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(54) **Paper material made from a fibrous pulp of industrial textile waste and exhausted sugarbeet pulp**

(57) A paper material of excellent characteristics is produced from industrial textile waste and exhausted sugarbeet pulp, which, derived from the diffusion extraction of sucrose, is pressed to bring the dry substance to a content of 22-28%, and is stored, in the absence of chemical additives, by inducing anaerobic fermentation. Following treatment in conventional pulping facilities, or in Bi-Vis machines, or in a steam explosion facility, a paper pulp of exhausted beet pulp (2-50%) and industrial waste cellulosic textile fibers is prepared with or without papermaking additives, and the pulp is used in traditional manner to produce paper comparable with that produced using currently used chemical pulp.

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Description

The present invention relates to paper material made from a fibrous pulp of industrial textile waste and exhausted sugarbeet pulp; to a method of industrially producing such a pulp from said waste raw materials; and to a method of preserving the damp exhausted beet pulp used in the fabrication method according to the invention.

Producing paper from textile waste is an ancient process. In fact, up to the seventeenth century, paper was produced almost exclusively from waste linen yarn and fabric glued using protein-based material of various sources.

Since that time, the traditional use of textile waste and the demand for large quantities of paper material has led to the introduction of new techniques based almost exclusively on the use of fibrous materials from a wide range of multi-annual plants, i.e. extensive use of cellulose for paper manufacture. Only a limited amount of poor quality paper and cardboard is still produced using agricultural waste, such as straw, and waste from the cultivation of cotton (linters), especially for producing paper money.

In recent years, however, environmental problems, a shortage of conventional wood fiber, and a surplus of human and animal food products, have led to renewed interest in the use of industrial and agricultural waste as a source of raw material for the paper industry.

The use of agricultural waste in the paper industry is, for example, the object of Czechoslovak Patent n. 174.308 and Italian Industrial Invention Patent Application n. VA93A000020 filed on 20.09.1993. The first proposes using only the cellulose present in beet pulp, which is extracted and added to conventional paper pulp to the amount of roughly 30% by weight; whereas the second proposes using the beet pulp as a whole, to the amount of up to 45% by weight, as an organic filler in conventional paper pulp of wood of various sources. In both methods, however, the material obtained from the beet pulp must be dried before use, thus greatly increasing cost as compared with conventional paper pulp. Moreover, in the case of the Czechoslovak patent, not all the beet pulp is used, thus further increasing production cost by requiring additional pressing, which cannot be performed at the paper mill; and both methods involve using considerable quantities of conventional wood pulp.

It is an object of the present invention to provide a method of producing good quality paper material, designed to overcome the aforementioned drawbacks, and which, in particular, provides for producing paper pulp exclusively from waste materials and at low cost.

According to the present invention, there is provided a method of producing paper material from industrial textile and agricultural waste, characterized by comprising the steps of:

- mixing damp exhausted sugarbeet pulp with waste textile fibers;
- diluting said mixture with water, with or without additives, to obtain a paper pulp compatible with a predetermined paper manufacturing technique; and
- manufacturing said paper material by applying said predetermined paper manufacturing technique to said paper pulp comprising the diluted mixture; said mixture forming the only cellulosic raw material in said paper pulp.

In other words, the present invention is based on the discovery that a fibrous pulp suitable for paper manufacture may be obtained easily and cheaply by mixing waste textile fibers, of acknowledged physical-mechanical properties, directly and in the right proportions with whole exhausted sugarbeet pulp resulting from diffusion extraction of sucrose, providing the exhausted pulp is used in the damp state. In particular, the exhausted beet pulp must contain a minimum of 40-50% by weight of humidity, and use is preferably made of pressed exhausted pulp in which the dry substance is limited to 22-28%, and more preferably 24-26%, of the total weight of the product.

yet a further basis of the present invention is the possibility of preserving the damp exhausted beet pulp for long periods of time to prevent the formation of mold or similar (which would impair and contaminate the raw material) or any chemical or morphological alteration in the solid structure of the pulp (pectins, hemicellulose, cellulose) due to degradation or the use of chemical preservatives.

