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F6966 XR 2,903,326
DSS REFERENCE SEARCH ROOM

United States Patent Office

2,903,326

Patented Sept. 8, 1959

2,903,326

IMPROVED PROCESS FOR BLEACHING CELLULOSE PULP USING CHLORATE

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No Drawing. Application October 17, 1956
Serial No. 616,377

7 Claims. (Cl. 8—105)

This invention is a continuation-in-part of my applications Serial Number 542,524, filed October 24, 1955, and Serial Number 594,346, filed June 28, 1956, both now abandoned.

This invention relates to a new use for chlorate, new and useful improvements in cellulose bleaching processes generally, and particularly to new and useful improvements in both the chlorination and oxidation stages of cellulose pulp bleaching.

The bleaching of cellulose pulp is a combination of chlorination, extraction and oxidation stages. Chlorination of unbleached cellulose pulp tends to solubilize colored lignin materials which are undesirable in the finished product. Oxidation of cellulose pulp materials decomposes chromophoric groups present in the lignin. The extraction stages in the overall bleaching process remove the soluble colored lignin materials and the decomposed chromophoric materials. The removal of the colored lignin materials and the decomposed chromophoric materials from the cellulosic pulp results in whitening of the treated material. In general, the processes of chlorination and extraction and oxidation are repeated until the desired whiteness of the finished product is obtained.

A general bleaching procedure consists first in the treatment of the aqueous slurry of cellulose pulp with chlorine (pH on the acid side) in one or more stages, followed by alkaline extraction and then by oxidation with an alkaline hypochlorite. The initial chlorine treatment stages primarily involve direct chlorination of some of the colored lignin impurities to make derivatives which are partially soluble in the acidic chlorine solution and particularly soluble in the subsequent alkaline extraction liquors. During the early chlorination stages, it is desirable that oxidation reactions with the cellulose be kept at a minimum since oxidation of the cellulose will cause degradation of the cellulose pulp with resulting loss of yield and strength. The chlorination of the ligneous materials prior to hypochlorite treatment results in the production of extractable chlorinated lignin derivatives which are further removed by alkaline extraction. The extraction of the lignin materials prior to the final oxidation treatments greatly improves the final brightness of the bleached material.

After the extraction stage it is customary in the art to further brighten the cellulosic pulp by means of one or more treatments with hypochlorite or other oxidizing agents, resulting in decomposition of the chromophoric groups associated with the lignin, thus directly decolorizing the lignin and, at the same time, making it somewhat extractable by water, thereby producing a brighter pulp. These latter oxidation stages are usually carried out using a hypochlorite solution containing sodium or calcium hypochlorite. However, in recent years some of the milder oxidizing agents such as sodium chlorite, chlorine dioxide, or peroxides have been used. The milder oxidizing materials have the advantage of not directly attacking the cellulose to the extent which is

normally encountered with the hypochlorites. This lessening of attack results in a strong pulp which is especially desirable for the making of paper. Unfortunately, the cost of the milder bleaching agents is considerably more than the cost of an equivalent amount, in terms of available chlorine, of the hypochlorites and this situation usually does not favor the use of the milder bleaching agents, even though a more satisfactory bleached pulp is obtained on the basis of strength. Further, the use of the milder bleaches sometimes requires special bleaching conditions which, in turn, makes necessary the costly changing of process equipment and operating conditions in the mill.

I have now discovered a novel process for reducing the oxidation degradation which normally accompanies chlorination of cellulosic materials in the early bleaching stages and also accompanies oxidation in the later bleaching stages, with the result that by use of the process of my invention loss of yield and strength is minimized. These desirable effects are particularly valuable in the bleaching of hard-to-bleach wood pulps such as groundwood, sulfate or kraft and soda pulps.

My invention comprises the use of a small amount of a material furnishing chlorate ion with the chlorine in the chlorination stage or stages of the bleaching of cellulosic materials and/or the use of a small amount of material furnishing chlorate ion with the hypochlorite in the oxidation stage or stages. In the practice of my invention the chlorine treatment of cellulosic materials is carried out in the conventional way, but with an amount of chlorate ion added in the bleach solution; likewise the oxidation phase, using a hypochlorite treatment, is carried out in the conventional way, but in the presence of added chlorate ion and with the same amount or less of hypochlorite in the bleach solution.

The process of my invention can be applied to both the chlorination and hypochlorination stages of the pulp bleaching operation or to individual parts of the process as herein described. Thus, the process may be applied to either the chlorination or oxidation stages only, resulting in beneficial improvements in brightness and strength of the pulp in each bleaching stage where the operation is carried out in the presence of chlorate ion.

While the mechanism of the action of the added chlorate is not fully understood, it is believed to inhibit oxidative degradation of cellulose, which ordinarily occurs as an undesired side reaction during both the chlorination and oxidation stages. This is a surprising action for chlorate which, under other conditions, is itself a strong oxidizing agent. My invention is not to be limited, however, to any particular theory of how the chlorate accomplishes the observed result.

