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Mannbro

[11] **3,830,688**

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[54] **METHOD OF REDUCING THE DISCHARGE OF WASTE PRODUCTS FROM PULP MILLS**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 83,371, Oct. 23, 1970, abandoned, which is a continuation-in-part of Ser. No. 654,998, June 21, 1967, abandoned.

[52] **U.S. Cl.** **162/29,** 8/156, 162/55, 162/60, 162/65, 162/66, 162/78, 162/88

[51] **Int. Cl.** **D21c 9/02,** D21c 9/08, D21c 11/00

[58] **Field of Search** 162/17, 31, 41, 51, 89, 162/60, 65–67, 78, 88, 87, 55, 96; 8/108, 109, 111, 156

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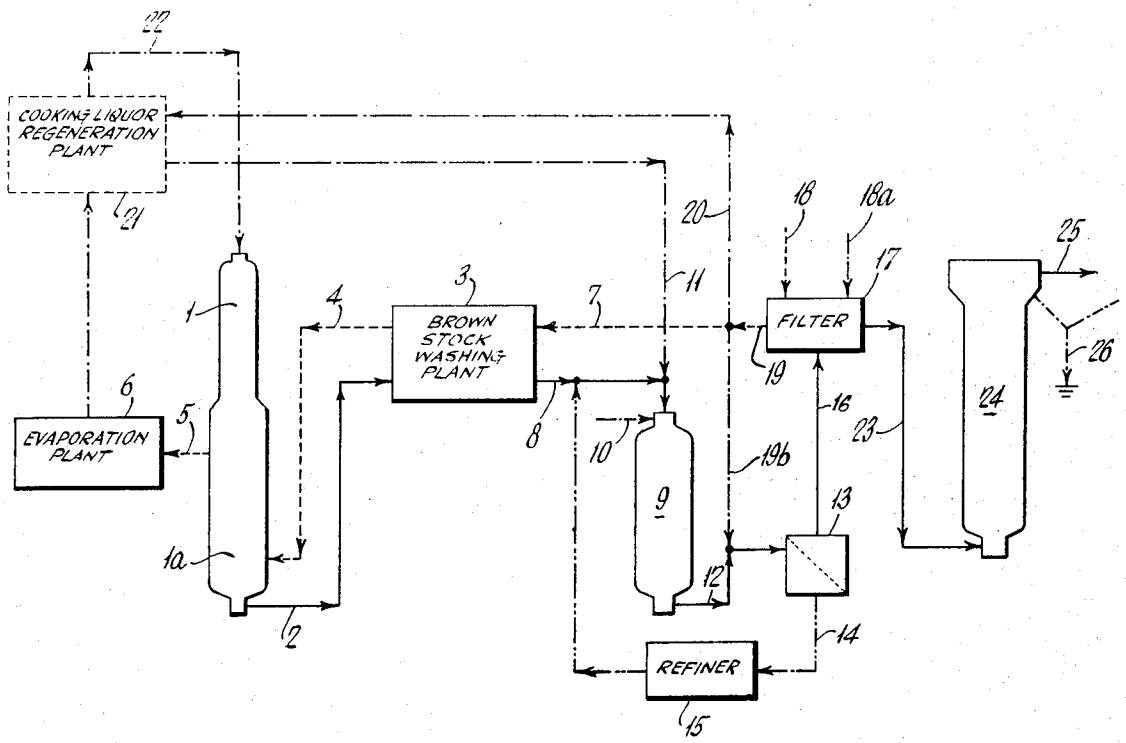
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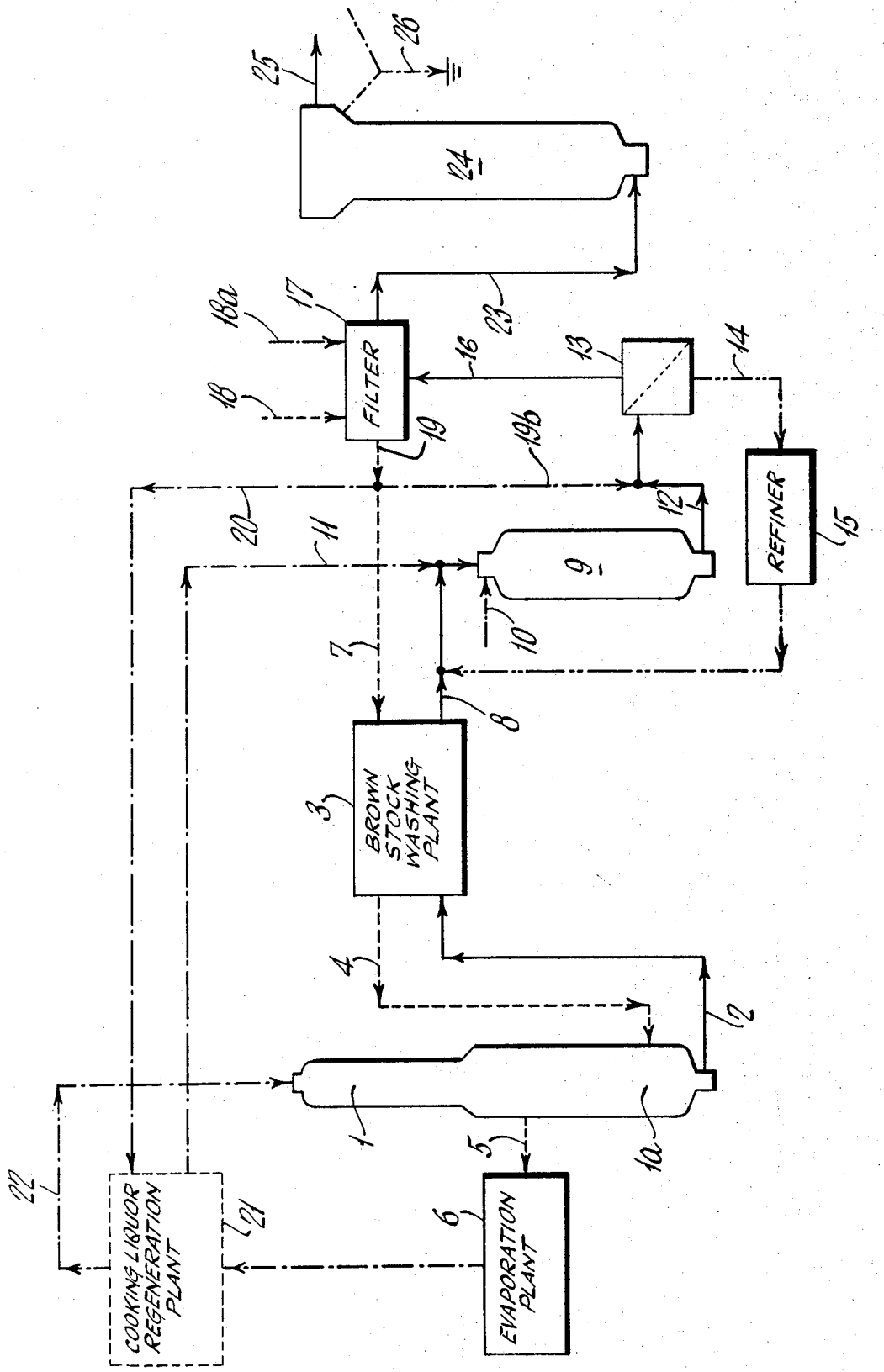
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[57] **ABSTRACT**

