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## LIGNIN-PRESERVING BLEACHING OF CELLULOSE PULP

Josef Franz Gierer, Lidings, and Carl Torbjorn Norin, Bromma, Sweden, assignors to Svenska Traforskningsinstitutet, Stockholm, Sweden  
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3 Claims

### ABSTRACT OF THE DISCLOSURE

A bleaching process for cellulose pulps and which enables the lignin in the pulp to be preserved comprises bleaching of the pulp in the presence of an organic peroxide, which is produced by contacting a peroxide forming organic compound with air or a gas containing free oxygen.

The present invention relates to a process for bleaching cellulose pulp while preserving the lignin therein.

There are known to the art a number of processes intended for bleaching cellulose pulps without adverse effect on the lignin therein. Reduction bleaching with dithionite and oxidizing bleaching with hydrogen peroxide or sodium peroxide are those methods which have obtained the greatest practical significance.

The reduction bleaching method with dithionite or other reduction agents, such as sulphite or boron hydride, is gentle and imparts to the pulp good properties of strength. The bleaching effect, however, is not long lasting. Pulps which have been bleached by the reduction method quickly turn yellow when coming into contact with air, particularly when subjected to light irradiation or high temperatures.

Oxidative bleaching with hydrogen peroxide or sodium peroxide produces a cellulose pulp with a high degree of brightness which is relatively stable, although at the cost of a certain deterioration in the mechanical properties of the pulps. The main disadvantages associated with peroxide bleaching, however, lie in the instability of the bleaching agent and its high price. In addition to oxidizing, and thereby removing chromophore systems in cellulose pulps, hydrogen peroxide undergoes a spontaneous decomposition which is difficult to calculate and to control. This decomposition can be reduced to a certain extent, although never entirely eliminated, by the addition of stabilizers, such as sodium silicate, magnesium sulphate, or complex builders, such as for example ethylene diamine-tetraacetic acid (EDTA). The stabilizers and complex builders are not recovered and hence create extra costs. Even when using these additives it is necessary to charge a large excess of peroxide to the system if the cellulose pulp is to obtain a high degree of brightness.

These disadvantages explain why peroxide bleaching processes have hitherto been mainly applied to cellulose pulps which respond well to bleaching per unit of weight of peroxide used i.e. in single stage bleaching of relatively bright starting pulps (semi-chemical pulps and mechanical wood pulps), in two stage bleaching in combination with a reducing bleaching stage (primarily dithionite bleaching) and in multi-stage bleaching as a terminating bleaching stage.

In accordance with the invention, cellulose pulps can be favourably bleached while preserving the lignin therein by performing the bleaching process in the presence of an organic peroxide. The organic peroxide is suitably produced, in accordance with the invention, by using air or some other oxygen bearing gas and a peroxide forming

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organic compound under correctly adjusted conditions with regard to pH, temperature, pressure, pulp consistency, reaction rate and, optionally, irradiation.

The process of the invention is suitable as a single-stage bleaching process, but may also be used to advantage in processes embodying two or more bleaching stages. Thus, it is not restricted to types of pulp which have a relatively high degree of initial brightness, such as for example mechanical, semi-chemical and pre-bleached pulps. Particularly when using air and easily recovering organic solvents for producing the active bleaching organic peroxide compounds it is possible in accordance with the invention to use the process, to advantage, for the partial or complete bleaching also of cellulose pulps which present a low initial brightness, e.g. unbleached sulphate pulp.

Processes for bleaching cellulose pulps with oxygen gas or air are well known to the art. According to these processes, the cellulose pulp, whilst suspended in caustic soda solution, is treated with air or oxygen gas at high temperatures and under pressure. During this treatment the major portion of the lignin is decomposed and separated and the bleaching process does not preserve the lignin. Furthermore, this treatment causes undesirable degradation of the cellulose and hence an inferior pulp yield and impaired strength properties of the pulp.

