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(54) MANUFACTURING PROCESS OF A PAPER SUBSTRATE INTENDED TO BE VULCANISED OR PARCHMENTISED

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(57) **ABSTRACT**

A manufacturing process of a paper substrate intended to be vulcanised or parchmentised, consisting in: subjecting, in a dry state, the cellulose fibres to energy radiation; defiberizing and refining in an aqueous environment the irradiated fibres until a homogenous fibre solution is obtained; forming a web from the obtained fibre suspension, which is then drained and dried to obtain the actual paper substrate.

MANUFACTURING PROCESS OF A PAPER SUBSTRATE INTENDED TO BE VULCANISED OR PARCHMENTISED

[0001] The invention relates to a manufacturing process of a paper substrate intended to be vulcanised or parchmentised. Thus, it also relates to the substrate obtained with the vulcanising or parchmentising process.

[0002] Those skilled in the art know the vulcanising and parchmentising operations so well that these processes will not be described more in detail hereinafter. The main thing is that the vulcanising is an operation consisting in treating a paper substrate by immersing it into a zinc chloride solution, and the parchmentising is a similar operation, in which the zinc chloride is replaced by sulphuric acid. The present invention does not relate to the actual vulcanising and parchmentising operations, but it relates to the manufacturing process of webs that can be treated with the operations of these two types.

[0003] The ability of a substrate to be treated by vulcanising or parchmentising depends mainly, if not exclusively, on the reactivity of the cellulose fibres making up the web with regard to the zinc chloride or sulphuric acid solutions. Thus, the more reactive i.e. accessible to chemical components contained in the ionic solutions the cellulose fibre is; the more satisfactory is the vulcanising or parchmentising. The reactivity of a fibrous web depends on several factors, one of which is especially the degree of polymerisation (DP) of the cellulose making up the fibre, the latter corresponding to the number of repetition units, which form the cellulose polymer. In general, it looks like the weaker the DP is, the more reactive is the fibre.

[0004] In the rest of the application, the efficiency of the vulcanising or of the parchmentising is controlled by evaluating the barrier level of the obtained vulcanised or parchmentised paper according to a technique, which will be made clear in the examples.

[0005] At the moment, the number of webs intended to be vulcanised is manufactured from textile waste coming especially from the "jeans industry", the jeans consisting 100% of long cotton fibres (staple), the size of which is between 20 and 50 mm. In practice, the jeans manufacturing clippings or rags are in the form of a bale, which is then opened and the size of the rags is reduced by different operations such as cutting and shredding. When these different steps have come to an end, the shredded pieces of jeans are cooked in a solution of soda concentrated to 7% in a closed reactor, under pressure, at a temperature of about 150° C. Then follows the tiresome step, in which the cooked fibres are washed with water in order to eliminate all of the cooking liquor. All these necessary operations of this discontinuous process may lead to duration of about 24 hours.

[0006] Soda cooking step allows both opening of the cotton fibres and reducing the degree of polymerisation of the cellulose. In practice, when the cotton fibres making up the jeans have, before cooking, an average degree of polymerisation of about 2000, this degree is only about 600, as far as vulcanising and parchmentising are concerned, immediately after the cooking step. The value of 600 seems in fact sufficient for obtaining reactivity, and consequently a satisfactory ability of the base paper to vulcanising or parchmentising.

[0007] The clusters of cooked fibres are processed in an aqueous environment so as to separate the fibres from each other, after which the individual fibres are refined, i.e. their structure is subjected to a deformation by mechanical action, allowing optimising the accessibility of the fibre. The suspension of the individual cotton fibres obtained right after these steps is then deposited on the wire of the paper machine, in the presence, or not, of fibres having different kind or same kind of nature such as e.g. wood fibres, so as to form in a known manner a web, which is then drained and dried until the actual paper substrate is obtained.

