

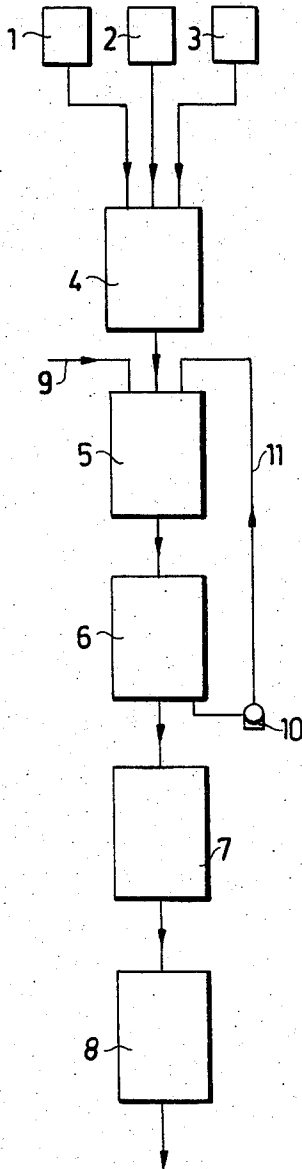
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PROCESS FOR MANUFACTURING CROSS-LINKED PAPER AND VISCOSE
PULP AND PRODUCTS PRODUCED ACCORDING TO THE PROCESS

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PROCESS FOR MANUFACTURING CROSS-LINKED PAPER AND VISCOSE PULP AND PRODUCTS PRODUCED ACCORDING TO THE PROCESS

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Continuation of application Ser. No. 597,794, Nov. 29, 1966. This application Sept. 14, 1970, Ser. No. 72,796

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U.S. Cl. 162—157 C

11 Claims

This application is a continuation of Ser. No. 597,794, filed Nov. 29, 1966 and now abandoned.

The present invention relates to a method of producing paper and viscose pulp, possessing improved absorption properties, softness and resistance to alkali, and products manufactured according to the method.

Although paper and viscose pulps produced in cellulose plants, and paper or other finished products produced from said paper and viscose pulps and intended for absorbing purposes, such as tissue papers, cellulose wadding, babies' napkins, towels, handkerchiefs, serviettes, bandaging material, sanitary towels etc. are well capable of absorbing such liquids as water, perspiration, body liquids, plastic solutions, etc., there exists a need, with respect to these products, for an increase in their absorption properties and an improvement in their softness and resistance to alkali. Improved properties in this respect, however, must not mean that the product in question becomes so expensive that it cannot be sold.

It is known that the properties of cellulose fibres can be modified by treating finished products based on cellulose fibres, e.g. cotton cellulose, with a cross-linking agent which reacts with the cellulose molecules and which provides cross-linkages between the same. It is also known that by treating paper pulp with cross-linking agents in strongly alkaline solution prior to the beating and sheet-formation processes it is possible to obtain a paper having improved porosity and absorption properties. The last mentioned method, however, is combined with considerable disadvantages in the form of high material losses and high manufacturing costs, and consequently it cannot be applied in practice when manufacturing paper or viscose pulp from wood.

The object of the present invention is to eliminate the disadvantages pertaining to previously known methods, and in a simple and economically advantageous manner produce new paper or viscose pulps possessing improved absorption properties, softness and resistance to alkali, whereby said pulps can either be used in their raw state, e.g. as adsorbing materials in bandages, babies' napkins, sanitary towels, dental and surgical absorption material, or be further treated to form a finished paper material of the type where high absorption properties and resistance to alkali is important, e.g. filter paper and laminate paper and various tissue products such as serviettes, household paper, towels, handkerchiefs, face towels, etc.

The method according to the invention is characterized in that the paper or viscose pulp is treated with a cross-linking agent from the group consisting of polyhalides, polyepoxides and epoxyhalides in the presence of an alkaline aqueous solution having a concentration of at the most 2.1% by weight alkali at a temperature at which cross-linking of cellulose takes place, for such a period of time that the resistance to 18% aqueous sodium hydroxide solution at 20° C. measured according to SCAN-C 2:61 is increased by 1-16%.