Method for reducing the amount of waste products discharged from cellulose pulp mills to limit the pollution of recipient water into which the wastes are finally discharged. The amounts of coarse pulp waste products as well as fines which pass the dewatering wire cloths are reduced in a single treatment stage, while sulphides and resin acids with black liquor residues left in the pulp are chlorinated and/or oxidized before they are discharged into the recipient water. The volume of waste water is kept small. The process is characterized by the omission of the conventional washed unbleached pulp screening operation and passage of the unbleached pulp and wash medium directly to the bleaching operation. The unbleached pulp washing step is performed with aqueous supplanter, e.g., white water or vapor condensate, and is to be distinguished from fresh water washing.

5 Claims, 1 Drawing Figure




25
26
24
18a
17
23
FILTER
16
13
14
18
19
19b
REFINER
15
20
11
12
9
10
7
8
BROWN STOCK WASHING PLANT
3
4
2
1
1a
5
22
21
6
COOKING LIQUOR REGENERATION PLANT
EVAPORATION PLANT

METHOD OF REDUCING THE DISCHARGE OF WASTE PRODUCTS FROM PULP MILLS

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of applicant's prior copending application, Ser. No. 83,371, filed Oct. 23, 1970 now abandoned, which bears the same title, and which was a continuation-in-part of application Ser. No. 654,998, filed July 21, 1967 now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a method of reducing the amount of waste products discharged from cellulose pulp mills, for the purpose of reducing pollution of the recipient water into which such waste products are discharged.

2. Description of the Prior Art

With rapid industrial growth and increasing population densities throughout the world, pollution of rivers, lakes and streams has become a very serious problem. One of the contributors to this contamination has been cellulose pulp mills which normally dump very large volumes of contaminated effluent water into recipient rivers, lakes and streams. It is a principal object of this invention to decrease the amount of waste products discharged from pulp mills.

The usual conventional process of sulphate pulping and bleaching has been described by Casey, in his book Pulp and Paper, which deals with brown stock washing in Chapter IV and with waste disposal in Chapter IX. In such a prior art process, pulp and black liquor from sulphate wood digestion pass on to a pulp washer for black liquor displacement. The diluted black liquor is passed to a regeneration plant. The washing cleans the pulp as thoroughly as possible of black liquor. The pulp, along with some remaining black liquor, is diluted with large quantities of water in a stock chest, producing a diffusion of sulphides, resins and other black liquor components.