The presence of added chlorate in the early chlorination stages of a pulp, kraft pulp for example, will produce a finished product of increased fiber strength, as shown by increased cupriethylenediamine disperse viscosity (TAPPI Method No. T230 sm-50, falling ball method), with an accompanying increase in yield. The advantages of increased yield and fiber strength obtained in using my process at this stage are further enhanced by the fact that the final chlorination product does not decrease in brightness, as determined by use of TAPPI Method No. T217 m-48, but, in fact, may even show a greater brightness as a result of the chlorate treatment.

In practicing my novel process in the chlorination stage of pulp bleaching, usually a 1 to 5% slurry of pulp in water would be chlorinated in one or more stages with about 2 to 25% chlorine, based on the weight of bone dry pulp, between the temperatures of 0° and 50° C. and at a pH below 7. The amount of chlorination of the cellulosic material does not affect the practice of my invention; thus the amount would normally be that used when

chlorate is not added to the process. The amount of chlorine applied will be varied by the number of chlorination stages used and the chlorine demand of the pulp.

According to my invention chlorates are added to this slurry in each chlorination stage in amounts up to a few percent, for example, up to 5% based on the weight of bone dry pulp.

The benefits to be obtained by adding chlorate ion to the direct chlorination stages in the bleaching of cellulose pulp are obtained particularly in the initial stages of direct chlorination. It is, of course, possible to use the added chlorate as well in the later direct chlorination stages but decreasing benefits result. The major benefits of adding chlorate to the direct chlorination stages are obtained when it is applied to the first and/or second chlorination stages.

The amount of chlorate ion needed in the practice of my invention in the chlorination stages may be as little as 0.01% and as high as 5% by weight of the bone dry pulp. Higher than optimum amounts may be used without obtaining any added advantage, as shown in the examples.

In the preferred application of my invention, it is desirable to ascertain the optimum amount of chlorate required for a particular pulp by making a number of test determinations of the increase in yield, brightness and strength versus amount of chlorate used. Conditions of bleaching vary widely in the industry and many combinations of bleaching stages are used. Further, mills are supplied with various types of wood and this wood is cooked by several different methods and innumerable variations thereof. It is, therefore, not possible to predict the exact amount of chlorate which will be suitable for use with chlorine in all types of pulp bleaching, but the amount useful with any given pulp can easily be determined by experimental bleaches on a laboratory scale. The results of these tests may then be applied on a commercial scale.

The temperatures at which chlorination stages using my process are carried out are those normally used in the direct chlorination of cellulosic materials. Temperatures of from 0° to 40° C. are conventional in the chlorination process of pulp generally and are equally applicable in carrying out the chlorination stages in the presence of added chlorate.

The pH of the liquors in which the direct chlorination of cellulosic pulps are carried out in the presence of added chlorate ion is generally the same as that used in processes in which the added chlorate is not present. The pH of the liquors is initially that of chlorine water at around 0.25% concentration, approximately a pH of about 2, and the liquors remain acid during the chlorination in the absence of added alkali. While it is possible to secure the effects of the chlorate addition in the presence of an initially higher acid concentration, it is not generally desirable since the acids convert the cellulose to sugars and other soluble compounds with a consequent loss in yield. The addition of alkali to the direct chlorination stages during the initial period is usually undesirable since it converts some of the chlorine to hypochlorite and results in oxidation. However, there are some pulp bleaching processes in use which involve the initial treatment of pulp with chlorine followed after a number of minutes by direct addition of calcium or sodium hydroxide, all in the same stage. This treatment converts the acid chlorination bleach to an alkaline hypochlorite bleach without washing between the treatments. My invention is also applicable to procedures of this nature in which the chlorate may act as an oxidation degradation inhibitor during the chlorination portion of the bleach stage and as a bleaching agent and oxidation degradation inhibitor in the hypochlorite portion as hereinafter described.

In addition to the pulp yield increase obtained in the early chlorination stages, my invention also results in a cumulative yield increase which carries on with the pulp through additional bleaching stages. In the conventional bleaching processes the fibers of cellulose comprising the pulp undergo a progressive degradation as a result of each successive bleach treatment. The degradation is greatest with wood pulps which by their nature or method of prior treatment are hard to bleach and consequently require a plurality of bleaching cycles. However, if the pulp treated in the early chlorination stages with added chlorate ion is not greatly degraded, as compared with pulp chlorinated without added chlorate ion, the cumulative degradation effect of further bleaching stages will not be as great as when chlorate has not been used. This cumulative effect is an important advantage of my invention.