The aim of the process of the invention is, however, to combine the economic advantages and effectiveness of, respectively, the air and the oxygen gas bleaching processes with the relative leniency of the peroxide bleaching process. This is achieved by incorporating the oxygen into organic compounds, to form organic peroxide substances which, in a lignin-preserving manner, bleach the cellulose pulps to a high and lasting degree of brightness. The process is lenient in respect of the values of the pH and temperature applied, which results therein that the yield losses caused by oxidative and/or hydrolytic decomposition are small and that the properties of strength of the resulting, bleached pulps are well comparable with the corresponding properties of pulps bleached to the same degree of brightness with hydrogen peroxide in a conventional manner.

In accordance with the invention, the preparation of the organic peroxidic substances of suitable organic compounds by reaction with air or oxygen bearing gas and reacting the formed peroxidic components with the chromophore groups of the pulps can take place either in two separate processes or simultaneously. In the first case both the preparation of the bleaching organic peroxide compounds and the reacting thereof can be carried out under optimal conditions in respect of the aforementioned variables. The advantage with this mode of procedure is primarily to be found therein that the pulp need not be subjected to high temperatures (and possibly high oxygen gas pressure) for long periods of time, whereby its strength properties are only slightly impaired. The best results have, therefore, been obtained when the step of preparing the peroxide and the step of reacting it with the cellulose pulp are carried out progressively under reaction conditions which are the most favourable one for each of these two stages.

It should also be understood, however, that the second mode of procedure, i.e. simultaneous preparation and reaction of the peroxidic compounds with the cellulose pulps, can present certain advantages. In this connection, the peroxidic compounds are formed and reacted either by introducing air or some other oxygen bearing gas continuously into a suspension of the cellulose pulp in a peroxide forming organic compound under the conditions given below, or by treating the pulp suspension with air or oxygen bearing gas under pressure in a closed system. Since this process does at the same time involve an effective extraction of the cellulose pulps, i.e. a re-

moval of lipophilic and hydrophilic low molecular constituents, e.g. resins, steroids, fats, mono- and oligosaccharides, there are obtained in addition to the bleaching effect, the same advantages as those when treated with solely the said compound (solvent). This combined bleaching and extraction effect is particularly advantageous in connection with lignin-preserving bleaching of mechanical, thermomechanical and semi-mechanical pulps which present a relatively high content of the extractive substances. Furthermore, the use of water-soluble, peroxide forming organic solvents has the advantage that the pulps are effectively dewatered during the bleaching operation.

In accordance with the invention, peroxide forming organic compounds are reacted with oxygen gas or oxygen bearing gas, preferably air, and the resulting peroxides are reacted with cellulose pulps. The following will discuss more closely the most suitable conditions for preparing the peroxides and their reaction with cellulose pulps.

Many peroxide forming organic compounds can be used for bleaching cellulose pulps while preserving the lignin therein. The best results, however, are obtained with organic compounds which with free oxygen give water-soluble peroxidic compounds, particularly such compounds which readily form organic hydroperoxides and which together with water swell the cellulose pulps and thereby render them more readily accessible to attacks by the organic peroxides. Dioxan, a commercially available solvent which is produced on a large scale, has the aforementioned properties. It forms together with air or free oxygen bearing gas a water-soluble hydroperoxide (M.P. 53–56° C.) and swells cellulose pulps. It can readily be recovered by distillation and be reused for the same type of lignin preserving bleaching process. The majority of the bleaching tests in accordance with the invention have therefore been carried out with dioxan as the peroxide forming organic compound. It should be mentioned, however, that also other peroxide forming organic compounds, such as other cyclic ethers such as tetrahydrofuran, tetrahydropyran, non-cyclic ethers and alcohols, e.g. isopropanol, 2-butanol, give satisfactory bleaching results.