The diluted pulp stock is screened and the screened pulp goes to a water extractor. The screened pulp passing to the extractor is accompanied by all of the dissolved waste products. The extracted waste water seriously contaminates the recipient body of water, for example a stream, river or lake. In ordinary processing as set forth the volume of waste water from unbleached pulp screening amounts to about 50 cubic meters per ton of pulp. The biochemical oxygen demand (BOD) of the wastes can be between 15–25 kg BOD per ton of pulp, that is, about 0.25 kg. BOD per kg of solids. The solids are, of course, dissolved wood substances derived from the black liquor which was entrained by the pulp stock since the pulp washing stage.

Not only do such wastes increase the BOD load on the recipient water, but also some of the waste components are poisonous. The undesirable results of such a process are particularly pronounced if the foul black liquor evaporation condensate is passed directly to the pulp washing stage undiluted by the addition of fresh water.

The waste water from the extractor also contains fines or Noll-fibres, which pass through the de-watering

wirecloths of the extractor in an unbleached state. These fines also contribute to the BOD load on the recipient. Screening rejects from conventional processes, that is, incompletely delignified material, represent a further solid waste disposal problem.

Also considered by Casey, cited above, is the conventional bleaching process for pulp. The pulp obtained from the water extractor as described above passes next to a bleaching operation. Bleaching is usually carried out in a multistage process, starting with an initial bleaching step using one of the common oxidizing agents, e.g. chlorine, hypochlorite, chlorine dioxide, oxygen or peroxide. If chlorine is used, the chlorination products must be dealt with, and these include chlorinated phenol compounds.

It is standard procedure in prior art multistage bleaching systems to wash the pulp between the several oxidizing bleaching stages and to solubilize the residual products of the initial oxidizing stage by alkaline extraction followed by washing with water. White liquor may be used for this treatment step. In oxidizing bleaching 5 percent to 10 percent NaOH is used simultaneously with the oxygen, and the alkaline pulp stock resulting from the oxygen bleaching is extracted under alkaline conditions by washing with water alone.

The subsequent conventional bleaching stages are well known to those skilled in the art. The bleach plant effluents contribute further to the BOD load resulting from the wastes in the previously extracted water. The total waste liquids to be disposed of after conventional sulphate pulping and bleaching is about 200 m^3 to 300 m^3 of waste liquids per ton of pulp. Depending on the particular type of bleaching and the kind of pulp treated, the BOD of the bleaching effluents is usually between 5–10 kg per ton of pulp, but this load may be as great as 20 kg/ton pulp. Adding the BOD of the bleaching effluents to the BOD of the extracted waste water, the total BOD has usually been over 40 kg/ton of pulp in prior art plants.

Attempts have been made to reduce the waste water volume and the BOD by in-process effluent recycling and the use of the alkali content of alkaline bleaching effluents in the pulp digestion process, e.g. for washing unbleached pulp prior to its screening. Products released from alkaline stage can, however, only be introduced to the cooking liquor regeneration process if the alkali is pure, i.e., contaminated only with a very small amount of chlorine compounds.

It is a common practice to treat the waste water in settling ponds, whose surfaces release foul gases, mainly originating from the sulphidic wastes. The ponds are often aerated to lower the BOD, but vast volumes of waste water are involved.

The weight of organic substances contained in the spent liquor obtained when digesting either sulphite or sulphate pulp is approximately equal to the weight of the recovered pulp. The sulphite pulp industry has caused serious water pollution problems. These problems have become less serious where combustion of sulphite spent liquor has been established as an economically acceptable process. With regard to water pollution, the sulphate pulp industry has had a much more favorable starting point. The use of relatively expensive but easily regenerable cooking chemicals explains the successful development of the recovery process for the manufacture of sulphate pulp. The complete success of the sulphate process has been limited

in that low concentrations of foul smelling substances are discharged in the form of gases to the atmosphere, and toxic substances to the sewage water and recipient water.

The spent sulphate digestion liquor (or so called black liquor) obtained during the digestion of sulphate pulp contains resin acids which are poisonous to fish and other animal life. Sulphides and mercaptans are also poisonous per se and also spoil surviving fish by imparting to them an unappetizing flavour and taste.

All of these compounds may cause serious damage even though they only appear in the recipient water in concentration of only a few milligrams per liter of water.

To assess the poison activity of sulphides and sodium salts of resin and fatty acids a more exhaustive study must be conducted, but as has been mentioned, the poison activity of the sulphides can be reduced by chlorinating the entire volume of water obtained when screening the unbleached pulp. Solid waste is separated from the screens at this stage of the process i.e., subsequent to washing and prior to bleaching. This solid waste presents a problem; whether it be flushed out into the recipient water or deposited on land. The screening of pulp from the digester is primarily intended to remove such solid waste as incompletely delignified wood chips, shives and bark residues and other constituents which resist fiber liberation by cooking and subsequent bleaching. These fractions are obtained as reject from screens and hydro-cyclone cleaners. If the rejects cannot be marketed as coarse pulp or e.g., utilized in the production of packaging materials, they represent a serious disposal problem.

