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PROCESS FOR THE BLEACHING OF CELLULOSE MATERIAL

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My invention relates to a process for the bleaching of cellulose material by a combined treatment with chlorine and hydrogen peroxide whereby the quantity of hydrogen peroxide is very low.

It is already known to bleach cellulose containing materials with peroxides or compounds which split up hydrogen peroxide hydrolytically. In this method the reaction of the baths was always more or less alkaline. The quantity of alkali in these bleaching baths was in general kept low but the presence of alkali was always deemed indispensable and favorable since the alkali exerts also a detersive action on the bleaching good. In the bleaching treatment of cellulose the absorption of oxygen in the fibre is sometimes very small because of the very low concentration of alkali and the low temperature of about 35°C; in these cases the alkalinity was increased by addition of caustic soda or the like to obtain an enhanced absorption of oxygen. All hitherto known exyperiences led to the conclusion that in using hydrogen peroxide in a neutrol region not only an insufficient bleaching effect but also heavy damages in the cellulose material would be expected.

Thorough and careful investigations have now revealed the fact that in working with commercial hydrogen peroxide in a neutral or nearly neutral region, unexpectedly great advantages over the working in the alkaline region were obtained. This experience is the main object of my invention. According to my invention these excellent effects are obtained by subjecting cellulose containing material to a bleaching treatment with chlorine and hydrogen peroxide whereby the quantity of hydrogen peroxide is maintained so low that only an insignificant damage of the material may be caused. It is therefore essential to combine the bleaching with chlorine and the treatment with hydrogen peroxide with each other and carry out the process in a neutral or nearly neutral region. The combination may thereby carried out in any form. The fibrous material to be treated may be first subjected to a bleaching treatment with chlorine, e. g. with calcium chloride, sodium hypochlorite or other hypochlorites. Then the good is introduced into a practically neutral bath containing hydrogen peroxide and finished, whereby another washing and acidifying process may follow, if desired. A special advantage was observed if the bleaching with chlorine was inserted after the treatment with hydrogen peroxide. It is, however, possible to combine the hydrogen peroxide and the chlorine treatment in any form and as it will be desired. Thereby I have found it advantageous to finish the bleaching treatment with hypochlorite. In another embodiment of my invention the material to be treated may be chlorinated, i. e. subjected to a treatment with elementary chlorine at the beginning and, after elimination of the decomposed incrustations and alkali and washing out, finally bleached according to the prescriptions of my new invention.

As raw material nearly every kind of cellulose material may be used, for instance, pine cellulose, straw celluose, beech celulose, hemp, cotton, fibres, fabrics and the like.

A further essential characteristic of my invention may be seen in the fact that the quantity of hydrogen peroxide is limited in such degree that only negligible damage of the fibres is caused. The upper limit of the quantity of hydrogen peroxide varies somewhat according to the starting material to be worked up. By a simple preliminary test the necessary maximum quantities of hydrogen peroxide which cause a remarkable damage of the fibres or a considerable decrease of the alpha-cellulose content or of the viscosity may be ascertained. In general this upper limit will be found at about 2% (absolute hydrogen peroxide), based on the dry starting material. In practice, I use an amount of hydrogen peroxide below 1%, preferably less than 0.5%. Especially in the latter case or in using even smaller quantities, for instance of about 0,1% a deleterious effect on the fibres will be practically avoided and an excellent grade of white obtained. If, according to my invention, the hydrogen peroxide concentration is kept below the above mentioned limits, the noxious action is even lesser than in the use of alkaline peroxide baths. The result is not only a higher content of alpha-cellulose but also an increased viscosity. This is of special importance in the manufacture of superior cellulose where a decrease of the high alpha-cellulose content must be prevented during the bleaching operation.

The following tables contain the results of various experiments which have been carried out according to my new invention.