Preparation of the bleaching organic peroxides by a separate process prior to the cellulose bleaching process is effected either by passing air or free oxygen containing gas through the peroxide forming compound at high temperature, preferably at the boiling point of the compound, or by heating the compound with air or oxygen bearing gas at pressures in excess of atmospheric in a closed system, at temperatures between the boiling point of the compound and 50° C. thereabove, generally between 80 and 150° C. Since the rate at which the peroxide is formed depends upon the amount of oxygen gas which is dissolved in the peroxide forming organic compound, and since this quantity is proportional to the partial pressure of oxygen over the compound, it is preferred for economic reasons to prepare the compound at pressures in excess of atmospheric. Generally an air pressure of between 3–50 atmospheres above atmospheric pressure is used, corresponding to an oxygen gas pressure of between 0.6–10 atmospheres above atmospheric pressure, preferably 20–30 and 4–6 atmospheres above atmospheric pressure respectively. The use of oxygen gas instead of air shortens the reaction rate for obtaining a specific peroxide content to approximately between one third and one fifth.

During the formation of peroxide, the pH falls because of the formation of acid decomposition products from the peroxidic compounds. Since the decomposition of the organic peroxides, active during the bleaching process, is catalysed by protons, the formation of the peroxides is compensated for after a certain length of time by the decomposition, i.e. the peroxide content passes through a maximum. For the purpose of avoid-

ing, or at least delaying, decomposition of the peroxides they can, in accordance with the invention, be prepared in the presence of stabilizers, such as sodium or magnesium salts, for instance, sodium silicate, sodium carbonate, magnesium sulphate etc. Such salts have been found essential when preparing peroxides in large quantities while using long reaction times.

If an open system is employed, the rate at which the peroxides are formed can be further increased by irradiating the system with UV-light in the presence of a sensitizer, e.g. benzophenone.

In principal, all types of cellulose pulps can be bleached by applying the method of the present invention. The majority of tests have heretofore been made with unbleached sulphate pulps which present a low initial brightness and with unbleached or pre-bleached neutral pulphite pulps and mechanical pulps having relatively high degree of initial brightness. The pulp consistency can be varied within wide limits e.g. from 1 to 25%. In practice a consistency of approximately 8% (8 g. of pulp/100 ml.) has been found advantageous. Under otherwise equal conditions the bleaching result is, primarily, determined by the relationship of organic peroxide to pulp.

The reaction between the organic peroxides and the cellulose pulps is suitably effected so that the brightness is increased by the largest possible extent within the shortest possible time. The optimum bleaching conditions vary of course with different types of pulp and different organic peroxidic compounds. Normally, temperatures between 40–100° C. and reaction times between 0.5–4 hours are applied. In the case of longer reaction times an addition of stabilizers, e.g. sodium silicate, provides a favourable effect on the bleaching result.

It is evident from the foregoing that the optimal conditions for, firstly, preparing the organic peroxides and, secondly, their reaction with cellulose pulps are not identical. If the preparation of the peroxides and their reaction with the pulps is to take place simultaneously, i.e. in one and the same process stage, the selection of the optimal bleaching conditions must therefore be based on compromises, primarily with respect to temperature, pressure, reaction time and pH. These process variables are suitably selected so that the highest possible increase in brightness is obtained with the least possible decomposition of the cellulose and of the lignin. Of course, the optimal bleaching conditions in this method of procedure are also dependent on the type of pulp to be bleached and on which peroxide forming organic compound and oxygen bearing gas is to be used.

Normally the cellulose pulps are suspended in the peroxide forming organic compound and bleaching is effected by introducing air or oxygen bearing gas through the suspension, heated to the boiling point of the compound, or by heating the suspension with air or oxygen bearing gas at pressures of atmospheres above atmospheric pressure (between 3 and 50 in respect of air, and 0.6–10 in respect of oxygen gas) to the boiling point of the compound or up to 50° C. above said boiling point in a closed system (autoclave tube). The reaction time is primarily determined by the degree of brightness to be obtained and the extent to which deterioration in the mechanical properties of the pulp can be tolerated. In this method of procedure reaction times of between 5 and 50 hours are normally chosen.

The invention will now be described with reference to a number of examples which illustrate the influence of different process variables on the formation of the organic peroxides, on their reaction with the different cellulose pulps and on the optical and mechanical properties of the bleached pulps.