A significant step forward has already been taken by removing coarse, unpulped material and knots before the pulp is washed and screened, these being returned with their black liquor content to the digestion step. After re-cooking a significant portion of the reject material will be accepted by screening. Re-cooking may, however, lead to a fraction of the acceptable material having relatively poor bleaching properties or increased consumption of bleaching chemicals.

Other disposal methods involve burning the waste either in incinerators or, suitably after shredding, together with black liquor in a soda recovery furnace. The deciding factor may, in certain cases, depend upon the value of the alkali remaining in the reject.

In some instances it is even considered to be industrially most economic to use knots and screen rejects for ground levelling.

In the foregoing there has been discussed the conditions for treating sulphate pulping waste, containing so-called knot pulp and screen rejects, sulphides with pulp from digestors and soap with resin acids as the most deleterious components in the black liquor loss. The present invention is based upon a study of how these constituents of the waste can be treated.

SUMMARY OF THE INVENTION

It has been found that the said constituents should not be treated individually, as has previously been the case, but that the waste should be subjected in its entirety to one common treatment. It has also been found that the treatment can be effected with no adverse effects on the quality characteristics of the bleached pulp. The invention provides a great advantage in modern methods for continuous digestion in direct connection with the washing of the pulp, where there has been a desire to effect screening in less space-demanding screening departments with small fresh water requirements. Quite simply, the invention improves measures previously applied only in successive, separate treatment stages in a novel, efficient and comprehensive method with a novel effect, to completely or partially eliminate the following large groups of waste products:

1. incompletely digested material
2. poisonous products from the digestion operation
3. dissolved wood substances which increase the oxygen demand of the recipient
4. fines in white water from thickeners and filters for screened, unbleached pulp.

The method of the invention has the following advantageous features:

1. The quantity of waste water and, to the same extent, the need for fresh water is reduced in that the entire screening procedure for washed unbleached pulp is omitted.

2. Equipment for black liquor recovery by washing the pulp is dimensioned so that all water used in one form or other for the final, clean washing of the pulp is utilized in counter current flow to the pulp and finally passed to the evaporation plant, instead of loading the recipient water with unbleached pulp screening white water.

3. Unbleaced pulp from the last washing stage filter and/or press for recovering liquor is passed directly to the first stage of the subsequent bleaching operation, where oxidation and/or chlorination agents react with the sulphide sulphur compounds and extracted substances of the pulp and liquor residues entrained therewith, at a concentration of said agents that is required for pulp bleaching.

4. Oxidation or chlorination products of sulphides and liquor residues present in aqueous solutions are extracted from the pulp while coarse material which has been delignified to some extent is subject, either directly or indirectly, to further processing.

5. Pulp from an alkaline bleaching stage is diluted with water recycled from the same or later alkaline stages, and is separated from the incompletely delignified material by means of suitable screen arrangements, cyclone cleaners and other separating means.

6. The fraction of incompletely delignified material separated according to item **5** above is mixed with the flow of unbleached pulp to the first bleaching stage. Preferably this material is first defibered in refiners and/or screened to remove constituents unsuitable for mixing with the flow to the first stage; these screening rejects are substantially free of sulphide sulphur compounds as compared to their composition when still present in the unbleached pulp.

7. In the continuous state of operation there is added to the initial bleaching stage an additional amount of oxidation agents, chlorine or other such substances, corresponding to the requirements for delignification of returned pulp and oxidation of poisonous sulphide sulphur compounds or black liquor residuals as well as conversion of extractives from pertinent wood species.

The novel method according to the invention provides, in one single treatment stage, a reduction of the coarse pulp of the waste products as well as fines which pass the de-watering wirecloths, while sulphides and

resin acids with black liquor residuals left in the pulp are chlorinated and/or oxidized before they are released to the recipient water, in a relatively small volume of waste water. The elimination of the screening of unbleached pulp causes a reduction of the requirements for fresh water in the plant, which may be of critical importance for expanding plants. (In certain instances sea water may be used in the bleaching plant up to the last washing stage, including also screening of the alkaline pulp suspension between the bleaching stages according to the present invention.)

For conventional screening the washed unbleached pulp is diluted. This step must be followed by corresponding thickening by water removal before bleaching can be effected. This dewatering process is accompanied by a loss of a fine fraction of fibres. If these fines are permitted as such to accompany the waste water into the recipient they add considerably to the load of the said recipient. This load is reduced if all pulp, without being subjected to losses, is passed to the introductory bleaching stage. Losses of delignified fibre from filters and thickeners subsequent to screening between bleaching stages cannot, on the other hand, be entirely avoided but they can easily be either recovered or rendered harmless by treating the relatively small volume of waste water that is released from the bleaching plant only. Naturally, the same amount of lost fibres imply a lower BOD after delignification with oxidation agents such as chlorine compounds, and elimination of the sulphide sulphur contents of the pulp which the lost fibres originate from.

