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A process for the manufacturing of paper, particularly corrugated paperboard, and resulting product.

By the treatment of paper, particularly the paper to be used for the intermediate layer of corrugated paper board, with black liquors of paper pulp, an improvement of the physical and mechanical properties of the paper, particularly of the crushing strength, is induced.

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The present invention relates to a process for the manufacturing of paper, particularly of paper useful as the intermediate layer ("medium") of corrugated paper board, and to the thus resulting product.

It is known that the corrugated paper boards in their simplest form, consist of three layers, namely two outer layers, forming the faces of the paper board and called "liners", and an intermediate, corrugated layer known in the related art as the "medium".

In the case of the five layer corrugated paper boards, there are provided two layers of corrugated "medium" paper, each one being interposed between two layers of "liner".

It is also known that, owing to the main use of the corrugated paper boards in the packing field the most significant properties of the single component layers, for an evaluation as a whole of the corrugated paper boards are the crushing strength (also known as the "Concora"), the water repellence and the wet strength.

In the past the "medium" papers were manufactured from straw, but such a technology is being almost worldwide abandoned, both because the straw handling costs became too much heavy, (particularly with respect to the transportation and the involved labour) and owing to the pollution problems of the industrial effluents deriving from such a raw material.

Presently the "medium" papers are produced according to technologies which can be essentially referred to two classes of raw materials:

- a) "medium" paper produced from mixtures of particles or chips of wood cooked by chemical processes (80%) and waste paper (20%); these papers are also called "semichemical" papers (or papers from semichemical pulp and are increasingly expensive due to the prevalence of a valuable material such as the wood.
- b) "medium" papers produced from mixtures of waste paper which are there improved by surface treatment of the resulting paper with starches or resins, the so-called "flutings" being thus obtained.

In this case too, apart from the lower quality of the resulting paper, the

manufacturing costs are increased not so mainly due to the raw material being used, but owing to the additional operations required.

It is enough to observe that the starch is added to the paper in the already substantially dried condition, as coming out of the drying section, in form of a thin surface layer, applied with a water solution having a concentration of about 2%, whereby the treated paper must be thereafter dried again with a relevant energy consumption.

Lastly it is worth to note that generally in the paper industry the effluent waters resulting from the attack of the wood particles (also known as the "black liquors") constitute a very serious problem from the point of view of the pollution and their treatment heavily affects the manufacturing costs.

The main purpose of the present invention is that of providing a process for the manufacturing of paper, particularly "medium" paper for corrugated paper board, which permit less valuable raw material to be used, the properties of crush resistance and water repellency being maintained at the same level or, the type and concentration of raw materials being the same, permits the afore said properties to be improved.

A more specific purpose of the present invention is that of providing a process of the afore said type which, in the case of the "semichemical" papers, and the physical and mechanical properties being the same, particularly the crush strength being the same, permits the contents of wood pulp to be reduced.

Another likely more specific purpose of the present invention is that of providing a process of the afore said type which in the case of "fluting" paper, permits the crush strength to be increased by about 20%.

A further purpose of the present invention is that of providing a process for the manufacturing of improved paper products, such as cardboards, wherein the "stiffness" it is a qualitatively important feature. These and other purposes are fulfilled by a process for the manufacturing of paper, particularly medium paper for corrugated board, characterized in that the paper, in the drying stage and having a content of dry matter of between

18% and 92%, is treated with black liquors previously concentrated to a value of the least 5% referred to the total dry material, whereby the ratio between the contents of dry material in the paper and the contents of dry material in the black liquors after the concentration is of between 50:10 and 92:10, and preferably of between 50:10 and 80:50.

In the preferred embodiment of the process of the invention the concentrated black liquor, before the application to the paper, is supplemented with a small percentage of alcohols, preferably polivinyl alcohol.

It has been in fact found that the property of the black liquors of improving the properties of the treated paper is thus enhanced.

According to a further embodiment of the invention, when the black liquors are to be used for the treatment of coloured papers, even of light colours, they can be previously treated by partial whitening and subsequent dyeing (for instance by means of H_2O_2) in a per se known manner.

It has been in fact surprisingly found that the black liquors, which to date had no use or had a limited use in different technical fields and were only a problem from the point of view of the depuration of the effluent waters of paper manufacturing industries, when are applied as a thin layer to the paper being dried, provided that they are previously concentrated to a contents of at least 5% of dry material, preferably of 30 to 50%, permit the following results to be achieved:

- 1) In the case of the semichemical papers, (80% of wood pulps and 20% of waste paper pulp), the crush strength (Concora) is increased by more than 20% whereby the use of semichemical paper of lower grams per square meter is permitted to obtain corrugated paperboard having the same crushing strength.
- 2) Alternatively, in the case of the semichemical papers, the rationn between wood pulp and waste paper pulp can be changed, passing for instance from 80:20 to 60:40, the physical and chemical properties, particularly the crushing strength, being maintained unvaried. The economical advantage is self-evident, if attention is paid to the fact that by the waste paper pulp an economy of 30 to 50% with respect to

the wood pulp is achieved.

- 3) In the case of the "fluting"papers, wherein to date the necessary crushing strength is obtained by applying starch or resins, there is not only achieved a saving of energy (in the previously stated sense) and of raw materials, since starches and resins are more expensive than the black liquors, but also better results are obtained as regards the increase of the crushing strength. In this specific embodiment it is preferable that the concentration of the black liquors is higher, of the order of 40 to 50%
- 4) in the case of paper products in which the "stiffness" effect is important as regards the quality and thus the price of the product, (as for instance cardboards for industrial packings, or the non white layers therefor an improved product can be obtained at a lower cost.
- 5) By the process of the invention there are again industrially acceptable the plants for the manufacturing of paper and cellulose from straw, since the problem of the effluent and of the realted pollution is advantageously solved.

Several attempts have been made in the past in order to reuse or recycle the black liquors, those attempts only involving the addition of the black liquors to the aqueous suspension of fibres before the forming of the paper sheet without any previous concentration step: these attempts were essentially useless since, although an increase of grams per square meter occurred, the physical and mechanical properties of the resulting paper got worse.

On the contrary, the qualifing and fully surprising feature, besides being novel, of the process of the invention is that by coating the paper, already dried to an optimum value of residual moisture content, with the black liquors, also previously concentrated, the resulting product is qualitatively and relevantly improved.

In this connection, the field tests demonstrated that a difference of the moisture content of 20 to 30% is necessary to ensure the desired results: otherwise stated, if the residual moisture content of the paper is about 30% it will be enough that the black liquours are concentrated to not more than 50%

to obtained the optimum results.

Tests of the crushing strength have been carried out, of type known as Flat Crush Test (FCT), on corrugated paperboard comprising an outer liner of kraft paper of 125 g/sq.m a medium semichemical paper of 130 g/sq.m., and an inner layer of liner paper of 125 g/sq.m.

Fours samples (samples A) of corrugated paperboard in which the medium layer had not been treated with black liquors, and four samples (samples B) of the same corrugated paperboard in which the medium paper had been treated with 10% concentrated black liquors were subjected to the FCT with following results:

	A	B
average weight	448	448
FCT crushing	151	188

The percent increase of the crushing strength in this case was higher than 24%.

Without imposing undue limitations to the present invention it seems plausible the hypothesis according to which the black liquors, owing to the concentration step, acquire the faculty of crystallizing and polimerizing (depending on the nature of the components), onto the surface of the paper being trated, thus giving place to the already mentioned "stiffness" effect, like or more than the traditional treatment agents, but with the previously mentioned advantages.

In this connection it seems reasonable to suppose that the better results, as obtained with the black liquors, can be attributed to a greater compatibility with the fiber substances which are treated therewith.

For the preparation of the black liquors to be used for the present invention there is carried out the washing and squeezing of the wood particles or chips after the chemical cooking the operation being repeated the most suitable number of times; like treatment is carried out on the pulp obtained from the beating operation as effected on the aforesaid chips, the resulting black liquors being recovered and combined.

As the black liquors useful for the present invention there are contemplated

not only those resulting from semichemical and chemical cooking treatments of annual or multiannual plants, as by-products of the paper and/or cellulose manufacturing, but also the black liquors which are purposely produced from plants or wastes of annual and multiannual plants (such as straws of various nature, canes, etc.) saw mill wastes, vine-shoots, sawdusts and generally wood flours.