In the method according to the invention the starting material may comprise pulp produced by digestion with

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the usual chemicals, examples of such pulps being sulphite and sulphate pulp of paper or viscose type. The pulp may be bleached or unbleached. Suitable viscose pulps usually have a composition corresponding to 88-100% cellulose, 11-0% hemicellulose and 1-0% rosin and other constituents. Suitable paper pulps usually have a composition of 80-88% cellulose, 18-15% hemicellulose, and 2-0% rosin and other constituents. One condition, however, is that the pulp shall be produced of wood cellulose, such as wood from pine, spruce, birch, aspen, poplar, beech, eucalyptus etc. Pulps based on other starting materials, e.g. cotton linters, cannot be treated according to the invention owing to, among other things, the low reactivity with cross-linking agents of the type used according to the invention.

The cross-linking agents used according to the invention comprise polyfunctional substances from the group consisting of polyhalides, polyepoxides and epoxyhalides, which during the cross-linking reaction with cellulose require an alkaline catalyst. The term polyfunctional is intended to indicate that the substances in question shall have at least two functional groups which can react with the cellulose to form cross-linkages within each fibre. This then does not mean cross-linking agents which give cross-linkages between cellulose molecules in different fibres. The cellulose chains are fixed in their position by means of the cross-linking provided according to the invention, within the fibre so that the chain molecules are prevented from sliding relative to each other at the same time as the swelling effect of the hemicellulose molecules on the fibres decreases. Suitable polyhalides for use according to the invention are, for instance, organic dihalides such as

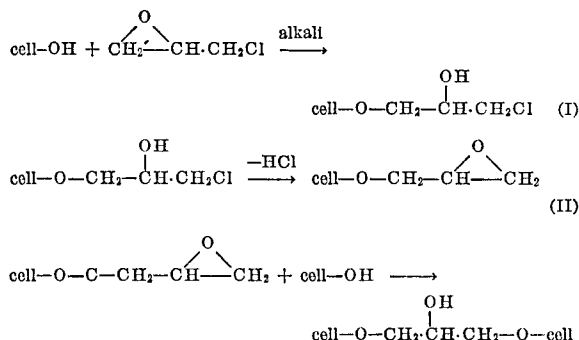
dichloroacetone,
dibromoacetone,
1,3-dichloropropane,
1,3-dibromopropane,
1,3-diiodopropane,
1,3-difluoropropane,
1,4-dichlorobutane,
1,4-dibromobutane,
1,4-diiodobutane,
1,4-difluorobutane,
1,3-dichloropropane-2,
1,3-dibromopropanone-2,
1,3-diiodopropanone-2,
1,3-difluoropropanone-2,
1,4-dichlorobutanedione-2,3,
1,4-dibromobutanedione-2,3,
1,4-diiodobutanedione-2,3,
1,4-difluorobutanedione-2,3,
1,5-dichloropentanedione-2,4,
1,5-dibromopentanedione-2,4,
1,5-diiodopentanedione-2,4,
1,5-difluoropentanedione-2,4,
1,3-dichloropropanol-2,
1,3-dibromopropanol-2,
1,3-diiodopropanol-2,
1,3-difluoropropanol-2,
1,4-dichlorobutanediol-2,3,
1,4-dibromobutanediol-2,3,
1,4-diiodobutanediol-2,3,
1,4-difluorobutanediol-2,3,
1,5-dichloropentanediol-2,4,
1,5-dibromopentanediol-2,4,
1,5-diiodopentanediol-2,4 and
1,5-difluoropentanediol-2,4, etc.

Suitable polyepoxides for use according to the invention are, for instance, butadiene dioxide, vinylcyclohexene dioxide etc.

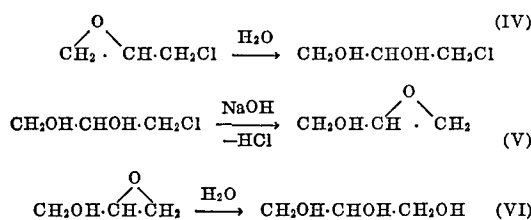
Suitable epoxyhalides for use according to the invention are, for instance, epichlorohydrin, epibromohydrin, epifluorohydrin, epiiodohydrin. Certain other cross-linking agents for cellulose, which require basic catalysts, can also be used according to the present invention, e.g. divinylbenzene, divinylsulfone, ethyleneimine and derivatives thereof etc.

The term "alkali" according to the above, indicates alkaline catalyst for the cross-linking reaction. Suitable alkaline catalysts are alkali metal hydroxides, calcium hydroxide and ammonia. Amines and quaternary ammonium bases, such as methylamine, ethylamine, isopropylamine, dimethylamine, trimethylamine, dimethylbenzylamine, and tetrabutylammonium hydroxide can also be used as alkaline catalysts according to the invention although the catalytic effect of these substances is lower in many cases, due among other things to reaction with the cross-linking agent, and the cost is high. It is particularly advantageous to use sodium hydroxide since this is found at hand in most cellulose plants.