Sedimentation ponds, filters and other purifying plants, and pipe lines and distributing means in the recipient need only be dimensioned for waste water from the bleaching department and subsequent treatment of the pulp. Foul smelling gases are often given off from surfaces of waste water in sedimentation ponds or settlers. According to the present invention such sulphide-sulphur compounds are eliminated, and as a result thereof also such hydrogen sulphide formation which takes place when waste water, containing sulphide containing liquor, is mixed with acidic waste from, inter alia, pulp bleaching stages. The more uniform and more concentrated the recovered fibre material the greater are the possibilities of usefully utilizing the same. The total volume of waste water for an average number of more modern sulphate plants which include bleaching plants is between approximately 200 and 300 m^3 per ton pulp. Of this the waste water from the screening of washed, unbleached pulp comprises 50 to 100 m^3 per ton pulp.

To render harmless sulphides and other poisonous sulphur compounds and resin acids together with other extractive substances from the liquor, a threshold value for the concentration of chlorine or other oxidation agents in the waste water must be passed. It is, therefore, important to work with the least possible volume of waste water. The present invention is therefore more favorable than chlorination or aeration of the excess of white water from thickeners and filters for unbleached pulp.

The practical performance of the described method is influenced by economic conditions concerning increased consumption of chlorine or chlorine compounds and other oxidation agents in the initial bleaching stage. The unpulped material from the digestion consumes more bleaching agent than the average pulp but, subsequent to delignification in the first bleaching stage, will result in an increased yield of liberated fibre. The value of the increased yield of pulp contributes to complete or partial compensation for the increased cost in chemicals for treating the waste water. Further, when manufacturing sulphate pulp it is possible to provide an optimal relationship between firstly, the return to the digester of the coarse fraction of the undigested material which is removed from the suspension of black liquor and pulp before the final washing stage and, secondly, bleaching of the remaining undigested material after it has passed the pulp washing department. Thus, the redigestion of screening rejects would finely divide non-desired material which cannot be bleached in a conventional system, but which according to the invention is liberated and separated by means of screening between bleaching stages.

To reduce the quantity of chlorine consuming constituents and black liquor present in the fibre after normal filter washing, the brown stock washing plant can include a diffusion stage before bleaching and preferably prior to the final washing stage or the pressing stage. Washing in continuous digesters and diffusers and similar washing apparatus give, in this respect, a better result than filter washers. Batch washing in diffusers can also be effected to advantage by means of the present invention.

Chlorination is normally effected at a pulp consistency of approximately 3 percent. It is therefore necessary to dilute, if the pulp from the washing filters with a consistency of approximately between 10 and 15 percent is to be chlorinated under normal conditions. Preferably, dilution can be effected with return water, e.g. from chlorine dioxide stages, in a manner known per se, with vapour condensate containing sulphide sulphur components.

Other processes use such high pulp concentrations, e.g. of about 20 percent to 60 percent as in U.S. Pat. No. 3,251,730, that fluffed pulp is treated with chlorine and/or chlorine dioxide gas. In the case of gas phase oxidation, the present invention affords the additional advantage that the relatively high pulp concentration from the last washing stage, filter or press, is utilized for pressing prior to fluffing. Gas phase chlorination is also particularly suited for unscreened pulp containing coarse, un-delignified material from the digester stage. Certain effects of a more penetrating delignification conducted in gas phase have also been noticed on coarser material subjected to redigestion, when it has been separated prior to the washing operation for the recovery of black liquor.

Modified sulphate digesting processes have been developed in latter years. One such process is digesting with liquor containing significant amounts of polysulphide. Another process utilizes substantially only sodium sulphide. These processes result in higher concentrations of sulphide and organic sulphur compounds in the products which accompany the pulp. In conventional washing and screening of such pulps the release of sulphides into the recipient must therefore be increased. This is counteracted by moving the screening stage to a position in the bleaching sequence according to the present invention. The vapour condensate from these modified pulping processes contains more sulphide sulphur than does the conventional sulphate process condensate. Therefore condensate from the evaporation stage, and to a certain extent from the digestion

stage, should be used for washing the pulp. If the condensate in the washing stage is not supplanted with fresh water sulphidic sulphur compounds follow the pulp from the filter, and thus not only is the discharge of deleterious substances into the recipient increased but also the odor level in the screening department. Thus the direct bleaching of the washed pulp according to the invention also presents obvious advantages in this respect. It provides for simultaneous discharge of black liquor losses and water-soluble chlorinating and oxidating products. Even though the total effect is favorable, chlorinated phenol compounds have certain poisonous effects. Chlorine dioxide may also in this respect favorably replace chlorine in the first bleaching stage. If chlorine dioxide is used in the application of the present invention, the black liquor and condensate residuals, containing sulphur and other compounds, entrained with the pulp will be oxidized at higher efficiency than when using chlorine. In this instance the invention can with the same advantage be applied to both sulphite and sulphate pulp bleaching. Irrespective of whether the invention is applied by using chlorine, hypochlorite, or chlorine dioxide in the first bleaching stage, the transport of reaction products to the subsequent alkaline stage is increased as compared to the conventional bleaching of pre-screened pulp.

