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3,135,613

IMPREGNATED PAPER WEB AND METHOD OF MAKING SAUSAGE CASINGS THEREFROM

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No Drawing. Filed Aug. 17, 1959, Ser. No. 833,944
6 Claims. (Cl. 99—176)

This invention relates to improvements in porous paper webs impregnated and bonded with regenerated cellulose. More particularly, the invention is concerned with improving the wet-strength of porous paper webs made from manila hemp fibers and of cellulose casings containing such paper webs as a fibrous reinforcement.

Heretofore, paper webs of relatively strong natural fibers such as manila hemp, flax and the like have been coated and impregnated with a viscose solution, the cellulose in the viscose solution being thereafter regenerated by immersion of the treated paper in a suitable acidic regenerating bath. The regenerated cellulose thus formed as a coating and impregnant on and in the fibers of the paper, strengthened the paper web and imparted some degree of resistance to water. Insofar as is presently known, the viscose solutions heretofore employed for treating hemp fiber paper webs were obtained by conventional xanthation technique of natural cellulose such as pulp or cotton linters, said cellulose having a content of alpha cellulose less than 92 percent by weight.

Regenerated cellulose impregnated paper webs have particular utility in the manufacture of fiber-reinforced tubular cellulosic casings which are used in the packaging of such meat products as sausage, bologna, butts, hams, hamburger and other ground meat products.

Such casings are conventionally manufactured by cutting the regenerated cellulose impregnated paper web into strips of suitable width, curving the strip about its longitudinal axis to form a tube with overlapping longitudinal margins which are thereafter permanently seamed together.

Immediately prior to forming the tubing, or simultaneously therewith or subsequently, the paper web is passed through a suitable viscose solution to internally and externally sheath the paper web with a viscose coating. The coated tube is then passed through a viscose regenerating bath such as an aqueous solution of sulphuric acid and sodium sulphate to convert the viscose coating to regenerated cellulose. The tube is then passed through one or more water baths to wash out the acid and salt of the regenerating bath, and then, if desired, through an aqueous bath containing in solution a plasticizer for regenerated cellulose, as for example glycerine. The tubing is thereafter dried by passing it in an inflated state through a heated drying chamber. The resultant product is essentially a cellulosic tubing having a paper web embedded therein.

The aforescribed process produces a tough, pliable, leak-proof regenerated cellulose casing having embedded therein the pre-bonded paper web, the latter serving to reinforce and strengthen the cellulose tubing. Because of the strength inherent in such a casing, it is particularly suitable for packaging boneless meats such as pieces of beef, pork, ham, fowl and the like which are stuffed in the casing under considerable pressure in order to produce a uniform, neat-appearing package.

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It is quite apparent that at various stages of manufacture of the casing from the regenerated cellulose impregnated paper web and in the use of the casing, there is more or less prolonged contact with water. The weakening effects of water on paper and other cellulose products is well known and hence precautions are taken to prevent tearing or rupture during manufacture or use of the casings. Rupture of the casing is apt to occur during meat stuffing operations whenever excessive stuffing pressures are used and when casings are presoaked in water to render them more pliable and extensible in the stuffing operation. Since the casing after being stuffed with moist meat products is therefore maintained in a moist condition it can be ruptured or torn by handling forces otherwise insufficient to damage a dry casing.

Accordingly it is an object of this invention to provide a regenerated cellulose impregnated porous paper web of manila hemp fibers having a higher wet-strength than heretofore known.

Another object of this invention is to provide fiber reinforced cellulosic tubular casings suitable for stuffing therein of meat products and having a higher wet-strength than casings heretofore made having equivalent dimensions and quantity of fiber reinforcement.

Another object is the impregnation of paper webbing prepared from manila hemp fibers with a viscose solution of essentially alpha cellulose.

Other objects will become apparent as the description of the invention proceeds.

It has now been found that the aforescribed objects can be realized by impregnating a porous paper web and particularly one containing manila hemp fibers with a dilute aqueous viscose solution prepared from a cellulose having at least a 93 percent by weight content of alpha cellulose, the balance if any being gamma cellulose and beta cellulose, drying the impregnated paper web, then passing the dried paper through a regenerating bath to regenerate the cellulose, washing the regenerated cellulose impregnated paper to remove the acids and/or salts carried over from the regenerating bath and thereafter drying the impregnated paper.

The resultant regenerated cellulose impregnated and bonded paper has particular utility in the manufacture of fiber reinforced, regenerated cellulose casings according to the process hereinbefore described.