The cross-linking reaction according to the invention progresses according to the diagram below, in which epichlorohydrin has been chosen as the cross-linking agent and "cell" represents a cellulose molecule.



Furthermore, in the alkaline environment a hydrolysis of epichlorohydrin according to the diagram below also takes place:



A certain formation of cellulose ethers also takes place parallel with the cross-linking reaction. The alkali hydroxide solution and epichlorohydrin solution form two separate liquid phases and thus the reaction requires good agitation of the pulp suspension if homogeneous reaction conditions are to be obtained. The system can be converted into a single liquid phase if a polar organic solvent is also added, which can partly dissolve both water and cross-linking agents of the type used without reacting with the same, and possess a boiling point preferably exceeding 50° C. It is of particular advantage if the solvent also has flash point which is so high that risk of explosion is avoided at the temperatures used during the treatment according to the invention. Solvents which can be used according to the present invention are, for instance, acetone, tetrahydrofuran, dialkyl sulphoxides, such as dimethyl sulphoxide etc.

It is also possible to produce a liquid one phase system by adding a water-soluble inorganic salt, which when

dissolved in water gives a pH of 6.5 to 7.5 and does not precipitate or react in any other way with the cross-linking agent, e.g. alkali metal chlorides, alkali metal bromides and alkali metal iodides, MgCl₂, CaCl₂, etc. By adding such a solvent or salt an improved homogeneity is obtained in the reaction conditions, which leads to an increase in the degree of cross-linking, and thus in this way it is possible to shorten the reaction time as compared with the two phase method.

The cross-linking reaction can be effected at room temperature or at higher temperatures. Suitable reaction temperatures for practical use are temperatures between 25 and 95° C., depending on the reaction time desired and the concentrations of alkali and cross-linking agent. The reaction time for obtaining the desired degree of cross-linking is, as a rule, from 0.15 to 10 hours. It has been found particularly suitable to use reaction temperatures of 30–50° C. and a reaction time of from 1 to 3 hours.

The cross-linking can be effected after the viscose or paper pulp has been produced, i.e. separately on the finished pulp, but it is also possible to effect the same in an alkaline stage during manufacture of the pulp itself, e.g. in conjunction with the bleaching process, if bleached pulp is to be treated. In this case it is particularly suitable to effect the cross-linking reaction in one of the alkali treatment stages which occur in the bleaching sequence. If several alkali stages are included in the bleaching process it is particularly suitable, when carrying out the treatment process according to the invention, to use the last alkali stage, thus preventing any of the cross-linking agents from being consumed by lignin products dissolved in the previous alkali stage. By carrying out the treatment in this way dewatering of the pulp in subsequent stages is facilitated, and it is possible to utilize the alkali already present from the pulp producing process.

The concentration of substances taking part in the cross-linking reaction, which is of great importance to the course of the reaction, and to economy, as well as the properties of the obtained product is, for the sake of clarity, indicated in the following both in terms of percent by weight based on the dry cellulose pulp and also in terms of percent by weight based on the treatment liquid.

Calculated in percent by weight based on the treating liquid, the reaction, when using a two phase system, can thus be effected with an alkali concentration of 0.01–2.1% and a cross-linking agent content of 0.05–8.8%. An alkali concentration of 0.2–0.6% and a cross-linking agent concentration of 0.5–4.4% have been found particularly suitable. When converting to percent by weight based on absolutely dry pulp the corresponding values of 0.5–12%, preferably 2–6% alkali and 0.5–50%, preferably 5–25% cross-linking agent are obtained. Thus the amount of cross-linking agent should be relatively high in relation to the amount of pulp to obtain good economy. On the other hand the amount of alkali should not exceed 2.1% based on the weight of the treatment liquid, since otherwise hemicellulose may be dissolved, making it impossible to carry out the process in practice. Furthermore, a low alkali concentration prevents etherification of the cellulose.