[0008] As already said, it is necessary, before vulcanising or parchmentising, to set out the most reactive cellulose fibres into the paper, this reactivity being obtained by lowering strongly the degree of polymerisation of the cellulose fibres.

[0009] The cooking step allowing obtaining this result has, however, some inconveniences. At first, the capital costs of an industrial chemical reactor are relatively high. Subsequently, the cooking consumes a lot of chemicals, in the case in question, soda. Finally and above all, the cooking leads to the formation of coloured effluents of concentrated soda having a pH of 13,5, the elimination of which is especially difficult and polluting. These operations of cooking and washing the rags take place generally with a yield in the order of 85% meaning a loss of the raw material of about 15%.

[0010] In other words, the invention tends to solve the problem by developing a clean and economical high yield (over 85%) manufacturing process of paper substrates intended to be vulcanised or parchmentised, which would be at least as reactive with regard to the zinc chloride or sulphuric acid solutions as the substrates obtained by the processes using a chemical cooking step of the cellulose fibres with a high degree of polymerisation.

[0011] To do this, the Applicant had the idea of substituting the cooking step in the concentrated soda solution with an energy radiation step, this radiation step being able to be performed, either, in a dry state, directly on the cellulose fibres, before the individualisation of the fibres and the refining in the aqueous environment, or in a dry state, on the final paper.

[0012] In other words and in a first embodiment, the invention relates to a manufacturing process of a paper substrate intended to be vulcanised or parchmentised, comprising the steps of:

[0013] subjecting, in a dry state, the cellulose fibres to energy radiation,

[0014] separating and refining in an aqueous environment the radiation-treated fibres until a homogenous fibre dispersion is obtained,

[0015] forming a web from the obtained fibre suspension, which is thereafter drained and dried to obtain the actual paper substrate.

[0016] The expression "homogenous fibre suspension" denotes a suspension, in which the cellulose fibres are dispersed into an aqueous solution to a consistency of about 1 to 10% by weight. This suspension is called homogenous insofar as the fibres have been correctly individualized due to hydration and mechanical agitation operations, thus avoiding the clustering of fibres.

[0017] In other words, the process consists first of all in lowering, with the energy radiation, in a dry state, the degree of polymerisation of the cellulose fibres, and once such a degree of polymerisation has been achieved, that the reactivity of the fibre is sufficient, separating the fibres in an aqueous environment and refining them, the fibre suspension next being settled on the wire of a paper machine to form a web, which is then drained and dried.

[0018] In another embodiment of the invention, the cellulose fibres are not exposed to energy radiation before the web formation, but thereafter, by the direct radiation of the final paper substrate intended to be vulcanised or parchmentised.

[0019] In this case, the process comprises the steps of:

[0020] separating and refining in an aqueous environment cellulose fibres contained in a mixture of fibres until a homogenous fibre suspension has been obtained,

[0021] forming a web from said suspension, which is next drained and dried until the actual paper substrate has been obtained, and

[0022] finally, exposing the paper substrate to energy radiation.

[0023] In the rest of the description and in the claims, the expression “cellulose fibres” denotes fibres formed by definition of cellulose, such as cotton fibres or any other annual plant fibres (flax, abaca etc.), wood fibres, these fibres of different origin distinguishing from each other by the structural characteristics such as the shape, the cross-section and thickness of the walls and the average degree of polymerisation (DP) of the cellulose making them up.

[0024] In the embodiment according to which the energy radiation is carried out before obtaining the sheet, it is possible to add to the fibre suspension, containing the cellulose fibres being exposed to energy radiation, cellulose fibres of the same origin, exposed to energy radiation or not, and/or cellulose fibres of different origin, exposed to energy radiation or not, and/or synthetic and/or mineral non-cellulose fibres.

[0025] In practice, the cellulose fibres treated with energy radiation are advantageously annual plant fibres and especially of cotton and represent at least 20%, advantageously at least 50% by weight, of the fibre suspension.

[0026] In the embodiment according to which the radiation is made directly on the paper substrate, all the cellulose fibres contained in the paper are irradiated by electron beams, regardless of their origin. It is clear that the mixture of fibres may further contain cellulose fibres, synthetic and/or mineral non-cellulose fibres. In practice, the cellulose fibres represent at least 20%, preferably at least 50% by weight, the most preferably 100% by weight of the fibre composition. In an advantageous embodiment, the cellulose fibres consist exclusively of cotton fibres.

[0027] When the paper substrate contains cotton fibres as cellulose fibres, the cotton fibres may have two essential sources.

[0028] First of all, the cotton fibres may be virgin cotton fibres, advantageously long fibres, the length of which is between 20 and 50 mm. In practice, these cotton fibres are received by the paper manufacturer in a dry state, either in the form of sheets, or in the form of compressed pulp thus comprising 100% of cotton fibres.

[0029] In this case, the energy radiation is in the form of a radiation by an electron beam or an X-ray beam.

[0030] When the irradiation treatment is carried out before the sheet formation and by means of X-ray, the penetration of the radiation is sufficient so that the cotton pulp is directly treated in a bale of about 1 m^3.

[0031] When the radiation is performed before the sheet formation and by an electron beam, the dry defibering of the sheet or of the compressed pulp starts prior to the radiation step and this, is done in such a way that the material passing under the beam is of low density (<0,6) and thin (in the order of a centimetre) so that the cotton fibres are treated in a homogenous and efficient manner.

[0032] As already said, the paper substrates intended to be vulcanised or parchmentised can also advantageously be obtained from cotton fibres coming from textile industry waste. In an advantageous embodiment, the cotton fibres coming to the composition of the fibre suspension come from jeans industry. In this case, the raw material is in the form of jeans manufacturing rags compacted in the form of bales.

[0033] In practice, the bale is first opened, the jeans rags are cut, possibly sorted to remove the foreign objects e.g. of metallic particle type, and finally shredded.

[0034] When the paper substrate is manufactured continuously, the cellulose fibres obtained after the shredding are separated and the refined in an aqueous environment.

[0035] When the paper substrate is manufactured discontinuously, the fibres obtained from shredded rags are stored again in the form of a bale, which is opened, and the cellulose fibres are separated and finally refined in an aqueous environment.

[0036] In a first embodiment, when the radiation is a radiation by electron beams and takes place before the paper sheet formation, the radiation treatment can be performed either immediately after the cutting step and prior to the shredding step or immediately after the shredding step.

[0037] In a second embodiment, the radiation is an X-radiation performed directly on the bale containing the cut and shredded rags of jeans.

[0038] As already said, the reactivity of a cellulose fibre depends on its DP.

[0039] The Applicant has noticed that for obtaining a cotton fibre treated by energy radiation that would be as reactive as the same fibre treated by cooking, it is necessary to reduce its degree of polymerisation under that of the cooked fibre.

[0040] Further and as already said, it is known that the degree of reactivity of a cotton fibre doesn’t necessarily have to be of the same level, depending on whether the fibre is intended to be vulcanised or parchmentised.

[0041] Further, the Applicant has noticed that for a same reactivity level, the DP of a cellulose fibre absorbing a given dose of irradiation before the sheet formation was higher than that of the same fibre having absorbed the same dose from the final paper.

Case in Which the Cotton Fibre is Exposed to Energy Radiation, Electron beam or X-Ray before the Sheet Formation:

[0042] When the degree of polymerisation of a cooked fibre intended to be vulcanised is in the order of 600, it is necessary, for obtaining a reactivity of at least equal to the same fibre treated by energy radiation, to reduce this degree of polymerisation to a value between 350 and 500, advantageously equal to 450. To obtain such DP-values, the irradiation dose absorbed by the cotton fibres is between 10 and 30 kGy.