The alpha cellulose useful in the present invention is obtained from natural cellulose such as is present in wood pulp, cotton linters, flax and the like. Natural cellulose is a carbohydrate having the empirical formula $(C_6H_{10}O_5)_x$ and by suitable treatment with aqueous sodium hydroxide solution can be separated into three different substances. The portion of cellulose which does not dissolve in the aqueous sodium hydroxide solution is named alpha cellulose. Acidification of the solution containing the dissolved portion of the cellulose causes part of the dissolved cellulose to precipitate, the precipitated portion being named beta cellulose. That part of the cellulose which remains in solution after acidification is called gamma cellulose. The proportions of alpha, beta and gamma cellulose vary with the source and with the conditions of extraction, such as the percentage amount of sodium hydroxide in the aqueous solution, immersion time of the cellulose in the aqueous caustic solution and the solution temperature.

For the purposes of this invention standard alpha cellulose is defined as that portion of a given weight of cellulose pulp which does not dissolve when immersed for 45 minutes in a given volume of a 17.5 percent by weight aqueous solution of sodium hydroxide maintained at 20° C. according to TAPPI test method T203-m58. (See also page 1021, Pulp and Paper Manufacture, volume I, J. N. Stephenson, published 1950 by McGraw-Hill Book Co., Inc.)

By purification procedures substantially as above described, there are obtained cellulose pulps of at least 93% weight content of alpha cellulose from conventional paper pulps as are made from wood, cotton rags, cotton linters, straw, esparto and the like by mechanical or semi-chemical processes; or by the soda process, acid sulphite process, neutral sulphite process, kraft process and the like.

The viscose for impregnating and bonding the paper web is prepared by subjecting a cellulose pulp of at least 93 percent by weight content of alpha cellulose to conventional xanthation techniques and preferably employing conditions well known to those skilled in the art to yield after regeneration of the cellulose in the viscose, a cellulose having a viscosity of at least 4.2 centipoises in a cupriethylene diamine solution containing 0.5% dry weight of cellulose and 0.5 molar in copper as prepared according to TAPPI test method T230-sm-50. This test is employed as a measure of the degree of polymerization of the cellulose.

It is also preferred that the viscose solution have an acetic acid index value between 30 and 50. The acetic acid index is defined as the number of cubic centimeters of a 10% by weight acetic acid solution needed to completely gel 100 grams of viscose at room temperature.

It should be understood that the index number of the viscose used in the paper manufacture is obtained on the standard 7% cellulose and 6% caustic compositions. These viscoses are diluted with water to yield a 1% cellulose composition used in the impregnation of the hemp fiber paper. The diluted viscoses are preferred to maintain porosity of the paper after regeneration of the viscose. The resultant porous paper is readily impregnated with additional viscose to form cellulosic tubing wherein the paper functions as a fibrous reinforcement.

Preferably, the total percent by weight quantity of cellulose in the viscose when ready for use in bonding the paper web is between 0.5% and 3% and optimally between 1% and 2%. Ordinarily, most viscose solutions are prepared at a concentration between 6% and 7% by weight of cellulose, but such solutions can be readily diluted with water to the aforescribed lower cellulose concentrations.

The aqueous regenerating bath preferably contains a 2% by weight or greater content of sulphuric acid and additionally, if desired, may also contain the usual small amounts of sodium sulphate.

In carrying out this invention, optimum operating conditions, such as speed of the paper web as it passes through the viscose solution, moisture content of the viscose-impregnated paper prior to regeneration, concentration of the regenerated cellulose in the impregnated paper, and the drying time of said paper can be easily determined by simple empirical tests known to those skilled in the art.

Tubular cellulosic casings are made from paper impregnated with regenerated cellulose of 93% or better content of alpha cellulose by coating and impregnating said impregnated paper in the usual manner with a conventional viscose solution, such as one containing 7% by weight of cellulose and 6% by weight of sodium hydroxide.

The practice of the invention is further illustrated in the following examples, but it is to be understood that the invention is not limited thereto except as defined in the appended claims.

EXAMPLES 1 to 8

Hemp fiber paper of substantially the same ream weight 75

was impregnated and prebonded with different viscose solutions prepared from wood pulps of different alpha cellulose contents. The impregnating viscose solutions for prebonding the paper in all the examples were prepared by diluting with water to a one percent cellulose concentration, a viscose solution containing 7% by weight of cellulose and 6% by weight of sodium hydroxide and having an acetic acid index value of 40. The cellulose upon regeneration of each viscose had in each instance a C.E.D. viscosity of at least 4.2. The paper was prebonded by passing it through a suitable viscose solution. One solution was made from a cellulose material containing 92.4% alpha cellulose and the other viscose solution was made from a cellulose material of 96.6% alpha cellulose content. The paper was then allowed to dry to a moisture content below about 5%. The dried viscose-impregnated paper was passed through a regenerating bath maintained at a content of between 4% to 8% by weight sulfuric acid to regenerate the cellulose. The resultant pre-bonded paper was washed free of acid and dried.