I have also found that the use of a chlorate in combination with hypochlorite in the oxidation stages of pulp bleaching will result in a stronger, bleached pulp as a result of decreased attack on the cellulose fibers. The degree of brightness obtained is about the same as that encountered with an equivalent amount of hypochlorite, used alone, and in some cases is slightly higher. When chlorate is used with hypochlorite in the oxidation stages of the bleaching process, not only are the brightness and pulp strengths increased, but the chlorate unexpectedly replaces a considerable part of the hypochlorite normally used. The effects resulting from the combination of chlorate and hypochlorite are not obtained when either is used alone. It also is possible, according to my invention, to add chlorate immediately prior to or during the hypochlorination stage or stages and, by so doing, obtain the aforementioned advantages. The effect of addition of chlorate to hypochlorite does not exactly parallel the results obtained when chlorate is used in conjunction with chlorine. The use of chlorate in the hypochlorination stage reduced degradation, as in the chlorination stage, but the chlorate also appears to act as a direct bleaching agent. In the hypochlorination stage, the effect of chlorate as a direct bleach is so marked that it is possible, and even advisable, to reduce the amount of hypochlorite present. By so doing, the amount of hypochlorite, which is a strong oxidizing agent under bleaching conditions, is lessened and replaced by chlorate, thus resulting in a milder bleach.

In the usual bleach process sequence the chlorinated pulp slurry is extracted between stages with an alkaline wash solution to remove soluble colored materials. The extracted pulp from the final chlorination treatment is then further bleached in one or more stages by oxidizing a 5 to 40% slurry of said pulp at a temperature of from 20 to 100° C. with a hypochlorite solution.

With respect to the use of my invention in the hypochlorite stages of pulp bleaching, I customarily add sodium chlorate to a sodium hypochlorite, the latter being the usual bleaching agent, for the final stages of pulp bleached. For example, a useful bleach can be prepared by adding to the bleach liquor an amount of chlorate equivalent in oxidizing power to the amount of hypochlorite usually employed (both being expressed in terms of available chlorine, with one mole of chlorate equivalent to 3 moles of available chlorine theoretically, but to about 2.5 in pulp mill practice). To this material can be added one-half mole of hypochlorite plus about a 30% excess (about 0.65 mole total) per mole of chlorate used. The above relationship of chlorate to hypochlorite may also be expressed on the basis of using about 1.5 moles of chlorate per mole of hypochlorite.

Combined oxidizing concentrations of hypochlorite and chlorate expressed as available chlorine, i.e. chlorine equivalent of the active oxygen, are usually on the order of from about 0.1% to about 20% depending on the chlorine demand of the pulp and based on bone dry pulp present. The total amount of the mixture used can be adjusted to the quantity of bleach required to perform the

desired degree of bleaching in that particular stage. However, pulps vary to a great extent and it may be necessary to vary the ratios of chlorate to hypochlorite outside the values given above. The amounts of each used would depend on the particular pulp which is to be bleached. The proper ratio and quantities can be established readily on the basis of simple laboratory tests.

The hypochlorite stages of pulp bleaching are generally carried out in the existing art at pulp consistencies of about 8 to 20% at temperatures in the range from about 20 to about 100° C. and for bleach periods of one-half to four hours. My process is also carried out under these conditions.

A further advantage of my invention lies in the fact that the use of chlorate sometimes permits bleach solutions in the oxidation stage to be at an acid pH, a practice which is not advisable in the conventional process of bleaching with hypochlorite alone. Acid hypochlorite solutions as usually used have a tendency to degrade the pulp excessively with a resulting lowering of its quality, therefore an alkaline hypochlorite is conventionally used. On the other hand, when a bleach solution containing chlorate and hypochlorite according to my invention is employed, it is sometimes possible to permit the pH of the solution to go below 7 without adversely affecting the pulp. I have found that in some cases it is even advisable to use an acid pH in conjunction with my invention since higher brightness values result.

When bleaching in the acid pH range with my invention, as an illustration, I may add to the hypochlorite-chlorate bleach solution about two moles of hydrochloric, or other, acid per mole of chlorate used. Under the conditions described, this acid addition usually gives the slurry a pH of about 5.

In the usual practice (i.e. without acid addition), the pH of the liquors in which the hypochlorite oxidation of cellulosic pulps is carried out in the presence of added chlorate ion is generally the same as in processes in which the added chlorate is not present, i.e. on the alkaline side. However, one can also use a pH of less than 7, which may be about 5; the liquors remain acid during the oxidation in the absence of added alkali. The resulting bleach solution will produce in a pulp a brightness which is about the same or slightly more than that obtainable with an amount of hypochlorite equivalent in available chlorine to the chlorate used, but which will have a strength in excess of pulp bleached with hypochlorite alone. The brightness of pulp bleached with the chlorate in combination with hypochlorite and acid may be slightly in excess of the brightness of pulp bleached with hypochlorite and chlorate with no acid being present. The use of acid with my invention is optional, however.