According to the present invention, the pulp is preserved by inducing lactic fermentation in anaerobic conditions to achieve and maintain in the damp pulp a pH of 4 to 4.5. In this condition, the pulp may even be preserved for over a year, thus enabling it to be stored safely and easily, and to be used as raw material all the year round despite being produced on a strictly seasonal basis. Using damp exhausted pulp also eliminates the drying process, thus greatly reducing production cost as compared with known processes also employing exhausted beet pulp.

To simplify mixing, in view of the widely differing morphological structures of the two components used (textile waste and exhausted beet pulp), the method according to the present invention also comprises the step of conditioning the damp exhausted sugarbeet pulp and waste textile fibers.

According to a first preferred embodiment of the invention, the conditioning step is performed simultaneously with said mixing step, by performing the mixing step in a known Bi-Vis™ machine capable of inducing a high shear rate in the mixed materials, and by operating in an aqueous suspension with a concentration of 2 to 20% by weight of solid substance, and in the presence of a strong base, preferably NaOH, dissolved in water to a concentration of 0.1 to 10 gr/l.

According to an alternative embodiment, said conditioning step is performed prior to said mixing step, by hot treating both the damp exhausted pulp and the waste textile fibers in an autoclave, and instantaneously releasing the pressure. Such a treatment, though used for entirely different materials, is known as "steam explosion".

The autoclave treatment is performed by placing the materials separately inside a respective reactor made of stainless steel or other material resistant to an aggressive acid environment and high temperature, and presenting a large release valve at the bottom; supersaturated steam is then fed into the reactor at 20 to 30 bar pressure to bring the material to within a given temperature range and keep it there for a given length of time; at which point, the pressure is reduced instantaneously to ambient pressure by expelling the steam and materials simultaneously through said valve at the bottom of the reactor used as an autoclave.

More specifically, the waste textile fibers are treated at a temperature of 190 to 230°C for 2 to 10 minutes; whereas the damp exhausted beet pulp is treated less severely, at a temperature of 170 to 200°C for 2 to 6 minutes.

The fiber structure and the supramolecular structure of both the textile fibers and the polysaccharide organic material in the pulp used in the method according to the invention are therefore so modified as to permit mixing using normal paper manufacturing methods. A similar variation in textile fiber structure is also obtained operating simultaneously with the mixing step according to the first embodiment described above, wherein the material for mixing, strongly diluted in soda water, is fed into mixers capable of developing very high shear rates, e.g. Bi-Vis™ machines. These are none other than a mixing channel several meters long and housing two side by side counter-rotating opposite-pitch screws, which provide for simultaneously mixing and feeding the material, fed in by a hopper, to the output end of the channel. With a throughput speed of 2 to 10 kg/h, such machines are capable of developing in the material, as it is being mixed, a very high shear rate, which provides for considerably transforming the textile fibers so that they are fully compatible with the cellulose in the beet pulp.

In both the embodiments described, the "conditioning" to which the materials for mixing are subjected enables any other raw materials, such as conventional wood pulp, to be eliminated, unlike other known processes employing agricultural and/or industrial waste.

The waste cellulosic textile fibers used in the method according to the invention are selected from a group comprising: cotton fibers and waste from the production of cotton or cotton yarn; linen fibers and waste from the production of linen or linen yarn; hemp fibers and waste from the production of hemp or hemp yarn; synthetic cellulosic fibers, particularly waste from the production of viscose yarn; and mixtures thereof. Waste cotton fiber from the manufacture of cotton products is, however, preferred.