Products released from the alkali stage can only be processed in the cooking liquor regeneration system if the recovered alkali contains small amounts of chlorine compounds. This is achieved with chlorine dioxide which, after all, has five times as great oxidative effect per chlorine atom. Thus, the present invention affords a particularly high effect if applied with chlorine dioxide in the first bleaching stage and with the recovery of filtrate from subsequent alkaline pulp extraction stages. This filtrate will also contain residues of products released during the digestion stage. Recovery can be effected by utilizing the alkaline filtrate for preparation of cooking liquor or be introduced in the waste liquor via the pulp washing stage. When washing sulphate pulp on filters the filtrate can be sprayed onto the pulp web to displace or supplant residual black liquor. Remaining alkaline filtrate is supplanted or displaced with water, either in the form of newly added water or in the form of vapour condensate or reuse of washing water from the process. The water employed can accordingly be called a "supplanter" or "displacing medium." The method can in itself contribute to a more effective washing out of sulphidic black liquor if the filtrate from the bleaching stage is free of sulphide. The amount of chlorine or oxidation agents introduced to the introductory bleaching stage can be reduced if the pulp is washed in the most effective manner possible.

The conditions are somewhat different if white liquor or possibly soda liquor (green liquor) is used in the alkaline stages of the bleaching department. The advantage of this process is that in this form the alkali is less expensive than in caustic liquor. It may be more expedient for pulp digestion purposes to utilize caustic liquor if sulphite is included in the cooking liquor. The disadvantage with white liquor for bleaching purposes is primarily that chlorine consuming sulphide residues accompany the alkali extracted and washed pulp to the next bleaching stage. Further, the risk of hydrogen sulphide formation must also be taken into account.

When filtrate from alkaline stages from the bleaching sequence contains sulphide it is still more important, from the aspect of water conservation, to recover the filtrate. If such filtrate is taken into the liquor regenerating process via the unbleached pulp washing this should suitably be undertaken before the last washing stage so that the first bleaching stage is not unnecessarily loaded.

The present invention is particularly effective in the case of the oxidation of sulphide e.g., introduced by vapour condensate, in the alkaline bleaching filtrate, which is used for recovering black liquor in later stages of the pulp washing prior to bleaching. Conventionally, the residual sulphide should follow the unbleached screening waste water to the recipient but, according to the present invention, these residuals are oxidized in the initial bleaching stage.

Methods for complete recovery of chlorine-containing bleach plant waste water are not yet available in actual practice. To obtain, according to the invention, an almost complete unloading of the recipient it is necessary to use oxidation agents in the initial bleaching stage, which enables the introduction of the washed-out reaction products into the cooking liquor (white liquor) regenerating process of the pulp plant. Suitable oxidation agents from this aspect are peroxide and air or oxygen, at suitable temperatures and pressure ratio. In the latter case catalysts may also be used. In latter years interest, inter alia, has increased in the use of initial bleaching stages with oxygen and alkali, accompanied by suitable bleaching sequences wherein chlorine, chlorine dioxide and alkali are included. In this way high brightness sulphite and sulphate pulps, having good quality characteristics in general can be produced. Since a fibre liberating delignification process takes place in the first bleaching stage the pulp can be screened directly. The present invention can therefore be adapted so that the otherwise less effective oxidation (aeration) of the waste water rather is operated as an optimated bleaching stage with recovery of alkali together with the oxidation products. A further advantage with regard to the quality of the pulp is obtained in that oxidation prevents the formation of chlorinated extractive substances. These chlorination products are, in hardwood pulps, often insoluble in subsequent alkali stages and therefore reduce the brightness stability of the bleached pulp.

The alkaline necessary for alkaline oxidation with oxygen can be added at the last washing filter for waste liquor recovery, or in connection with the last washing stage. Certain pulp lignin oxidation processes use significant amounts of alkali in the order of up to 5 or 10 percent NaOH calculated on the pulp. If the alkali balance of the pulp plant is upset thereby, regenerated liquor should be used for the bleaching process. In certain other processes for alkaline treatment of pulp, sulphur compounds in, for instance, white liquor have been found to protect against cellulosic decomposition. In the present instance oxidization to sulphate takes place at high temperatures. If the said alkaline bleaching waste liquor is to be used for digestion purposes with sulphite in the cooking liquor it is more advantageous to have converted sulphide and thiosulphate by oxidization.

BRIEF DESCRIPTION OF THE DRAWING

The drawing shows a system for performing the method of the invention in schematic form.