The benefits obtained by adding chlorate ion to the hypochlorite in the oxidation stages in the bleaching of cellulose pulp are obtained in each stage of the oxidation. Cumulative benefits are obtained when it is applied with each hypochlorite oxidation stage after the chlorination and extraction stages, especially when pulps of the hard-to-bleach variety are being treated. In the oxidation stages of the conventional bleaching process, as during the chlorination stages, the fibers of cellulose comprising the pulp normally undergo a progressive degradation in each successive oxidation bleach treatment. On the other hand, pulp treated in the oxidation stages with added chlorate ion is not as greatly degraded compared to pulp oxidized without added chlorate ion. Consequently, the cumulative degradation effect through both the chlorination and oxidation bleaching stages will be less than that experienced when chlorate has not been used. The net result is that a higher yield of stronger pulp with brightness equivalent to or better than that obtained by conventional commercial processes is obtained. This is one of the outstanding features of my invention.

It should be noted that my invention is also useful when used only in the last stage of a pulp bleaching operation, where highest brightness values with least loss of strength are desired. It is at this point that serious loss of strength occurs in bleaching carried out according to the existing art. In some cases, the brightness values obtained when my invention is applied to pulps which are darker than normal may be less than may be obtained by use of hypochlorites alone, because of the more intense oxidizing action provided by use of hypochlorite; but degradation will be less and strengths will be higher in proportion.

Bleaching processes are in use which involve the addition of an alkali, such as caustic soda or lime, initially, to the pulp followed by chlorination. In such a combination alkali and hypochlorination stage the pulp is not washed between reagent treatments. When chlorate is added to the bleach, so that it is present in the hypochlorination portion of the stage, it will act in the previously described beneficial manner.

On bleaching pulps having a low lignin content, or in cases in which it is desired to bleach to a low degree of brightness, chlorination or caustic extraction stages may be omitted. In such situations my invention may be used in the hypochlorination stages without the necessity of using it in the chlorination stage.

My invention is particularly applicable to the bleaching of kraft pulp as hereinafter shown in most of the examples. It can also be used advantageously in the bleaching of soda, semi-chemical pulps and other cellulose pulps and fibrous materials such as are used in the manufacture of paper, textiles and other cellulosic materials. Sulfite pulps, which are commonly known to be easy to bleach, can also be bleached with my process with beneficial results. Generally, the pulp is prepared for bleaching in the normal manner, and no particular preparation of pulp is necessary to obtain the beneficial effects of chlorinating the pulp in the presence of the chlorate ion. The chlorate is merely added to the chlorination stage as previously described. The use of chlorate in the hypochlorite stage is similar to the process when hypochlorite is used alone, except that the amount of hypochlorite is reduced and chlorate is added. Acid may also be added if desired.

Any type of soluble chlorate which produces chlorate ions in aqueous solution is satisfactory in practicing my invention. For example, soluble metal chlorates, soluble alkali and alkaline earth metal chlorates and/or chloric acid are useful and will produce the same beneficial results when added to the cellulose chlorination and oxidation stages. Preferably, the chlorate ion is furnished by sodium chlorate since it is relatively inexpensive, readily soluble in water, and does not color the bleach solutions or pulp.

The use of chlorate does not appreciably add to the cost of the pulp bleaching process since, according to my invention, the quantity of chlorine used in the chlorination stages is not increased, and the quantity of hypochlorite commonly used in the oxidation stages may be considerably reduced. Furthermore, sodium chlorate is a relatively common chemical of commerce and lies in a price range which is somewhat less than that of the milder oxidizing agents referred to above, such as chlorine dioxide, sodium chlorite, and peroxides.

The following examples show that important advantages in strength and yield can be obtained when chlorate is used in the chlorination stages of cellulose pulp bleaching. Examples 1 and 2 show the increase in fiber strength and brightness obtained after a direct chlorination stage, and alkaline extraction stage, a hypochlorination stage and a second extraction stage. In all of the examples the chlorine, chlorate, hypochlorite, caustic and chlorite percentages are weight percentages based on the bone dry pulp.

EXAMPLE 1

A sample of kraft pulp was obtained which had a brightness of 23.3 (TAPPI method No. T217 m–48), and a cupriethylenediamine disperse viscosity (TAPPI

Method No. T230 sm-50, falling ball method) of 216 cp. This sample was bleached in two runs as are shown below in the table.