#### EXAMPLE 1

Oxygen gas or air was introduced into 250 ml. of the peroxide forming organic compound during a reflux di-

gestion cycle and during the times given in Table 1. In a number of the tests benzophenone (50 mg.) was added as a sensitizer. The amount of peroxide formed was determined by iodometric titration with 0.1 N sodium thiosulphate solution.

TABLE 1.—PEROXIDE FORMATION IN DIFFERENT ORGANIC COMPOUNDS WITH AIR OR OXYGEN GAS AT BOILING POINT

Peroxide forming organic compound (250 ml.)	Air or oxygen	Temperature, ° C.	Reaction time (hours)	With (+) or without (—) benzophenone (50 mg.)	ml consumed at 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution per 5 ml.
Isopropanol.....	Air.....	82	68	—	1.60
Do.....	Air.....	82	27	+	1.60
2-butanol.....	Oxygen.....	100	24	—	25.60
Tetrahydrofuran.....	do.....	65	48	—	10.00
Tetrahydropyran.....	do.....	81	60	—	15.00
Do.....	do.....	81	103	—	60.00
Dioxan.....	do.....	100	24	—	12.50
Do.....	do.....	100	30	—	18.10
Do.....	Air.....	100	24	—	4.50
Do.....	Air.....	100	48	—	10.00
Do.....	Air.....	100	24	+	8.10
Do.....	Air.....	100	30	+	12.30

### EXAMPLE 2

In order to show the effect of different stabilizers on the formation of peroxide the method of procedure in accordance with Example 1 was repeated with dioxan

dioxan, was added to the suspension. Bleaching was effected under the conditions disclosed in Table 3, which also shows the values of brightness, viscosity and the most important mechanical properties of some of the bleached mechanical pulps.

TABLE 3

[Bleaching of mechanical pulp (50 g.) (58.8% G.E., 153 cp.) with peroxide from dioxan (4 g.) in the presence of sodium silicate (2.5 g.)]

Temperature, ° C.	Reaction time (hours)	Brightness (percent G.E.)	Intrinsic viscosity (cp.)	Beating degree (° S.R.)	Breaking length (m.)	Rupture strength (kp./cm. <sup>2</sup> )	Tearing factor	Double foldings
60.....	2	67.3	145	52	1,921	0.7	43	2
60.....	4	69.5	152	53	2,322	0.9	46	4
80.....	2	68.2	186	53	1,897	0.7	42	2
Unbleached mechanical pulp								
.....	.....	58.8	153	52	2,560	0.8	44	2

(250 ml.) and oxygen gas at 100° C., with the addition of different inorganic salts.

TABLE 2.—FORMATION OF PEROXIDE IN DIOXAN WITH OXYGEN GAS AT 100° C. IN THE PRESENCE OF INORGANIC SALTS

Added inorganic salt (mg.)	Reaction time (hours)	ml. consumed 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution/5 ml.	Remarks
MgCO <sub>3</sub> (100).....	24	12.5	MgCO <sub>3</sub> added in 3 portions at 50 mg. after 24, 40 and 44 hours.
MgCO <sub>3</sub> (150).....	24	14.2	
MgCO <sub>3</sub> (150).....	54	25.5	
MgCO <sub>3</sub> (150).....	54	42.0	Na <sub>2</sub> CO <sub>3</sub> added in 2 portions at 50 mg. after 24 and 44 hours.
Na <sub>2</sub> CO <sub>3</sub> (100).....	24	15.5	
Na <sub>2</sub> CO <sub>3</sub> (100).....	48	36.5	
MgSO <sub>4</sub> (150).....	66	75.5	
Na <sub>2</sub> SO <sub>4</sub> (150).....	48	43.3	

Tests at 40° C. and a reaction time of 1 hour gave a bleached pulp having a brightness of 66.1% G.E.

