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**Trichet**(10) **Pub. No.: US 2005/0155729 A1**(43) **Pub. Date: Jul. 21, 2005**(54) **METHOD FOR OZONE TREATMENT OF  
USED PAPER**(30) **Foreign Application Priority Data**

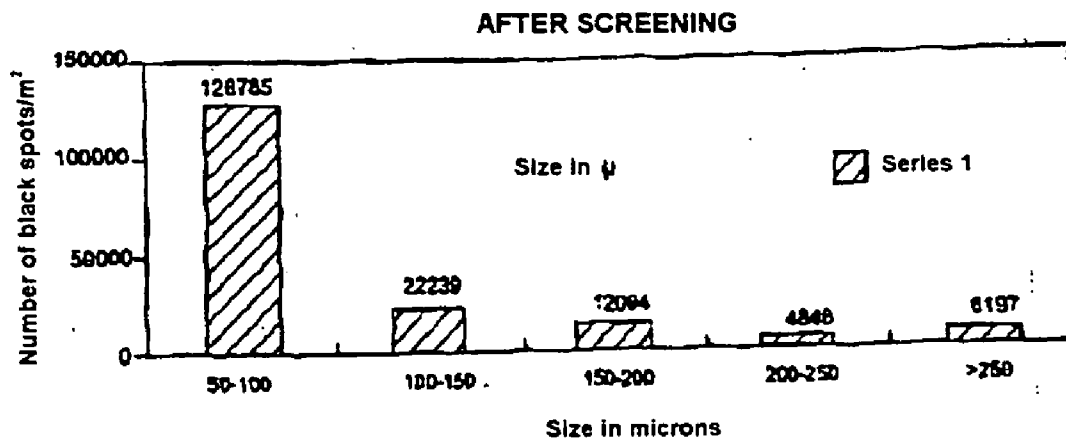
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(76) **Inventor: Alain Trichet, Montelier (FR)****Publication Classification**

Correspondence Address:

**Air Liquide****Intellectual Property Department****Suite1800****2700 Post Oak Boulevard****Houston, TX 77056 (US)**(51) **Int. Cl.<sup>7</sup> ..... D21B 1/32; D21C 5/02**(52) **U.S. Cl. .... 162/4; 162/6; 162/7; 162/8;  
162/55**(57) **ABSTRACT**

The invention concerns a novel method for ozone treatment of used paper which consists in transforming used paper into pulp in an aqueous medium, screening then de-inking said paper by liquid flotation, the method further comprising an ozone treatment step carried out at latest prior to the liquid flotation step.

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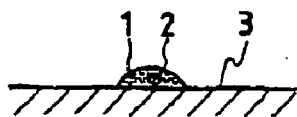