When utilizing a system with one single liquid phase the amount of added organic solvent of the type which dissolves both water and cross-linking agents should constitute 5–50, preferably 8–15% of the weight of added cross-linking agent. Thus, in this case, the treating liquid, in addition to the percentages disclosed above for alkali and cross-linking agent, also contains 0.25–4.4, preferably 0.4–1.2%, based on the weight of the treating liquid, of said organic solvent. If an inorganic salt is used instead so as to provide a system with one single liquid phase the amount of said salt should reach to 40–70, preferably 45–60% of the added amount of cross-linking agent. In this case, the treating liquid, in addition to the alkali and cross-linking agent, thus contains 0.2–6.2, preferably 0.5–2.2%, based on the weight of the treating liquid, of the

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inorganic salt. The remaining amount of treating liquid is comprised of water, including any water which may be added with the cellulose.

To facilitate dispersion of the cross-linking agent in the alkaline aqueous phase it is also possible to add a small amount of surfactant of arbitrary constitution, e.g. anionic, cationic or nonionic surfactants of known types. Suitable surfactants are, e.g. nonionic surfactants such as alkylene oxide adducts of fatty alcohols, alkylphenols etc., anionic alkylene sulphates and alkylarylsulphonates, e.g. lauryl sulphate, and cationic cetylpyridinium sulphate. The wetting agent can be added to the pulp before, after or at the same time as the addition of alkali and/or cross-linking agent, to facilitate the direct dispersion of the latter in the alkaline aqueous phase. Suitable amounts of surfactants are 0.005–0.5%, preferably 0.01–0.1%, calculated on the amount of dry pulp.

It is desirable that the pulp consistency is as high as possible during the cross-linking reaction so as to suppress secondary reactions, but it must not be so high that good mixing of the reaction medium is made impossible. Thus the reaction can be effected with pulp consistencies of over 10%. Suitable pulp consistencies during the reaction have been found to be 25–60%, preferably 35–50%.

When carrying out the method according to the invention in practice, the aforementioned suitable conditions for the reaction can be created by means of a method including the blending of paper or viscose pulps with a solution containing both alkali and cross-linking agent, effecting the cross-linking reaction and washing the reacted pulp. A particularly suitable example of the method is shown diagrammatically in the figure. According to this method, subsequent to mixing the pulp with the treating liquid to a pulp consistency of 1–15%, preferably 5–10%, the treating liquid is separated by being squeezed out, e.g. in a press or centrifuge, whilst returning the separated liquid to the mixing stage and simultaneously supplying thereto the requisite amounts of fresh treating liquid to replace that which has been used. According to the figure the cross-linking agent is passed from the tank 1 to the container 4 where it is mixed with aqueous alkaline hydroxide solution from the tank 2. A dissolving aid in the form of an organic solvent or an inorganic salt may also be supplied from the container 3, if a single liquid phase is required. The complete treating liquid is then passed to the mixing vessel 5 which is provided with an agitating device, where it is mixed with pulp supplied through the conduit 9. The treated pulp is transferred to the squeezing means 6 where it is given the required pulp consistency. The separated treating liquid is returned by the pump 10 via the conduit 11 to the mixing vessel 5, while the squeezed pulp is transferred to the reaction vessel 7, where it is allowed to react with the treating liquid to the desired degree of cross-linking. The reacted pulp is then washed in the container 8.

The method can be carried out continuously as well as batchwise. It is favourable to the economy of the process if the separated solution containing alkali and cross-linking agent is recirculated in the process. If, for instance, a pulp consistency of 8% is used in the mixing stage and 15% cross-linking agent based on dry pulp, is charged, it is possible, by means of pressing to a pulp consistency of 35–50%, to return 83–90% of the charged amount of cross-linking agent in the process, while supply of fresh cross-linking agent can be kept at 2.5–0.8% based on the dry pulp. Consequently the process is very economical. Washing subsequent to the reaction stage is suitably effected with the addition of a neutralizing substance, e.g. an acid or aqueous SO_2 , for neutralizing the pulp and removing possible excess cross-linking agent. The pulp treated according to the above can be further processed without difficulty, e.g. by bleaching or some other treatment stage, desirable in the pulp process.

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The invention will now be illustrated by the following examples. The following measuring methods have been applied:

WATER ABSORPTION ACCORDING TO KLEMM

The method is described in SCAN-P 13:64 (Papper och Trä 46 (1964) 10, pages 603–605) and relates to the suction height in mm. per 10 minutes for water in a vertically suspended paper strip the lower end of which is submerged in water.

