

[54] METHOD OF DECOLORIZING PAPER
MILL EFFLUENT LIQUID

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[56]

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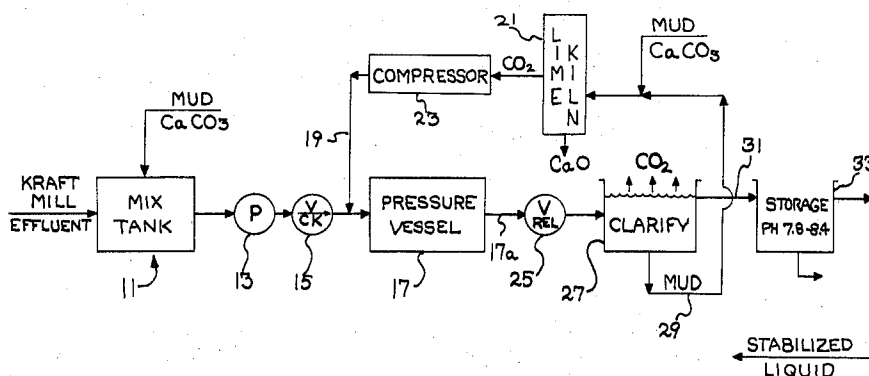
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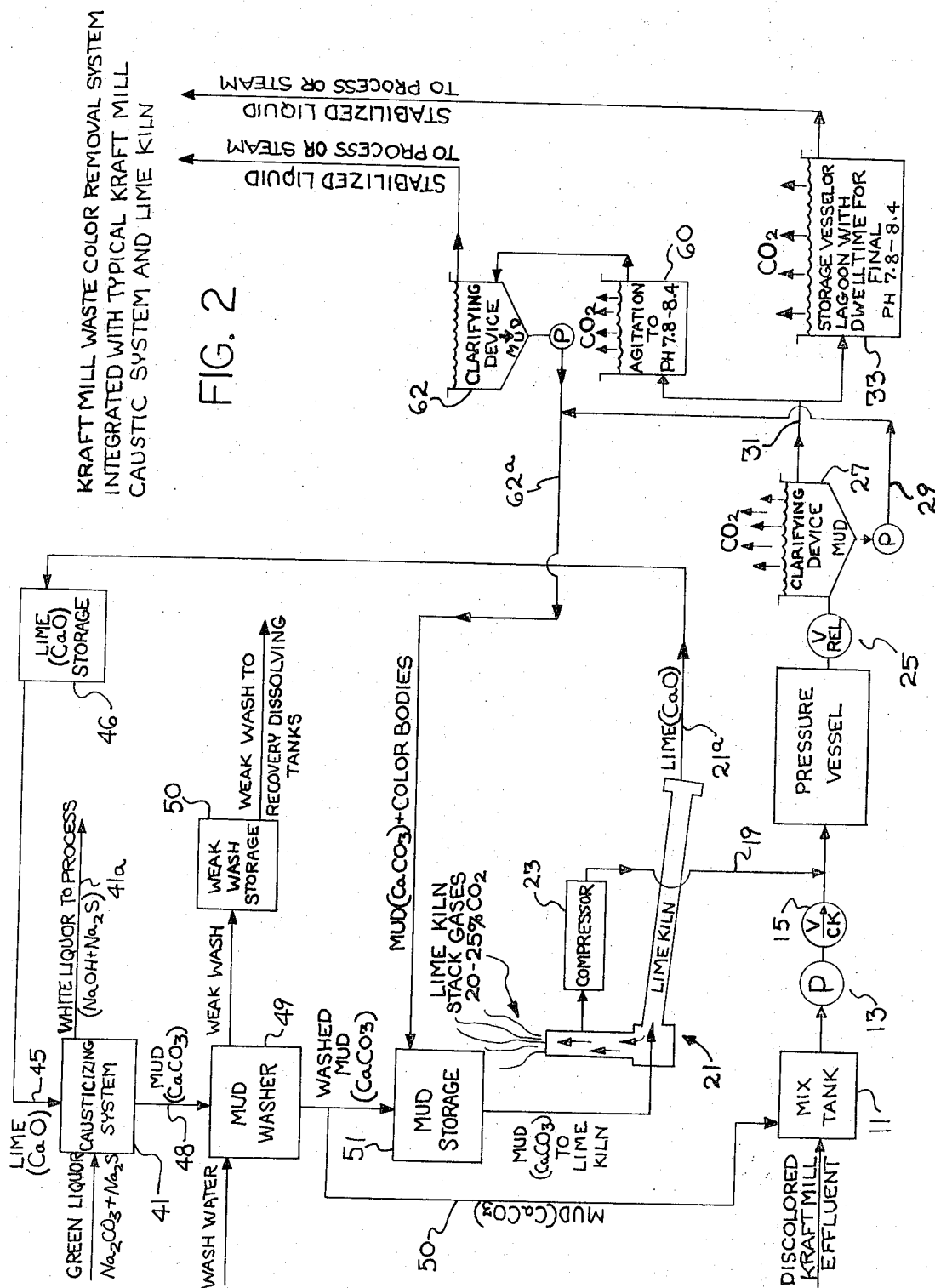
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ABSTRACT