Charge:
- Brown stock brightness 23.3
- Brown stock viscosity, cp. 216

Bleaching process:
- Stage 1—
  - Pulp used, grams 20
  - Temperature, ° F. 70
  - Time, Minutes 60
  - Consistency, percent 3.5
  - Cl_2 and $NaClO_3$ ..... Tabulated below
- Stage 2—
  - NaOH used, percent 2.5
  - Temperature, ° F. 160
  - Time, minutes 60
  - Consistency, percent 10
- Stage 3—
  - NaOCl used, percent 1.25
  - Pulp used, grams 10
  - Temperature, ° F. 90
  - Time, minutes 180
  - Consistency, percent 10
- Stage 4—
  - NaOH used, percent 1.2
  - Temperature, ° F. 160
  - Time, minutes 60
  - Consistency, percent 10

Summary

Run No.	Percent Cl_2 Used, 1st Stage	Percent $NaClO_3$ Used, 1st Stage	Stage 2		Stage 4	
			Brightness	Viscosity, cp.	Brightness	Viscosity, cp.
1	5	0	23.7	270	38.2	234
2	5	1	24.6	297	39.5	260
Increase: Run 2 vs. Run 1			3.9%	10%	3.5%	11%

It can be seen from Example 1 that both strength and brightness are improved through the use of chlorate in the first stage of pulp bleaching and that this improvement is reflected as the bleach stages are continued. The strength is indicated by the viscosity which is a measure of fiber length. Higher viscosities indicate longer fibers and less degradation.

EXAMPLE 2

Charge:
- Brown stock brightness 23.3
- Brown stock viscosity, cp. 216

Bleaching process:
- Stage 1—
  - Pulp used, grams 20
  - Temperature, ° F. 70
  - Time, Minutes 60
  - Consistency, percent 3.5
  - Cl_2 and $NaClO_3$ ..... Tabulated below
- Stage 2—
  - NaOH used, percent 2.5
  - Temperature, ° F. 160
  - Time, minutes 60
  - Consistency, percent 10
- Stage 3—
  - NaOCl used, percent 1.25
  - Pulp used, grams 10
  - Temperature, ° F. 90
  - Time, minutes 180
  - Consistency, percent 10
- Stage 4—
  - NaOH used, percent 1.25
  - Temperature, ° F. 160
  - Time, minutes 60
  - Consistency, percent 10

Summary

Run No.	Percent Cl_2 Used, 1st Stage	Percent $NaClO_3$ Used, 1st Stage	Stage 2		Stage 4	
			Brightness	Viscosity, cp.	Brightness	Viscosity, cp.
3	7.5	0	29.0	206	52.1	196
4	7.5	1.67	28.6	277	52.5	209
Increase: Run 4 vs. Run 3			−1.3%	10.3%	0.7%	6.8%

As in Example 1, both strength and brightness are improved through the use of chlorate in the chlorination stage of pulp bleaching.

EXAMPLE 3

As another example of brightness improvement caused by the use of chlorate in the chlorination stage, a kraft pulp was bleached in three separate stages with 7.5% chlorine, 2.5% caustic, and 1% sodium hypochlorite. Sodium chlorate in the amount of 0.5% was used in the chlorination stage. The final brightness of the chlorate treated pulp was 67.0 as compared to a brightness of 61.7 in a sample which was treated without chlorate, an improvement of 8.5%. Other kraft pulps bleached in a similar manner but to a higher brightness also showed a brightness increase, but the improvement was smaller in pulps bleached to a brightness of the order of 75.

EXAMPLE 4

A sulfite pulp of 19.4 permanganate number was bleached in three separate stages with 6.5% chlorine, 2.5% caustic soda, and 0.5% sodium hypochlorite, respectively. Sodium chlorate in the amount of 1% was added in the first, or chlorination, stage. The final brightness of the chlorate treated pulp was 84.1, compared to a brightness of 77.8% in a comparable sample treated without chlorate.

EXAMPLE 5

Example 2 was repeated with an additional hypochlorite stage being added. The bleach in this stage consisted of one percent sodium hypochlorite in terms of available chlorine. In this stage the pulp was at 10 percent consistency; bleaching was two hours at 90° F. The increase in yields for the individual stages as well as the actual cumulative yield for the overall process is shown.

	Run 5, No chlorate	Run 6, 1.67% chlorate
2nd Stage:		
Pulp used, grams	20	20
Yield after Stages 1 and 2	17.88	18.36
Gain in yield, percent		2.7
4th Stages:		
Pulp used, grams	17	17
Yield after Stages 3 and 4	15.95	16.18
Gain in yield, Percent		1.4
5th Stage:		
Pulp used, grams	15	15
Yield after Stage 5	14.3	14.4
Gain in yield, percent		0.7
Total composite sample [1] (all stages)	16.3	16.9
Mean gain in yield from TCS, percent		3.7

[1] All samples dried and weighed together.
(Brightness of each sample at end of bleach series equalled 76.)

Examples 6 and 7 further illustrate the increase in pulp yield obtained in practicing my invention. For comparison purposes permanganate numbers (TAPPI Method T214 sm-50) were determined for each pulp sample after drying. Permanganate numbers give an indication of the residual lignin in the pulp and illustrate, in the following examples, that the use of chlorate, while greatly increasing the yield, does not lessen the degree of lignin removal.