RESISTANCE TO ALKALI ACCORDING TO SCAN-C 2:61 (R18)

According to the method, which was published in Papper och Trä 43 (1961):4, pages 301–312, pulp is treated with 18-percent aqueous sodium hydroxide solution and dissolved substances are oxidized with dichromate. Excess of dichromate is determined volumetrically. R18 relates to the amount of alkali-resistant pulp, as percent of absolutely dry pulp.

Example 1

Used as the starting material was a paper pulp produced from pine by digestion according to the sulphate method, and bleaching with chlorine, sodium hypochlorite and chlorine dioxide, which had the following starting characteristics: Alkali resistance R18 according to SCAN-C 2:61:83.0%. Water absorption according to Klemm: 80 mm./10 min. 6.5 g. epichlorohydrin and 4 g. NaOH were introduced into a container holding 980 grams of water and provided with an agitator, after which 370 grams of pulp of 27% solids content were added under agitation, corresponding to 100 g. absolutely dry pulp. The pulp consistency was thus 8% and the treating liquid, amounting to 1150 ml., contained 0.57% by weight epichlorohydrin and 0.35% by weight NaOH. Agitation was continued for 5 minutes, after which the obtained pulp suspension was transferred to a laboratory press where it was pressed to a pulp consistency of 40%. In this way 70% of the added amount of epichlorohydrin could be used again. The pressed pulp was transferred to a container which was submerged in a water bath at 40° C., where the pulp was allowed to react for 3 hours. The pulp was then washed four times, at 3% pulp consistency with water, with intermediate centrifuging, the second wash being effected with water containing 1% SO_2 . A portion of the pulp was then slurried in water and made in a laboratory press at a pressure of 7 kg./cm.² into hand sheets having a weight of 100 g./m.², for determining the water absorption, while another portion was slurried in 18-percent NaOH for determining the resistance to alkali.

The pulp treated with epichlorohydrin had an alkali resistance of 86.9% and a water absorption according to Klemm of 170 mm./10 min. The yield of cross-linked pulp was 100.7% and no loss of hemicellulose was observed. Corresponding treatment of pulp without epichlorohydrin gave an alkali resistance of 84.5% and a water absorption of 101 mm./10 min. If, by way of comparison, a two stage treating process comprising strong alkali in the first stage (8% NaOH), removing alkali by centrifugation and treating with 0.57% epichlorohydrin at 40° C. for 5 hours at a pulp consistency of 8% without intermediate removal of epichlorohydrin was used instead, an alkali resistance of 94.6% and a water absorption of 197 mm./10 min. was obtained. The yield of pulp, however, was only 84%, and thus a significant dissolution of hemicellulose had taken place. If the last mentioned test is carried out under the same conditions but without epichlorohydrin treatment an alkali resistance of 92.3% and a water absorption of 180 mm./10 min., and a yield of 93% is obtained, solely due to the adopted short alkalization.

Thus, this test shows that while a desirable increase in alkali resistance and water absorption can be effected by means of treatment with strong alkali or by means of such

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treatment combined with an epichlorohydrin treatment, in this case the dissolution of hemicellulose and cellulose degradation products is so great that these methods cannot be used in practice. In addition to an increase in the amount of hemicellulose dissolved, high alkali concentrations also imply considerable losses of cross-linking agent owing to hydrolysis of the same, which is shown in a lower degree of cross-linking (R18) based on the amount of cross-linking agent used. If, on the other hand, treatment according to the invention is undertaken with alkali in low concentration in combination with a cross-linking agent, the desired alkali resistance and water absorption can be obtained without appreciable losses of pulp and with a minimum loss of cross-linking agent.

Example 2

This test was carried out under the same conditions as Example 1, but with an addition of 14.0 grams epichlorohydrin. The concentration of epichlorohydrin in the treating liquid was thus 1.22% by weight. The obtained cross-linked pulp had an alkali resistance of 87.9% and a water absorption of 220 mm./10 min. The yield was 100.1%.

Example 3

Example 1 was repeated but with the difference that the treating liquid contained 4.1% by weight epichlorohydrin and 0.8% by weight NaOH. In this way 88% of added epichlorohydrin could be regained. The obtained cross-linked pulp presented an alkali resistance of 95.3% and a water absorption of 345 mm./10 min. The yield was 101.5%.

Example 4

Example 1 was repeated but with the difference that the treating liquid contained 3% by weight epichlorohydrin, 0.38% by weight NaOH and 0.2% by weight acetone, and thus existed in only one liquid phase, and that the treating temperature was 50° C. and the treatment time after pressing was 2 hours. The obtained cross-linked pulp and an alkali resistance of 92.1% and a water absorption of 300 mm./10 min. while the yield was 100%. Corresponding treatment but without acetone gave an alkali resistance of 90.2%, a water absorption of 264 mm./10 min. and a yield of 99.8%.