### EXAMPLE 4

A neutral sulphite pulp from spruce (50 g.) having an initial brightness of 48.6% G.E. and an intrinsic viscosity of 781 cp. was suspended in 625 ml. of water, optionally containing sodium silicate (2.5 g.), and was treated in the manner described in Example 3. Table 4 discloses the bleaching conditions and the brightness; intrinsic viscosity and mechanical properties of the bleached pulps.

TABLE 4

[Bleaching of neutral sulphite pulp (50 g.) (48.6% G.E., 781 cp.) with peroxide from dioxan (4 g.) with and without sodium silicate (2.5 g.)]

Temperature, ° C.	Reaction time (hours)	With (+) or without (—) $\text{Na}_2\text{SiO}_3$	Brightness (percent G.E.)	Intrinsic viscosity (cp.)	Beating degree (° S.R.)	Breaking length (m.)	Rupture strength (kp./cm. <sup>2</sup> )	Tearing factor	Double foldings
40.....	2	—	57.4	.....	.....	.....	.....	.....	.....
40.....	2	+	50.7	.....	.....	.....	.....	.....	.....
40.....	4	—	62.4	.....	.....	.....	.....	.....	.....
40.....	4	+	54.1	.....	.....	.....	.....	.....	.....
60.....	1	—	58.7	567	50	9,003	6.9	89	1,508
60.....	2	—	60.9	593	53	8,793	6.5	91	2,131
60.....	4	—	58.2	567	48	8,717	6.4	91	1,984
80.....	2	+	62.1	856	71	10,579	7.9	80	4,617
Unbleached neutral sulphite pulp									
.....	.....	—	48.6	781	43	9,437	7.1	64	1,574

Test with the bleaching of a corresponding pulp with hydrogen peroxide at the temperature of 60° C. and a reaction time of 4 hours showed that bleaching to ac-

washed with distilled water, dried in air and examined in respect of brightness, intrinsic viscosity and mechanical properties. The results are disclosed in Table 6.

TABLE 6

[Bleaching of different types of pulp (40 g.) with air in dioxan (2 l.) during refluxed digestion for 48 hours.†]

Type of pulp (40 g.)	With (+) or without (-) Na <sub>2</sub> SiO <sub>3</sub> (2 g.)	With (+) or without (-) benzo-phenone (0.4 g.)	Brightness (percent G.E.)	Intrinsic viscosity (cp.)	Beating degree (° S.R.)	Breaking length (m.)	Rupture strength (kp./cm. <sup>2</sup> )	Tearing factor	Double foldings
Mechanical pulp.....	-	+	60.1	176	27	9,852	0.45	25	1
Do.....	+	-	58.4	210	27	12,059	0.41	27	1
Neutral sulphite pulp.....	+	-	64.0	688	68	8,843	6.3	75	1,884
Do.....	+	+	61.9	604	61	7,936	5.6	74	2,239
Sulphate pulp.....	-	-	44.2	735	36	9,182	7.6	138	4,040
Do.....	-	+	48.4	679	46	9,562	7.8	125	4,356

† Corresponding values for the starting pulps are found in Tables 3-5.

ceptable brightness can only be achieved in the presence of a stabilizer.

## EXAMPLE 5

Unbleached sulphate pulp from pine (50 g.) having an initial brightness of 23% G.E. and an intrinsic viscosity of 1128 cp. was suspended in 625 ml. of water, optionally containing sodium silicate (2.5 g.), and was treated in the manner described in Example 3. Table 5 discloses the bleaching conditions and the values of the brightness, intrinsic viscosity and mechanical properties of the bleached sulphate pulps. For comparison purposes, the

## EXAMPLE 7

20 Oxygen gas was forced into an autoclave tube made of stainless steel and containing a suspension of pulp (40 g.) in dioxan (2 l.), and optionally sodium silicate (2 g.) as a stabilizer, to a pressure of 5 atmospheres above atmospheric pressure. The sample was rotated for 6, 12 and 23 hours, respectively, in a polyglycol bath heated to 100° C. The obtained pulp was washed with distilled water, dried in air and examined in respect of brightness. Table 7 discloses the measuring values and the bleaching conditions.