FIG. 1

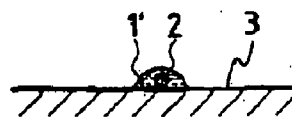


FIG. 2  
PRIOR ART

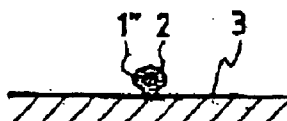


FIG. 3

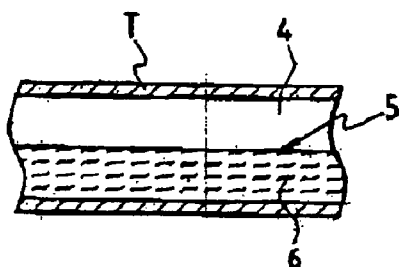


FIG. 4

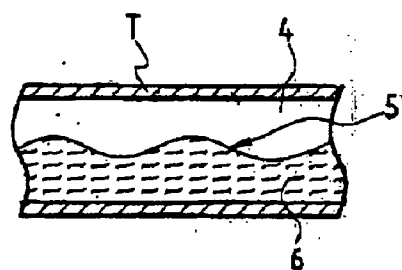


FIG. 5

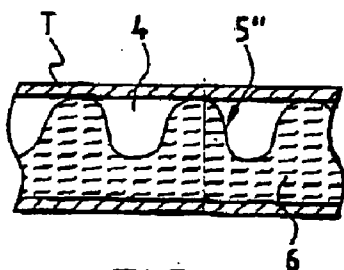


FIG. 6

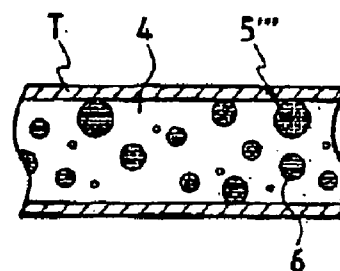
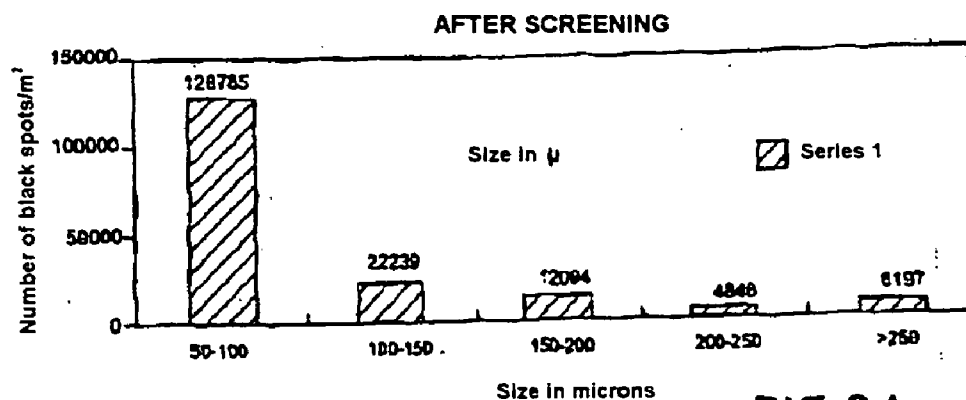
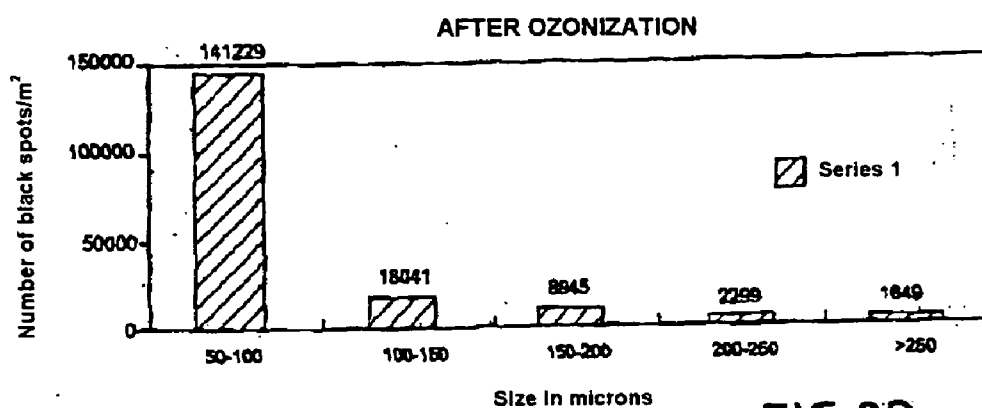


