United States Patent Office 3,433,663 Patented Mar. 18, 1969

3,433,663

IMPREGNATED POROUS PAPER WEBS AND METHOD OF OBTAINING SAME

William F. Underwood, Oak Park, Ill., assignor to Union Carbide Corporation, a corporation of New York

No Drawing. Filed May 4, 1964, Ser. No. 364,771
The portion of the term of the patent subsequent to June 2, 1981, has been disclaimed
U.S. Cl. 117—62.1 7 Claims
Int. Cl. D21h 1/42

ABSTRACT OF THE DISCLOSURE

A viscose bonding agent comprising a dilute aqueous viscose solution prepared from a cellulose having an alpha cellulose content of at least 93% by weight and a degree of polymerization as measured by cupriethylene diamine (CED) viscosity in excess of 4.2 centipoises can be utilized in the preparttion of porous paper webs which can then be impregnated with cellulose and regenerated to obtain fibrous cellulose casings.

This invention relates to porous paper webs impregnated and bonded with regenerated cellulose. More particularly, this 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 cellulosic fibers such as hemp, flax and the like have been bonded and impregnated with a viscose solution, the cellulose in the viscose solution being thereafter dried, coagulated and regenerated. The regenerated cellulose thus formed as a bonding agent and impregnant 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 in the art for treating hemp fiber paper webs were obtained by conventional techniques utilizing dissolving cellulosic fibers from pulps, said cellulose having an alpha cellulose content of less than 93 percent by weight, and a cupriethylene diamine (CED) viscosity of less than 4.2

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 bonded 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 sealed together by application of viscose between the overlapping margins.

Immediately prior to forming the tubing, or simultaneously therewith or subsequently, the paper web is passed through a suitable viscose solution to externally and/or internally sheath the paper web with a viscose coating. The viscose is allowed to penetrate through the paper web to result in the web being embedded in the viscose. The coated and impregnated tubing is immersed in a salt bath containing ammonium sulfate to coagulate the viscose and then immersed in a viscose regenerating bath such as an aqueous solution of sulphuric acid and sodium sulfate to convert the viscose 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 and is transversely cut in appropriate length to form sausage or meat casings known in the trade as "fibrous casings."

The aforedescribed process produces a tough, pliable, leak-proof regenerated cellulose casing having embedded therein the pre-bonded paper web, in the form of a tube, 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 stufffed in the casing under considerable pressure in order to produce a uniform, neat-appearing package.

Recently it was discovered that regenerated cellulose bonded porous paper webs, exhibiting outstanding wet strength properties could be prepared by utilizing as a viscose bonding agent, a dilute aqueous viscose solution prepared from a cellulose having at least a 93 percent by weight content of alpha cellulose, and a degree of polymerization as measured by cupriethylene diamine viscosity (CED) in excess of 4.2 centipoises.

This recent discovery, inter alia, is disclosed in detail in copending application, Serial No. 833,944, filed Aug. 17, 1959.

Until the present invention, it was believed that porous paper webs exhibiting outstanding wet strength characteristics could only be obtained through the utilization of viscose bonding agents prepared from cellulose containing at least 93 percent alpha cellulose and exhibiting a C.E.D. viscosity in excess of 4.2 centipoises.

In accordance with the present invention it has been found that regenerated cellulose bonded paper webs exhibiting increased wet strengths can be realized by bonding and impregnating a porous paper web and particularly one containing hemp fibers with a regenerated cellulose bonding agent having a CED viscosity of at least 4.2 centipoises using a dilute aqueous viscose solution prepared from a cellulose having an alpha cellulose content of greater than 85 and less than 93 percent by weight, the balance, being gamma cellulose and beta cellulose, drying the bonded and impregnated porous paper web, then passing the dried paper through a regenerating bath to regenerate the cellulose, washing the regenerated cellulose bonded 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.

Alpha cellulose is obtained from natural cellulose sources such as wood pulp, cotton linters, flax and the like. 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 called 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. The percentage of alpha cellulose in low cost dissolving wood pulps is generally less

than 93 percent and is usually from about 86 to 90 percent.

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 the Technical Association of the Pulp and Paper Industry (TAPPI), test method T203–os61. (See also page 1021, Pulp and Paper Manufacture, volume I, J. N. Stephenson, published 1950 by McGraw-Hill Book Co., Inc.)

By purification procedures there are obtained cellulose pulps of from 85% to 93% weight content of alpha cellulose from dissolving pulps chiefly from wood sources. Purification processes that can be used are the soda process, acid sulphite process, neutral sulphite process, kraft process and the like, as well as the hydroxide procedure described above.