EXAMPLE 6

One kilogram samples of fresh dry kraft pulp were diluted to 3.5% consistency with water at 10° C. 7.5%

of chlorine was used. The pulp, after vigorous stirring, was allowed to stand for one hour after which time it was placed on a screen and washed with six buckets of water (2.5 gallons per bucket). The pulp was then squeezed about 20% consistency and was subsequently treated with 2.5% caustic soda at 10% consistency and 50° C. After one hour the pulp was screened, washed with 12 buckets of water, and dried to constant weight. This experiment was repeated using various amounts of chlorate with the yield being determined after each run. Results are tabulated below:

Run No.	$NaClO_3$ Used, Percent	Yield, Grams	Yield Increase, Percent	$KMnO_4$ No.
7	0	910	0	8.5
8	0.05	927	1.87	8.1
9	0.125	933	2.53	9.5
10	0.25	934	2.64	9.0
11	0.5	938	3.08	9.5
12	1.0	940	3.29	8.3
Raw Pulp				24.9

EXAMPLE 7

A second sample of fresh dry kraft pulp was obtained and was treated as described in Example 6 with various amounts of sodium chlorate being added. The results are tabulated below:

Run No.	$NaClO_3$ Used, Percent	Yield, Grams	Yield Increase, Percent	$KMnO_4$ No.
13	0	954	0	6.5
14	0.125	964	1.05	6.4
15	0.250	972	1.89	6.25
16	0.5	981	2.83	6.1
17	1.0	981	2.83	6.9
Raw Pulp				21.5

The results from Examples 6 and 7 indicate that the optimum level of sodium chlorate use for these particular pulps lies in the vicinity of 0.5%. Further addition of chlorate gives small, if any, increase in bleached pulp yield.

Example 8 is further illustrative of the inhibition of oxidation that takes place when chlorate is present in the direct chlorination of cellulose pulp.

EXAMPLE 8

Two 50 gram samples of kraft pulp were chlorinated at 3% consistency and 7.5% chlorine at 20° C. 0.5% sodium chlorate was added to one sample. After one hour the liquor was drained from each sample and allowed to stand for 24 hours. The two solutions were then compared in a spectrophotometer and results tabulated as shown in the table:

Wave Length, A.	Percent Transmittance, 0.5% $NaClO_3$ Compared to 0% $NaClO_3$
3,500	50
3,750	66
4,000	78
4,250	86
4,500	91
4,750	95
5,000	96
5,250	98
5,500	99
5,750	100
6,000	99
6,250	102
6,500	102

The solution containing the chlorate was considerably darker than the non-chlorate containing solution. Direct visual observation showed that the non-chlorate containing solution had bleached to a much lighter color than the chlorate containing solution after 24 hours standing. A slight color difference was also noticeable immediately after removal of the solution from the pulp.

When chlorate was not present in the chlorination of the pulp sample the solution color was much lighter immediately after removal from the pulp and was almost colorless after standing for a twenty-four hour period, indicating the oxidation of the lignin materials to almost colorless compounds. When chlorate was present during the chlorination the lignin was not oxidized and the resulting solution was darker in appearance and remained dark on standing, showing that oxidation was inhibited by the presence of the chlorate.

The following examples of oxidation bleaching show that important advantages in strength and brightness can be obtained also when chlorate is used with hypochlorite in the oxidation stages of cellulose pulp bleaching. These results are especially noticeable in acid mediums.

In preparation to carrying out the examples described below a lot sample of kraft pulp was obtained which had previously been bleached in chlorination, extraction and hypochlorite stages, a total of four stages having been used. The pulp sample had a brightness of 78.6 (TAPPI Method No. T217 m–48) and a strength of 61.1 cp. (cupriethylenediamine disperse viscosity (TAPPI Method No. T230 am–50, falling ball method)). Pulp samples taken from the lot sample were used in each of the runs. Upon completion of the bleach step in each run, the pulp was washed with water containing a small amount of sodium thiosulfate and acidified with hypochloric acid to a pH of 5. The wash served to destroy residual bleach in the pulp and prevented loss of color during drying. This stabilization treatment is equivalent to the final touch-up with sulfur dioxide and acid customarily used in pulp mills. In each run the pulp was used at a consistency of 10%, and the oxidation bleaching was done at 90° F. for a period of 2 hours.

EXAMPLE 9

Since sodium hypochlorite is widely used in pulp oxidation bleaching stages and results obtained through its use are well-known by those working in the art, this agent serves as an excellent standard of comparison for other bleaching agents.

Comparative runs were made using sodium hypochlorite alone, sodium hypochlorite with sodium chlorate, and sodium hypochlorite with sodium chlorate and hydrochloric acid in the ratio of two moles of hydrochloric acid per mole of chlorate.

Results of these runs are shown in the tabulation below. It is seen that the pulps from runs containing chlorate, runs 19 and 20, each have strengths superior to that of run 18 in which an amount of hypochlorite equivalent in available chlorine to the amount of chlorate was used. The brightness is in the same order of magnitude. Runs 19 and 20 which contain chlorate also gave superior results in both strength and brightness compared to chlorate-containing run 21 which had an amount of hypochlorite equivalent to that used with runs 19 and 20.