Table I lists the wet breaking strength of paper prebonded with regenerated cellulose from viscose prepared from pulp of varying alpha cellulose content. It is to be noted that paper bonded with the higher alpha cellulose content (96.6%) regenerated cellulose had greater wet breaking strength in both the machine and transverse directions than did the paper bonded with the lower alpha cellulose content (92.4%) regenerated cellulose.

In Table II it can be seen that casings made from the prebonded papers of Table I have higher burst pressures when made from paper containing the higher alpha cellulose content. The effect of higher alpha cellulose content on burst pressures is emphasized in the ratio of burst pressure to ream weight. The casings were prepared in the conventional manner by curving a strip of paper about its longitudinal axis to form a tube with overlapping longitudinal margins and impregnating with a viscose solution containing 6% by weight of sodium hydroxide 7% by weight of cellulose (98% alpha cellulose content), said viscose having an acetic acid index of about 40, and the cellulose thereof after regeneration having a C.E.D. viscosity as heretofore defined of 4.3 centipoises. After impregnation, the viscose impregnant and coating was regenerated by passing the tube through an aqueous sulphuric acid regenerating bath containing from 15% to 25% by weight ammonium sulfate and about 1% to 4% by weight of sulphuric acid. After washing of the regenerated cellulosic casings to remove acid therefrom, the washed casings were plasticized with glycerin (10% to 25% by weight of the casing) and thereafter dried.

Table I.—Wet Breaking Strength of Paper Bonded With Different Viscoses

Example No.	Percent Alpha Cellulose ¹	Ream Wt. (lbs.) ²	Wet Breaking Strength (g./in. width)	
			MD	TD
1-----	92.4	13.7	1,377	1,134
2-----	96.6	13.2	1,535	1,271
3-----	92.4	13.2	1,341	1,260
4-----	96.6	12.9	1,423	1,316
5-----	92.4	13.0	1,260	1,120
6-----	96.6	12.5	1,311	1,200
7-----	92.4	13.8	1,334	1,285
8-----	96.6	13.0	1,423	1,363
9-----	92.4	15.0	1,461	1,358
10-----	96.6	15.2	1,540	1,400
11-----	92.4	13.7	1,339	1,192
12-----	96.6	13.7	1,470	1,327
13-----	92.4	13.9	1,412	1,328
14-----	96.6	13.8	1,461	1,372
15-----	92.4	14.8	1,468	1,351
16-----	96.6	14.5	1,501	1,388
Control-----	Not impregnated.	-----	0	0

¹ Content of alpha cellulose in wood pulp used to prepare the viscose solution.

² Weight of paper after impregnation and drying.

Table II.—Burst Pressure Values of Casings Made From Paper Bonded With Different Viscoscs

Example No.	Percent Alpha Cellulose ¹	Ream Wt. (lbs.) ²	Burst Pressure (mm. of Hg)	Ratio of Burst Pressure/ Ream Wt.
1.....	92.4	13.7	589	43.0
	96.6	13.2	591	44.8
2.....	92.4	13.2	643	48.7
	96.6	12.9	650	50.4
3.....	92.4	13.0	418	32.15
	96.6	12.5	424	33.9
4.....	92.4	13.8	454	32.85
	96.6	13.0	459	35.3
5.....	92.4	15.0	384	25.6
	96.6	15.2	407	26.8
6.....	92.4	13.7	389	28.4
	96.6	13.7	398	29.05
7.....	92.4	13.9	361	26.0
	96.6	13.8	378	27.4
8.....	92.4	14.8	403	27.3
	96.6	14.5	407	28.1

¹ Content of alpha cellulose in wood pulp used to prepare the viscose solution.

² Weight of paper after impregnation and drying.

In Examples 9–11, the dry hemp fiber paper was passed over a doctor roll which transferred the dilute viscose to the paper. The paper was then passed over a drying chamber where the viscose-impregnated paper was dried. The dried paper was then passed under a dip roll in a sulfuric acid bath in order to regenerate the cellulose. The paper, after passing through the acid bath, passed through six feet of air travel and then into a water bath. The paper, in the water bath, covered approximately three feet of travel and included first, dipping into the water under a dip roll, passing over a transfer roll where water was sprayed continuously upon the paper, and then under a final dip roll. Under the final dip roll, ammonia may be added to bring about neutralization. The paper was then dried and reeled.