The viscose for impregnating and bonding the paper web is prepared by conventional viscose processing techniques and conditions well known to those skilled in the art.

While the prior use of viscose solutions made from cellulose exhibiting an alpha cellulose content of at least 93 percent and a CED viscosity (determined as the viscosity of a cupriethylene diamine solution containing 0.5 percent dry weight of cellulose and 0.5 molar in copper as prepared in accordance to TAPPI test method T230–sm–50) in excess of 4.2 centipoises, provides porous paper webs with optimum wet strength characteristics after cellulose regeneration, such cellulose must be obtained directly from natural sources rich in alpha cellulose or from sources containing a lower percentage of alpha cellulose by concentration techniques.

The discovery that paper webs having increased wet strength can be made using viscose solutions prepared from dissolving cellulosic pulps containing less than 93 percent alpha cellulose which cellulose is depolymerized to an extent that it exhibits a viscosity no lower than 4.2 centipoises in a cupriethylene diamine solution containing 0.5 percent dry weight of cellulose and 0.5 molar in copper as prepared according to TAPPI test method T230–sm–50, permits manufacture of said paper utilizing a strong bonding viscose from low cost sources of cellulose.

It has been found desirable to use a viscose bonding agent within the definition of this invention in which the cellulose exhibits a CED viscosity of from 4.2 to 5.75 centipoises.

The preparation of viscose from cellulose has long been known in the art. The cellulose is usually steeped for a period of time in an aqueous solution of an alkali such as sodium hydroxide, potassium hydroxide or the like. The cellulose is thereby converted to a product known as "alkali cellulose." The alkali cellulose is recovered from the treating baths as a filter cake. This cake is then shredded and placed in covered contains where it is aged under controlled conditions of temperature and humidity. The aging step causes the alkali cellulose to partially depolymerize. The period of time for which the alkali cellulose is aged is dependent upon the desired CED viscosity, and the aging conditions. The aged alkali cellulose is then reacted with carbon disulfide to produce cellulose xanthate. The cellulose xanthate is dissolved in an aqueous solution of a caustic such as sodium hydroxide to produce a solution which is known as viscose. The viscose solution is diluted with water prior to use to give the cellulose and caustic concentration desired.

The alkali cellulose aging step in the manufacture of viscose is influenced by such factors as the time of contact between cellulose and sodium hydroxide solution, the concentration of this solution and the ratio of sodium hydroxide to cellulose, as well as the temperature, humidity, and the presence of certain metal ions, such as iron, manganese, etc. These factors are all carefully controlled during the process of aging to produce the desired viscosity.

It is also preferred that the viscose solution useful in the present invention 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 containing 7% cellulose and 6% alkali at room temperature.

The viscose solutions used as bonding agents in the preparation of the fibrous papers are used as dilute aqueous caustic solutions. These viscose bonding solutions are preferably maintained and applied at a sufficiently dilute level so that the porosity of the paper is maintained after the regeneration of the cellulose from the bonding viscose. Since the resultant porous paper is embedded in a regenerated cellulosic casing, it must be readily impregnable to a viscose impregnating and coating agent having a relatively high concentration of cellulose and caustic, usually a standard 7 percent cellulose and 6 percent caustic. The porosity of the paper of this invention should be maintained at a level sufficient to permit impregnation of the paper by the viscose impregnating and coating agent to be used.

Preferably the total percent by weight of cellulose in the viscose bonding agent, used for bonding the fibers of the paper web, is between 0.5 percent and 3 percent and optimumly between 1 percent and 2 percent. The viscose bonding agent usually contains from 0.5 percent to 3 percent caustic and desirably from 0.8 to 1.5 percent. Viscose compositions can be readily diluted with water or dilute aqueous caustic solution to prepare the viscose bonding agent for the paper web having the concentration given above.

The coagulating or salt bath generally contains a sufficient concentration of salts such as ammonium sulfate, sodium sulfate or mixtures of the same and from 0 to 5 percent by weight of sulfuric acid, to coagulate the viscose solution in immersion. These salts and the acid if used are in aqueous solution.

The aqueous regenerating bath preferably contains a 2% by weight or greater content of sulfuric 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 bonded 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 the porous paper bonded with regenerated cellulose, by cutting a strip of bonded paper, curving said strips about its longitudinal axis to form a tube. The edges of the paper are overlapped and cemented in place with impregnating viscose so that a uniform tube is maintained. This tube is then internally and externally impregnated and coated with a viscose impregnating and coating agent. The impregnated and coated paper tube is passed through a coagulating bath and then through an acid regenerating bath to regenerate the cellulose casing or tubing. The resulting casing is a cellulose tube having embedded therein a coextensive tube of fibrous paper. These casings are known as fibrous reinforced casings.