Effluent liquid normally discharged by paper mills is ecologically undesirable for return to streams, lakes or the like by reason of the presence of color-imparting substances, e.g., color bodies, desirably removed by a process which includes mixing therewith an excess of calcium carbonate, followed by a combination at a pressure above atmospheric with a fluid rich in carbon dioxide, serving to convert the calcium carbonate to soluble calcium bicarbonate which is in turn discharged to atmospheric pressure whereby the calcium bicarbonate reconverts to calcium carbonate precipitate, said precipitate attracting and sweeping said color-imparting color bodies; the precipitate and color bodies being readily separable from the color-free effluent which may be returned to the source, stream, river or lake or reintroduced as fresh water into the pulping process as needed.

7 Claims, 2 Drawing Figures





METHOD OF DECOLORIZING PAPER MILL EFFLUENT LIQUID

The present invention relates broadly to paper manufacture. More particularly, the present invention relates to pulping and, even more specifically, to the pulping of wood by the so-called kraft pulping system employing sodium hydroxide and sodium sulfide as the active pulping chemicals. Generally, of course, in the pulping industry, timber, that is, cut timber or trees, is cut and converted to chips which are thereafter digested in a paper mill either by physical, semi-chemical or totally chemical techniques to form a pulp or slurry of the cellulose fibers which are separated from the liquor and collected by means of a Fourdiner machine, following which water is extracted and the formed sheet of fibers is collected, dried and rolled into sheet stock. Pulping or digesting can be accomplished by a variety of chemical substances such as sodium sulfate, sodium sulfite, sodium sulfide, alkali metal bisulfites, hydroxides, etc.; which chemicals are employed as cooking liquors to attack the lignins and other binding constituents which hold the cellulose fibers together in the form of the wood as it grows and matures. Over the years, pulping economy has made necessary the employment of a variety of chemical recovery operations. These chemicals, for example, sodium chemicals, can be treated after pulping and essentially recovered, revitalized by treatment and addition of makeup chemicals to yield active liquors available for reintroduction as fresh pulping chemicals to effect digesting separation of the desired cellulose fibers.

Pulping and the various chemical recovery techniques require tremendous amounts of water, usually taken from rivers, streams, lakes and the like. By reason of the contact of the water with the wood, with pulping chemicals, with the various by-products of the chemical reactions taking place and the pickup in the water of the waste fiber binding constituents such as lignins, organic by-products, etc., the water becomes very contaminated and considerably discolored.

Water which is discolored is, of course, very undesirable and unacceptable as a replacement for water drawn from natural supplies. In view of the tremendous amounts of water employed in industrial paper mill and similar operations, the problem of discoloration is of considerable importance which takes the form of a stimulus to remove or reduce contamination and discoloration.

It has been determined that the coloration, which is in part a by-product of pulping, is imparted to the water by what are referred to in the art as color bodies. These color bodies include chemical entities such as lignins, tannins and long chain organic polymers of resinous character which are by-products of the chemical attack of the various pulping chemicals employed on the above referred to bonding cements which hold the cellulose fibers which make up the wood or timber together.