At the diluting step, additives compatible with said paper manufacturing technique may be added to the pulp mixture to obtain specific characteristics of the finished paper material. For example, limited amounts (about 2% by weight, calculated on the total weight of dry pulp, i.e. not taking into account the weight of the water) of known cationic starch to improve retention of the fine parts during the paper manufacturing process, and so provide for cleaner waste water from the mill; limited amounts (about 2-20% by weight, calculated on dry pulp) of inorganic fillers, such as calcium carbonate, china clay, etc.; and any other known additive, such as sizing agents, adhesives (synthetic or rosin-based), and bleaching agents may be added to the paper pulp according to the invention.

More specifically, if the paper pulp is to be used for producing "white" paper, e.g. for printing, the method according to the invention also comprises the step of "bleaching" the mixture of beet pulp and fibers, which is preferably done during the mixing step in a Bi-Vis machine, by adding to the mixture 3-5% by weight (calculated on dry pulp only, i.e. without calculating the water) of hydrogen peroxide (or any other non-chlorine-based oxidizing bleaching agent, such as ozone, peracids, etc.), which provides for obtaining an excellent degree of whiteness of 70 to 75% (measured to ISO standards). In addition to being pollutant, chlorine-based bleaching agents may also affect the cellulosic fiber structure of the beet pulp, and are therefore to be avoided.

In general, therefore, the paper pulp obtained using the method according to the invention comprises water, 2 to 50% of beet pulp, and, say, up to 80% of industrial waste cotton fiber or other cellulosic fibers.

The present invention therefore also relates to a paper pulp which may be produced exclusively from cellulosic and fibrous raw materials in the form of industrial waste, characterized by comprising a mixture of 2 to 50% of exhausted sugarbeet pulp, and 88 to 40% of waste textile fibers selected from a group comprising: cotton fibers and waste from the production of cotton or cotton yarn; linen fibers and waste from the production of linen or linen yarn; hemp fibers and waste from the production of hemp or hemp yarn; synthetic fibers, particularly waste from the production of viscose yarn; and mixtures thereof.

The present invention also relates to an ecological paper material, characterized by comprising textile fibers mixed with a cellulosic matrix exclusively comprising exhausted sugarbeet pulp.

The fibrous pulp according to the present invention may be used for producing widely different types of paper, by virtue of featuring a mixture of materials with complementary and synergic structural and morphological characteristics; and the invention also provides for a new ecological, low-energy paper manufacturing method capable of meeting the requirements of leading ecological brands.

The present invention and further characteristics and advantages thereof will now be described in detail and purely by way of example with reference to the following non-limiting practical embodiments.

EXAMPLE 1

Beet pulp preparation and preservation - Sugarbeet pulp from the diffusion extraction of sucrose is partially dehydrated by pressing it to obtain a dry substance content of 22 to 28% (preferably 24 to 26%) by weight. The residual sucrose content may vary from 1.1 to 3% (on average, from 1.5 to 2%) by weight, calculated on dry pulp; the temperature of the pulp just after pressing is about 50°C; and the content of antifermenting products (such as formaldehyde, glutaraldehyde, quaternary ammonium salts, etc.) must not exceed the normal amount remaining in exhausted pulp following normal antiseptic diffusion treatment.

After regulating the composition, the damp exhausted beet pulp is ensiled anaerobically. Three different ensiling methods were experimented, all of which gave more or less the same results: conventional "trench" and "concrete platform" methods; and a new method limited so far to the conservation of forage, and wherein the damp exhausted pulp is placed inside cylindrical plastic bags of about 2.5 m in diameter, about 30 m long, and made of synthetic acid-resistant material of low oxygen permeability and good mechanical characteristics; the pulp is tamped into the bags by a special machine; and the bag is sealed hermetically and left resting directly on the ground with no flooring.

In all cases, and with no need for inoculum, ensiling results in anaerobic lactic fermentation of the damp pulp, wherein the remaining sugar in the pulp is mainly converted into lactic acid to lower the pH to about 4 and, on average, to 3.8 to 4.1. Such pH values provide for preserving the solid structure of the pulp (pectins, hemicellulose, cellulose) intact and so preventing the formation and/or development of mold and yeast which might destroy the structure of the pulp. To achieve this, the pH value must in no case exceed 4.5.