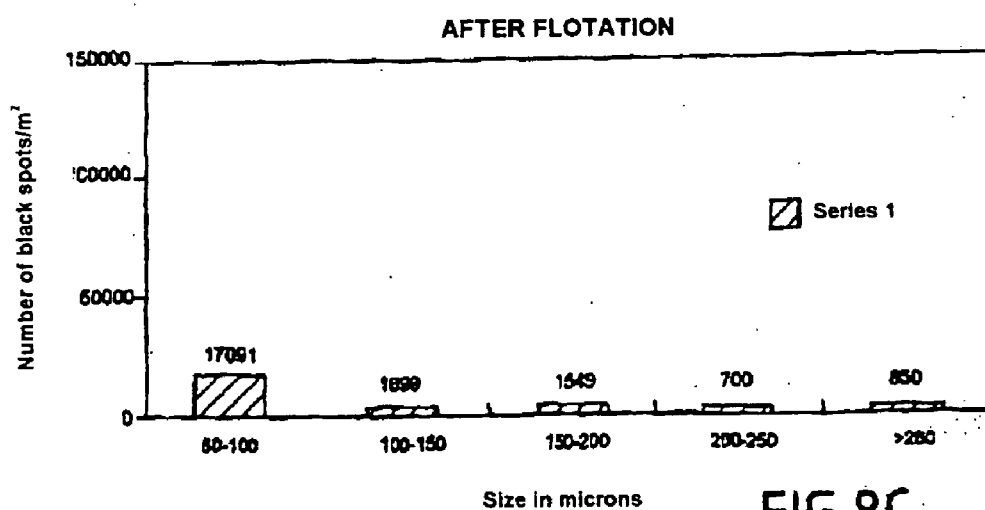
FIG. 7



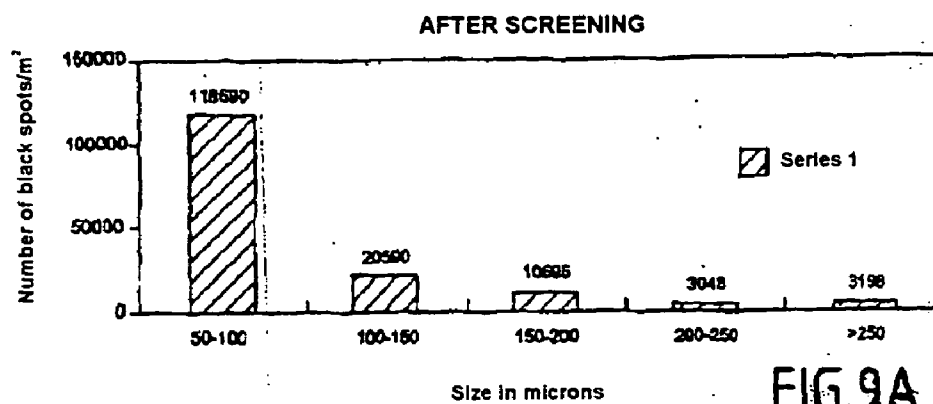
**FIG.8A**



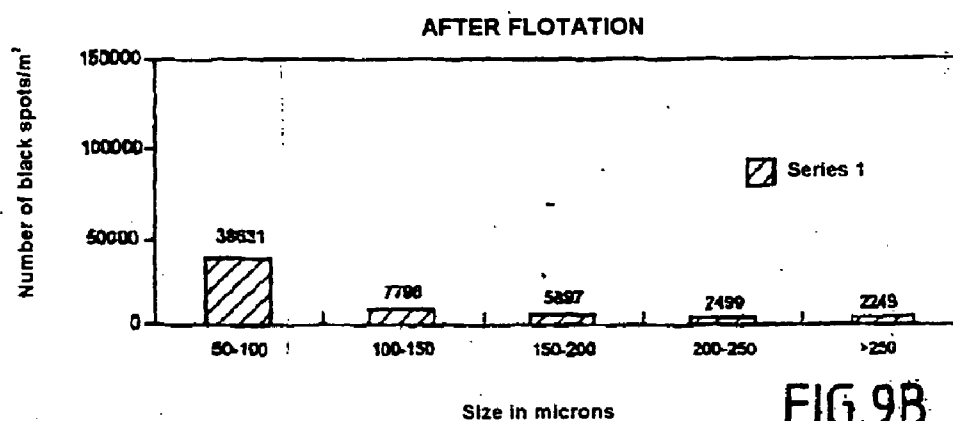
**FIG.8B**



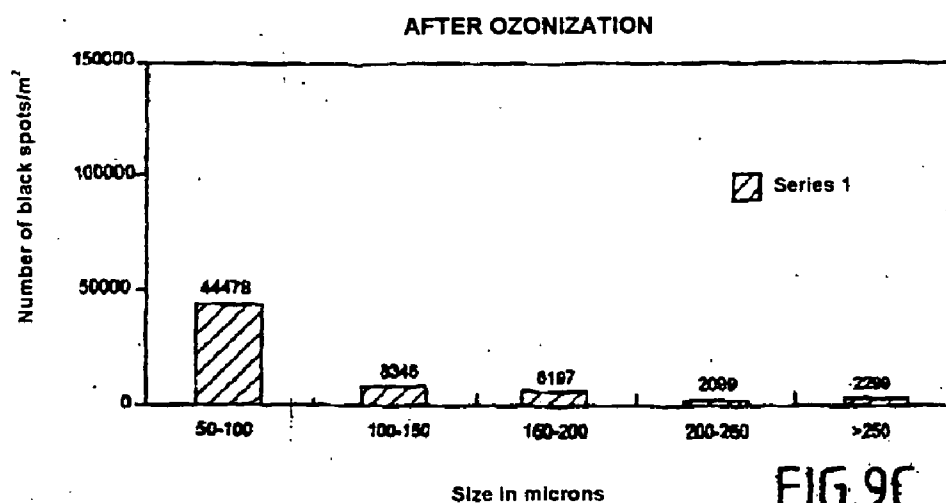
**FIG.8C**



**FIG. 9A**



**FIG. 9B**



**FIG. 9C**

## METHOD FOR OZONE TREATMENT OF USED PAPER

[0001] The invention relates to a method for treating used paper.

[0002] There is a strong world demand today for recycling used paper, in particular to limit deforestation. Used paper is recovered and treated to produce new paper sheets or new paper or cardboard packaging materials, for example.

[0003] The present method for treating used paper for the recycling thereof begins with pulping of the paper recovered for recycling.

[0004] This pulp is screened one or more times to remove the coarse particles such as paperclips, staples, coarse ink particles, etc.

[0005] This is followed by one or a plurality of flotation steps to further complete the removal of the ink which served to print the waste paper.

[0006] In fact, used paper is generally printed. The printing ink consists of organic or inorganic dyes and organic binders which, on drying, imprison the dye particles and maintain them on the paper.

[0007] Moreover, used paper is often coated with glues or adhesives, for example binding glues and adhesives for sealing envelopes.

[0008] Used paper is also soiled, by food and other materials; the pulp obtained therefore contains microorganisms such as bacteria, fungi, yeasts, and enzymes such as the enzyme catalase.

[0009] To permit waste paper recycling, all the foreign bodies must be removed, such as paperclips, staples, traces of food and other materials, as well as the printing ink and glues and adhesives, and the microorganisms and, in particular, catalase enzyme, because the latter pollute the circuits of the installation in which the paper is treated.

[0010] For this purpose, at the present time, various chemicals are added during or immediately after the paper is pulped. This serves to improve the results of the various steps.

[0011] Caustic soda is introduced in particular to swell the paper fibers and to permit a better separation of the solids. Hydrogen peroxide and/or oxidizing chlorine products are also added to destroy the microorganisms and to improve deinking. Chelating agents, such as sodium silicate, of which the action mechanism is poorly known, are also added to further facilitate deinking. They form complexes with the binders and dyes which are then more easily removed.

[0012] Hydrogen peroxide and/or chlorine products have the function not only of destroying the microorganisms present in the pulp but also of purifying the circuits of the installation. However, since hydrogen peroxide is destroyed by the catalase enzyme present in the pulp, this causes high overconsumption of this compound during bleaching.

[0013] Once these pulping, screening and flotation steps have been completed, very fine particles of ink may still remain in the pulp.

[0014] A series of mixings is accordingly carried out, followed by flotations of the pulp, to remove the fine ink

particles mechanically or at least to coat them in the mass of the pulp in order to obtain a uniform "whiteness".

[0015] Used paper to be recycled generally consists of a mixture of papers of different types: newspapers, lined papers, magazines or higher grade papers.

[0016] The differences in quality of the papers mean that, once the preceding treatment steps have been completed, the paper pulp obtained may yield a paper of which the "whiteness" may not be satisfactory for its final use.

[0017] In this case, the pulp obtained can be subjected to a bleaching step. This bleaching step is carried out, as for new paper pulps, by treatment with oxidants such as hydrogen peroxide or chlorine products, or with reducing agents such as sodium dithionite.

[0018] Used paper may also contain paper that has been treated with optical brighteners (optical brighteners are fluorescent compounds that make the paper appear whiter via an optical mechanism), and these fluorescent compounds have been suspected of being carcinogenic; it may therefore be desirable to proceed with a defluorescence of the pulp, and, here also, hydrogen peroxide is used.

[0019] The pulp is then converted into paper sheets by known methods.