TABLE 7

[Bleaching of different types of pulp (40 g. of each) in dioxan (2 l.) with oxygen gas (5 atmospheres above atmospheric pressure) at 100° C.‡]

Type of pulp (40 g.)	With (+) or without (-) Na <sub>2</sub> SiO <sub>3</sub> (2 g.)	Reaction time (hours)	Brightness (percent G.E.)	Intrinsic viscosity (cp.)	Beating degree (° S.R.)	Breaking length (m.)	Rupture strength (kp./cm. <sup>2</sup> )	Tearing factor	Double foldings
Mechanical pulp.....	-	23	66.3	49.3	-----	-----	-----	-----	-----
Neutral sulphite pulp.....	-	23	49.3	-----	-----	-----	-----	-----	-----
Do.....	+	23	49.9	-----	-----	-----	-----	-----	-----
Sulphate pulp.....	-	6	33.2	874	26	8,975	7.7	134	5,096
Do.....	+	6	32.7	872	42	10,047	8.2	126	5,173
Do.....	-	12	39.7	-----	-----	-----	-----	-----	-----
Do.....	-	23	45.4	697	30	9,387	7.7	116	4,594
Do.....	+	23	44.0	739	32	9,038	7.6	123	5,680
Do.....	-	23	38.2	943	37	9,842	8.4	126	5,777

‡ Corresponding values for the starting pulps are given in Tables 3-5.

‡ Treated with air instead of oxygen.

table also discloses corresponding values for the unbleached sulphate pulp.

What is claimed is:

1. A process for bleaching cellulose pulps while pre-

TABLE 5

[Bleaching of sulphate pulp (50 g.) (23.2% G.E., 1,128 cp.) with peroxide from dioxan (4 g.) with and without sodium silicate (2.5 g.)]

Temperature, ° C.	Reaction time (hours)	With (+) or without (-) Na <sub>2</sub> SiO <sub>3</sub>	Brightness (percent G.E.)	Intrinsic viscosity (cp.)	Beating degree (° S.R.)	Breaking length (m.)	Rupture strength (kp./cm. <sup>2</sup> )	Tearing factor	Double foldings
60.....	4	-	33.4	1,127	36	9,973	8.9	124	6,312
60.....	4	+	36.6	1,150	43	10,164	8.9	121	5,690
80.....	1	+	34.5	1,124	41	10,037	8.5	123	5,003
80.....	2	-	35.9	1,045	40	10,164	8.8	121	6,330
80.....	2	+	36.7	1,065	49	10,204	8.9	125	6,123
Unbleached sulphate pulp									
-----	-----	-	23.2	1,128	50	10,992	9.1	120	7,114

Tests with the bleaching of a corresponding pulp with hydrogen peroxide at a temperature of 60° C. and a reaction time of 4 hours resulted therein that bleaching to an acceptable brightness can only be achieved in the presence of a stabilizer.

## EXAMPLE 6

Different types of pulp (40 g. of each type) were suspended in dioxan (2 l.), optionally containing sodium silicate (2 g.) as a stabilizer and/or benzophenone (0.4 g.) as a sensitizer, and the suspension was refluxed digested on the water bath during constant percolation of air for 48 hours. The pulp was subjected to filtration,

serving the lignin therein comprising adding to unbleached cellulose pulp an organic compound selected from the group consisting of alcohols and ethers, contacting the cellulose pulp and organic compound with free oxygen under a pressure of from about 0.6 to about 10 atmospheres above atmospheric pressure at a temperature of from about 80° C. to about 150° C. during a reaction time from about 5 to about 50 hours whereby an organic peroxide is formed and the cellulose pulp is bleached thereby in one stage.

2. A process as claimed in claim 1 wherein the organic compound is an ether selected from the group consisting of dioxan, tetrahydrofuran and tetrahydropyran.

3. A process as claimed in claim 1 wherein the organic compound is an alcohol selected from the group consisting of isopropanol and 2-butanol.

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