Table III gives the wet breaking strength results of paper pre-bonded with viscoscs of different alpha cellulose content. The results show a greater wet breaking strength for paper pre-bonded with viscose of higher alpha cellulose content.

Table III.—Wet Breaking Strength of Paper Bonded With Different Viscoscs

Example No.	Ammonia Neutralization	Acid Bath Conc. (Percent)	Percent Alpha Cellulose ¹	Ream Wt. (lbs.) ²	Wet Breaking Strength (g./in. width)	
					MD	TD
9.....	Yes.....	1-2	96.6	13.06	2,146	830
10.....	No.....	1-2	92.4	12.53	1,691	610
11.....	Yes.....	1-2	92.4	12.72	1,534	688

¹ Content of alpha cellulose in wood pulp used to prepare the viscose solution.

² Weight of paper after impregnation and drying.

In Tables I to III supra the term "ream-weight" refers to the weight in pounds of 480 sheets of paper, each being 24 inches wide and 36 inches long according to the method described in ASTM D-646-50.

The term "breaking strength" is the force in grams required to break a test sample of a paper sample one inch wide and 3 inches long and of any thickness.

The burst pressure referred to in Table II was determined by inflating with air the casing after being soaked in water until it burst.

In the practice of this invention it is preferred to impregnate with high alpha cellulose viscoscs those papers prepared from purified hemp fibers. However, similar

improvements as to wet-strength values are obtained by employing papers prepared from a mixture of hemp fibers and other fibers known to be useful in reinforcing webs for use in regenerated cellulose casings.

What is claimed is:

1. A porous paper web of improved wet-strength comprising essentially hemp fibers impregnated and bonded together with a regenerated cellulose having an alpha cellulose content of at least 93 percent by weight and a cupriethylene diamine viscosity of at least 4.2 centipoises as determined by TAPPI test method T230-sm-50, and wherein said regenerated cellulose is present in an amount which essentially maintains the porosity of said paper web.
2. A porous paper web of improved wet-strength comprising essentially hemp fibers impregnated and bonded together with a regenerated cellulose having an alpha cellulose content of about 96.6 percent by weight and a cupriethylene diamine viscosity of at least 4.2 centipoises as determined by TAPPI test method T230-sm-50, and wherein said regenerated cellulose is present in an amount which essentially maintains the porosity of said paper web.
3. A porous tubular regenerated cellulose casing of improved wet-strength comprising tubing of regenerated cellulose having encased therein a porous fibrous reinforcement of hemp fiber paper in which the fibers are bonded together and impregnated with a regenerated cellulose having an alpha cellulose content of at least 93 percent by weight and a cupriethylene diamine viscosity of at least 4.2 centipoises as determined by TAPPI test method T230-sm-50.
4. Method for producing porous hemp paper webs of improved wet-strength which comprises impregnating the hemp web with a viscose solution containing between 0.5 and 3 percent by weight of cellulose having at least a 93 percent by weight content of alpha cellulose and a cupriethylene diamine viscosity of at least 4.2 centipoises according to TAPPI test method T230-sm-50, drying the viscose impregnated hemp web, regenerating the cellulose in the viscose present in said dried web to form a regenerated cellulose having a cupriethylene diamine viscosity of at least 4.2 centipoises according to TAPPI test method T230-sm-50 by contacting the web with an aqueous regenerating solution containing at least 2 percent by weight of sulfuric acid, thereafter washing the web with water to remove the acid therefrom and then drying the washed web, said regenerated cellulose being present in an amount which essentially maintains the porosity of said paper web.
5. The method according to claim 4 and wherein the viscose solution contains between 1 and 2 percent by weight of said cellulose.
6. Method of preparing cellulosic sausage casings of improved wet-strength which comprises impregnating a paper web formed of hemp fibers with a viscose solution containing between 0.5 and 3 percent by weight of cellulose, said viscose having been prepared from a cellulosic pulp containing at least 93 percent by weight of alpha cellulose, said cellulose after regeneration having a cupriethylene diamine viscosity of at least 4.2 centipoises according to TAPPI test method T230-sm-50, drying the viscose impregnated paper, regenerating the viscose in the dried paper by contacting the paper with an aqueous regenerating solution containing at least 2 percent by weight of sulfuric acid, then washing and drying said regenerated cellulose impregnated paper web, said regenerated cellulose being present in an amount which essentially maintains the porosity of said paper web, curving a strip of said web into tubular form with the opposite edges of said strip forming a single overlap seam, im-

pregnating and coating said paper tube with a viscose solution, contacting the impregnated tube with an aqueous regenerating solution to regenerate the cellulose in said viscose, and thereafter washing and drying the cellulose impregnated and coated paper tube.

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