[0020] It is known that ozone has been used for treating used paper. However, ozone treatments are performed after the flotation steps, that is during the subsequent bleaching and defluorescence steps. Moreover, ozone is always used as a supplement to other chemicals, that is hydrogen peroxide, chlorine products, caustic soda, and the chelating agents already present in the method.

[0021] The method of the prior art, in these different variants, has a number of drawbacks.

[0022] Firstly, this method is highly pollutant because of the many chemicals used, which are found in the effluents discharged by the used paper treatment plants.

[0023] Moreover, this process incurs high overconsumption of hydrogen peroxide due to the presence of catalase enzyme, and sometimes of metals, which degrade the hydrogen peroxide.

[0024] Finally, the flotation step for deinking purposes may not be sufficient and, as it has been observed, it then becomes necessary to carry out a plurality of mixing steps followed by flotation steps to complete the deinking.

[0025] It is necessary here to emphasize the distinction between: the deinking step, which is aimed at removing the printing ink present on the used paper to be treated and serves to obtain a corresponding whiteness close to that of the original paper and the actual bleaching step, which is practised both on pulps produced from used paper and on new paper pulps, that is obtained directly from cellulose. The bleaching as such consists in removing the lignin present in the pulp (new or recycled). The deinking step is unnecessary in the case of new paper pulps.

[0026] It is an object of the invention to overcome the drawbacks of the method of the prior art by proposing a method for treating used paper that serves to reduce or indeed eliminate the overconsumption of hydrogen peroxide and to improve deinking. This allows for a shorter treatment

method comprising fewer or no mixing steps, followed by flotation steps aimed at completing the deinking.

[0027] In a variant, the invention further proposes a method for treating waste paper which serves to significantly reduce the pollution of the effluents discharged by the treatment plants.

[0028] For this purpose, the invention proposes a method for treating used paper of the type comprising the successive steps of: a) pulping of the used paper in an aqueous medium, b) at least one screening to remove coarse particles, c) at least one flotation to deink the pulp, characterized in that it further comprises an ozonization step d) carried out at the latest before the flotation step c).

[0029] Advantageously, the ozonization step d) is carried out at a used-paper pulp consistency of between 0.5 and 5%.

[0030] Preferably, the ozonization step d) is carried out at a used-paper pulp consistency of 0.5 to 3%.

[0031] According to a preferred embodiment of the method of the invention, the steps a), b), c) and d) are carried out in water, without the addition of chemicals other than ozone in step d).

[0032] According to another embodiment of the method according to the invention, the steps a), b), c) and d) are carried out in the presence of caustic soda, hydrogen peroxide and/or chlorine products, sodium silicate and/or chelating agents.

[0033] In these two embodiments, the step d) is preferably carried out after the screening step b).

[0034] Advantageously, the ozonization step d) is carried out in a two-phase tubular contactor of the gas-liquid type.

[0035] In this case, according to a first variant, the ozonization step d) is carried out in the tubular contactor operating in wave mode.

[0036] According to a second variant, the ozonization step d) is carried out in the tubular contactor operating in plug mode.

[0037] Preferably, the ozonization step d) is carried out with an air-ozone or oxygen-ozone gas mixture comprising between 50 and 200 g of ozone per m<sup>3</sup> of gas mixture.

[0038] Advantageously, the ozonization step d) is carried out in a two-phase gas-liquid tubular contactor in which the ozone is introduced in the form of an air-ozone or oxygen-ozone gas mixture at a rate above 0.5 m/s and less than or equal to 10 m/s while the used-paper pulp is introduced at a rate above 0.5 m/s and less than or equal to 10 m/s.

[0039] However, most advantageously, the ozonization step d) is carried out in a two-phase tubular contactor in which the ozone is introduced in the form of an air-ozone or oxygen-ozone gas mixture at a rate between 0.5 and 2 m/s while the used-paper pulp is introduced at a rate between 0.5 and 2 m/s.

[0040] The invention will be better understood and other details, advantages and features thereof will appear more clearly from a reading of the description that follows, made with reference to the figures appended hereto in which:

[0041] FIG. 1 shows an enlarged view of a particle of printing ink bonded to the surface of a used paper,

[0042] FIG. 2 shows an enlarged view of the ink particle of FIG. 1, on the same scale, after the deinking step of the prior art method,

[0043] FIG. 3 shows an enlarged view of the ink particle of FIG. 1, on the same scale, after the deinking step of the method of the invention,

[0044] FIG. 4 shows a cross section of a two-phase gas-liquid tubular contactor in segregated mode,

[0045] FIG. 5 shows a cross section of a two-phase liquid-gas tubular contactor in wave mode,

[0046] FIG. 6 shows a cross section of a two-phase gas-liquid tubular contactor in plug mode,

[0047] FIG. 7 shows a cross section of a two-phase gas-liquid tubular contactor in dispersed bubble mode,

[0048] FIG. 8 shows, in the form of bar graphs, the number of points of ink remaining, as a function of their size, in a used-paper pulp after the screening step (FIG. 8A), the ozonization step (FIG. 8B), and the flotation step (FIG. 8C), according to a first embodiment of the method of the invention, and

[0049] FIG. 9 shows, in the form of bar graphs, the number and size of the points of ink remaining in a used-paper pulp after the screening step (FIG. 9A), the flotation step (FIG. 9B) and the ozonization step (FIG. 9C), carried out according to the prior art method.

[0050] The method for treating used paper to be recycled according to the invention comprises, like the method for treating used paper of the prior art, a step of pulping of the mass of paper to be recycled in an aqueous medium. The pulp then undergoes a plurality of solid-solid separation steps in order to remove the undesirable elements such as paperclips, staples and coarse ink particles.

