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BLEACHING OF CELLULOSIC PULP

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The present application is a continuation-in-part of my application Serial No. 520,089, filed July 5, 1955, now abandoned. The present invention has for its object a process of lignin removal from and bleaching of cellulosic fibers. It is characterized in that the fibers in a slightly acidulated aqueous suspension are treated with metallic chlorates in the presence of a catalyst.

It has already been proposed to treat cellulosic fibers in the form of wood chips with large quantities of chlorates in an acid medium in order to obtain a raw pulp. The present invention is differentiated from these prior processes first, by the fact that it accomplishes a different result, being directed to the treatment of specifically different types of materials, namely, straw, chemical and semi-chemical cellulose. It is further differentiated from prior processes in that in accordance with the present invention, there is used a quantity of chlorate corresponding to that which is to be absorbed (consumed) by the fibers being treated whereas, in the former processes this quantity is several times, indeed tens of times, larger than said quantity.

Further, the quantity of the acid used in the present invention can be 200–300 times smaller than that used in the processes alluded to. The temperatures and reaction times can, on the contrary, remain of comparable magnitude.

This enormous difference in the means used in the present invention not only has an economic advantage, which is self-evident, but makes it also possible to limit the attack on the cellulosic fibers, which is inevitable in any acidic medium. This attack is the more intensive the more concentrated the medium. It becomes even more intensive as the fibers, as the result of the bleaching, attain (approach) a progressively higher degree of purity.

It is known that a cellulosic fiber having a degree of purity approaching that of the complete bleached state, is very much degraded if exposed for a few hours to the action of an acidic medium having a H_2SO_4 concentration higher than 0.5%, for example, 1% at a temperature higher than the ambient temperature but lower than 80° C., for example, 40–70° C.

The use of chlorates in acid concentrations not higher than 0.2% and at temperatures not higher than 80° C. is made possible, according to the present invention, by the use of certain catalysts.

The quantity of chlorates used in the present invention ranges from 0.2% to 10% based on the weight of the material treated. Since the material treated is always in the form of an aqueous suspension, it is important to reduce the quantity of water to the minimum possible. Preferably, suspensions are used having a density of at least 10% (i.e. 10 litres of water contain 1 kilo of dry fibers) which corresponds to the densities ordinarily used in bleaching pulp. However, higher densities can be used, for example, a density of 50%.

The quantities of acid to be used are in all instances 1–2 grams per litre of liquid present during the treat-

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ment (namely, 0.1–0.2%). As acids, there can be used H_2SO_4 , HCl, or any other acid capable of yielding a pH lower than 3.

The temperatures to be used are lower than 80° C., for example, a temperature of 60–70° C., at which the consumption (exhaustion) of the chlorate requires 4–8 hours, or a temperature of 20° C. which requires a treatment period of 3–4 days.

While it is possible that under these conditions formation of ClO_2 takes place (which, however, cannot be established by known analytical means), the oxidizing action exerted by the chlorate on the cellulosic fibers can be considered as being different from that exerted by the ClO_2 by the simple fact that the ClO_2 utilizes two atoms of oxygen for oxidizing the fibers whereas, when chlorates are used—for example, $NaClO_3$ —three atoms of oxygen participate in the oxidation of the fibers, NaCl being the only residue of the operation.

In carrying out the present invention, there is added to the suspension of cellulosic fibers the requisite quantity of chlorate—for example, $NaClO_3$ —which it is desired shall be consumed (absorbed) by the material being treated.

Applicant's experience has shown that this quantity of chlorate depends on the quantity of lignin contained in the material being treated and on the desired subsequent treatments. Indeed, the operation, the ultimate aim of which is bleaching, is completed by a treatment subsequent to that with the chlorate, for example, with hypochlorites or peroxides. The bleaching can also be initiated with the usual treatments and be completed by means of chlorates in accordance with the present invention. The use of a larger quantity of chlorates renders possible a reduction in the quantity of reagents used in the subsequent treatments, and vice versa.

According to a preferred form of the invention, there is used a catalyst containing vanadium. A catalyst having a base of vanadium and tin gives excellent results. The operation proceeds as if the reaction takes place directly between the chlorate and lignified constituents contained in the cellulosic fibers, the residue of the operation being NaCl.

The process according to the invention makes it possible to obtain for the same degree of whiteness a greater yield in weight of bleached pulp and viscosities higher than there can be obtained with other bleaching processes which do not use chlorates.