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. In these examples and throughout this specification, unless otherwise noted, all percentages are by weight.

Example 1

Paper webs were prepared by general commercial paper making techniques. The paper web was bonded by passing

it through a viscose bonding solution. The paper was then allowed to dry to a moisture content below about 5%. The dried viscose-bonded paper was passed through a coagulating bath, and then through a regenerating bath maintained at a concentration 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.

These paper webs were bonded with viscose bonding solutions in which the cellulose used varied in alpha cellulose content as well as CED viscosity as shown in the attached table. The paper webs used to evaluate the viscose bonding were made consecutively on the same paper making apparatus to insure each paper web would be as similar as possible. The bonding viscose solutions used were as follows:

1

Low α-cellulose ---------- percent -- 92.4
High CED viscosity ---------- centipoises -- 4.33

2

Low α-cellulose ---------- percent -- 92.4
Low CED viscosity ---------- centipoises -- 2.91

The relative ratio of cellulose used to bond the fibers in the paper making process was about 3 to 5 percent by weight of the finished paper product or a ratio of 0.03 part cellulose binder to 1 part hemp fiber.

All of the papers were then made into casings by impregnating the paper web with a viscose impregnating and coating solution having a high alpha cellulose (greater than 93%) and a heigh CED viscosity (greater than 4.2 centipoises). The ratio of cellulose to paper used to make the casing was about 200 percent by weight of the paper fiber or a ratio of 2.0 parts cellulose to one part hemp fiber.

Physical properties of the paper webs and of the casings made from the paper webs were then determined. These properties are disclosed in the tables which follow:

TABLE I.—WET MULLEN'S BURST STRENGTH OF PAPER BONDED WITH VISCOSE SOLUTIONS OF VARYING ALPHA CELLULOSE CONTENT AND CUPRIETHYLENE DIAMINE (CED) VISCOSITY

Ref. No.	Bonding viscose solution		Paper ream weight in pounds	Mullen's burst strength in pounds per square inch	Comparison percentage burst strength
	Alpha cellulose content in percent	CED viscosity in centipoises			
1	92.4	4.33	13.4	8.1	142.1
2	92.4	2.91	13.3	5.7	100

TABLE II.—SIX PERCENT SODIUM HYDROXIDE WET TENSILE STRENGTH OF PAPER BONDED WITH VISCOSE SOLUTIONS OF VARYING ALPHA CELLULOSE CONTENT AND CURPIETHYLENE DIAMINE CED VISCOSITY

Ref No.	Alpha cellulose content in percent	CED viscosity in centipoises	Ream weight of bonded paper in pounds	6% NaOH wet tensile strength		Comparison of 6% wet tensile strength, percent increase	
				Machine direction in grams/inch	Transverse direction in grams/inch	Machine direction in percent	Transverse direction in percent
1	92.4	4.33	13.4	315	240	176.9	200
2	92.4	2.91	13.3	178	120	100	100

TABLE III.—WATER WET TENSILE STRENGTH OF PAPER BONDED WITH VISCOSE SOLUTION OF VARYING ALPHA CELLULOSE CONTENT AND CUPRIETHYLENE DIAMINE CED VISCOSITY

Ref. No.	Bonding Viscose Solution		Ream weight of bonded paper in pounds	Water Wet Tensile Strength		Comparison of water wet tensile strength, percent increase	
	Alpha cellulose content in percent	CED viscosity in centipoises		Machine direction in grams/inch	Transverse direction in grams/inch	Machine direction in percent	Transverse direction in percent
1	92.4	4.33	13.4	1,400	1,191	127.6	138.6
2	92.4	2.91	13.3	1,097	859	100	100

TABLE IV.—BURST STRENGTH OF CASINGS MADE FROM PAPER BONDED WITH VISCOSE SOLUTIONS OF VARYING ALPHA CELLULOSE CONTENT AND CUPRIETHYLENEDIAMINE CED VISCOSITIES

Ref. No.	Bonded paper, bonding viscose solution		Ream weight in pounds [1]	Fibrous casings			
	Alpha cellulose content in percent	CED viscosity in centipoises		Casing diameter at burst in inches	Burst pressure (uncorrected) in millimeters of mercury	Burst pressure corrected for diameter at burst in millimeters of mercury [2]	Burst pressure corrected for diameter at burst and resin weight in millimeters of mercury [3]
1	92.4	4.33	13.4	5.16	407	404	404
2	92.4	2.91	13.3	5.16	394	391	394

[1] Ream weight: Weight in pounds of 414,720 square inches of paper.