It has also been theorized that the color bodies are composed of a reaction product of calcium ion with either phenolic or enolic groups which are by-products of the hydrolysis or lignin. The color bodies or complexes, if you will, are extremely small, measuring in the colloidal range, which makes the removal of these color bodies quite difficult.

There are known in the art a number of techniques for attempting to deal with the problem of discoloration, impurities and contaminants in paper mill effluent. Thus, in U.S. Pat. No. 3,120,464, there is disclosed a method wherein spent liquor, containing organic color bodies, is treated with lime, that is, calcium oxide, serving to absorb the color bodies for separation from the spent liquor. The so-called lime technique has been refined by the expedient of employing massive dosages of lime which, unfortunately, adds considerably to the expense. Reducing the amount of lime to reduce the attendant expense results in the formation of a gelatinous precipitate which is difficult to separate by filtering or like separation operations. The gelatinous precipitate is believed to be a complex reaction product of lime with the organic constituent of the binding cement holding the fibers together.

U.S. Pat. No. 3,531,370 also discloses a process for removing color bodies by the use of lime and additionally a cellulosic fiber to obtain effective settling.

U.S. application Ser. No. 149,534, filed June 3, 1971, entitled "System For Removing Color From Paper Mill Liquid Waste" now U.S. Pat. No. 3,736,254 issued May 29, 1973, and U.S. application Ser. No. 301,132, filed Oct. 26, 1972, entitled "Method Of Decolorizing Waste Process Liquid Discharged By A Paper Mill," said applications being assigned to the same assignee as the present application, are also disclosive of processes for overcoming the problem of discoloration of mill effluent.

It is an object of the present invention to provide a method of effectively accomplishing removal of coloration or discoloration present in paper mill liquid effluent, said effluent including both liquid from the pulping process and liquid from the machine room.

It is a particular object of the present invention to provide such a method which is effectively integrated into existing pulping operations and attendant and collateral chemical recovery operations.

It is a particular object of the present invention to provide such a method which employs as additives readily available materials and substances and which result in by-products which are redirectable and are reemployable in the recovery and/or pulping system.

It is a significant object of the present invention to provide a system which does not feature the utilization of the relatively expensive lime and furthermore is avoidative of the production of any gelatinous by-product but rather results in a relatively easily separable precipitate which is easily handled and is advantageously directed to recovery operations already employed.

The foregoing and, as well, other objects of the present invention will become apparent to those skilled in the art from the following detailed description taken in conjunction with the annexed sheets of drawings on which there are presented, for purposes of illustration only, several embodiments of the present invention including a schematically illustrated sequence of steps and, additionally, a somewhat diagrammatic illustration of the inventive method integrated into a kraft pulping and chemical recovery system.

IN THE DRAWINGS

FIG. 1 is a schematic block and line flow diagram illustrating the flow of the kraft mill effluent through the sequence of operational steps for combination with

various additives to yield the final substantially color-free liquid; and

FIG. 2 is a somewhat more detailed block and line flow sheet illustrating the movement of the mill effluent as in FIG. 1 but additionally showing the flow movement of the additives from and to the various streams of liquids in a typical kraft chemical recovery system.

Considered most basically, the present invention envisions a technique for accomplishing removal of color bodies by purposefully causing an in situ precipitation, within the mass of discolored liquid effluent, of insoluble calcium carbonate; the discolored effluent having been previously treated in such manner as to contain a sufficient concentration of soluble calcium bicarbonate, whereby the precipitate attracts and carries color bodies along in a subsequent gravity separation thereof. In accordance with one embodiment of the present invention, this treatment is effected by conjointly mixing, with the discolored effluent, lime mud and carbon dioxide at a pressure greater than atmospheric as will favor a chemical reaction converting the calcium carbonate to soluble calcium bicarbonate.

Considered in a more commercial sense, the present invention envisions the employment of readily available calcium carbonate combined, in excess, with the mill effluent liquid to be decolorized, followed by a combination, under pressure, with readily available carbon dioxide, preferably in the form of lime kiln stack gases, to convert the calcium carbonate to soluble calcium bicarbonate, following which the pressure is released, resulting in a reversal of the pressure-induced reaction and consequently the formation of insoluble calcium carbonate once again, which precipitation together with gravity effectively attracts and carries color bodies in conglomeration therewith; the precipitate and color bodies being easily separated by simple clarification; the effluent being available for re-introduction into the source, stream, or employed for process liquid free of any coloration. The re-precipitated calcium carbonate and the color bodies carried thereby can be readily directed to the lime kiln for conversion to reusable lime.

Reference should now be had to FIG. 1 for a brief and simplified illustration of the sequence of steps and operations constituting the treatment, in accordance with the present invention, of the discolored aqueous kraft mill effluent proceeding from the entire kraft mill operation. As can be seen, starting at the left of FIG. 1, the discolored mill effluent is directed together with a slurry of calcium carbonate mud to mixing tank 11. The resulting mixture is pumped by pump 13 through pressure-maintaining check valve 15 to pressure vessel 17 into which is essentially simultaneously introduced, through line 19, pressurized carbon dioxide present in by-product stack gases emanating from lime kiln 21; the stack gases containing the carbon dioxide being pressurized by compressor 23. The pressure vessel is designed in terms of capacity or volume to provide a residence time, of the mixture of Kraft effluent and calcium carbonate in admixture with pressurized carbon dioxide, of from about 2 to 5 minutes, whereby essentially all of the calcium carbonate is converted at the higher pressure to water soluble calcium bicarbonate. Pressure is maintained within the pressure vessel by a pressure relief valve 25 in the outlet line 17a of vessel 17; said valve being predeterminedly set to maintain a

desired pressure desirably within the range of about 20 to 100 pounds per square inch. It will be appreciated that the quantity of effluent to be treated together with the amount of calcium carbonate slurry and quantity of carbon dioxide, bearing in mind the concentration of the carbon dioxide in the lime kiln exhaust gases, will determine the size and capacity of the pressure vessel 17. The pressure relief valve 25, in addition to maintaining the desired pressure within the vessel, serves to release the liquid, e.g., aqueous calcium bicarbonate, to clarifier tank 27 maintained at atmospheric pressure; the release in pressure initiating the formation of insoluble calcium carbonate. The calcium carbonate precipitate increases in amount and propagates, gradually falling to the bottom of the tank, sweeping with it as it grows in size the color bodies. The efficiency of color removal according to this method is believed in part due to the fact that the initial precipitate is quite small and serves to attract in admixture therewith the extremely small, in fact, colloiddally sized, color bodies. The precipitate continues to form and grow, carrying with it differing sized color body entities. In accordance with a preferred embodiment, the removal of the color bodies is very efficiently accomplished by an excess of calcium carbonate which is first solubilized in the pressure vessel and then is reprecipitated in the clarifier tank, providing thereby a vast multitude of formed insoluble molecules of insoluble calcium carbonate which propagate and grow in the manner above described, resulting in a mass sweeping action upon the body of liquid in the clarifier tank. The precipitate falls, as indicated, to the bottom of the tank, carrying with it the color bodies; all of which are removed through line 29 as mud and redirected to calcium carbonate mud storage and/or to the lime kiln for recovery of calcium oxide and reproduction of carbon dioxide. Simultaneously with the initiation of precipitation of the calcium carbonate, there is initiated a release of carbon dioxide as a gas which bubbles, as it were, to the surface and passes harmlessly to the surrounding atmosphere.

Liquid constituting the "tops" in the clarifier tank 27 is passed via line 31 to a secondary treatment and storage tank 33, providing additional time for stabilization of the liquid to a final pH ranging from about 7.8 to about 8.4. Here again, any residual precipitate which may and frequently does form is withdrawn at the bottom and directed to the calcium carbonate while effluent water is drawn off as stabilized, essentially color-free water adapted for reintroduction into the stream, river or lake from which originally obtained or available for reintroduction to the mill operation at whatever point fresh color-free water is desired or needed. The stabilization of the clarified liquid in tank 27 may be hastened by utilizing a violent mixing operation.

To more clearly understand and visualize the integratability of the process of the present invention into a commercial mill operation, reference should be had to FIG. 2 wherein the sequence of operations of FIG. 1 are illustrated again, utilizing the same reference numbers for the same illustrated elements, lines, tanks, etc., but additionally showing the various collateral kraft mill operations and line flow of various streams, particularly those integratively adjunctive to the sequence of steps illustrated in FIG. 1. A description of the flow diagram of FIG. 2 is best begun by referring to the block 41 entitled "Causticizing System." By causticizing sys-

tem is generally meant the reactivation of green liquor by the addition of lime to form white liquor which is composed of the active chemicals, sodium hydroxide and sodium sulfide. This white liquor is utilized as the prime active chemical for the pulping operation not illustrated. As is readily known, however, the pulping proceeds in large tank digesters where the timber in the form of wood chips are essentially cooked in the white liquor. The cellulose fibers of the wood are liberated by the attack of the active chemicals on the binding constituents such as lignins, etc., with the chemical becoming gradually depleted in activity and the liquor discolored by the by-products, ultimately resulting in a mass of unrefined cellulose fibers in black liquor. The fibers are separated, washed, continuously collected as a sheet on the Fourdiner machine and dried into paper roll stock, while the black liquor, rich in sodium values, is concentrated in a large capacity evaporator, and finally burned to drive off organic and combustible constituents, resulting in a molten smelt which is passed into a dissolving tank containing water and, as well, amounts of various wash water from other operations as will be described. The liquid in the dissolving tank containing the dissolved smelt is referred to as green liquor. It is composed principally of sodium carbonate and sodium sulfide and is pumped via line 43 to the causticizing system 41 where lime, calcium oxide, is introduced, as previously described, resulting in the formation of fresh white liquor for further digestion of the next batch of wood chips.

The causticization of green liquor to white liquor involves a chemical reaction having, as a by-product, a slurry of calcium carbonate, CaCO_3 , referred to as mud. The mud is drawn through line 48 to a mud washer and thence to mud storage 51. It may be incidentally noted that the calcium carbonate mud wash water is stored as "weak wash" in a storage tank 50 from which it is directed to the smelt dissolving tanks to assist the solubilizing of the molten smelt to produce green liquor. Calcium carbonate mud is a plentiful by-product of the causticization system employed in the typical kraft mill and in fact historically presented a problem of disposal. However, it was soon realized that the calcium carbonate could be converted to lime, CaO . Thus, as shown, an amount of the lime mud is burned in lime kiln 21 employing whatever fuel is economically available, usually natural gas; the calcium carbonate at the temperatures maintained decomposing to ultimately form calcium oxide powder which is conveyed via line 21a to the lime storage 46. The burning of the fuel results, of course, in flue gases while the decomposition of the CaCO_3 yields carbon dioxide gas typically measuring 20 to 25 percent of the lime kiln stack gases. These are normally passed to the atmosphere as they are largely ecologically harmless.

It can be appreciated from the description hereinabove that the practice of kraft chemical recovery process inherently yields a plentiful supply of calcium carbonate and a plentiful supply of carbon dioxide.

In accordance with the present invention, both of these materials are employed and their use was described in the description of FIG. 1. By way of reiteration and referring back to FIG. 2, an amount of the calcium carbonate mud is mixingly combined in tank 11 (appearing in the lower left of FIG. 2) with the discolored kraft mill effluent and pumped via pump 13, through check valve 15, into the pressure vessel 17. Sim-

ultaneously, stack gases emanating from the lime kiln 21, or at least a portion thereof, are compressed in compressor 23 and piped to the pressure vessel 17 for reaction with the mixed slurry components, resulting in the formation, usually 2 to 5 minutes residence time, of soluble calcium bicarbonate which is released via the relief valve 25 into the clarifier tank 27. The harmless carbon dioxide gas is given off simultaneously with the formation of insoluble calcium carbonate precipitate which falls, together with attracted color bodies, to the bottom, as described, and is pumped via line 29 back to the mud storage 51. The aqueous effluent from clarifier 27 passes via line 31 into the storage vessel 33 in the manner described hereinbefore in FIG. 1 or in accordance with a subsidiary embodiment of the present invention, violently agitated in tank 60 to hasten the stabilization and residual precipitation, if any. A secondary clarifier tank 62 may then be used to separate the stabilized liquid which may be returned to the process or stream while any residual precipitate with agglomerated color bodies can be directed back to mud storage via line 62a.

From the foregoing description, it will be appreciated that readily available by-product materials are utilized in treating discolored kraft mill effluent by a sequence of steps which are easily integrated into the Kraft mill operation, thereby accomplishing effective removal of the color bodies causing the discoloration and at the same time regeneration of one by-product, namely, calcium carbonate, for further conversion to lime which is, as described, usable in producing digesting liquor.

It has thus been further demonstrated that the process in accordance with the present invention is eminently practicable for a kraft mill operation since the kraft pulping process inherently yields an abundance of calcium carbonate and carbon dioxide by-products of use in the process of the invention.

Contemporaneous with the foregoing, it is an advantage of the present invention that different levels or concentrations of discoloration of the mill effluent can be readily accommodated. For example, should it be observed that the effluent discoloration is or has increased to a higher level, the efficiency of removal of the color bodies causing the discoloration can be increased in any one or more of the following ways. In the first place, efficiency of color body removal can be improved by increasing the amount of soluble calcium bicarbonate since the reconversion of the calcium bicarbonate to insoluble calcium carbonate precipitate will result in a larger amount of precipitate, serving as sites for attracting the color bodies and ultimately sweeping them as the precipitate forms and falls by gravity to the bottom of the storage vessel or clarifying tank. The increase in production of soluble calcium bicarbonate can be accomplished by an increase in the pressure within the pressure vessel and/or an increase in the amount of lime mud combined with the kraft mill effluent and/or an increase in the amount of lime kiln stack gases (carbon dioxide) introduced into the mixture of lime mud and discolored kraft mill effluent. By way of example, it has been determined that a kraft mill having a daily operating production measuring about 850 tons of pulp will necessarily discharge about 10 million gallons of effluent and, if the kraft mill referred to includes a lime kiln recovery system for production of reusable calcium oxide, will yield or produce lime mud (calcium carbonate) at a rate of about 475-500 pounds per min-

ute. The lime kiln combustion of this lime mud to recover the lime will necessarily yield stack gases, measuring approximately 20–25 percent carbon dioxide, at a rate of about 45,000 cubic feet per minute. The just-described values in terms of effluent, yield of lime mud and stack gases have been correlated with the practice of the present invention, conducted with differing pressures within the pressure vessel 17, as illustrated in either of FIGS. 1 and/or 2. Table 1 below contains the tabulated data, at different pressures, of dry mud and lime kiln stack gas capacity, envisioning a kraft mill effluent throughput of 7,000 gallons per minute; which rate corresponds to the 10 million gallon per day yield.

TABLE 1

Pressure psig	Dry Mud (CaCO ₃) lbs/min (100% excess)	Lime Kiln Stack Gases cu ft/min 20% CO ₂ (100% excess)
30	89.6	1740
50	101.0	1950
100	122.0	2360

As can be seen, higher rates as to lime mud and carbon dioxide are achieved at the higher pressure values which necessarily results in an increase in the production of soluble calcium bicarbonate and necessarily in an increase in the amount of insoluble calcium carbonate as the composite liquid is passed from the pressure vessel to the clarifier tank whereby the increased amount of precipitate is capable of efficiently attracting and sweeping therewith a greater amount and quantity of discoloration-causing, color bodies.

The practice of the present invention, in addition, of course, to removing coloration, desirably affects the biological oxygen demand (BOD) and the chemical oxygen demand (COD). Color has been found to be reduced by as much as 95.3 percent, while the BOD has been reduced by as much as 50 percent and the COD has been reduced by as much as 78 percent.

While there has been disclosed with considerable detail certain preferred manners of performing this invention, it is not intended or desired to be solely limited thereto, for the procedure may be modified, the precise proportions of the materials utilized may be varied, and other materials having equivalent properties may be employed if desired without departing from the spirit and scope of the invention unless such departures would offend and violate the language of the appended claims.

I claim:

1. A method of reducing color present in paper mill effluent liquid which comprises:

1. mixing, into the effluent liquid, a liquid including an excess of calcium carbonate, CaCO₃,
2. pressurizing said liquid to greater than atmospheric in the presence of a fluid including an excess of carbon dioxide, CO₂, whereby said calcium carbonate, CaCO₃, is substantially converted to soluble calcium bicarbonate, CaHCO₃, and
3. discharging the pressurized liquid to atmospheric pressure whereby said calcium bicarbonate, CaHCO₃, substantially converts to insoluble calcium carbonate, CaCO₃, as a precipitate carrying therewith color-imparting substances present in said paper mill effluent liquid.

2. The method as claimed in claim 1 which includes the step of (4) separating the precipitate containing color-imparting substances from the remainder of the liquid.

3. The method as claimed in claim 2 which includes the step of (5) directing the separated precipitate to a lime kiln for combustion conversion of CaCO₃ to CaO.

4. A method of reducing color present in paper mill effluent liquid which comprises:

1. mixing into the effluent liquid a liquid including an excess of calcium carbonate, CaCO₃,
2. pumping said mixture under pressure into a tank together with a fluid including an excess of carbon dioxide, CO₂, and maintaining said mixture therein under a pressure greater than atmospheric for a time sufficient to effect substantial conversion of calcium carbonate, CaCO₃, into soluble calcium bicarbonate, CaHCO₃,
3. discharging the pressurized liquid comprising essentially calcium bicarbonate, CaHCO₃, to atmospheric pressure whereby said calcium bicarbonate, CaHCO₃, essentially converts to insoluble calcium carbonate, CaCO₃, as a precipitate, carrying with said precipitate, in agglomerated fashion, color-imparting substances and entities carried in said paper mill effluent,
4. separating effluent liquid from precipitate and
5. exposing said effluent to a stimulus to effect residual precipitation, formation of color bodies and stabilization of effluent pH to from 7.8 to 8.4.

5. In a system of pulping wood by the kraft process wherein sodium hydroxide and sodium sulfide are the active pulping chemicals combined with wood chips to attack the binding components and resulting in the liberation of cellulose fibers and wherein black liquor recovered from the pulping reaction is concentrated and burned to recover sodium values in the form of green liquor including sodium carbonate and sodium sulfide, which green liquor is thence causticized with recovered lime to yield fresh pulping chemicals and a by-product comprising calcium carbonate mud, a portion of said calcium carbonate being desirably burned to yield reusable lime for said causticizing and resulting in by-product gases rich in CO₂, said pulping process and recovery process resulting in a considerable amount of mill effluent liquid which is normally ecologically undesirable due to discoloration caused by the presence of color bodies; the improvement wherein said effluent mill liquid is treated in accordance with the following series of steps integrated into the pulping process just described, said steps being as follows:

1. mixing with the discolored mill effluent liquid an amount of said calcium carbonate slurry liquid separated from the causticizing reaction of lime with sodium carbonate and sodium sulfide,
2. combining said mixture under a pressure greater than atmospheric with said CO₂ by-product of the burning of calcium carbonate mud, thereby converting calcium carbonate to soluble calcium bicarbonate,
3. discharging the liquid comprising calcium bicarbonate into a settling tank at atmospheric pressure whereby said calcium bicarbonate converts to insoluble calcium carbonate as a solid precipitate which attracts and carries color bodies in agglomeration or admixture therewith,

4. separating calcium carbonate precipitate and color bodies from said liquid whereby said liquid is essentially decolorized and
5. returning said precipitated calcium carbonate to said lime recovery.
6. A method of reducing color present in paper mill effluent liquid which comprises the following steps:
 1. combine said liquid effluent with a slurry of calcium carbonate,
 2. combine said step (1) mixture under a pressure greater than atmospheric with carbon dioxide, CO_2 , thereby converting said calcium carbonate to soluble calcium bicarbonate,

3. expose the resultant of steps (1) and (2) to a reduction in pressure to atmospheric pressure to convert soluble calcium bicarbonate to insoluble calcium carbonate which forms a precipitate of said calcium carbonate, said precipitate attracting and carrying color bodies therewith, and
4. separate said precipitate and color bodies from said effluent.
7. The method as claimed in claim 6, wherein said pressure measures about 20 to 100 pounds per square inch gauge.

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