DESCRIPTION OF A PREFERRED EMBODIMENT

The drawing illustrates a system adapted for the performance of the method of the invention. The reference character **1** denotes a continuous digester having a washing zone **1***a*. A conduit **2** leads from the zone **1***a* of the digester **1** to a brown stock washing plant **3.** A pipe **4** for returning black liquor also connects the brown stock washing plant **3** and the digester **1.**

The pipe **5** leads from the digester **1** to an evaporation plant schematically shown at **6.**

An outlet line **8** of the brown stock washing plant **3** leads to a bleaching unit **9,** which is preferably for the initial bleaching stage of a series of successive bleaching stages (not illustrated). An oxygen feed line to the bleaching unit **9** is shown at **10,** and a feed line for alkali is shown at **11.**

The oxidation products of the initial bleaching stage leave the unit **9** through a conduit **12,** travelling to a screen arrangement **13,** whence screening rejects leave at **14** to pass to a refiner **15.** The refiner **15** is connected to the bleaching unit **9** for recycling of refine screening rejects.

Line **16** carries screened stock to a filter **17** fed with vapor condensate at **18** and water as shown at **18***a*. Conduit **19** for filtrate branches into a line **20** leading back to a cooking liquor regeneration plant **21** (shown in dashed lines), and also into a branch to line **7** leading back to the brown stock washing plant **3.**

The conduit **22** carries regenerated cooking from the plant **21** to the digester **1.**

The right hand end of the figure of the drawing shows a conduit **23** leading to a subsequent bleaching unit **24.** Although only one unit **24** is illustrated, there would preferably be a series of such units. The outlet **25** is for bleached pulp and the final recipient of wastes is shown at **26.**

The method of the invention will be more clearly understood from the following example:

EXAMPLE

Wood was digested according to the sulphate process with an alkaline cooking liquor containing sulphide. The digestion was carried out in a continuous digester **1** and in cooperation with a washing of the pulp at a zone **1***a* of the digester **1.** The digestion products comprised pulp and incompletely digested wood such as knots, as well as black liquor. The products were passed through a conduit **2** to a brown stock washing plant **3** for final washing of the pulp stock. Black liquor from washing was passed in counter-current flow to the pulp through a pipe **4** to the digester **1** and was then introduced through pipe **5** to the evaporation plant **6.** Washing was accomplished by adding washing water partly comprising evaporation condensate through the pipe **7.** This evaporation condensate contained sulphides and mercaptans of which a fraction added to other BOD and toxic components of the black liquor residue at the outlet **8** from the washing plant **3.** The washed pulp stock was transferred directly to the initial stage, at **9,** in a series of successive bleaching stages, thereby avoiding the dilution in the waste water producing pulp screening procedure which is characteristic of previously known pulp treatment methods.

The fines accompanying the pulp as well as the diffusible soap and other potential contaminants all flowed along with the pulp stock up to the oxidizing bleaching treatment stage. The initial bleaching stage at **9** comprised treatment with oxygen fed in at **10** and with alkali shown entering at **11,** the alkali containing a residue of sulphide emanating from the cooking liquor recovery process. A catalyst was also added. For pulp delignification, 6 percent NaOH, calculated on pulp at a suitable temperature and pressure ratio, was used. Simultaneously incompletely digested materials, i.e., knots, were subjected to a fibre-liberating delignification to form useful cellulose pulp, while the various BOD and toxic components were oxidized.

The initial bleaching stage oxidation products were discharged at **12** and treated in an arrangement of screens **13.** After oxidation any remaining liberated material was separated as screening reject and left the screens at **14** to be treated in a refiner **15** prior to mixing the pulp entering the first bleaching stage **9** through the conduit **8.**

The screened stock passed from the screen as shown at **16** to be treated on a filter **17** using vapor condensate introduced at **18** and some water shown entering at **18***a* to supplant the oxidation spent liquor. The filtrate removed at **19** contained not only comsumed alkali added for bleaching, but also alkaline compounds released with the digested pulp. Recovery of the alkali value was accomplished by passing a first part of the filtrate through the conduit **7** to the washing plant **3** for washing digested pulp while a second part of the filtrate flowed as shown at **20** to be used in the preparation of cooking liquor at the plant **21.** Dilution for screening was provided for by recycling filtrate to the screens **13** as shown at **19***b*.

Alkali was introduced at **11** to the oxygen-alkali bleaching stage **9.** The alkali was supplied by the cooking liquor regeneration plant **21,** which also supplied regenerated cooking liquor to the digester **1** through a conduit **22.** By this means the alkali balance of the entire pulp plant was controlled.

The stock containing delignified and washed pulp and remaining condensate was conveyed through the conduit **23** to a subsequent bleaching stage **24** with bleaching agents of high oxidizing power such as chlorine and chlorine dioxide. The bleached pulp finally was removed at **25** and treated by conventional means. The waste products discharged from the final bleaching and treatments, e.g. delignified and bleached fines, had relatively low BOD and contained no sulphidic sulphur compounds. The waste water containing these wastes, and leaving the mill at **26,** was free from foul smelling substances. The total volume of waste water discharged by the sulphate mill was cut to approximately 100 cubic meters or less per metric ton of bleached pulp.