[2] Corrected by use of formula: $\frac{\text{(Burst pressure) (burst diameter)}}{\text{Basis diameter: 5.20}}$

[3] Corrected by use of formula: $\frac{\text{(Burst pressure corrected for burst diameter) ream weight basis (13.4)}}{\text{Ream weight}}$

From the foregoing it is clearly seen that a considerable strength increase of the paper is obtained when bonding viscose is used which is prepared from a dissolving cellulose having a low alpha cellulose content (below 93%) when the CED viscosity of the cellulose is maintained above 4.2 centipoises, over that obtained when the CED viscosity is maintained below 4.2 centipoises. When it is considered that the ratio of cellulose used to bond the fibers to the fibers is only 0.03 to 1, it can be appreciated that this increase is surprising. It

should also be noted that an increase in strength in casings is obtained when using these improved papers. It is to be noted that the casing strength is usefully increased also even though the amount of the bonding cellulose in comparison to the fiber and the regenerated cellulose of the casing is extremely small.

In a similar manner viscose prepared from other cellulosic dissolving pulps containing for example 85%, 87% and 90% alpha cellulose content can be used with the cellulose having CED viscosities of 4.2, 5.5, 5.75 centiposes, inclusively, can be used to prepare bonded paper webs within the teaching of this invention.

The papers of the present invention are used as reinforcements in cellulose casings such as are used in the manufacture of sausage and other meat products.

What is claimed is:

1. A porous paper web of improved wet strength consisting essentialy of natural cellulosic fibers, bonded together with a regenerated cellulose having an alpha cellulose content greater than 85% and less than 93% by weight, and a cupriethylene diamine viscosity of at least 4.2 centipoises as determined by TAPPI test method T230–sm–50.

2. A porous paper web of improved wet strength consisting essentially of natural cellulosic fibers, bonded together with a regenerated cellulose having an alpha cellulose content greater than 85% and less than 93% by weight and a cupriethylene diamine viscosity of at least 4.2 to 5.75 centipoises as determined by TAPPI test method T230–sm–50.

3. A porous paper web of improved wet strength consisting essentially of hemp fibers, bonded together with a regenerated cellulose having an alpha cellulose content greater than 85% and less than 93% by weight and a cupriethylene diamine viscosity of at least 4.2 to 5.75 centipoises as determined by TAPPI test method T230–sm–50.

4. A regenerated cellulose casing of improved wet strength comprising tubing of regenerated cellulose having encased therein a hemp paper in which the fibers are bonded together and impregnated with a regenerated cellulose having an alpha cellulose content of greater than 85% and less than 93% by weight and a cupriethylene diamine viscosity of at least 4.2 centipoises as determined by TAPPI test method T230–sm–50.

5. A method for producing fibrous porous paper webs of improved wet strength which comprises impregnating a natural cellulosic fibrous web with a viscose solution containing between 0.5% and 3% by weight cellulose and from 0.5 to 3 percent caustic having an alpha cellulose content greater than 85% and less than 93% by weight and a cellulose 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 by contacting the web with an aqueous regenerated solution containing at least 2% by weight of sulfuric acid, thereafter washing the web with water to remove the acid therefrom and then drying the washed web.

6. The method according to claim **5** wherein the cellulose has a cupriethylene diamine viscosity of from 4.2 to 5.75 centipoises according to TAPPI test method T230–sm–50.

7. The method according to claim **5** wherein the viscose bonding solution contains from 1 and 2 percent by weight of cellulose, and from 0.8 to 1.5 percent caustic.

References Cited

UNITED STATES PATENTS

1,701,543	2/1929	Richter et al.	162—176 X
1,745,557	2/1930	Richter et al.	117—11 X
2,033,481	3/1936	Richter	117—157
2,686,725	8/1954	Cornwell	99—174
2,910,380	10/1959	Shiner	117—157 X
3,135,613	6/1964	Underwood	117—157 X

OTHER REFERENCES

Ott, Emil, Cellulose and Cellulose Derivatives, 1943, pp. 810 and 811.

WILLIAM D. MARTIN, *Primary Examiner.*

M. LUSIGNAN, *Assistant Examiner.*

U.S. Cl. X.R.

99—176; 117—102, 157, 166

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,433,663 March 18, 196[illegible]

William F. Underwood

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 16, "at least" should read -- less than --; after line 24, insert as a new paragraph -- This application is a continuation-in-part application of application Serial No. 833,944 filed August 17, 1959, now U.S. Patent 3,135,613 issued June 2, 1964. --. Column 3, line 57, "contains" should read -- containers --. Columns 5 and 6, TABLE IV, eighth column, line 6 thereof, "resin" should read -- ream --.

Signed and sealed this 7th day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, J
Commissioner of Paten