Example 5

100 grams of absolutely dry bleached pine sulphate pulp was carefully mixed at 8% pulp consistency with a treatment solution containing 0.5% NaOH and 0.52% 1,3-dichloropropane. The suspension was pressed to 40% pulp consistency and the pressed pulp was allowed to react for 3 hours at 40° C., after which the reaction was interrupted and the product washed in accordance with Example 1.

Test data of the starting pulp:

R18=83.5%
Water absorption 80 mm./10 min.

The test data of the pulp treated according to the invention:

R18=85.2%
Water absorption 123 mm./10 min.
Yield 98.6%.

Example 6

Example 5 was repeated but using 1,3-dichloropropanol instead of 1,3-dichloropropane. The treated pulp obtained the following test data:

R18=86.3%
Water absorption 156 mm./10 min.
Yield 99.0%

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Example 7

Example 5 was repeated but with 1,3-dichloropropane instead of 1,3-dichloropropane. The treated pulp obtained the following test data:

R18=85.6%
Water absorption 134 mm./10 min.
Yield 98.7%

Example 8

Example 5 was repeated but with epibromohydrin instead of 1,3-dichloropropane. The treated pulp obtained the following test data:

R18=86.6%
Water absorption 164 mm./10 min.
Yield 99.3%

Example 9

100 grams of dry, bleached spruce sulphite pulp (paper pulp type) was carefully mixed at 8% pulp consistency with a treatment solution containing 1.5% NaOH and 2% 1,3-dichloropropane. The suspension was pressed to 40% pulp consistency and the pressed pulp was allowed to react for 2 hours at 50° C., after which the reaction was interrupted and the product washed in accordance with Example 1.

The test data of the starting pulp:

R18=83.2%
Water absorption 63 mm./10 min.

Pulp treated with NaOH alone:

R18=85.4%
Water absorption 102 mm./10 min.
Yield 94.2%

Pulp produced according to the invention:

R18=87.8%
Water absorption 138 mm./10 min.
Yield 97%

Example 10

Example 9 was repeated but with 1,3-dichloropropanol-2 instead of 1,3-dichloropropane. The treated product had the following test data:

R18=92.8%
Water absorption 194 mm./10 min.
Yield 98.6%

Example 11

Example 9 was repeated but with 1,3-dichloropropane instead of 1,3-dichloropropane. The treated pulp had the following test data:

R18=90.2%
Water absorption 165 mm./10 min.
Yield 97.1%

Example 12

Example 9 was repeated but with epichlorohydrin instead of 1,3-dichloropropane. The treated pulp obtained the following test data:

R18=96.4%
Water absorption 232 mm./10 min.
Yield 99.2%

Example 13

100 grams of absolutely dry bleached spruce sulphite pulp (viscose pulp) was mixed at 8% pulp consistency with a treatment solution containing 1% NaOH and 4% epibromohydrin. The suspension was pressed to 45% pulp consistency and allowed to react for 4 hours at 40° C., after which the reaction was interrupted and the pulp washed in accordance with Example 1.

Test data of the starting pulp:

R18=93.5%

Water absorption 100 mm./10 min.

Pulp treated with NaOH alone:

R18=94.7%

Water absorption 136 mm./10 min.

Yield 96.7%

Pulp produced according to the invention:

R18=98.7%

Water absorption 268 mm./10 min.

Yield 98.6%

Example 14

100 grams of absolutely dry bleached pine sulphate pulp was treated with a solution containing 0.35% NaOH and 0.87% epichlorohydrin at 8% pulp consistency during a reaction time of 3 hours at 40° C., after which the reaction was interrupted and the pulp washed in accordance with Example 1.

Test data of the starting pulp:

R18=83.5%

Water absorption 88 mm./10 min.

Pulp treated with NaOH alone:

R18=84.5%

Water absorption 101 mm./10 min.

Yield 97.3%

Pulp produced according to the invention:

R18=88.0%

Water absorption 225 mm./10 min.

Yield 99.8%

Pulp produced in a corresponding manner but with the difference that the treatment solution was supplied with 0.1% of a surfactant fatty alcohol ethylene oxide adduct (Berol Visco 07) calculated on the dry pulp, had further improved absorption properties according to below.