Run No.	Principal Bleach Agent as Percent Available Cl_2	Principal Bleach Agent	Brightness (stabilized)	Viscosity, cp.
18	0.5	NaOCl	85.5	41.1
19	0.5	$NaClO_3$	84.7	50.3
20	0.5	$NaClO_3$+HCl	85.1	51.1
21	0.13	NaOCl	83.2	46.1

EXAMPLE 10

The runs shown in the present example were carried out using twice as much of each reagent as was used in the runs of Example 9. The ratios of hypochlorite and

hydrochloric acid to chlorate were the same as those in Example 9. Test results are summarized below.

Run No.	Principal Bleach Agent as Percent Available Cl_2	Principal Bleach Agent	Brightness (stabilized)	Viscosity, cp.
22	1	NaOCl	86.6	42.8
23	1	$NaClO_3$	85.2	45.8
24	1	$NaClO_3$+HCl	86.3	49.2
25	0.26	NaOCl	85.3	44.6

Again, it is seen that hypochlorite bleach containing chlorate ion is superior to hypochlorite bleach used alone for pulp treatment. This result is also obtained in the presence of acid. Pulp brightness is about equal to that obtained with hypochlorite alone. Pulp degradation is much less, leaving the pulp with more strength. The viscosities tabulated in Example 10 are not as good as those in Example 9 inasmuch as more bleach was used in each run in the present example.

EXAMPLE 11

A retabulation of the runs of Examples 9 and 10, shown below, indicates that the strengths of pulps processed with chlorate treated bleaches in accordance with my invention are from about 4 to 24% above strengths, as shown by viscosities, of pulps processed only with hypochlorite. This result occurs even though the total amounts of bleach in terms of available chlorine when chlorate and hypochlorite as used in accordance with my invention are in excess of those used with hypochlorite alone.

Run No.	Bleaching Agent		Equivalent Percent Available Cl_2			Brightness (stabilized)	Viscosity cp.
	A	B	A	B	Total		
18	NaOCl		0.5		0.5	85.5	41.1
19	NaOCl	$NaClO_3$	0.13	0.5	0.63	84.7	50.3
20	NaOCl	$NaClO_3$+HCl	0.13	0.5	0.63	85.1	51.1
21	NaOCl		0.13		0.13	83.2	46.1
22	NaOCl		1.0		1.0	86.6	42.8
23	NaOCl	$NaClO_3$	0.26	1	1.26	85.2	45.8
24	NaOCl	$NaClO_3$+HCl	0.26	1	1.26	86.3	49.2
25	NaOCl		0.26		0.26	85.3	44.6

EXAMPLE 12

Example 12 was carried out in the same manner as preceding examples and shows that chlorate, even with acid present, has little effect as a bleaching agent for pulp in the absence of hypochlorite. This fact is shown by the brightness values obtained from runs 26, 27, 28 and 29 when compared with the brightness results shown in the previous examples. A slight improvement is apparent in each of the runs in the present example, but this improvement is probably a result of additional washing and the effect of acidification on residual chromophores remaining with the pulp. The HCl and H_2SO_4 used in the example were in chemically equivalent amounts. In each run the pH of the batch was adjusted to about 4 with the acid.

Run No.	Bleaching Agent	Equivalent of Available Chlorine	Brightness (Stabilized)	Viscosity, cp.
26	$NaClO_3$+HCl	1.0	80.1	51.6
27	$NaClO_3$+H_2SO_4	1.0	80.1	47.4
28	HCl		79.7	48.8
29	H_2SO_4		80.1	48.5

The foregoing Examples 9, 10, 11, and 12 illustrate that a distinct advantage in strength is obtained through the use of chlorate in the brightening stages of pulp bleaching. It should be especially noted that, with this particular pulp, the use of sodium chlorate in an acid hypochlorite bleach results in a relatively strong pulp without the fiber degradation and brightness loss that is customarily associated in the art with the use of hypochlorite alone in an acid bleach.

My invention is not to be limited by the quantities or conditions cited in the above examples as these examples are only illustrative of the general methods of use of my invention.

In cases where various strength and brightness combinations are required, it is obvious that it might be advisable to vary the chlorate-hypochlorite and chlorate-acid ratios. While the advantages of my invention can be realized, over a wide range of concentrations and ratios, for a particular pulp it would be advantageous to determine optimum ratios and amounts on the basis of laboratory scale tests, and then apply these to mill-scale operations. The essence of my invention is that chlorate may be used with chlorine or hypochlorite, as an adjuvant in the bleaching of pulp, cellulose and similar materials and that desirable results will be obtained. Several examples are given to illustrate the use of this material but are not necessarily cited as limitations or most desirable combinations for every pulp.

