

Sept. 18, 1973

U. T. GREENE

3,759,784

METHOD OF BLEACHING PULP WITH AN AQUEOUS CHLORINE SOLUTION
WHILE SUPPRESSING VAPORIZATION OF LIQUID CHLORINE

Original Filed June 12, 1969

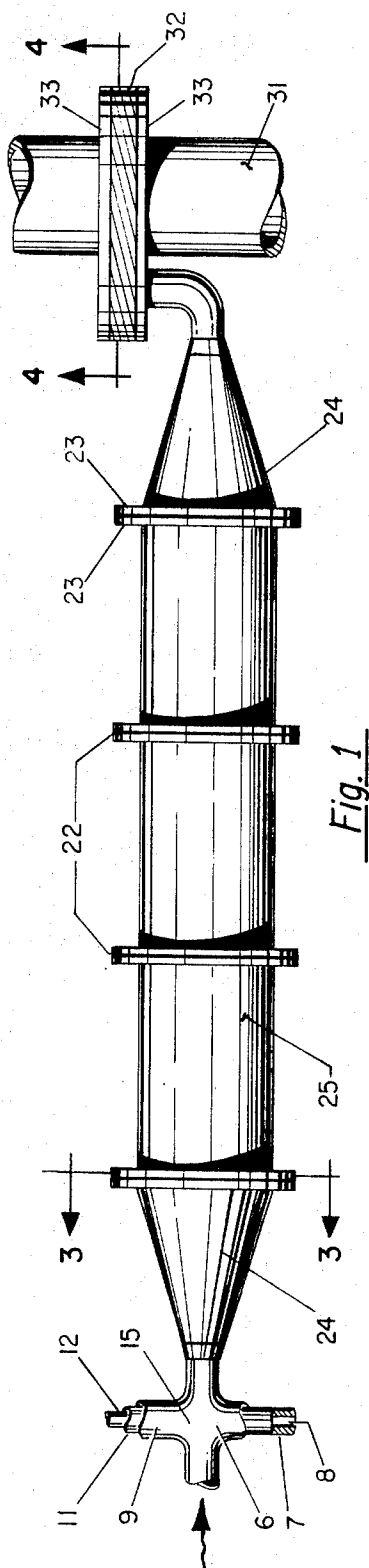


Fig. 1

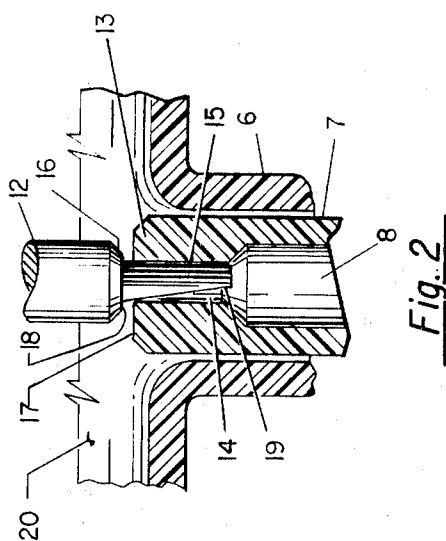


Fig. 2

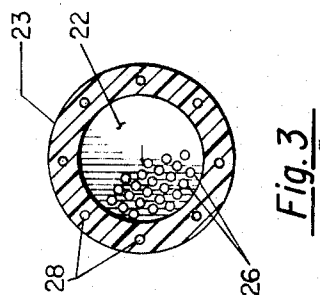


Fig. 3

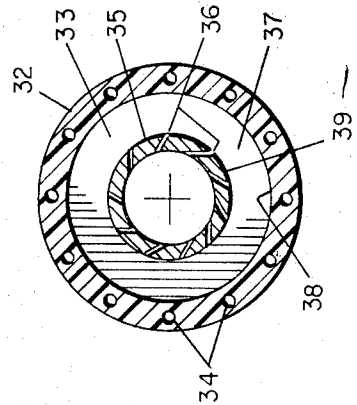


Fig. 4

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METHOD OF BLEACHING PULP WITH AN AQUEOUS CHLORINE SOLUTION WHILE SUPPRESSING VAPORIZATION OF LIQUID CHLORINE
 Udell T. Greene, Florham Park, N.J., assignor to
 Diamond Shamrock Corporation, Cleveland, Ohio
 Original application June 12, 1969, Ser. No. 832,633.
 Divided and this application Oct. 29, 1970, Ser.
 No. 85,260

Int. Cl. D21c 9/12

U.S. Cl. 162—87

2 Claims

ABSTRACT OF THE DISCLOSURE

Method for bleaching pulp with a solution of a soluble liquefied gas in a liquid chlorine solvent while permitting at least substantially full pressure on the liquefied gas to the point of incipient solution and thereafter desirable dispersion of the liquefied gas dissolving the solvent as well as providing fast and efficient flow of the resulting solvent into a liquid processing medium. The method provides for suppressed vaporization of gas, even though such suppression occurs during an accompanying pressure drop, when the liquefied gas dissolves in the solvent, and further when the resulting solution disperses in the liquid processing medium.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a divisional application of Ser. No. 832,633, filed June 12, 1969, now U.S. Pat. No. 3,582,047.

BACKGROUND OF THE INVENTION

The introduction of a soluble liquefied gas into a liquid solvent can often lead to flashing of the liquefied gas and thus to the formation of discrete gaseous bubbles within the solvent. Moreover, where such resulting solution of liquefied gas is thereafter injected into a liquid processing medium the pressure drop commensurate with such injection may lead to further flashing within the liquid processing medium. Thus at both the introduction of the liquefied gas into the solvent and of the resulting solution into the processing medium retarded solution efficiency and prolonged solution time and hence undesirable processing efficiency can often be encountered.

This may be a particular problem with a substance which is normally gaseous at standard temperature and pressure and thus may be under a pressure of 2-3 atmospheres or greater when in liquid condition. Therefore, although solution is slower, many substances which are typically shipped and/or stored in the liquid state may be permitted to become gaseous before combining with a solvent.

SUMMARY OF THE INVENTION

Dispersing apparatus is now provided which affords direct introduction of the liquefied gas into a stream of liquid solvent. Next the dispersing apparatus provides for enhanced dispersion of the liquefied gas as it dissolves in the solvent and subsequently provides for excellent dispersion of the resulting solution into a liquid processing medium, all the while suppressing flashing of gas within the apparatus. Moreover the apparatus permits at least substantially full pressure on the liquefied gas to the zone of incipient solution in the solvent.

Broadly, the dispersing apparatus of the present invention comprises a conduit confining a stream of the liquid solvent; a single-seated valve assembly, having a valve passage therethrough forming a part of the conduit, the valve assembly having means whereby a controlled flow of soluble liquefied gas is introduced directly into the stream

of solvent flowing within such passage; mixing means downstream from the valve assembly, enhancing dispersion of the soluble liquefied gas dissolving in the solvent; and a nozzle assembly downstream from such mixing means for passing the resulting solution into the liquid processing medium.

The foregoing single-seated valve assembly comprises: a valve body having a valve passage therethrough connecting spaced apart inlet and outlet ports, and forming a portion of a conduit confining the liquid solvent, with the body having two hollow side protrusions, the first of which extends outwardly from the body between the ports, and the second of which extends outwardly from the valve body at least substantially coaxial with the first and opposite same across the valve passage. A substantially rigid, stationary valve seat forms with the first protrusion a side passageway terminating in an end port opening at an end surface of such valve seat, with the end surface being positioned so that the end port opens directly into the valve passage at least along a wall thereof.

A movable valve stem within the second protrusion opposite such end port and across the valve passage, terminates in an end section adapted for at least partial insertion within the end port and for sealing thereof. The end section has at least one beveled surface longitudinally along same providing diminishing cross-sectional area for the end section toward the end port. The valve assembly lastly has means for reciprocally transporting the shaft to remove and insert the end section within the end port. Thus the end section seals the end port when in snug engagement therewith and the beveling of the end section permits fluid to flow from the end port into the valve passage in amounts increasing with the increasing removal of the shaft from the side passageway.

The invention is further directed to a method of first dissolving a soluble liquefied gas into a liquid solvent and thereafter dispersing the resulting solution into a liquid processing medium. The invention is further most particularly directed to use with substances which are normally gaseous at standard temperature and pressure and are often available in liquid condition, such as sulfur dioxide and chlorine, that can be first dissolved in concentrated solution and the solution employed in subsequent processing medium, e.g., a concentrated aqueous solution of chlorine for bleaching a pulp stream or a concentrated aqueous solution of sulfur dioxide for treating an industrial waste water.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of representative dispersing apparatus of the present invention.

FIG. 2 is a sectional view of a portion of a representative valve assembly for apparatus of the present invention.

FIG. 3 is a sectional view of an orifice plate assembly useful in the apparatus of the present invention and taken along the line 3—3 of FIG. 1, as viewed in the direction indicated by the arrows.

FIG. 4 is a sectional view of a nozzle assembly for the apparatus of the present invention taken along the line 4—4 of FIG. 1 and viewed in the direction indicated by the arrows.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In the dispersing apparatus of FIG. 1 fluid feeding from a source not shown first enters a valve assembly containing a valve housing 5 having a valve passage therethrough, not shown. From the valve housing 5 there extends a side protrusion 6 containing a side conduit 7 provided with an inlet channel 8. The valve body 5 has a second side protrusion 9 housing a guide ring 11 around

a movable valve stem 12 connecting to operating means, not shown. The valve assembly is connected to mixing apparatus containing perforated plates 22, spaced apart one from the other by hollow cylindrical sections 25, and maintained in place by flanges 23. A hollow conical section 24 connects the mixing apparatus with the valve assembly and a hollow conical section 24 also connects the mixing apparatus with the balance of the dispersing apparatus. This balance of the dispersing apparatus consists of a nozzle assembly positioned around a conduit 31. The nozzle assembly contains a second annular member 32 maintained between radial flanges 33.

Referring to FIG. 2, the side conduit 7 within the side protrusion 6 terminates in a valve seat 13. The valve seat 13 contains an end port 14 at the top of the inlet channel 8, and the valve seat 13 extends into the valve passage 20. The end section of the valve stem 12 terminates in a finger 15 extending from a shoulder 16 around the valve stem 12. The valve seat 13 ends in an end surface 17 opposite a coplanar end surface 18 of the shoulder 16. The finger 15 is provided with a beveled surface 19 extending along the finger 15 and affording diminishing cross-sectional area away from the shaft 12. For this assembly, it can be seen that the zone of incipient solution for liquefied gas entering the solvent includes the region where solvent flows between the coplanar surface 18 and the valve seat end surface 17 and around the portion of the finger 15 emerging from the end port 14.

In FIG. 3 the perforated plate 22 contains apertures 26 through the plate 22 and is positioned behind a flange 23 having bolting holes 28 through same. In FIG. 4, a second annular member 32 has an inner surface 38 and further has bolting holes 34 extending through the member 32 from a radial flange 33. The second annular member 32 surrounds a first annular member 35 having an outer surface 39 from which slots or ports 36 extend through the first annular member 35 and the inner surface 38 of the second annular member 32, a portion of the radial flange 33 forms with such annular members 32, 35 and annular opening 37.

Referring again to FIGS. 1 and 2, liquid solvent feeding from a source not shown enters the valve housing 5 in a direction as shown by the arrow. As the liquid solvent flows within the valve passage 20 it flows around the valve seat 13 and across the portion of the end surface 17 of the seat 13 not engaged by the coplanar end surface 18. The liquid solvent is at a pressure substantially as great as, to higher than, the vapor pressure of the liquefied gas, to be introduced into the solvent, based on the temperature of the solvent. Liquefied gas feeding from a source not shown and at a pressure above that of the solvent within the valve housing 5 is fed through the inlet channel 8 into the end port 14 and thus into contact with the finger 15 within the end port 14. Withdrawal of the valve stem 12 permits a flow of the liquefied gas from the end port 14 along the beveled surface 19 of the finger 15 and into immediate contact with the flow of liquid solvent within the valve passage 20. Reverse movement of the valve stem 12 places the coplanar end surface 18 of the stem 12 back in snug engagement with the end surface 17 of the valve seat 13 thereby sealing the end port 14.

As shown in FIG. 1 and FIG. 3, the liquid solvent passing from the valve housing 5 and containing the dissolving liquefied gas flows through hollow conical section 24 and then through apertures 26 in a series of perforated plates 22 spaced apart by hollow cylindrical sections 25. Referring then to FIG. 1 together with FIG. 4, resulting liquid solvent containing an enhanced dispersion of dissolved liquefied gas therein flows from a hollow conical section 24 of the mixing apparatus and into an annular opening 37 in the nozzle assembly. The resulting solution within the annular opening 37 then continues through the slots 36 in the first annular member 35 and

feeds into liquid processing medium flowing within the conduit 31.

The valve assembly need not be directly connected to the mixing means but can be spaced apart therefrom by a conduit. The mixing means can be any mixing means employed for enhancing the solution of a dissolving liquid solute in a liquid solvent such as mechanical mixing means, e.g., typically propeller agitated tanks, pumps including centrifugal pumps, and turbine mixers, as well as being hydraulic mixing assemblies such as an orifice column or turbulence mixers including the baffle-plate mixers that may have a column diameter, or the like, the same as the valve passage diameter. Moreover, the feed from the valve assembly can be divided and passed through a number of mixing apparatus in parallel. The nozzle assembly for introducing the resulting solvent from the mixing apparatus can also be one or more injector means which need not be circular but can have other cross-sectional shape. Moreover, the slots or ports in the inner or first annular member can be one or more slots which may be radial or at varying angles to radius lines and unevenly spaced.

The feed from the mixing apparatus to the nozzle assembly can enter same through the outer annular member such as in radial or tangential manner or can be divided and enter the nozzle assembly through more than one entry port in the radial flanges or outer annular member or both. Also, where perforated plates are employed in the mixing apparatus, each plate may have one or more holes and the holes can have axes which are not transverse to the plane of the plate. Typically the side flanges of the nozzle assembly are integral with the conduit through which the processing medium flows and the inner annular member of such assembly is fastened to the flanges by cementing or welding, which can include solvent welding when assembly parts are receptive to same. However, any other conventional fastening means may be employed, for example, the inner annular member can have an inner lip extending around and within the conduit, thereby holding it in place.

The end surface of the valve seat should be at least along a wall of the valve passage to insure introducing the liquefied gas directly into contact with the solvent liquid flowing within the valve passage. Also, the side protrusions of the valve body need not be at the mid-section thereof and need not be transverse to the valve passage but can be canted either against the flow of the liquid solvent within the passage or away from same, so long as these protrusions are substantially coaxial with one another across the valve passage to permit sealing of the end port with the end section of the shaft. Preferably, the side protrusions are completely solid and/or filled up to the wall of the valve passage thereby preventing flow of solvent liquid into such side protrusions. The beveled surface for the end section of the shaft, or valve stem, can be more than one such surface or a beveled surface completely around such section, as a conical surface, e.g., so that the finger in FIG. 2 is a truncated cone. Also, the end surface of the valve seat need not be flat but can be a rounded surface projecting into the valve passage.

The dispersing apparatus can be typically employed in commercial operation involving the introduction of a soluble liquefied gas such as chlorine into the aqueous medium to form a concentrated solution wherein the downstream use in the processing medium might simply be water purification, or liquid chlorine into a liquid hydrocarbon, or a concentrated liquefied carbon dioxide solution in water for downstream introduction into a liquid beverage concentrate, or liquefied sulfur dioxide first into water and then the solution into waste waters, e.g., industrial waste waters. In the special application of liquid chlorine into an aqueous medium, such medium can typically be at a temperature within the range from about 35°-120° F. and under a pressure of between about 20-200 p.s.i.g. For such conditions the pressure on the liquid

chlorine is advantageously between about 10–40 p.s.i.g. above the pressure of the aqueous medium although greatly higher pressure differences, e.g., 100 p.s.i.g. or more, are operational. A pressure differential below about 10 p.s.i.g. can provide inefficient introduction of liquid chlorine into the aqueous medium and a pressure differential above about 40 p.s.i.g. over an extended period may lead to a jet effect within the valve assembly and deleterious mechanical erosion of assembly parts.

For the application wherein the processing medium is a suspension of pulp in a liquid medium and an aqueous chlorine solution is used in bleaching the pulp, the pulp suspension is typically at a pressure of between about 10–80 p.s.i.g., which pressure is established substantially by the hydrostatic head of the bleaching tower and by the friction presented in the apparatus piping from the introduction of the aqueous chlorine solution to the point of entry for the suspension into the tower. The pressure of the aqueous chlorine solution before feeding into the pulp suspension is typically above the vaporization pressure for the liquid chlorine at the temperature of the aqueous medium and for the concentration of the chlorine therein. For example, with an aqueous medium at 100° F. and for a saturated solution, the pressure established on the aqueous chlorine solution is typically above about 142 p.s.i.g., whereas for such saturated conditions where the temperature of the aqueous medium is at 120° F. the pressure would be above about 188 p.s.i.g.

However, when the liquid chlorine is introduced into the aqueous medium, the apparatus provides that elevated pressures above the pressure at which chlorine will vaporize need not be attained for excellent suppression of chlorine vaporization. For example, results have shown that at a water temperature of 107° F. and a pressure of 150 p.s.i.g. under which conditions of temperature and pressure liquid chlorine can otherwise be expected to vaporize, virtually no deleterious formation of chlorine vapor has been experienced with such apparatus. Nonetheless, it can be seen from the foregoing that pressure differentials between the aqueous chlorine solution and the pulp suspension for water temperatures from 100°–120° F. can be up to about 150 p.s.i.g. or more.

For this typical application, i.e., of chlorine into water and then chlorine water into a pulp suspension, the entire surface area of the valve assembly exposed to the liquid chlorine or to the liquid chlorine dissolving in the water is best provided by a vinylidene fluoride resin or a fluorinated ethylene-propylene resin. At the elevated pressures for the liquid chlorine, e.g., approaching 200 p.s.i.g., a fluorinated ethylene-propylene resin valve seat such as the valve seat 13 in FIG. 2 can show some deflection under pressure which, when the pressure is relaxed, will return to a normal state. For example, the inner section of the valve seat 13 around the entry port 14 in FIG. 2 can be displaced slightly inwardly toward the center of the valve passage 20. Thus the valve seat can be somewhat flexible. The balance of the apparatus downstream of the valve assembly, i.e., the mixing means and a nozzle assembly, may then be any of the materials useful for confining an aqueous solution of chlorine, e.g., ceramic lined apparatus and polyvinyl chloride lined apparatus, or elements such as the annular members of the nozzle assembly can be completely fabricated from titanium or polyvinyl chloride or the like.

More particularly, in referring again to the drawings, water under a pressure of 115 p.s.i.g. and at a temperature of 73° F. is passed through the valve passage 20 at a rate of 6.6 gallons per minute. As the water is flowing through the valve passage 20, the end port 14 of the valve seat 13 is closed by the end section of the valve stem 12. Thereafter the valve stem 12 is gradually moved upwardly so that liquid chlorine, feeding into the end port 14 of the valve seat 13 at a pressure of about 175 p.s.i.g. is fed through the valve port 14 into the valve passage 20. Such

feed is gradually increased to a chlorine feed rate of 1.0 pound per minute.

The liquid chlorine dissolving in the water in the valve passage 20 is fed downstream through a pipe having a constant inside diameter the same as the valve passage except that the pipe contains four perforated plates 22 placed between hollow cylindrical pipe sections 25. Each perforated plate 22 has a single aperture 26 which decreases the inside pipe diameter by a factor of one-half. This mixing apparatus was constructed so that the flow of the liquid therethrough could be visually inspected for chlorine flashing and/or hydrate formation.

In a conduit 31 having an inside diameter three times as great as the inside diameter of the hollow cylindrical sections 25 there is fed 62 gallons per minute of water at a temperature of 73° F. and a pressure of 13 p.s.i.g. The solution of chlorine in water is fed from the mixing assembly into an injector assembly and flows from the injector assembly through a single orifice having a $\frac{3}{16}$ inch diameter. The conduit 31 simulating a conduit for carrying a pulp slurry is also constructed for visual inspection of chlorine flashing and/or hydrate formation within the conduit. During operation both the mixing assembly and the conduit 31 are thus visually inspected and no chlorine flashing or hydrate formation is visually observed, although hydrate formation would not be expected. Some gas is visually observed to be present in the conduit 31 downstream from the injector assembly but such gas is not regarded as significant and is not observed to be attributable to chlorine flashing.

Moreover the flow from the conduit 31 is collected, chlorine dissolved therein neutralized by sodium hydroxide, and the neutralized medium analyzed to determine actual chlorine content in the conduit 31 out-flow. By this method and by comparing the results with the flow of chlorine into the valve passage 20 from the end port 14, it is found that 98 percent of input liquid chlorine is contained in the liquid out-flow from the downstream conduit. These results are deemed to be excellent and the apparatus is regarded as highly suitable for bleaching of pulp suspensions.

Another run is made with the apparatus with water passing through the valve passage 20 at a temperature of 40° F. and a pressure of 80 p.s.i.g. at a rate of 5 gallons per minute. Liquid chlorine entering the end port 14 at a temperature of 83° F. and a pressure of about 165 p.s.i.g. is fed into the water within the valve passage 20 at a rate of 1.5 pounds per minute. At such a rate the chlorine feeding into the water at the valve as well as in the downstream mixing apparatus is in an amount of 0.3 pound per gallon of water. Under these conditions there is observed by visual inspection to be no chlorine flashing and to be no noticeable formation of chlorine hydrate, even though with a water temperature of 40° F. and a pressure of 80 p.s.i.g., a chlorine content of 0.3 pound per gallon in water can be expected to provide appreciable amounts of hydrate formation. The conditions under which hydrate formation, i.e., $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ formation, can be expected, may be best understood by referring to the data presented, for example, in Perry, "Chemical Engineer's Handbook," 3rd edition, page 674 and re-charting such data, as equal pressure lines, on a chart showing solubility of chlorine in water vs. temperature of the water.

The solution leaving the mixing assembly is passed into the pulp simulator conduit 31 through which conduit water at a pressure of 14 p.s.i.g. and a temperature of about 72° F. is flowing at a rate of 62 gallons per minute. Since no visual chlorine vaporization or hydrate formation is found by visual observation of the apparatus, the apparatus is deemed in addition to being excellently suited for the chlorine bleaching of a pulp suspension to also be excellently suited for such operation free from chlorine vaporization and hydrate formation where such might otherwise be expected.

For the typical application of dissolving chlorine into an aqueous medium and then feeding the resulting solution into a pulp suspension, the ports or slots through which the solution feeds into the suspension, where such ports are at least essentially circular in cross section, they have a diameter advantageously on the order of about $\frac{3}{8}$ inch or less to enhance fast dispersion of such solution into the pulp suspension. The size employed for each slot or port, which size can vary from port to port, will be dependent upon the number of ports available and the flow of chlorine solution desired into the pulp suspension, which in turn will be dependent upon the pressure drop. For example, with a pulp suspension at a pressure of about 30–35 p.s.i.g. and an aqueous chlorine solution at a pressure of about 110–125 p.s.i.g., a circular port of 0.25 inch diameter will pass about ten gallons per minute of chlorine solution into the pulp suspension. The number of such quarter-inch slots thus employed will then depend upon the total amount of such solution desired to be passed into the pulp suspension for a given time period, which in turn can be readily determined by the concentration of chlorine in the aqueous solution and the desired concentration of chlorine in the treated pulp suspension.

Although the total amount of the liquefied gas which will be introduced into the liquid solvent is dependent upon a number of factors including type of solvent and type of liquefied gas as well as the pressure under which the solvent is flowing through the valve passage, for the typical introduction of liquid chlorine into an aqueous medium at a pressure for example of 120° p.s.i.g., useful solutions of liquid chlorine in aqueous medium typically contain not substantially above about 0.5 pound of chlorine per gallon of aqueous medium. Moreover, the amount of dissolved liquefied gas that should be present in the liquid processing medium can also be dependent upon a number of factors such as those discussed hereinabove. For the typical introduction of liquid chlorine into water and for introduction then of the dissolved chlorine in the water into a pulp stream the desired amount of chlorine is almost always not above about 20 weight percent and is typically ten weight percent or less, such percent being based on the total downstream weight of the dry pulp content of the slurry. In conventional pulping operations such content is often desirably between about 3–7 weight percent chlorine by weight of the dry pulp content of the slurry.

It is to be understood that, although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

What is claimed is:

1. The method of bleaching pulp, suspended in a liquid medium, with an aqueous solution of chlorine where, before bleaching, liquid chlorine is dissolved directly into the aqueous medium while retarding chlorine hydrate formation and permitting at least essentially full pressure

on the liquid chlorine to the zone of incipient solution, and while suppressing vaporization of liquid chlorine dissolving in aqueous medium, as well as suppressing vaporization of liquid chlorine from the resulting chlorine solution upon passage into the pulp suspension for bleaching, including freedom from subsequent formation of a separate chlorine vapor phase, which method comprises:

- (A) passing a flowing aqueous medium at a temperature above about 35° F., within and through a valve passage housed in a valve body, at a pressure substantially as great as, to higher than, the vapor pressure of chlorine at the temperature of the aqueous medium and at least above about 20 p.s.i.g.;
- (B) feeding said liquid chlorine into a side passageway of said valve body at a pressure of about 10–100 p.s.i.g. above the pressure of the aqueous medium in the valve passage, and into contact with a valve stem end section for sealing an end port of said side passageway, said end port being positioned at least partially within said valve passage;
- (C) feeding a controlled flow of liquid chlorine from said end port directly into said aqueous medium flowing within the valve passage in an amount sufficient to provide not substantially above about 0.5 pound of chlorine per gallon of aqueous medium;
- (D) passing the resulting flow of liquid chlorine solution in liquid aqueous medium downstream from said valve passage through mixing means;
- (E) providing a suspension of pulp in an aqueous liquid medium at a pressure below the pressure of the aqueous chlorine solution passing through said mixing means; and
- (F) feeding said aqueous chlorine solution, with an attendant pressure drop, from said mixing means into the pulp suspension in an amount sufficient to provide not substantially above about 20 weight percent chlorine, based on the dry pulp content of said pulp suspension.

2. The method of claim 1 wherein said suspension of pulp is at a pressure between about 10–80 p.s.i.g., and said pulp suspension is fed with sufficient solution to provide below about 10 weight percent chlorine, basis dry pulp content of said suspension.

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S. LEON BASHORE, Primary Examiner

A. L. CORBIN, Assistant Examiner

U.S. Cl. X.R.

62—48; 137—605