R18=88.5%

Water absorption 238 mm./10 min.

Yield 99.7%

Example 15

100 grams of dry, bleached pine sulphate pulp was mixed at 8% with a solution containing 0.35% NaOH and 0.87% epichlorohydrin. After being homogenized the suspension was pressed to 17% pulp consistency after which the pressed solution was used as an additive for fresh pulp, together with a fresh supply of an amount of NaOH and epichlorohydrin corresponding to that which was used in the preceding batch. The pressed pulp was allowed to react for 3 hours at 40° C., after which the reaction was interrupted and the pulp washed in accordance with Example 1. The procedure was repeated a further six times and the following test data were obtained. (The R18 of the starting pulp=83.2%).

Batch No.	R18, percent	H ₂ O absorption, mm./10 min.
1-----	88.6	220
2-----	89.2	218
3-----	88.6	224
4-----	88.5	230
5-----	88.4	223
6-----	88.4	196
7-----	88.5	220
8-----	88.5	208

As can be seen from the above table, R18 is constant without extra supply of epichlorohydrin over the amount used, thus the principle of recirculation of the cross-linking agent can be used to advantage in the practical application of the invention.

Example 16

A babies' napkin 32 x 11.5 x 1 cm. in size was produced from paper pulp manufactured according to item No. 1 in Example 15, of an approximately 1 cm. thick layer of dry defibred pulp (fluff) surrounded by a thin protective casing of cellulose wadding and above this a thin layer of fibrillated rayon fibre (non-woven). The absorption capacity of this napkin was determined according to a standard method whereby the napkin was secured to the bottom of a domed plate, in the center of which was located a hole, over which was mounted a burette containing 300 ml. of water. Water was supplied in portions from the burette until the first drops penetrated to the bottom of the napkin. Corresponding tests were made on a babies' napkin sold on the market, having the same construction but the absorption layer of which comprised non-cross-linked pulp. The following results were obtained:

	Absorbed water amount
Babies' napkin:	g./gram napkin
The cross-linked absorption layer according to the invention	8.1
Non-cross-linked absorption layer	6.4

The babies' napkin produced according to the invention thus had 26% improved absorption ability and was able to absorb almost 100 ml. more water than the napkin used as a comparison.

Example 17

A compress for bandaging and blood-adsorbing purposes size 0.5 x 10 x 10 cm. of similar construction as the napkin in Example 16 was produced from pulp according to item 1 in Example 15. The compress thus contained an absorption layer of dried defibred pulp (fluff) treated according to the invention and compressed at a pressure of 2 kg./cm.², enclosed in a thin layer of fibrillated rayon fibre (non-woven) as a dust shield. The absorption capacity of this compress was then determined as in Example 16 and compared with a compress appearing on the market, of the same structure including non-cross-linked pulp. The following results were obtained:

	Absorbed water amount
Compress:	g./gram compress.
The cross-linked absorption layer according to the invention	8.7
Non-cross-linked absorption	6.8

The compress produced according to the invention thus had a 28% improved absorption ability as compared with the standard compress.

Example 18

Dentist pads for absorbing saliva for dental purposes, having a length of 4.5 cm. and a diameter of 1 cm. were manufactured from pulp according to item 1 in Example 15, said pads being provided with a thin protective casing of fibrillated rayon fibre. The absorption capacity for these pads was 8.8 g. per gram of pad whereas corresponding pads containing non-cross-linked fluff absorbed 6.3 g. per gram of pad. The pads according to the invention thus presented 40% improved absorption ability.

Example 19

A sanitary towel, 1.5 x 5.5 x 19 cm. in size and substantially oval in shape, produced from the pulp according to item 1 in Example 15 and constructed of two layers of fluff enclosed in a thin layer of tissue paper, the outer surface of one fluff layer, furthermore, being provided with a thin plastic sheet located outside the tissue paper and serving as a protective barrier. The two fluff layers were held together by a further casing of two-ply tissue paper which was compressed (embossed) along all the edges of the towel to hold the plies together. A casing of voluminous cotton wool, approximately 22 mm. thick was placed outside the outer tissue paper. A stitched net was

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placed around the towel. Absorption tests showed that the sanitary towel according to the invention could absorb 6.6 g. water per gram of towel, while sanitary towels produced in a corresponding manner containing non-cross-linked fluff could only absorb 5.2 g. water per gram of towel. The sanitary towel produced according to the invention thus presented an increase in absorption of 27%.