The pressed ensiled pulp with correct lactic fermentation presents the following average composition:

dry substance	25-27	% of total weight
raw fiber	21-22	% of total weight
pH	3.8-4.1	
lactic acid	5.0-5.5	% by weight of dry pulp
acetic acid	1-2	% by weight of dry pulp
propionic acid	<0.01	% by weight of dry pulp
L-butyric acid	<0.01	% by weight of dry pulp
n-butyric acid	<0.01	% by weight of dry pulp
valeric acid	<0.01	% by weight of dry pulp
ethanol	0.1-0.20	% by weight of dry pulp

In the above conditions, the damp pulp is preserved perfectly for long periods, even for over a year.

The preservation method according to the invention was also tested, and gave the same results, using cold pressed exhausted pulp (at ambient temperature of, on average, 10 to 25°C). In this case, however, the sucrose content must be controlled and, if necessary, integrated to keep it at least equal to 1.5-2% by weight of dry pulp. If below this value, a sufficient amount of sugar, usually molasses, is added to the pulp, or *Lactobacillus delbrückii* is inoculated to reach the above value.

Since oxygen encourages the formation of mold and yeast, anaerobic conditions must be guaranteed during ensilage. For this reason, the third method described above, using plastic bags, is preferable, and also presents the added advantages of ensuring the pulp is tightly packed, thus assisting fermentation, and of reducing storage cost by requiring no building work.

EXAMPLE 2

Paper production using the Bi-Vis method - Cotton waste and waste from other industrial textile processes (spinning, weaving, manufacture) are mixed - as they are or carded beforehand - with exhausted beet pulp preserved damp as in Example 1. Mixing is performed initially in a normal pulper equipped with a screw mixer, and in the presence of an aqueous solution of NaOH with a concentration of 4% by weight of dry pulp. The mixture, diluted with water to a concentration of 2% by weight of dry pulp, is then fed at the rate of 7 kg/h into a standard semiindustrial Bi-Vis™ facility. After adding standard additives (8% by weight, calculated on dry pulp, of calcium carbonate, and 2% by weight, calculated on dry pulp, of cationic starch), the resulting pulp is subjected to a conventional paper die cycle using a standard Britannico sheet forming facility. The paper die cycle comprises: dispersion in water, addition of additives, mixing, cloth

draining, damp pressing, and drying on a plate heated to 105°C, at the end of which, the paper sheet presents a residual humidity of 5-10% by weight.

The sheets of different substance so formed are then conditioned in a conditioned chamber maintained at a temperature of 23°C and 50% relative humidity, and then subjected to mechanical and technological testing to ISO/UNI standards.

The results are shown in comparison Table 1.

As can be seen, the values relative to the sheets produced from the pulp according to the invention are comparable with the normal values of paper produced from conventional chemical pulp with a cellulosic content derived entirely from wood. Moreover, the pulp containing absolutely no beet pulp results in paper of slightly poorer properties, and above all with excessively high permeability values.

TABLE 1

PULP PROPERTIES	IR	IRB1	IRB2	IRB3
Waste cotton (% by weight)	90	80	75	60
Beet pulp (% by weight)	0	10	15	30
Cationic starch (% by weight)	2	2	2	2
Calcium carbonate (% by weight)	8	8	8	8
Freeness (SR)	33	32	37	45
SHEET PROPERTIES (1)				
Permeability (sec.)	42	148	150	202
Apparent consistency (kg/m ³)	468	492	501	525
Tear length (km)	3.82	3.85	4.21	4.06
Stretch (%)	2.90	2.97	2.50	2.43
Tear energy (J/kg)	376	384	371	365
Tear resistance (Nm ² /kg)	13.58	12.25	10.15	9.43
CMT (2) (N)	142	157	159	171
SCT (3) (kN/m)	2.43	2.46	2.63	2.77
Ash (% by weight)	4.83	4.92	5.12	5.19

(1) Measured using sheets of about 70 g/m² if not otherwise stated.