As stated earlier in this specification, my invention is especially valuable when applied in the chlorination and hypochlorination stages of bleaching of difficult-to-bleach wood pulps. Pulp from wood, which by its nature is difficult to bleach, and which furthermore is prepared by mechanical or semi-chemical or soda or sulfate chemical processes presents the most difficulty in bleaching operations, particularly if paper grade stock is being prepared and a high degree of whiteness with a maximum of strength is desired. In the bleaching of easy-to-bleach pulps, such as pulps prepared by the sulfite process from woods naturally easy to bleach, improvement of brightness by use of my process may not be very great. On the other hand the degradation of the pulp will be less and strength will be higher than if bleached in the absence of chlorate.

By way of example of this point, the modest improvement in brightness obtained in the hypochlorination bleaching of a sulfite pulp using the teaching of my method is shown in Example 13.

EXAMPLE 13

A sulfite pulp of permanganate number 19.4 was chlorinated with 6.5% chlorine for one hour at 70° F. and 10% consistency. The pulp was further treated by caustic extraction with 2.5% caustic soda for one hour at 160° F. and 10% consistency. A sample was then bleached for two hours at 100° F. and 10% consistency using a bleach solution containing 1% sodium chlorate and 0.65 moles of sodium hypochlorite per mole of chlorate used. Another sample was treated under the same conditions except without the sodium chlorate. Brightness values obtained were 71.4 for the sample treated in the presence of chlorate and 70.6 for the sample treated in the absence of chlorate.

It is emphasized that bleach procedures vary greatly in the industry because of variations in type of wood, method of cooking, degree of bleach and strength de-

sired, number of stages, temperature, bleach period, consistency, bleach concentration, etc. Because of these variations, it is not possible to illustrate all combinations of the above conditions in which my invention would be useful. I have illustrated general methods, however, and have given sufficient information to one skilled in the art so that my invention can be applied to a great variety of bleaching conditions.

It will be quite obvious to one skilled in the art that the preceding examples will be equally as operable with potassium chlorate, calcium chlorate, magnesium chlorate, chloric acid or any other material which furnishes chlorate ion in aqueous solution.

I claim:

1. In a conventional commercial process for bleaching cellulose pulp comprising the step of contacting an aqueous suspension of said pulp with chlorine in at least one stage of said process at a pH in the range from about 2 to below 7 and at a temperature in the range from about 0° C. to about 50° C., the improvement which consists of carrying out said contacting in further contact with from about 0.01% to about 5% of an added amount of an inorganic chlorate selected from the group consisting of alkali metal chlorates, alkaline earth metal chlorates and chloric acid based on the weight of said pulp for a period of time at least sufficient to solubilize a substantial portion of colored lignin materials in said cellulose.

2. The process of claim 1 wherein the inorganic chlorate is sodium chlorate.

3. In a conventional commercial process for bleaching cellulose pulp comprising the step of contacting an aqueous suspension of said pulp with an inorganic hypochlorite in at least one stage of said process at a pH in the range from about 5 to above 7 and at a temperature in the range from about 20° C. to about 100° C., the improvement which consists of carrying out said contacting in further contact with an added amount of an inorganic chlorate selected from the group consisting of alkali metal chlorates, alkaline earth metal chlorates and chloric acid for a period of time at least sufficient to decompose a substantial portion of chromophoric groups in the lignin of said cellulose, said hypochlorite and said chlorate being in the molar ratio of 1 to about 1.5.

4. The process of claim 3 wherein the inorganic chlorate is sodium chlorate.

5. The process of claim 3 wherein the inorganic hypochlorite is selected from the group consisting of sodium hypochlorite and calcium hypochlorite.

6. In a conventional commercial process for bleaching cellulose pulp comprising the steps of contacting an aqueous suspension of said cellulose with chlorine in at least one stage of said process at a pH in the range from about 2 to below 7 at a temperature in the range from about 0° C. to about 50° C. and with an inorganic hypochlorite in at least one other stage of said process at a pH in the range from about 5 to above 7 and at a temperature in the range from about 20° C. to about 100° C., the improvement consisting of the steps of carrying out said contacting of said cellulose with chlorine in further contact with from about 0.01% to about 5% of an added amount of an inorganic chlorate selected from the group consisting of alkali metal chlorates, alkaline earth metal chlorates and chloric acid based on the weight of said cellulose for a period of time at least sufficient to solubilize a substantial portion of colored lignin materials in said cellulose, and carrying out said contacting of said cellulose with said hypochlorite in further contact with an added amount of said chlorate for a period of time at least sufficient to decompose a substantial portion of chromophoric groups in the lignin of said cellulose, said hypochlorite and said chlorate being in the molar ratio of 1 to about 1.5.

7. The process of claim 6 wherein the inorganic chlorate is sodium chlorate and the inorganic hypochlorite is selected from the group consisting of sodium hypochlorite and calcium hypochlorite.

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