Example 20

The pulp according to Example 15, item 1, was wet beaten in a Jordan beater to a degree of beating of 23 Schoppe-Riegler. The pulp suspension obtained, which had a consistency of 0.2%, was transferred to a sheet-forming apparatus to be drained and shaped into a paper strip, which was taken up on a Yankee cylinder and creped. Hand towels were made from the creped paper, the towels presenting 28% better absorption capacity when compared with corresponding hand towels produced from non-cross-linked pulp.

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A method of manufacturing paper and viscose pulp having improved water-absorption properties according to SCAN-P-13:64, improved softness, and improved resistance to alkali according to SCAN-C2:61, which comprises reacting cellulose pulp with an alkaline aqueous solution containing alkali in an amount of at most about 2.1% by weight of the solution and from about 0.5 to about 12% by weight of the dry pulp, and a cross-linking agent selected from the group consisting of polyhalides, polyepoxides, and epoxyhalides in an amount within the ranges from about 0.05 to about 8.8% by weight of the solution and from about 0.5 to about 50% by weight of the dry pulp, at a temperature of between 25° C. and 95° C. at which cross-linking of the cellulose takes place, for a period of time sufficient to increase resistance to an 18% aqueous sodium hydroxide solution by from about 1 to about 16%.

2. A process in accordance with claim 1, in which the aqueous solution includes an organic solvent which is a solvent both for water and the cross-linking weight, in an amount within the ranges from about 5 to about 50% by weight of the cross-linking agent, and from about 0.25 to about 4.4% by weight of the treating liquid.

3. A process in accordance with claim 1 in which the aqueous solution comprises an inorganic salt in an amount

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within the ranges from about 40 to about 70% by weight of the cross-linking agent and from about 0.2 to about 6.2% by weight of the treating liquid.

4. A process in accordance with claim 1 in which the reaction is effected in the presence of an anionic, cationic or nonionic surfactant in an amount within the range from about 0.005 to about 0.5% by weight of the dry pulp.

5. A process in accordance with claim 1 in which the cross-linking agent remaining at the completion of the reaction is recovered and recycled.

6. A process in accordance with claim 1 in which the pulp is separated from the alkaline aqueous solution in an amount sufficient to increase the pulp concentration in the solution to within the range from about 25 to about 60%, the alkaline aqueous solution that is recovered is recycled, and the treated pulp is neutralized and washed.

7. A process in accordance with claim 1 in which the cross-linking agent is reacted with the pulp at a temperature within the range from about 25 to about 95° C. for from 0.15 to about 10 hours.

8. A process in accordance with claim 1 in which the reaction is effected in an alkali bleaching stage.

9. A cellulose paper pulp having improved water absorption capacity, softness and resistance to alkali, improved water absorption properties according to SCAN-P-13:64, and having an alkali resistance within the range from about 83 to about 99% according to SCAN-C-2:61 (R-18), having a cross-linking agent reacted therewith according to the process of claim 1.

10. Paper prepared from the cellulose paper pulp according to claim 9.

11. Absorbent material prepared from the cellulose paper pulp according to claim 9.

References Cited

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HOWARD R. CAINE, Primary Examiner

U.S. Cl. X.R.

8—120; 162—158

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,700,549 Dated October 24, 1972

Inventor(s) Ingemar Liss-Albin Croon et al.

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

Column 1, Between
lines 12 and 13

: Please insert
--ABSTRACT OF THE DISCLOSURE

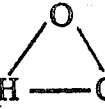
A process is provided for manufacturing paper and viscose pulp having improved absorption properties, softness and resistance to alkali, by reacting the pulp with an alkaline aqueous solution containing at most about 2.1% by weight of alkali, and a cross-linking agent.--

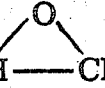
SPECIFICATION--

Column 1, line 53

: "adsorbing" should be --absorbing--

Column 3, line 38

: "cell-O-C-CH₂-CH  + cell -OH--
should be

--cell -O-CH₂-CH  + cell -OH--

<u>Column 4, line 56</u>	:	"weigh" should be --weight--
<u>Column 4, line 75</u>	:	"2,2%" should be --2.2%--
<u>Column 10, line 47</u>	:	insert --layer-- after "absorption"
<u>Column 10, line 72</u>	:	"whcih" should be --which--
<u>Column 11, line 42, Claim 2</u>	:	"weight" should be --agent--

Signed and sealed this 23rd day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents