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2,178,696 11/1939 Muskat et al. .... 8/108  
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[54] **BLEACHING OF SHREDDED OR FLUFFED**  
**CELLULOSIC PULP WITH GASEOUS CHLORINE**  
**MONOXIDE**  
**17 Claims, 2 Drawing Figs.**

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8/108, 8/109, 162/63, 162/67, 162/73, 162/76,  
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**ABSTRACT:** A process for bleaching a fibrous cellulosic pulp which comprises bleaching the pulp at high consistency and in the form of fluffed or shredded fibers and fiber aggregates with chlorine monoxide in the gaseous phase.

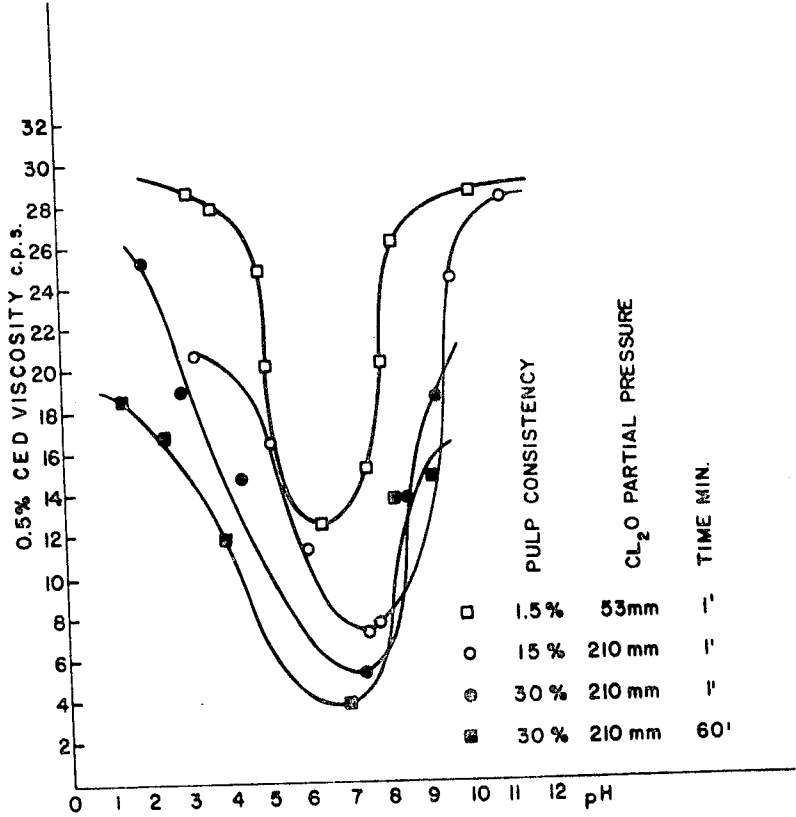


FIG 1

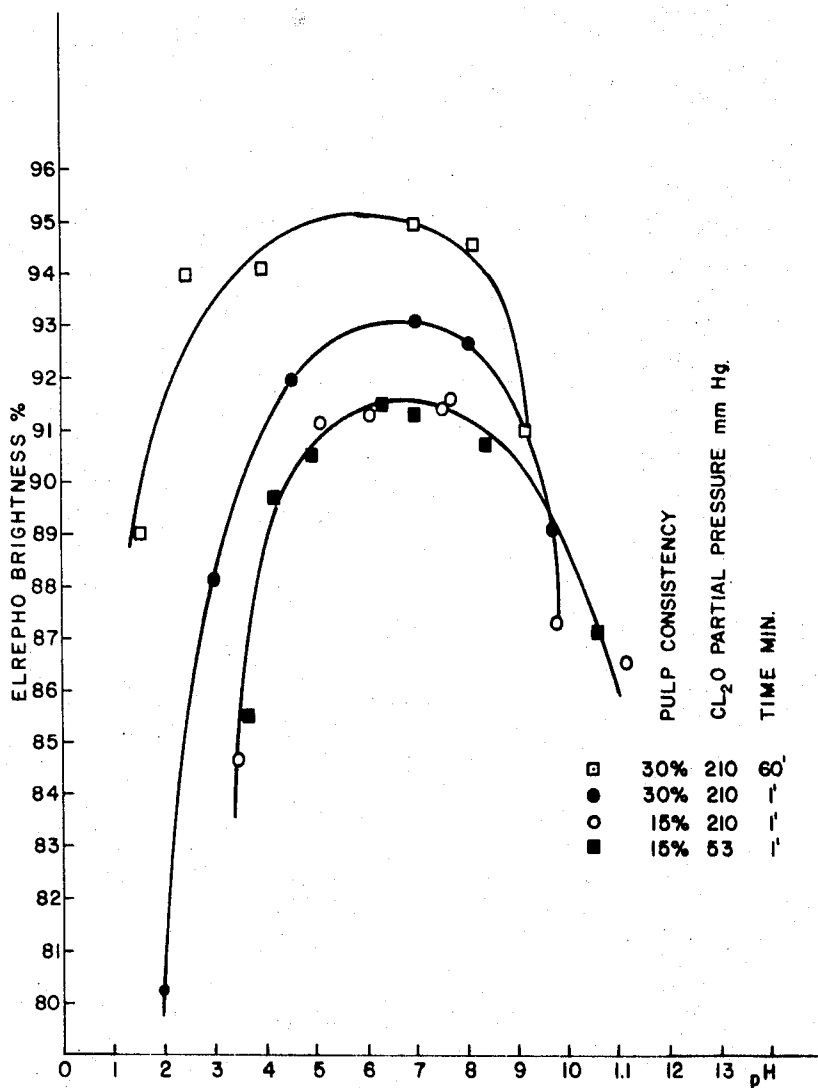


FIG 2

# BLEACHING OF SHREDDED OR FLUFFED CELLULOSIC PULP WITH GASEOUS CHLORINE MONOXIDE

The present invention relates to the bleaching of cellulosic pulp and in particular relates to the bleaching of cellulosic pulp at high consistency in fluffed or shredded form, with gaseous chlorine monoxide.

In the multistage bleaching of an unbleached chemical cellulosic, e.g. wood, pulp, the pulp from the digestion stage in for example the kraft, soda or sulfite process, normally after washing, is treated to render at least a portion of the ligneous impurities readily soluble in water, whilst, of the ligneous impurities not readily soluble in water, at least a portion is readily soluble in a dilute aqueous alkali such as dilute aqueous solutions of sodium hydroxide, sodium sulfite or ammonium hydroxide. To render these ligneous impurities of the wood pulp soluble in water and dilute aqueous alkali the pulp is conventionally treated with agents such as chlorine, chlorine dioxide or the oxides of nitrogen, more usually chlorine or chlorine dioxide or mixtures thereof.

The aforesaid "pretreated" pulp after washing with water is subjected to caustic extraction with for example sodium hydroxide to remove the water insoluble ligneous impurities therefrom, this extraction being generally conducted on the pulp at low consistency in the range 10 to 14 percent, a temperature in the range 40° to 70° C. and at a retention time of 60 to 120 minutes.

Subsequent to the caustic extraction stage and normally after water washing, the extracted pulp is oxidized with chlorine dioxide generally at a low consistency of from 6 to 15 percent, at a temperature of from 60° to 75° C. for a retention time of 3 to 5 hours.

The aforesaid three stages are present in all multistage bleaching processes for chemical cellulosic pulps although variations are possible with regard to the stages. For example, with pulps made from certain wood species treatment with sodium or calcium hypochlorite may be desirable between the extraction with for example sodium hydroxide and the chlorine dioxide oxidative treatment. Further, with kraft pulps, the chlorine dioxide treatment is normally repeated a caustic extraction stage being interposed between the two chlorine dioxide oxidation stages.

However, regardless of the number of stages the treatment of the pulp is carried out in slurry form at low consistencies varying from 3 to 15 percent, at temperatures ranging from ambient to about 75° C. and for retention times from about 30 minutes to about 5 hours.

In an improvement in the conventional multistage bleaching of chemical cellulosic pulp in which the pulps are treated with aqueous solutions of the reagents, it has been found as set forth inter alia in Canadian Pat. Nos. 733,412 and 752,864 and Canadian Pat. applications 940,952 and 988,372 filed Sept. 20, 1965 and Apr. 20, 1967, respectively, that by treating the pulps at high consistency suitably in the range 15 to 60 percent and in the form of fluffed and shredded fibers and fiber aggregates with gaseous reagents such as chlorine, chlorine dioxide, or ammonia depending upon the particular stage of the multistage bleaching process, it is possible to greatly reduce the reaction time between the reagent and the pulp. As set forth in Canadian patents and Canadian applications fluffed chemical cellulosic pulp (sometimes referred to as shredded chemical cellulosic pulp) is the product obtained by the fragmentation of a chemical cellulosic pulp into fibers and fiber aggregates or flocks, substantially each discrete fiber aggregate or flock being spongy compressible and readily gas permeable. Each of said fiber aggregates or flock is usually an average of an eighth to 1 inch in diameter and prevents a fluffed up dry appearance even with about 70 to 80 percent moisture in the cellulosic pulp. Thus reference to fluffing or shredding of chemical cellulosic pulp is directed to a process of producing this pulp by fragmentation. In particular, in Canadian Pat. application 988,372 according to the invention set forth therein, in order to realize fully the advantages of gas phase reaction between the reagent and the high consistency

pulp in the multistage bleaching of fibrous chemical cellulosic pulp the comminution of the pulp, i.e. the shredding or fluffing of the pulp, must be of a specific nature to produce fragments which independent of their size are of low density, of porous structure throughout, and substantially free from any highly compacted portions, i.e. compacted fiber bundles. By operating according to the invention set forth in the aforesaid Canadian patents and Canadian patent applications it is possible to obtain a relatively high-speed process in which the fluffed pulp is contacted with the gaseous reagent over a substantially reduced periods of time as compared with the conventional process and which involves the use of substantially reduced volumes of water for evaporation. In particular by adjusting the consistency of the pulp to be of high consistency and by contacting the reagent in gaseous form with the pulp shredded or fluffed into fiber or fiber aggregates, it is possible to obtain a fast intimate contact of the gaseous reagent with the interior of the fibers or fiber bundles and as a result to reduce the time necessary for obtaining the extent of reaction necessary for high brightness in the pulp. Due to the speed of the process of the invention set forth in the aforesaid Canadian patents and Canadian applications the retention time in continuously operated reactions is greatly reduced which allows the use of small equipment of lower capital cost. Also the presence of smaller quantities of pulp in the process makes for more precise control of the operation and furthermore the sharp reduction in the quantity of water involved in the use of high pulp consistency results in substantial reduction of heat input to the reaction and corresponding savings. Finally it has been found generally that there is a saving of the gaseous reagent over and above that necessary in the conventional process.

It has now been found that it is possible with substantial advantage to bleach cellulosic fibrous pulp by subjecting said pulp at high consistency and in the form of fluffed or shredded fibers or fiber aggregates of the oxidative action in the gaseous phase of chlorine monoxide.

According to the present invention therefore there is provided a process for bleaching of a fibrous cellulosic pulp particularly a chemical cellulosic pulp which comprises contacting the pulp at a high consistency and in the form of fluffed or shredded fibers and fiber aggregates with chlorine monoxide in the gaseous phase.

In particular applicants have found that in the bleaching of chemical cellulosic fibrous pulps in the gaseous phase at high consistency and in fluffed and shredded form, chlorine monoxide can be used with advantage in those stages where chlorine dioxide is hitherto been used. In particular applicants have found that by using chlorine monoxide to achieve a similar oxidative bleaching effect on chemical cellulosic pulp with chlorine dioxide, the period of contact between the chlorine monoxide gas and the pulp to achieve a similar pulp brightness is substantially reduced yielding an even greater cost saving in the bleaching of the pulp and inter alia and more precise control over the bleaching operation and a further saving in bleaching chemicals.

Thus it has been found that in bleaching a chemical cellulosic pulp, in particular a wood pulp, such as a Kraft or sulfite pulp, at high consistency in the gaseous phase with chlorine monoxide it is possible to achieve high Elrepho brightness of about 91 in a very short period of time of the order of about 1 minute which high brightness using chlorine dioxide in the gaseous phase would only be achieved after a substantially larger period of time up to about 30 minutes. Again the brightness achieved with gaseous phase chlorine monoxide bleaching of high consistency fluffed or shredded pulp increases with time and further it is found that the increase in brightness continues for a period up to about 60 minutes in contrast to chlorine dioxide where maximum brightness is achieved after 30 minutes. In particular it is found possible to achieve higher brightness values up to about 95 Elrepho brightness with the gaseous chlorine monoxide bleach of the present invention.

Further, it is well known that bleaching chemicals corrode the equipment and more serious cases of corrosion are found in equipment used for stages in which chlorine dioxide is used. Chlorine dioxide in combination with the chloride formed during the bleaching reaction attacks the equipment such as washers, circulation water pipe lines and tanks even if such equipment is made of stainless steel or acid-proof steel. In contrast thereto, using chlorine monoxide in the bleaching of chemical cellulosic pulp, neither the chlorine monoxide nor the products of the reaction with the pulp are corrosive to the equipment which is a decisive commercial advantage over the use of chlorine dioxide.

According to a particular embodiment of the present invention there is provided a process for bleaching of a chemical cellulosic pulp, particularly wood pulp, which comprises contacting the pulp at a high consistency and in the form of fluffed or shredded fibers or fiber aggregates with chlorine monoxide in the gaseous phase.

The pulp on contact with the gaseous chlorine monoxide is a high consistency pulp, suitably having a consistency of at least 15 percent, preferably a consistency in the range 15 to 50 percent and more desirably in the range 15 to 30 percent, at which consistency it is shredded and fluffed particularly by the method set forth in Canadian Application 988,372 into fibers and fiber aggregates. In general the higher the consistency of the pulp in the process of the present invention, all other parameters being the same, the higher the brightness achieved but the lower the viscosity of the pulp obtained. It is critical to the present invention to have a high consistency pulp as with a conventional low consistency pulp the chlorine monoxide is reacted in aqueous solution and the pulp is thus reacted with a dilute hypochlorous acid solution. Such a process is disclosed in U.S. Pat. No. 2,178,696 and subject to may problems including purity of the reactant hypochlorous acid and the results of the process are substantially inferior both in the properties of the bleached pulp obtained particularly brightness and the process involved such that this process has not achieved commercial use. In contrast to the process of the U.S. patent which cannot tolerate impurities such as hydrogen chloride, chlorine, chlorides etc. the presence of impurities in the process of the present invention has no significant effect, the gaseous chlorine monoxide being able to contain for example substantial amounts of chlorine.

For safe and economical usage, the chlorine monoxide gas should be diluted with a nonreactive gas such as air, carbon dioxide or nitrogen to a partial pressure not greater than about one-third of an atmosphere, i.e. about 253 mm. of mercury. This is in contrast to chlorine dioxide gas which must be diluted with a nonreactive gas to a much lower partial pressure of not greater than 100 mm. of mercury to avoid the risk of explosion. The process of the present invention may be operated at a high partial pressure of chlorine monoxide suitably above 100 mm. of mercury which for a pulp of the same consistency, same pH during the process and period of contact with the chlorine monoxide will yield a brighter pulp but the viscosity of the pulp is lower than when operating at a low partial pressure of chlorine dioxide below 100 mm. of mercury.

The temperature of reaction between the gaseous chlorine monoxide and the pulp is not particularly critical and is desirably in the range from 30° C. to 50° C. It has been found that chlorine monoxide bleaching of pulp according to the present invention produces an exothermic reaction. If the partial pressure of chlorine monoxide is above 100 mm. of mercury, and the consistency of the fluffed pulp is in the range of 25 to 35 percent, the temperature of the mixture is found to rise from 23° C. to 46° C. Thus when operating with a high concentration of chlorine monoxide at a high pulp consistency, no external heat is necessary for the bleaching process. When the partial pressure of the chlorine monoxide is below 100 mm. of mercury and especially in the range of from 1 to 20 mm. of mercury, it is beneficial to heat the mixture to about 40° C. and to maintain the temperature during the reaction or retention period.

The pH of the pulp maintained in the process of the present invention has a substantial effect in the brightness of the pulp obtained and on the viscosity of the pulp obtained. Thus it is found that the highest brightness values are achieved at pH's in the range of from about 5.5 to about 8 but at the same time the viscosity of the pulp falls markedly in this pH range. While the high brightness—low viscosity pulp produced in the aforementioned pH range has certain end uses when bleaching pulp for use in the paper industry wherein pulp with 0.5 percent CED viscosity below about 15 is not useful, it is preferred to operate below 5.5 and suitably in the range 3.5 and 5.5 i.e. in the acid range or alternatively above 8 and suitably in the range 8 to 11, i.e. the alkali range. Being able to operate the process in the alkali range of pH gives the process of the present invention flexibility over the gaseous chlorine dioxide process which can only be operated under acidic conditions. The pH of the reaction mixture may be controlled by adding a buffering agent, such as an alkali metal salt of a weak acid, e.g. sodium carbonate, to the pulp before contact with the gaseous chlorine monoxide. With the above conditions it has been found that a contact period of from about 1 to 60 minutes is sufficient to effect the desired bleaching action of the chlorine monoxide on the pulp.

It is further found according to the present invention that by the addition of ammonia or compounds of ammonia, such as sulfamic acid in small amounts (1–3 percent) to the pulp before contact with the gaseous chlorine monoxide and suitably prior to the fluffing and shredding of the pulp protects the pulp against excessive lowering of the viscosity thereof during the process. This aspect of the invention has particular application when operating at high partial pressures of chlorine monoxide suitably in the range 100 to 200 mm. of mercury and at higher temperatures in the range 45° to 50° C. when the viscosity of the product pulp obtained is lowest. It has been found that small amounts of chlorine dioxide e.g. up to 0.05 percent in pulp admixed with the gaseous chlorine monoxide has a similar effect in protecting the pulp viscosity when operating in the acid range. Again it is found that when the pulp treated according to the present invention is one which has been subjected to a previous ammonia extraction the viscosity of the product pulp of the process of the present invention is higher than one which has been previously subjected to a caustic soda extraction.

The present invention will be further illustrated by way of the following examples in conjunction with the accompanying drawings in which:

FIG. 1 is a graph showing the variation of the brightness of the pulp produced according to the present invention with pH and

FIG. 2 is a graph showing the variation in 0.5 percent CED viscosity of the pulp produced according to the present invention with pH.

#### EXAMPLE 1

(a) An unbleached sulfite pulp from coniferous wood having a Roe chlorine number of 7.9, a CED viscosity of 35.6 c.p.s. and a Kappa number of 33.0, was chlorinated, extracted with dilute sodium hydroxide and washed with water. The pretreated, i.e. partially delignified pulp had a Kappa number of 1.0, a CED viscosity of 33.1 c.p.s., and a Elrepho brightness of 57.7 percent. A portion of the pretreated pulp was pressed to 35 percent consistency and the pressed pulp was sprayed with a solution containing sodium carbonate equal to 1 percent by weight of the pulp and water sufficient to reduce the consistency to 30 percent, i.e. to a moisture content of 70 percent. The pulp was then shredded into fiber and fiber aggregates, by the method set forth in Canadian Pat. application 988,372 and the fluffed pulp was placed in a tower at room temperature. Chlorine monoxide diluted with air to a partial pressure of 210 mm. of mercury was passed into the tower until 0.6 percent chlorine monoxide based on oven-dry pulp was added to the pulp. The reaction temperature rose from

23° C. to 46° C. within 1 minute reaction time. The final pH of the pulp was 4.6. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 91.8 percent on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 14.9 c.p.s.

(b) Another portion of the chlorinated, extracted, pressed sulfite pulp was shredded at 30 percent consistency, placed in a tower, the tower set in the heating bath, the temperature being maintained at 40° C. in the tower. Chlorine monoxide, diluted with nitrogen to a partial pressure of 5 mm. of mercury, was passed into the tower until 0.6 percent chlorine monoxide based on oven-dried pulp was added to the pulp and the pulp was held at 40° C. for 5 minutes. The final pH of the pulp was 5.0. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 88.4 on the Elrepho meter and the pulp had a 0.5 CED viscosity of 28.7 c.p.s.

Chlorine monoxide is a well-known gas and may be prepared for example by the methods disclosed in U.S. Pat. Nos. 2,155,281; 2,157,524; 2,157,525; and 2,157,559.

### EXAMPLE 2

In a similar manner as in example 1(a) a series of pulps the same as in example 1(a) were treated at 30 percent consistency and at a partial pressure of 210 mm. of mercury with gaseous chlorine monoxide diluted with air until from 0.61 to 0.66 percent chlorine based on oven dry pulp was added to the pulp. The period of time in one series of pulps was 60 minutes, the results being given in table I and in a second series of pulps 1 minute the results being given in table II. The temperature during the process rose from 23 to 46° C.

TABLE I

Pulp 30 percent consistency, time 1 hour, partial pressure of chlorine monoxide 210 mm. of mercury.

| pH   | Elrepho Brightness % | 0.5% CED<br>Viscosity cps. |
|------|----------------------|----------------------------|
| 1.75 | 85.0                 | 18.5                       |
| 2.5  | 94.0                 | 16.8                       |
| 4.0  | 94.1                 | 11.9                       |
| 7.0  | 95.2                 | 3.8                        |
| 9.2  | 91.3                 | 17.8                       |

TABLE II

Pulp 30 percent consistency, time 1 minute, partial pressure of chlorine monoxide 210 mm. of mercury.

| pH  | Elrepho Brightness % | 0.5% CED<br>Viscosity cps. |
|-----|----------------------|----------------------------|
| 2.1 | 80.2                 | 25.1                       |
| 3.0 | 88.1                 | 19.0                       |
| 4.6 | 91.8                 | 14.9                       |
| 7.2 | 93.1                 | 5.3                        |
| 8.2 | 92.6                 | 13.8                       |
| 9.7 | 89.1                 | 18.6                       |

It will be seen from tables I and II that the longer the process in the range 1 minute to 1 hour the higher the brightness of the pulp and the lower its viscosity.

Operating as in tables I and II but modifying the pulp to a viscosity of 15 percent a further series of pulps were treated according to the present invention for 1 minute at various pHs. The temperature the process rose from 23° to 31° C. The results are given in table III below.

TABLE III

Pulp 15 percent consistency, time 1 minute, partial pressure of chlorine monoxide 210 mm. of mercury.

| pH  | Elrepho Brightness % | 0.5% CED<br>Viscosity cps. |
|-----|----------------------|----------------------------|
| 3.4 | 84.6                 | 20.6                       |

|      |      |      |
|------|------|------|
| 5.2  | 91.1 | 16.3 |
| 6.0  | 91.2 | 11.2 |
| 7.5  | 91.6 | 6.7  |
| 7.6  | 92.1 | 7.2  |
| 9.8  | 87.2 | 24.3 |
| 11.0 | 86.6 | 28.1 |

It will be seen from table III that the lower the pulp consistency the lower the brightness and the higher the viscosity of the product pulp.

Operating as in table III but with the chlorine dioxide diluted to a partial pressure of 53 mm. of mercury with nitrogen a further series of pulps were treated according to the present invention for 1 minute at various pHs, the temperature during the process rising from 23° to 27° C. The results obtained are given in table IV.

TABLE IV

Pulp 15 percent consistency, time 1 minute, partial pressure of chlorine monoxide 53 mm. of mercury.

| pH   | Elrepho Brightness % | 0.5% CED<br>Viscosity cps. |
|------|----------------------|----------------------------|
| 3.2  | 85.5                 | 28.5                       |
| 3.8  | 89.2                 | 28.1                       |
| 5.0  | 90.4                 | 24.8                       |
| 6.4  | 91.6                 | 12.3                       |
| 7.6  | 91.4                 | 15.2                       |
| 8.4  | 90.6                 | 26.2                       |
| 10.2 | 87.2                 | 28.5                       |

It will be seen from table IV that the lower the partial pressure of the chlorine monoxide the higher the viscosity and the lower the brightness achieved in the product pulp.

The results of tables I, II, III, and IV were plotted as graphs in FIGS. 1 and 2 of the accompanying drawings.

It will be seen from FIGS. 1 and 2 that a pulp of a desired brightness and desired viscosity, can be obtained by adjusting the pH of the mixture. When a brightness of from 85 to 91.5 percent is required and the required viscosity of such a pulp is in the range of 15 to 28, the pH may be adjusted to range between 3.5 and 5.5 or from 8 to 11. When it is desired to reduce the viscosity of the pulp a pH range from 5.5 to 8 may be employed.

### EXAMPLE 3

An unbleached kraft pulp from coniferous wood having a Roe chlorine number of 4.6, a Kappa number of 26.8 and a CED viscosity of 29.2 cps. was chlorinated, extracted with dilute sodium hydroxide and washed with water. The pretreated, i.e. partially delignified pulp had a Kappa number of 7.3, a CED viscosity of 28.6 cps. and an Elrepho brightness of 31.6 percent. The pretreated pulp was pressed to 35 percent consistency and three different portions of this pulp were sprayed respectively with a solution containing 1, 2 or 3 percent sodium carbonate on pulp and water to bring the consistency of each portion to 30 percent. The three portions were then shredded or fluffed into fiber and fiber aggregates in a similar manner as in example 1 and each portion was placed in a tower maintained at 40° C. in a heating bath. Chlorine monoxide diluted to a partial pressure of 5 mm. of mercury was passed into each tower until 1.25 percent chlorine monoxide based on oven dry pulp was added to each portion the retention time in each case being 5 minutes. The final pH of each portion of the pulp, the brightness and the viscosity of the pulps after washing and air drying are set out in the table below.

TABLE V

| Sample | End pH | Elrepho<br>Brightness % | 0.5% CED<br>Viscosity cps. |
|--------|--------|-------------------------|----------------------------|
| 1.     | 3.0    | 74.5                    | 24.3                       |
| 2.     | 3.9    | 79.2                    | 27.2                       |
| 3.     | 4.2    | 79.8                    | 24.1                       |

## EXAMPLE 4

In this example the bleaching process of the present invention was conducted in the following alternative ways;

- a. no additive is added to the chlorine monoxide bleaching stage.
- b. sulfamic acid is premixed with the pulp prior to the addition of the chlorine monoxide, and
- c. a small quantity of chlorine dioxide, 0.05 percent on O.D. pulp, is added to the chlorine monoxide gas simultaneously as the gas is added to the pulp.

(a) The unbleached sulfite pulp from coniferous wood used in example 1, after chlorination and caustic extraction and subsequent washing, had a Kappa number of 1.0, a CED viscosity of 33.1 cps. and an Elrepho brightness of 57.7 percent.

One portion of the pretreated pulp was pressed to 30 percent consistency and then shredded into fiber and fiber aggregates. Chlorine monoxide, diluted with air to a partial pressure of 210 mm. of mercury, was passed into the tower until 0.6 percent chlorine monoxide, based on oven dry pulp, was added to the pulp. The reaction temperature rose from 23° C. to 46° C. in 1 minute reaction time. The final pH of the pulp was 3.0. The bleached pulp was washed, air-dried and the final brightness and CED viscosity measured. The brightness was 88.1 on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 19.0 cps.

(b) Another portion of the chlorinated, extracted and washed pulp was pressed to 35 percent consistency. The pressed pulp was sprayed with a solution containing sulfamic acid (1 percent based on available chlorine content) and water sufficient to reduce the pulp consistency to 30 percent. The pulp was then shredded into fiber and fiber aggregates, and placed in a tower. Chlorine monoxide, diluted with air to a partial pressure of 210 mm. of mercury was passed into the tower until 0.6 percent chlorine monoxide based on oven-dry pulp was added to the pulp. The reaction temperature rose from 23° C. to 42° C. within 1 minute reaction time. The final pH of the pulp was 2.8. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 87.9 percent on the Elrepho meter and the pulp had a viscosity of 32.8 cps.

(c) Another portion of the chlorinated, extracted and washed pulp was pressed to 30 percent consistency. The pulp was shredded into fiber and fiber aggregates and placed in a tower. Chlorine monoxide, diluted with air, and chlorine dioxide (0.05 percent on O.D. pulp) to a partial pressure of 210 mm. of mercury was passed into the tower until 0.6 percent chlorine monoxide based on oven-dry pulp was added to the pulp. The reaction temperature rose from 23° C. to 42° C. within 1 minute reaction time. The final pH of the pulp was 2.7. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 87.3 percent on the Elrepho meter and the pulp had a 0.5 CED viscosity of 23.8 cps. Under similar conditions with the final pH 4.5 the Elrepho brightness was 91.3 percent and the 0.5 percent CED viscosity was 21.3 cps. in the product pulp.

## EXAMPLE 5

This example compares the effect of chlorine-monoxide and chlorine dioxide on chlorinated and extracted (pretreated) sulfite pulp, 15 percent consistency at a temperature of 27° C.

A portion of the chlorinated and extracted pulp from example 4 was pressed to 20 percent consistency and sprayed with a solution containing sodium carbonate equal to 1 percent by weight of the pulp and water sufficient to reduce the consistency to 15 percent. i.e. a moisture content of 85 percent. The pulp was then shredded into fiber and fiber aggregates.

(a) An aliquot of the above pulp was placed in a tower at room temperature 23° C. Chlorine monoxide diluted to a partial pressure of 53 mm. of mercury was added to the pulp. The reaction temperature rose to 27° C. within 1 minute reaction

time. The final pH of the pulp was 5.0. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 90.4 percent on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 24.8.

(b) Another aliquot of the chlorinated, extracted and shredded pulp was placed into a tower at room temperature, 23° C. Chlorine dioxide, diluted to a partial pressure of 60 mm. of mercury, was added to the pulp. The temperature rose from 23° C. to 24° C. within 1 minute reaction time. The final pH of the pulp was 5.2. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 81.0 percent on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 30.2 c.p.s.

(c) Another aliquot of the chlorinated, extracted and washed pulp, shredded with the carbonate already added to the pulp, was placed in a tower and was set in a bath and temperature maintained at 80° C. Chlorine dioxide, diluted with nitrogen to a partial pressure of 30 mm. of mercury, was passed into the tower until 0.6 percent chlorine dioxide on pulp O.D. basis was passed into the tower and the pulp was held at 80° C. for 30 minutes. The final pH of the bleached pulp was 5.2. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 92.8 percent on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 30.1 cps.

## EXAMPLE 6

This example demonstrates the use of ammonia as the extractant in the alkali extraction stage in the pretreated pulp, rather than caustic soda, and how it helps to protect the viscosity in the chlorine monoxide bleaching stage. The example can be compared to example 4(a).

The unbleached sulfite pulp, having a Roe number of 7.9 and CED viscosity of 35.6 and a Kappa number of 33, was chlorinated and extracted with an ammonia/steam gaseous mixture, by the method set forth in Canadian Pat. application 752,864. The pretreated, i.e. partially delignified pulp, had a Kappa number of 1.3, a CED viscosity of 32.8 and an Elrepho brightness of 56.1 percent. A portion of the pretreated pulp was pressed to 20 percent consistency and the pressed pulp was sprayed with a solution containing sodium carbonate equal to 1 percent by weight of the pulp and water sufficient to reduce the consistency to 15 percent, i.e. moisture content of 85 percent. The pulp was then shredded into fiber and fiber aggregates, and the fluffed pulp was placed in a tower at room temperature. Chlorine monoxide, diluted with air to a partial pressure of 53 mm. of mercury, was passed into the tower until 0.6 percent chlorine monoxide based on oven-dry pulp was added to the pulp. The reaction temperature rose from 23° C. to 25° C. The final pH of the pulp was 5.2. The bleached pulp was washed, air-dried and the brightness and CED viscosity measured. The brightness was 88.4 percent on the Elrepho meter and the pulp had a 0.5 percent CED viscosity of 29.7 c.p.s.

Under similar conditions with the final pH 3.6 the pulp had an Elrepho brightness of 88.0 percent and a 0.5 percent CED viscosity of 29.9 c.p.s. With a final pH of 7.1 the pulp had an Elrepho brightness of 90.4 percent and a 0.5 percent CED viscosity of 18.2 c.p.s. and at the final pH of 10.6 the pulp had an Elrepho brightness of 86.8 percent and a 0.5 percent CED viscosity of 29.1 c.p.s.

We claim:

1. A process for bleaching a fibrous cellulosic pulp which comprises bleaching the pulp at high consistency and in the form of fluffed or shredded fibers and fiber aggregates with chlorine monoxide in the gaseous phase.

2. A process as claimed in claim 1 in which the pulp is a chemical cellulosic pulp.

3. A process as claimed in claim 2 in which the pulp is a Kraft or sulfite pulp.

4. A process as claimed in claim 2 in which the pulp is a partially delignified pulp.

5. A process as claimed in claim 2 in which the pulp has a consistency of at least 15 pH

6. A process as claimed in claim 2 in which the pulp has a consistency of 15 percent to 50 percent.

7. A process as claimed in claim 2 in which the pulp has a consistency of from 15 percent to 30 percent.

8. A process as claimed in claim 2 in which the chlorine monoxide is diluted with a nonreactive gas to a partial pressure below 253 mm. of mercury.

9. A process as claimed in claim 2 in which the chlorine monoxide is diluted with a nonreactive gas to a partial pressure in the range from 100 mm. to 253 mm. of mercury.

10. A process as claimed in claim 2 in which the chlorine monoxide is diluted with a nonreactive gas to a partial pressure below 100 mm. of mercury.

11. A process as claimed in claim 2 in which the pH of the pulp is maintained in the range from 3.5 to 5.5.

12. A process as claimed in claim 2 in which the pH of the pulp is maintained in the range from 8 to 11.

13. A process as claimed in claim 2 in which the temperature is in the range 23° C. to 50° C.

14. A process as claimed in claim 2 in which the reaction period is in the range 1 to 60 minutes.

15. A process as claimed in claim 2 in which the pulp contains ammonia or a compound of ammonia in an amount sufficient to reduce the degradation in the viscosity of the pulp.

16. A process as claimed in claim 2 in which the pulp contains from 1 to 3 percent of sulfamic acid or ammonia to reduce the degradation in the viscosity of the pulp.

17. A process as claimed in claim 2 in which the chlorine monoxide contains up to about 0.05 percent of chlorine dioxide to reduce the degradation in the viscosity of the pulp.

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