[0051] For this purpose, at least one screening step is carried out.

[0052] This is followed by one or a plurality of flotation steps in order to remove the very fine ink particles.

[0053] In the prior art method, these steps are put into practice in an aqueous medium in the presence of caustic soda to adjust the pH and to swell the paper fibers in order to permit an easier detachment of the ink particles and other impurities, in the presence of hydrogen peroxide and/or sodium hypochlorite in order to facilitate removal of the ink particles, eliminate the microorganisms, such as bacteria, fungi and yeasts, as well as the enzymes such as catalase enzyme, so as to clean up not only the pulp itself but also the circuits of the installation in which the method is put into practice. Chelating agents such as sodium silicate are also added to complex the metals, originating for example from the dyes of the printing inks, in order to be able to subsequently remove them with hydrogen peroxide or the chlorine products already mentioned. Any other chemical may be added, as known in the art.

[0054] The method for treating used paper of the invention differs from the method of the prior art in that, at the latest before the flotation steps, the paper pulp is subjected to an ozonization step.

[0055] This ozonization step serves to improve the effectiveness of the flotation steps for deinking the paper pulp and, moreover, it destroys the microorganisms and, above all, the catalase enzyme.

[0056] Thus, by making the deinking step by flotation more effective, the number and duration of the subsequent treatment steps intended to further complete the deinking, for example by carrying out a series of mixings followed by flotations, are reduced in comparison with the prior art or indeed eliminated.

[0057] Furthermore, since ozone destroys the catalase enzyme which reduces the activity of the hydrogen peroxide, this eliminates the overconsumption of hydrogen peroxide in the event that the hydrogen peroxide treatment step is maintained.

[0058] The high reactivity of ozone enables it to degrade the unsaturated products with which the waste paper is impregnated.

[0059] The following products are thereby found, rich in unsaturated and aromatic groups:

[0060] dyes, particularly printing inks,

[0061] optical brighteners to improve the whiteness of the paper,

[0062] glues, commonly called "stickies" in the art, which are present, for example, as glue for binding, for example, of the reams of paper, or as an adhesive for envelopes, and

[0063] binders of the inks which serve to fix the printing dyes on the paper, when the paper is dried.

[0064] All these products are easily degraded by ozone in aqueous medium or in another solvent.

[0065] Although the most important unsaturated product in the products to be treated is usually the lignin in different forms, it is important to note here that the ozone used in the method of the invention is used to react with the unsaturated products impregnating the used paper and less with the lignin present, because the latter is "coated" by these products and others such as mineral fillers.

[0066] The destruction by ozone of these products impregnated on the surface of the fibers automatically causes changes in the wettability properties of the paper fibers. This gives rise to substantial modifications during the flotation of the inks and fillers.

[0067] In fact, in the liquid state, printing inks consist of particles of carbon or another dye dispersed in a liquid binder. When the binder dries, it coats the carbon particles and other particles and fixes them to the surface of the paper sheet.

[0068] FIG. 1 shows an enlarged cross section of a particle of dried printing ink on the paper surface. The carbon particle 2 is enveloped and bonded to the paper surface 3 by the dried binder 1.

[0069] FIG. 2 shows a cross section of the ink particle of FIG. 1, on the same scale, after the pulping, screening and flotation steps according to the prior art method. As may be observed in FIG. 2, the carbon particle 2 is still coated and bonded to the paper surface 3 by the binder 1' which has decreased in thickness.

[0070] Thus, in the prior art, it is necessary to separate, by mechanical action, that is by mixing, the binder 1' from the paper surface 3 to release the carbon particle 2, and then

carry out a flotation step to remove the particles of binder and carbon from the paper pulp.

[0071] When the method according to the invention is applied, that is when the ozonization step has been put into practice before the flotation step, fewer particles of ink remain adhering to the paper surface. However, if one considers the ink particles which still adhere to the paper surface, for each of these ink particles, as shown in FIG. 3, which is a cross section of the same ink particle as the one shown in FIG. 1, on the same scale, but after the flotation steps for deinking according to the method of the invention, the binder 1" is more strongly degraded and coats the carbon particle 2 "less well".

[0072] The mechanical action necessary to detach this ink particle 2 from the paper surface 3 is less than that required to separate the ink particle 2 shown in FIG. 2. The number of mixing-flotation steps necessary to completely deink the paper to be recycled according to the method of the invention is smaller.

[0073] Furthermore, the ozone destroys the microorganisms and, above all, the catalase enzyme. Since catalase enzyme destroys the activity of the hydrogen peroxide used in the prior art method, this allows a more effective use of the hydrogen peroxide. Its overconsumption is decreased, and it can even be eliminated for certain end uses of the paper.

[0074] The ozone also serves to clean up the circuits of the installation to which the method for treating used paper is put into practice.

[0075] It has also been discovered surprisingly that the ozone can be used without adding any of the reagents commonly used in the prior art method.

[0076] The method of the invention, in a particularly advantageous embodiment, hence consists in pulping the mass of paper to be recycled, in water, in proceeding with the solid-solid separation steps by screening followed by the flotation steps, always exclusively in water and without the addition of any reagent, provided that an ozonization step is put into practice at the latest before the flotation steps.

[0077] This method, which uses ozone only without other chemical reagents, offers considerable advantages, its simplicity and its economy, and, furthermore, it is a method for treating used paper from which the effluents have a very low level of pollution.

[0078] In the two embodiments of the method of the invention, the ozonization step must be carried out at the latest before the flotation step for deinking. It can be carried out before, during or just after the pulping step or after the screening step.