(2) CMT = Concora Medium Test: resistance to plane compression of laboratory undulated paper of about 120 g/m²

(3) SCT = Short-span Compression Test: resistance to short-span compression of sheets of about 120 g/m².

EXAMPLE 3

Paper production using the steam explosion method -Waste cotton of the same type as in Example 2 is first steam explosion treated in a pilot facility. Supersaturated steam is used, and the cotton fibers maintained at a temperature of 210°C for about 4 minutes. The beet pulp in Example 1 is pretreated in the same facility at a lower temperature (170°C) for 2 minutes. The fibrous material so formed is mixed in varying proportions (% by weight) in the Example 2 pulper, and, operating as in Example 2, is subjected to a standard paper die cycle to produce 200 cm² sheets using the same facility as in Example 2.

The physical-mechanical characteristics (measured to ISO standards) are shown in Table 2 and, as can be seen, are fully comparable with those of Example 2.

TABLE 2

PULP PROPERTIES	IR	IRB1	IRB2	IRB3
Waste cotton (% by weight)	90	80	75	60
Beet pulp (% by weight)	0	10	15	30
Cationic starch (% by weight)	2	2	2	2
Calcium carbonate (% by weight)	8	8	8	8
Freeness (SR)	29	29	32	43
SHEET PROPERTIES (1)				
Permeability (sec.)	54	166	185	238
Apparent consistency (kg/m ³)	512	566	576	624
Tear length (km)	3.51	3.55	3.76	4.16
Stretch (%)	2.01	2.07	2.90	2.78
Tear energy (J/kg)	257	268	316	275
Tear resistance (Nm ² /kg)	12.43	11.15	10.61	9.22
CMT (2) (N)	154	161	178	202
SCT (3) (kN/m)	2.85	2.91	3.41	3.92
Ash (% by weight)	4.64	4.62	4.85	5.31

(1) As for Table 1

(2) CMT = as for Table 1

(3) SCT = as for Table 1

EXAMPLE 4

Operating in the same way as in Example 2, white 200 cm² sheets of paper are produced by adding to the mixture, as it is mixed in a Bi-Vis™ machine, from 3 to 5% by weight, calculated on dry pulp (odp), of 12-volume hydrogen peroxide. The physical-mechanical properties are the same as in Table 1. In addition, the degree of whiteness of the finished paper is assessed to ISO standards and found to range from 70 to 75%, which is more than enough to enable the paper according to the invention, and with the addition of normal bleaching agents, to be used in applications requiring a high degree of whiteness (writing and printing paper, etc.).

Claims

1. A method of producing paper material from industrial textile and agricultural waste, characterized by comprising the steps of:
 - mixing damp exhausted sugarbeet pulp with waste textile fibers;
 - diluting said mixture with water to obtain a paper pulp compatible with a predetermined paper manufacturing technique; and
 - manufacturing said paper material by applying said predetermined paper manufacturing technique to said paper pulp comprising the diluted mixture; said mixture forming the only cellulosic raw material in said paper pulp.
2. A method as claimed in Claim 1, characterized in that, in the course of said diluting step, respective additives compatible with said paper manufacturing technique are added to said mixture from which to prepare said pulp to achieve specific characteristics of the finished paper material.

3. A method as claimed in Claim 1 or 2, characterized by also comprising a conditioning step for conditioning said damp exhausted sugarbeet pulp and said waste textile fibers, to assist the mixing of the waste textile fibers with the exhausted pulp.
- 5 4. A method as claimed in Claim 3, characterized in that said conditioning step is performed simultaneously with said mixing step, by performing the mixing step in a Bi-Vis type machine capable of inducing a high shear rate in the mixed materials, and by operating in an aqueous suspension with a concentration of 2 to 20% by weight of solid substance, and in the presence of a strong base dissolved in water to a concentration of 0.1 to 10 gr/l.
- 10 5. A method as claimed in Claim 3, characterized in that said conditioning step is performed prior to said mixing step, by hot treating both the damp exhausted pulp and the waste textile fibers in an autoclave, and instantaneously releasing the pressure.
- 15 6. A method as claimed in Claim 5, characterized in that said autoclave treatment is performed by placing the materials for treatment separately inside a respective reactor, feeding supersaturated steam into the reactor at 20 to 30 bar pressure to bring the material to within a given temperature range, keeping the material within said given temperature range for a given length of time, and then instantaneously reducing the pressure to ambient pressure by expelling the steam and materials simultaneously from the reactor.
- 20 7. A method as claimed in Claim 6, characterized in that said waste textile fibers are treated at a temperature of 190 to 230°C for 2 to 10 minutes.
8. A method as claimed in Claim 6, characterized in that said damp exhausted sugarbeet pulp is treated at a temperature of 170 to 200°C for 2 to 6 minutes.
- 25 9. A method as claimed in any one of the foregoing Claims, characterized in that said waste textile fibers are selected from a group comprising: cotton fibers and waste from the production of cotton or cotton yarn; linen fibers and waste from the production of linen or linen yarn; hemp fibers and waste from the production of hemp or hemp yarn; synthetic cellulosic fibers, particularly waste from the production of viscose yarn; and mixtures thereof.
- 30 10. A method as claimed in any one of the foregoing Claims characterized in that said paper pulp comprises water, soda, 2 to 50% of beet pulp, and, for the remainder, industrial waste cotton fiber.
- 35 11. A method as claimed in any one of the foregoing Claims characterized in that said damp exhausted beet pulp is derived from the diffusion extraction of sucrose, is pressed to obtain a dry substance content of 22 to 28% by weight of the total weight of damp pulp, and is stored in the absence of chemical additives pending the mixing step, by inducing lactic fermentation in the damp pulp in anaerobic conditions, to achieve and maintain a pH of the damp pulp of 4 to 4.5.
- 40 12. A method as claimed in any one of the foregoing Claims, characterized by comprising a "bleaching" step for "bleaching" the mixture of beet pulp and fibers; said "bleaching" step comprising adding to the mixture from 3 to 5% by weight, calculated on the dry substance only, of a non-chlorine-based oxidizing agent; said oxidizing agent preferably being hydrogen peroxide or ozone.
- 45 13. A paper pulp which may be produced exclusively from cellulosic and fibrous raw materials in the form of industrial waste; characterized by comprising 2 to 50% of exhausted sugarbeet pulp mixed with waste textile fibers selected from a group comprising: cotton fibers and waste from the production of cotton or cotton yarn; linen fibers and waste from the production of linen or linen yarn; hemp fibers and waste from the production of hemp or hemp yarn; synthetic fibers, particularly waste from the production of viscose yarn; and mixtures thereof.
- 50 14. A paper pulp as claimed in Claim 13, characterized in that the content of textile fibers in said mixture of exhausted beet pulp and textile fibers is such that the paper pulp contains up to 80% by weight of textile fibers.
- 55 15. An ecological paper material, characterized by comprising textile fibers mixed with a cellulosic matrix exclusively comprising exhausted sugarbeet pulp.
16. An ecological paper material producible from industrial waste, characterized by being produced using a method as claimed in any one of the foregoing Claims from 1 to 12.

17. An ecological paper material producible from industrial waste, characterized by being produced from a paper pulp as claimed in Claim 13 or 14.

18. A method of preserving, without additives, exhausted sugarbeet pulp derived from the diffusion extraction of sucrose; the method comprising: a step wherein the humidity and sugar content of said pulp is regulated by bringing the content of dry substances of the pulp to 22 to 28% by weight, and the sugar content to at least 1.5 to 2% by weight, calculated on the dry pulp; and a step wherein anaerobic lactic fermentation is induced in said pulp to bring the pH of the pulp to 4 to 4.5.

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