It will be understood that brown stock washing, after digestion and before bleaching according to the invention, provides for washing of the pulp and the return of cooking chemicals to the digestion stage, before the pulp is passed on for bleaching. The washing is accomplished with "supplanter" or "displacing medium" — water which has been recycled or added. This arrangement separates the digestion from the bleaching stages, but allows the fines, and other incompletely digested solid materials, toxic materials, etc. to be subjected to the oxidizing action of bleaching chemicals along with the pulp before the pulp is separated from such materials as are to be discharged to a waste recipient.

Various modifications and substitutions falling within the spirit and scope of this invention will suggest themselves to those skilled in the art of pulp process. The example stated above is merely intended as a non-limiting illustration of a preferred embodiment.

Having described my invention, what I claim is:

1. A method of reducing fresh water requirements and the discharge of solid and liquid wastes from mills producing bleached pulp from ligno-cellulosic material, by non-oxidative digestion of the major part of the lignin and then by oxidative bleaching of the cellulosic residue wherein solid material which was incompletely digested in converted into useful cellulose pulp and screening wastes while simultaneously alleviating the malodorous and toxic character of composite wastes comprising digestion effluents and discharged solid wastes, including fines in white water, and limiting the BOD of such composite wastes, comprising the steps of:

a. passing the solid residue of the ligno-cellulosic material and spent liquor mixture from a pulp mill digestion stage directly to a brown stock washing step using a liquid aqueous supplanter containing BOD-increasing volatile digestion residues from spent liquor evaporation condensate that is recycled for the recovery of the spent digestion chemicals from the pulp and, to render the brown stock suitably free of original spent liquor;

b. passing the brown stock and any spent liquor entrained thereby along with incompletely digested solid material, from the brown stock washing step directly to an oxidation stage of a bleaching plant utilizing the brown stock consistency from the final brown stock washing stage, and subjecting said brown stock, incompletely digested solid material and entrained liquor as well as remaining BOD-increasing aqueous supplanter to the oxidizing action of an accordingly increased charge of bleaching chemicals selected from the group consisting of oxygen, peroxides, chlorine dioxide and chlorine for the simultaneous bleaching of the pulp, oxidative delignification of incompletely digested material and oxidation of spent liquor chemicals including resins and other toxic or BOD-increasing digestion products;

c. increasing the yield of useful bleached cellulose fibre and to the same extent reducing the polluting discharge comprising coarse solid waste material by converting the incompletely digested coarse material to useful cellulose pulp in the simultaneous waste alleviation and fibre liberating delignification of the oxidation step (b), into which step all fines material with BOD is contained and oxidized before any fraction thereof can escape with a reduced volume of deodorized white water either to a pulp mill effluent purifying plant for fibre recovery or to recipient water; and

d. passing the material from step (b) to a bleach plant alkaline extraction and washing stage supplied with liquid aqueous supplanter, for extraction of the aqueous solubilized chemicals-pregnant discharge from said oxidation stage.

2. A method according to claim **1** wherein a fraction of incompletely converted material passing from the oxidation step (b) is separated by immediate screening of pulp in suspension with the aqueous solubilized chemicals-pregnant discharge and then added to the brown stock and returned therewith to the oxidation step with an additional amount of the oxidizing chemical for repeated fibre liberating delignification, thereby reducing the discharge of oxidized waste materials and further increasing the yield of finally bleached cellulose fibre.

3. A method according to claim **1** wherein sodium compounds are used with oxygen in step (b), producing an aqueous extraction discharge from step (d), said chemicals-pregnant discharge containing alkaline solubilized oxidation products, and including passing said sodium compounds to a digestion liquor regeneration process.

4. A method according to claim **1** in which the pulp manufacturing process is the sulphate process and pulp-entrained black liquor containing toxic and malodorous sulphide compounds from the brown stock washing step (a) is recovered to a digestion liquor regeneration process as a component of the discharge of step (d).

5. A method according to claim **1** when chlorinating chemicals are selected for oxidation in step (b) wherein an amount of the chlorinating oxidizer is consumed in addition to the demand of the actual pulp bleaching and wherein chlorine dioxide replaces chlorine to achieve high efficiency oxidation of black liquor and vapor condensate residues which are extractable by water, while the transport of aqueous solubilized chemicals-pregnant and incompletely digested material to the subsequent alkaline extraction washing stage is adjusted by recovery of solubilized products containing alkaline filtrate with only small amounts of chlorine compounds to a digestion chemicals regeneration process by supplanting residual black liquor from the brown stock in step (a) with said alkaline filtrate from step (d) and then with vapor condensate and a chlorinating stage effluent.

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