[0079] Preferably, it is carried out after the screening step in order to permit good contact between the ozone and the pulp to be treated, for greater effectiveness of the ozone; the coarse particles and undesirable elements can be removed easily by the screening, and the ozone is therefore used more efficiently and without overconsumption to remove the fine ink particles, purify the installation circuits and/or react with certain additives.

[0080] The effectiveness and extent of the degradation of the products to be removed in the used paper for the same

contact time depend on the extent and effectiveness of the contacting of the ozone with the products to be degraded. In other words, the effectiveness of the ozonization reaction depends on the rate of dissolution of the ozone in the pulp.

[0081] As previously stated, ozone has already been used in methods for producing paper pulps to bleach virgin pulps. At the present time, these ozonization methods take place at a solids concentration between 8 and 40 g of solids per 100 g of pulp.

[0082] The paper pulps are treated as a liquid medium, generally an aqueous medium, in which the solid particles are in suspension.

[0083] The ozonization reaction therefore produces a situation of a two-phase mixture: a gas phase and a liquid phase containing solids. Since the chemical ozonization reaction is fast, it is necessary to have a very rapid gas dissolution rate in the liquid phase containing the solids so that the ozone reacts with the solids.

[0084] When operating at atmospheric pressure, because of the high solids concentration of the pulp and the high reactivity of the ozone, risks of heterogeneous treatment exist. In order to increase the dissolution rate of the ozone in the liquid-solid phase, another method accordingly proposes to carry out the ozonization reaction under pressure in units of the centrifugal pump type, which requires compressing the ozone.

[0085] This raises problems already discussed, that is the fact that the paper fiber is subjected to high mechanical stresses which can damage it, and the need to compress the ozone, which entails the use of compressors which are costly to purchase and maintain.

[0086] It has now been discovered that all these drawbacks are overcome by carrying out the ozonization step on paper pulps with low or very low consistencies.

[0087] In the above discussion and in what follows, the expression "low consistency paper pulp" means a paper pulp in which the paper concentration is between 0.5 and 5% by weight of the total weight of the pulp.

[0088] In the above discussion and in what follows, the expression "very low consistency paper pulp" means a paper pulp in which the paper concentration is about 1% by weight of the total weight of the pulp. For such pulps, it is possible to use two-phase gas-liquid tubular contactors which serve to obtain very high gas dissolution rates in the paper pulp.

[0089] The invention proposes to put the ozonization step into practice in a two-phase tubular contactor of the gas-liquid type and to introduce the paper pulp at low or very low consistency.

[0090] The tubular contactor for putting into practice the method of the invention can be a horizontal or vertical tubular contactor operating in cocurrent flow of the liquid phase containing the solids.

[0091] The gas can be introduced via a simple pipe or via a more sophisticated system, for example a static mixer.

[0092] The ozone dissolution rate in the paper pulp depends on the gas-liquid mass transfer coefficients and, more particularly, on the interfacial area between the two phases.

[0093] The aim here is to obtain a good gas-pulp emulsion.

[0094] Depending on the respective rates of introduction of the gas and the pulp, the reactor will operate in segregated mode, in wave mode, in plug mode or in dispersed bubble mode.

[0095] FIG. 4 shows a cross section of a horizontal tubular contactor T operating in segregated mode in which the gas phase has the numeral 4 and the pulp has the numeral 6. In FIG. 4, the interfacial area is shown by the contact surface 5 between the gas phase 4 and the pulp 6.

[0096] This contact surface 5, when the tubular contactor T is in segregated mode, as shown in FIG. 4, can be treated as a plane surface.

[0097] In this case, the interfacial area corresponding to the contact surface 5 is smaller than in the cases shown in FIGS. 5 to 7, which are discussed below. For this reason, the ozone dissolution rate is less favorable.

[0098] Such a segregated mode is obtained when the respective rates of introduction of the gas phase and the pulp are lower than 1 m/s, more particularly higher than 0.5 m/s and lower than 1 m/s.

[0099] The contact surface between the gas phase and the liquid phase containing solids is improved when the contactor T operates in wave mode, as shown in FIG. 5.

[0100] As may be observed in FIG. 5, the contact surface with the numeral 5' between the gas phase 4 and the pulp forms waves. It is increased in this domain. Hence the gas is dissolved more rapidly in this case than in the case shown in FIG. 4, that is in segregated mode.

[0101] The ozone dissolution rate, and hence the reaction rate of the ozone with the pulp, is further improved when, as shown in FIG. 6, the tubular contactor T operates in plug mode. As may be observed in FIG. 6, when the tubular contactor T operates in plug mode, the pulp 6 is actuated with a movement which makes it touch the two inside horizontal walls of the contactor.

[0102] The gas phase 4 therefore has a large contact surface with the numeral 5" for contact with the pulp 6 when the contactor operates in such a plug mode.

[0103] The contactor T operates in wave mode or in plug mode when the respective gas phase and pulp introduction rates are between 1 and 2 m/s.

[0104] The best results are obtained when the contactor is in dispersed bubble flow mode, as shown in FIG. 7. In this case, the pulp 6 forms bubbles which are dispersed in the gas phase 1 and the contact surface 5''' for contact between the gas phase 4 and the pulp 6 is very large.

[0105] Such a dispersed bubble mode is obtained for respective gas and pulp introduction rates above 2 m/s and up to 10 m/s.

[0106] However, to obtain such an operation in dispersed bubble mode, it is necessary to use very high gas pressures and this is not preferable in the method of the invention, because it entails the use of a gas compressor with the attendant purchase and maintenance costs. Furthermore, the drawback associated with the mechanical stresses applied to the pulp, and in particular to the paper fiber, is observed here.

[0107] Hence, for the reasons stated above, although the ozonization step can be put into practice in the contactor T operating in segregated mode, in wave mode, in plug mode or in dispersed bubble mode, it is preferably put into practice in wave mode or in plug mode, that is with gas introduction rates between 0.5 and 2 m/s and pulp introduction rates between 0.5 and 2 m/s.

[0108] The introduction rates mentioned above and below are rates obtained when the contactor T is empty. In other words, the gas introduction rate is calculated as a function of the internal cross section of the contactor used, in order to obtain a gas introduction rate between 0.5 and 2 m/s when the contactor contains no pulp.

[0109] Similarly, the pulp introduction rate is calculated as a function of its introduction rate in the empty contactor and as a function of the internal cross section of the contactor.

[0110] To obtain a high reaction rate, it is advantageous to use a gas mixture containing ozone in a high concentration in a carrier gas such as air, for example. In fact, as already stated, ozone is highly reactive and the quantities of ozone to be consumed are generally small. By way of example, in the case of paper pulps, they are lower than 20 kg/t of pulp.

[0111] Thus it has been determined that an ozone-air gas mixture containing between 50 and 200 g of ozone per m<sup>3</sup> of gas mixture is perfectly suitable.

[0112] However, an oxygen-ozone or nitrogen-ozone gas mixture or any other mixture of ozone in a carrier gas compatible with ozone can also be used.

[0113] In order to better understand the invention, several examples of application will now be described. These examples are given purely for illustration and are not limiting.

#### EXAMPLE 1

##### Treatment of Used Paper According to the Method of the Invention in the Presence of the Usual Reagents

[0114] Pulping Step

[0115] 1.5 kg of waste papers consisting of a mixture of old newspapers and magazines are mixed with 13.5 l of water and the usual prior art quantities of hydrogen peroxide, caustic soda and sodium silicate.

[0116] The mixture is stirred in a pulper marketed by Lamort for 20 min. The pH is close to 10.5.

[0117] Screening Step

[0118] The paper pulp obtained is then screened through screens, following the usual methods of the profession.

[0119] Ozonization Step

[0120] The ozonization is carried out at a consistency of 3% in a glass reactor, the ozone is introduced in the form of an oxygen-ozone gas mixture containing 150 g of ozone per m<sup>3</sup> of gas mixture, until 10 kg of ozone are consumed per metric ton of dry paper.

[0121] Flotation Step

[0122] The pulp obtained is diluted to a consistency of 1% and transferred to a Lamort type flotation cell. The flotation is carried out for 6 min and prolonged for 4 min. A foaming agent is added.

[0123] In all these steps, the temperature has remained close to 40° C.

[0124] After each step, a sample of pulp is taken and converted into a sheet of paper. The whiteness of this sheet of paper is measured with UV according to standard ISO (2420).

[0125] The fluorescence of the pulps is measured by an identical method, by inserting a UV blocking filter in the optical path (application of the operating mode described in "TAPPI T 452 appendix C"). The results are given in Table 1 below:

TABLE 1

| Step              | WH iso %<br>with UV | WH iso %<br>without UV | Fluorescence<br>% |
|-------------------|---------------------|------------------------|-------------------|
| After screening   | 61.9                | 57.3                   | 4.6               |
| After ozonization | 59.2                | 59.7                   | -0.4              |
| After flotation   | 65                  | 65.2                   | -0.2              |

[0126] The results given in Table 1 show that when the method of the invention in its first variant, that is comprising an ozonization step, is put into practice with the usual chemical reagents of the profession, the sheet of paper finally obtained has an improved whiteness and a decreased fluorescence.

[0127] The number and size of the black spots was also measured on each sheet per m<sup>2</sup> of surface area.

[0128] The results are shown in FIG. 8.

[0129] As shown in FIG. 8, with the method of the invention in its first variant, the number of black spots remaining after flotation is very small.

[0130] This means that the ozonization step, when introduced before flotation, improves the effectiveness of the flotation step itself, that is of the deinking.

[0131] The number of black spots per m<sup>2</sup> and the size in microns of these black spots were determined by image analysis.

#### EXAMPLE 2

##### Application of the Method of the Invention without Addition of any Chemical Reagent Other than Ozone

[0132] The method was followed as in example 1 but without adding hydrogen peroxide, caustic soda and sodium silicate. The pH was close to 7.5.

[0133] The same measurements of whiteness with UV and without UV and of fluorescence were carried out on the sheets of paper obtained after the screening, ozonization and flotation operations respectively.

[0134] The results are given in Table 2 below:

TABLE 2

| Step              | WH iso %<br>with UV | WH iso %<br>without UV | Fluorescence<br>% |
|-------------------|---------------------|------------------------|-------------------|
| After screening   | 58                  | 54                     | 4                 |
| After ozonization | 54                  | 53.4                   | -0.2              |
| After flotation   | 58.6                | 56.5                   | 0.7               |

[0135] Here also, a significant decrease in fluorescence and a significant increase in whiteness are observed.

## COMPARATIVE EXAMPLE 3

[0136] By way of comparison, the prior art method was put into practice in which the ozonization is carried out after the flotation step. To do this, the method was followed in the same way as in example 1, but by carrying out the ozonization step only after the flotation step.

[0137] Measurements were taken of the whiteness with and without UV, of the fluorescence and the number of black spots per m<sup>2</sup> of sheets of paper obtained by this method, as well as their size in microns, on each sheet of paper obtained after the screening step, after the flotation step and after the ozonization step.