TABLE I

Straw cellulose bleached with a preliminary treatment with peroxide at various pH, rinsed and finished with 2,50 of active chlorine

	Preliminary bleaching treatment	Consumption	pH		Content of alpha-cellulose	Viscosity
			Beg.	End		
		Per cent			*Per cent*	*Centipoises*
1	0,3% Na_2O_2	0, 18	9, 2	8, 1	90, 18	61, 6
2	0,2% Na_2O_2 + 0,1% H_2O_2(40)	0, 16	8, 5	7, 2	90, 52	63, 7
3	0,1% Na_2O_2 + 0,2% H_2O_2	0, 13	7, 5	6, 8	90, 57	65, 3
4	0,3% H_2O_2	0, 21	6, 9	6, 8	90, 60	68, 7
5	1,00% H_2O_2	0, 21	6, 9	6, 8	90, 79	71, 6
6	2,00% H_2O_2	0, 30	6, 9	6, 8	88, 46	44, 2
7	5,00% H_2O_2	0, 55	6, 8	6, 7	87, 76	43, 3

With the same expenditure of hydrogen peroxide (test 1–4)—it is always a hydrogen peroxide of 40 Vol. %—but with varying pH the content of alpha-cellulose as well as the viscosity are increasing with an approach to the neutral point. With a higher consumption of hydrogen peroxide these values increase further but they decrease rapidly when the consumption of hydrogen peroxide is too high. In the experiments with the same expenditure of hydrogen peroxide (1–4) the grade of white is nearly the same. With a higher consumption of hydrogen peroxide the white improves considerably but at the expense of the other desired qualities of the fibrous material.

TABLE II

Pine cellulose, preliminarily treated with peroxide, washed and finished with 3% active chlorine

	Preliminary bleaching treatment	Consumption	pH		Content of alpha-cellulose	Viscosity
			Beg.	End		
		Percent			*Percent*	*Centiposes*
1	0,3% Na_2O_2	0,10	8,6	7,2	85,30	54,8
2	0,2% Na_2O_2					
	0,1% H_2O_2	0,07	8,0	7,0	85,34	59,6
3	0,1% Na_2O_2					
	0,2% H_2O_2	0,06	7,5	6,9	85,26	60,1
4	0,3% H_2O_2	0,04	6,9	6,8	86,45	60,6
5	0,5% H_2O_2	0,08	6,9	6,8	85,24	55,5
6	1,0% H_2O_2	0,14	6,9	6,8	84,15	51,4

Nearly the same observation as stated in Table I have also been made here with the difference that the values with respect to the contents of alpha-cellulose and viscosity already diminish if more than 0,3% peroxide are employed. Test 4 shows the best white of all four experiments with the same expenditure of hydrogen peroxide but with the lowest consumption. The grade of white in test 5 is even better but the fibres are already slightly attacked. This corresponds nearly completely with test 1 where sodium peroxide is used; only the degree of white is better in test 5. Test 6 is more strongly attacked and not as white as 5.

Nearly the same results will be obtained with a simple after-treatment with peroxide in using a cellulose which has first been treated with chlorine.

TABLE III

	Subsequent treatment	Consumption	Ph		Content of alpha-cellulose	Viscosity
			Beg.	End		
		Per cent			*Per cent*	*Centipoises*
1	0,5% act. chlorine.	0,40	------	------	84,86	66,7
2	0,3% Na_2O_2	0,09	9,1	7,5	87,51	74,2
3	0,1% H_2O_2	0,01	6,9	6,9	87,55	94,3
4	0,2% H_2O_2	0,02	6,9	6,9	87,82	97,7
5	0,3% H_2O_2	0,04	6,9	6,9	87,96	95,6
6	0,5% H_2O_2	0,05	6,9	6,9	87,24	94,5

The considerably enhanced viscosity of the tests which are finally treated with hydrogen peroxide is remarkable with respect to the test which was finished with sodium peroxide. The maximum of the content of alpha-cellulose and of the viscosity will be obtained in using an amount of 0,2 to 0,3% hydrogen peroxide. An increased expenditure of hydrogen peroxide causes only a decrease of these values.

According to my invention it is also possible to carry out the bleaching treatment with oxygen together with wetting or frothing agents which latter exert a maximum effect in a neutral or only slightly acid region.

In carrying out my invention at a large scale I prefer to use the commercial hydrogen peroxide which generally contains also traces of acids and can therefore be used without any further preparation to adjust the necessary neutral or slightly acid reaction.

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