In the latter case these raw materials are chemically attacked with either acid or basic solutions, the chemical attack being effected to get the maximum yield of black liquors, whereas cellulose or hemicellulose, useful too in the paper industry, are obtained as the by-products.

The black liquors are then passed to a concentration plant, comprising two or more stages (depending on the sought concentration degree).

Clearly, the higher is the resulting concentration, the more economical is the use of the resulting black liquors, since the energy consumption for the drying of the treated paper will be lower.

As already mentioned, for the purposes of the invention, a concentration degree of 5% is already sufficient.

However, especially when "fluting" papers are to be treated, it is convenient to bring the concentration of the black liquors to values of 40 to 50%.

The black liquors, as it is evident, are produced in the plants for the manufacturing of chemical or semichemical paper starting from wood.

They can be used again in the same paper mill or even used in paper mills producing "fluting" paper, namely from waste paper pulp. In the latter case, of course, the concentration of the black liquors is brought to at least 35 to 40% for transport saving.

The resulting black liquors, having greater or lesser viscosity and consistence, depending on the concentration degree, are coated onto the paper during its drying step, by means of coating rollers, or of any other suitable device depending on the type of black liquors.

The coating of the paper can take place onto one or both surfaces, or between one sheet and the other in the case of doubled paper, card board or paperboard, by using known coupling, coating and impregnating machines.

It has been further assessed that the addition of alcohols (particularly polivinyl alcohol) even in small percentages of the order of 0.2-0.3% by weight referred to the weight of the paper, to the concentrated black liquors, causes their behaviour, as an additive for the improvement of the basic qualities of the treated paper, to be enhanced.

Lastly it is to be noted that, as already assessed in the filed tests, the vegetal source of the black liquors must be selected as a function of the mainly desired results.

For instance, whereas the black liquors obtained from multiannual plants by semichemical or soda/sulfate cooking mainly give place to an improvement of the crushing strength, those obtained from annual plants (straw and the like) by the same cooking treatments mainly give place to an improvement of the bursting strength, whereby the former shall be more advantageous for the treatment of papers to be used for "medium", whereas the latter shall be useful for the "liners".

Lastly the bisulfphite type cooking of multiannual plants gives black liquors qualitatively increasing the crushing strength and the bursting strength without any of the two improvements substantially prevailing with respect to the other.

There are also a subject of the invention the papers and paperboard when obtained by the process of the present invention since ,the content of wood pulp being the same, show better properties of crushing strength and resistance to moisture.

CLAIMS

1. A process for the manufacturing of paper characterized in that to the paper being dried, having a moisture content not greater than 50%, a surface coating of black liquors, previously concentrated to at least 5%, is applied.
2. A process according to claim 1, characterized in that the ratio between the content of dry material of the paper and the content of dry materials of the black liquors after concentration is of between 50:10 and 92:10.
3. A process according to claim 2, characterized in that said ration is of between 50:10 and 80:50.
4. A process according to claim 1, characterized in that a semichemical paper is treated in order to increase the crushing strength thereof.
5. A process according to claim 1, characterized in that a semichemical paper having a reduced content of wood pulp is treated, the crushing strength being maintained unchanged.
6. A process according to claim 5, characterized in that said semichemical paper has a content of wood pulp not greater than 60%, the remaining part being waste paper pulp.
7. A process according to claim 1, characterized in that paper entirely manufactured from waste paper pulp is treated and said black liquors are previously concentrated to 30-50%.
8. A process according to claim 1 to 7, characterized in that "medium" paper for corrugated paperboard is manufactured.
9. A process according to any of the claims 1 to 7, characterized in that cardboards and paperboards are produced.
10. A process according to claim 1, characterized in that said concentrated black liquors are added with an alcohol.
11. A process according to claim 10, characterized in that said alcohol is polyvinyl alcohol.
12. A process according to claim 1, characterized in that said black liquors are treated with a whitening process.
13. Paper and paperboard, as obtained with the process according to each of the claims 1 to 12.