[0043] The degree of polymerisation of a cellulose fibre treated by cooking and intended to be parchmentised is about 1000. To obtain a reactivity vis-à-vis the concentrated sulphuric acid at least equal to the same fibre treated by energy radiation, it is necessary to reduce this degree of polymerisation to a value less then 700, so that the irradiation dose absorbed by the fibres should be between 5 and 20 kGy.

[0044] Generally, the absorbed irradiation dose necessary to the cellulose fibre for obtaining an optimal reactivity of the substrate with regard to vulcanising and parchmentising depends on the treatment conditions and in particular of the type of equipment used.

Case in Which the Cotton Fibre is Irradiated after the Sheet Formation:

[0045] When the paper sheet manufactured exclusively of cotton fibres is intended to be vulcanised, the degree of polymerisation of the fibres making up the paper sheet obtained is less than 700, advantageously between 200 and 300, preferably 250. To obtain such a value, the Applicant has noticed that the irradiation dose absorbed by the cotton fibres should be between 10 and 50 kGy. However, these values can be applied only to vulcanising.

[0046] In the case of parchmentising, when the paper is manufactured solely from cotton fibres, the degree of polymerisation of the fibres making up the paper sheet obtained is between 400 and 600, advantageously 500. To obtain such a value, the Applicant has noticed that the irradiation dose absorbed by the cotton fibres should be between 5 and 30 kGy.

[0047] The manufacturing processes of the paper substrate of the invention, depending on whether the energy radiation treatment is performed before or after the sheet formation, can be carried out continuously or discontinuously.

[0048] The invention and the advantages, which stem therefrom will become more apparent from the following embodiment examples.

EXAMPLE 1

[0049] In this example, the process is a discontinuous process consisting in cutting the textile waste, removing the foreign bodies and shredding the pieces before forming a bale. This sequence of steps is made continuously on suitable cutting, sorting and shredding machines, known to those skilled in the art.

[0050] The baling step makes it easier to store the ready-made raw material for a subsequent dispersion step of the fibres in an aqueous environment.

[0051] When the paper manufacturer takes again the jeans waste bale, he opens it in a dry state so that the bale is broken. The pieces of the jeans are then separated, defiberized and then refined in an aqueous environment, the obtained fibre suspension then being deposited on a paper machine, which assures, after draining and drying, the manufacturing of the final paper.

[0052] In the prior art, the obtained shredded pieces of jeans, after the dry disintegration of the bale, are subjected to a cooking step in a cooker at the temperatures of about 150° C. in soda solutions concentrated to 7%, the matter obtained being washed and defiberized, and finally refined in an aqueous environment.

[0053] In the process object of the an exemplary embodiment of the present invention, this cooking and washing step is replaced by a radiation step by electron beams.

[0054] This irradiation step can be performed on the cotton fibres before manufacturing the paper and this, either immediately after the sorting step or immediately after the shredding step, or directly on the finished sheet.

EXAMPLE 2

[0055] In this example, a paper intended to be vulcanised is produced containing 100% of cotton fibres treated either by cooking or by irradiation before the sheet formation.

A/Method

[0056] For the two samples, the degree of polymerisation of the cooked cotton fibres or those exposed to radiation by an electron beam has been determined before transformation operation of the paper by vulcanising, as well as the reactivity of the final sheet has been determined after the vulcanising. The degree of polymerisation of the cotton fibres is determined by calculations from the viscosity measurements of a solution based on cupriethylenediamine (CED), into which the cellulose fibres are dissolved.

[0057] The precise test from which the DP-values are obtained is done as follows:

[0058] placing the fibres in a polyethylene flask containing 10 ml of de-ionized water under agitation,

[0059] then adding 10 mm of cupriethylenediamide,

[0060] eliminating the air from the flask by pressure on its walls,

[0061] closing the flask with its plug,

[0062] agitating the solution for 40 minutes until the fibres have been completely dissolved,

[0063] filtering the solution by means of a mechanical filter,

[0064] measuring the viscosity of the lower part of the filtrate by means of a capillary viscosimeter CANON-FENSKE 200.

[0065] The reactivity of the paper (DL) is evaluated after the vulcanising by measuring the barrier level with a coloured solvent. The test is done as follows:

[0066] preparing a sample of the paper to be tested, the size of which is 10×10 cm,

[0067] putting the side of the sample to be tested on a transfer paper,

[0068] applying a coloured solution of turpentine on the whole surface of the paper to be tested: the contact time being 3 minutes.

[0069] The evaluation is made in the following table:

SCALE	SIDE OF THE PAPER TO BE TESTED	TRANSFER PAPER
5	no stains	no stains
4	4 spots maximum	no stains
3	several spots	no stains
2	—	4 spots maximum
1	—	several spots
0	—	1–2 stains, size 5–20 mm
−1	—	more than 2 stains, 5–20 mm
−2	—	size of the stains over 200 mm
−3	—	the whole surface is coloured

[0070] Generally, the higher the DL-value of the paper transformed by the vulcanising is; the higher is the reactivity of the base paper. The reactivity of a paper is consequently estimated by the barrier level of the final product obtained.

B/Results

[0071] 1/ The DP's and DL's concerning the fibres treated by radiation with different doses of absorbed energy before the sheet formation are given in the following table:

Dose in kGy	Basic Weight g/m^2	DP	DL
0	111	2010	0
10	109	640	1
15	109	525	2
20	107	515	2
25	112	370	2
30	110	390	3
50	110	330	3

[0072] It may be seen from the results that it is necessary, in order to obtain a degree of reactivity of a paper treated by radiation of the same level as that of a paper obtained from cooked fibres (DL=3), to lower the degree of polymerisation of the treated fibres to a value of about 390.

[0073] 2/ The DP and DL of a paper, the cotton fibres of which have been cooked or treated by an electron beam, are given in the following table, but we must bear in mind that the DP is evaluated on the fibres before the transformation operation of the paper by vulcanising.

	DP	DL
1 Cooked cotton fibres	600	3
2 Paper irradiated with 50 kGy	250	3
3 Fibres irradiated with 30 kGy	390	3

[0074] The examples 2 and 3 of the table reveal the difference due to raw material irradiation before manufacturing of the paper in comparison with an irradiation on the finished paper. For the same paper transformation level after vulcanising, that is to say for the same reactivity level of the paper, a much more important dose of irradiation has to be applied to the finished paper than to the raw material.

EXAMPLE 3

[0075] In this example, a paper intended to be parchmentised is manufactured, containing 100% of cotton fibres treated by irradiation before the sheet formation.

A/Method

[0076] The samples are characterized by the degree of polymerisation of the cotton fibres exposed to radiation by an electron beam, before the transformation operation of the paper by parchmentising, as well as by the reactivity of the sheet with regard to the parchmentising.

[0077] The degree of polymerisation DP of the cotton fibres is determined by calculation from the measurements of the viscosity of a solution based on cupriethylenediamine (CED), in which the cellulose fibres are dissolved.

[0078] The reactivity of the paper (DL) is evaluated after the parchmentising, by measuring its barrier level with a coloured solvent.

B/ Measurements		
Dose in kGy	DP	DL
0	2010	1
10	640	5
30	400	5
50	320	5

[0079] As can be seen from the measurements, an irradiation by electrons of the cotton fibres before the paper manufacturing with a dose of 10 kGy is sufficient for lowering the DP of the cellulose under 700 and making it capable of a good parchmentising.

1. A manufacturing process of a paper substrate intended to be vulcanised or parchmentised, comprising the steps of

subjecting, in a dry state, the cellulose fibres to energy radiation,

separating and refining in an aqueous environment the radiation-treated fibres until a homogenous fibre solution is obtained,

forming a web from the obtained fibre suspension, which is then drained and dried to obtain the actual paper substrate.

2. A process according to claim 1, characterized in adding to the fibre suspension being exposed to energy radiation, cellulose fibres of the same origin, exposed to energy radiation or not, and/or cellulose fibres of different origin, exposed to energy radiation or not, and/or synthetic and/or mineral non-cellulose fibres.

3. A process according to claim 1, characterized in that the fibre suspension contains at least 20%, advantageously at least 50% by weight of the cellulose fibres exposed to energy radiation.

4. A process according to claim 1, characterized in that the cellulose fibres exposed to energy radiation are cotton fibres.

5. A process according to claim 4, characterized in that the cotton fibres exposed to energy radiation are virgin cotton fibres coming from sheets or compressed pulp.

6. A process according to claim 5, characterized in that the energy radiation is a radiation by electron beams or by x-radiation.

7. A process according to claim 4, characterized in that the cotton fibres exposed to energy radiation come from textile industry waste.

8. A process according to claim 7, characterized in that the cotton fibres come from jeans waste first cut, then sorted and shredded, the fibres being exposed to a radiation by electron beams either right after the cutting step, and prior to the shredding step, or right after the shredding step.

9. A process according to claim 7, characterized in that the cotton fibres come from jeans waste in the form of bales containing the jeans manufacture rags, possibly cut and then shredded, the entire bale being exposed to X-radiation.

10. A process according to claim 4, characterized in that, when the paper is intended to be vulcanised, the irradiation dose absorbed by the cotton fibres is between 10 and 30 kGy.

11. A process according to claim 4, characterized in that, when the paper is intended to be vulcanised, the DP of the irradiated cotton fibres is between 350 and 500.

12. A process according to claim 4, characterized in that, when the paper is intended to be parchmentised, the irradiation dose absorbed by the cotton fibres is between 5 and 20 kGy.

13. A process according to claim 4, characterized in that, when the paper is intended to be parchmentised, the degree of polymerisation of the irradiated cotton fibres is less then 700.

14. A manufacturing process of a paper intended to be vulcanised or parchmentised comprising the steps of:

separating and refining in an aqueous environment cellulose fibres contained in a mixture of fibres until a homogenous fibre suspension is obtained,

forming a web from the suspension, which is next drained and dried until the actual paper substrate has been obtained, and

lowering the degree of depolymerisation of the fibres by exposing the paper substrate to energy radiation.

15. A process according to claim 14, characterized in that the mixture of fibres contains at least 20%, preferably at least 50% by weight, most preferably 100% by weight of the cellulose fibres.

16. A process according to claim 14, characterized in that the cellulose fibres are exclusively virgin cotton fibres coming from sheets or compressed pulp.

17. A process according to claim 14, characterized in that the cotton fibres, defiberized and then refined in an aqueous environment, come from textile waste.

18. A process according to claim 17, characterized in that the textile waste comes from jeans industry.

19. A process according to claim 14, characterized in that the fibre suspension contains 100% by weight of cotton fibres.

20. A process according to claim 14, characterized in that the energy radiation is a radiation by electron beams.

21. A process according to claim 19, characterized in that, when the paper is intended to be vulcanised, the radiation dose absorbed by the cotton fibres is between 10 and 50 kGy.

22. A process according to claim 19, characterized in that, when the paper is intended to be vulcanised, the degree of polymerisation of the irradiated cotton fibres is less then 700, advantageously between 200 and 300.

23. A process according to claim 19, characterized in that, when the paper is intended to be parchmentised, the degree of polymerisation of the irradiated cotton fibres making up the obtained paper sheet is between 400 and 600, advantageously 500.

24. A process according to claim 19, characterized in that, when the paper is intended to be parchmentised, the irradiation dose absorbed by the cotton fibres is between 5 and 30 kGy.

25. A process for vulcanizing a paper substrate comprising providing a paper substrate obtained by the process of claim 1, and subjecting the paper substrate to a vulcanizing operation.

26. A process for parchmentising a paper substrate comprising providing a paper substrate obtained by the process of claim 1, and subjecting the paper substrate to a parchmentising operation.

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