[0138] The results of the measurements of whiteness with and without UV and of fluorescence are given in Table 3 below:

TABLE 3

| Step              | WH iso %<br>with UV | WH iso %<br>without UV | Fluorescence<br>% |
|-------------------|---------------------|------------------------|-------------------|
| After screening   | 61.9                | 57.3                   | 4.6               |
| After flotation   | 67.1                | 62                     | 5.1               |
| After ozonization | 66.9                | 62.1                   | 4.8               |

[0139] The results in Table 3 show, when compared with the results of the measurements of whiteness with and without UV and of fluorescence carried out on the sheets of paper obtained in example 1, that with the method of the invention the sheets of paper finally obtained have a higher whiteness and a lower fluorescence in the case of the sheets treated by the method of the invention than in the case of the prior art method.

[0140] The results of the measurements of the number of black spots per m<sup>2</sup> present on the sheets of paper obtained according to the prior art method as described in the present example, and of their sizes, are given in FIG. 9.

[0141] By comparing the results of these measurements with those obtained with the method of the invention as described in example 1, it is observed that the method of the invention permits a better deinking than the prior art method.

## COMPARATIVE EXAMPLE 4

[0142] The method is followed as in example 2, without the addition of any chemical reagent other than ozone but by carrying out the ozonization step after the flotation step.

[0143] The whiteness with and without UV and the fluorescence of the sheets of paper obtained with the pulps

obtained after the screening, after the flotation and after the ozonization are given in Table 4 below:

TABLE 4

| Step              | WH iso %<br>with UV | WH iso %<br>without UV | Fluorescence<br>% |
|-------------------|---------------------|------------------------|-------------------|
| After screening   | 57.9                | 54                     | 3.9               |
| After flotation   | 60.4                | 56.1                   | 4.3               |
| After ozonization | 54.7                | 53.6                   | 1.3               |

[0144] By comparing the results of the measurements given in Table 4 above with those of the measurements given in Table 2 of example 2, it may be observed that by putting into practice the method of the invention without the addition of any reagent other than ozone, with the method of the invention, a better whiteness with UV is obtained and a better defluorescence of the paper pulp obtained from the UV papers.

## EXAMPLE 5

[0145] The test in example 2 was reproduced using a horizontal stainless steel tubular contactor having an inside diameter of 4.5 cm and a length of 100 m supplied with a used-paper pulp with a consistency of 2.5%.

[0146] The paper pulp introduction rate was selected in order to obtain pulp rates (in empty contactor) between 1 and 2 m/s.

[0147] The same rates were used for the gas mixture consisting of a mixture of oxygen and ozone having an ozone content of 100 g/m<sup>3</sup> of mixture.

[0148] Under these conditions, the pressure drops are between 2 and 3 bar.

[0149] The ozone transfer capacity is accordingly 1.5 to 3 kg/t of pulp for a residence time of one-and-a-half minutes.

[0150] The same results were obtained as in example 2.

[0151] All these measurements show that the method of the invention serves to obtain sheets of recycled paper presenting a better whiteness, a better defluorescence and a better deinking, with fewer subsequent treatment steps, without overconsumption of hydrogen peroxide, and even without the addition of any reagent other than ozone, than the sheets obtained according to the prior art.

[0152] Evidently, the invention is not at all limited to the embodiments described and shown which are only given as examples.

[0153] On the contrary, the invention comprises all the technical equivalents of the means described as well as combinations thereof if these are carried out in its spirit.

1-12. (canceled)

13. A method for treating used paper comprising:

- pulping said paper in an aqueous medium;
- screening said pulp at least once to remove coarse particles;
- deinking said pulp with at least on flotation; and
- performing an ozonization step prior to said flotation.

14. The method of claim 13, wherein said ozonization step is performed at a used paper pulp consistency of between about 0.5% and about 5%.

15. The method of claim 14, wherein said consistency is between about 0.5% and about 3%.

16. The method of claim 13, further comprising performing said method in water, without adding chemicals other than ozone.

17. The method of claim 13, further comprising performing said method in the presence of caustic soda NaOH, hydrogen peroxide  $H_2O_2$ , and sodium silicate  $Na_2SiO_3$ .

18. The method of claim 13, wherein said ozonization is performed after said screening.

19. The method of claim 13, wherein said ozonization further comprises being performed in a two-phase tubular contactor, wherein said contactor comprises a gas-liquid type.

20. The method of claim 19, further comprising performing said ozonization in said contactor in wave mode.

21. The method of claim 19, further comprising performing said ozonization in said contactor in plug mode.

22. The method of claim 13, further comprising performing said ozonization with a gas mixture wherein said mixture comprises between about 50 g and about 200 g of ozone per  $m^3$  of gas mixture.

23. The method of claim 13, further comprising performing said ozonization with a gas mixture wherein said mixture comprises at least one member selected from the group consisting of:

a) an air-ozone gas mixture; and

b) an oxygen-ozone gas mixture.

24. The method of claim 19, further comprising:

a) introducing said ozone in a gas mixture at a rate greater than about 0.5 m/s and less than or equal to about 10 m/s;

b) introducing said pulp at a rate greater than about 0.5 m/s and less than or equal to about 10 m/s.

25. The method of claim 24, wherein:

a) said gas mixture rate is between about 0.5 m/s and about 2 m/s; and

b) said pulp rate is between about 0.5 m/s and about 2 m/s.

26. The method of claim 25, wherein said gas mixture comprises at least one member selected from the group consisting of:

a) an air-ozone mixture;

b) an oxygen-ozone gas mixture; and

c) a nitrogen-ozone mixture.

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