20

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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