The examples set out below, which are not given by way of limitation, but only by way of illustration, describe various embodiments of the present invention:

Example 1

100 gr. of straw, suitably cut into pieces about 3–4 cm. long, are suspended in 500 gr. water containing 6 gr. sodium chlorate, to which is added 1 gr. H_2SO_4 and a catalyst consisting of a mixture of vanadium and tin salts, for example, 0.06 gr. V_2O_5 and 0.025 gr. $SnCl_4$. The suspension is maintained at a temperature of 70° C. with stirring, until the chlorate has been exhausted, which can be effected in 6 to 8 hours at a temperature of 70° C.; the resultant product is extracted with NaOH and washed, and can be separated into fibers by the use of known apparatus. The resultant pulp has a bleaching index (TAPPI T 219–M48) of 6–8 and can be bleached later by known means.

Example 2

100 gr. of semi-chemical coniferous cellulose, having a bleaching index of 12.5 were suspended in 1 litre cold water. 1 gr. HCl, 5 gr. $NaClO_3$ and 0.02 gr. NH_4VO_3 +0.01 gr. SnO_2 were added while agitating continuously. The suspension was gently heated and main-

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tained at 65° C. temperature for 6 hours, agitating all the while. Thereafter, the cellulose was washed with water at 40° C., slightly alkalized with NaOH, yielding a pulp with a bleaching index of 1.00. This pulp can be bleached further by known means.

Example 3

100 gr. kraft cellulose, having a bleaching index of 12.5 were treated in exactly the same way as in Example 2, yielding a pulp with a bleaching index of 1.50.

Example 4

100 gr. sulfite cellulose derived from leafy wood and having a bleaching index of 7.00 were treated exactly in the same way as in Example 2, but using 2.5 gr. NaClO₃, 0.01 gr. NH₄VO₃, 0.005 gr. SnO₂ and 0.5 gr. HCl. The resulting pulp has a bleaching index of 0.5.

Example 5

100 gr. sulfite cellulose, derived from coniferous plants and having a bleaching index of 8, were treated as in Example 2 with 2.2 gr. NaClO₃, 0.45 gr. HCl, 0.009 gr. NH₄VO₃, and 0.0045 SnO₂. There was obtained a pulp having a bleaching index of 1.

Example 6

100 gr. sulfite cellulose having a bleaching index of 8 were treated as in Example 2 with 2.2 gr. NaClO₃, 0.70 gr. H₂SO₄, and 0.09 gr. NH₄VO₃. A pulp was obtained having a bleaching index of 1.00.

Example 7

100 gr. of sulfite cellulose were bleached by a known process, without the use of chlorites or of ClO₂, so as to attain a whiteness (brightness) of 76 GE while retaining a satisfactory viscosity. The pulp was dispersed in 1 litre of water and there were added: 1 gr. NaClO₃, 0.01 gr. V₂O₅ and 0.5 gr. H₂SO₃. The pulp was heated to 70° C. and kept at this temperature for 6 hours with light stirring. A pulp was obtained having a whiteness (brightness) of 87 GE and viscosity equal to about 90% of the initial viscosity.

Example 8

100 gr. of the same pulp as in Example 7, but dispersed in only 100 gr. water, are treated with an aqueous solution of the same chemicals as in said example, the dispersion being permitted to stand for a period of 3-4 days at the ambient temperature. There is obtained a whiteness (brightness) of 87 GE and a pulp having a viscosity in excess of 90% of that of the original pulp. It is apparent that the consistency (density) of the pulp suspension does not affect the results of the treatment.

Example 9

100 gr. of kraft cellulose having a bleaching index of 12.75 are dispersed in 0.5 litre of cold water to which are added 3 gr. sodium chlorate and 0.02 gr. V₂O₅. The resultant suspension is then mixed with 0.5 litre water having 3 gr. of chlorine dissolved therein. The mixture, constantly stirred, is heated to 70° C. which temperature is maintained until the chlorate employed disappears, which takes about 3 to 5 hours. The resultant pulp is washed with a 2% NaOH solution, and dried at 60° C. for 1 hour; its bleaching index is 0.3.

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Instead of using a solution of chlorine in water, gaseous chlorine can be injected into the aqueous suspension.

Various treatments can be applied to these same cellulosic fibers by interposing intermediate washings or other treatments.

It is evident that the actual (practical) treating conditions of the process according to the invention depend on the nature of the cellulosic material submitted to treatment, as well as on the treatments to which the starting material has been subjected.

All the reagents employed in the application of the present invention can be added separately, and at the time of use, to the aqueous suspension of cellulosic fibers to be treated. Nevertheless, the chlorate and the catalysts can be mixed preliminarily.

While sodium chlorate has been used in the examples set out above, the chlorates of other alkali and alkaline earth metals can also be employed in the performance of the present invention. Particularly useful in this connection are the chlorates of potassium, calcium and barium.

The term "chemical cellulose" as used in the specification and in the appended claims denotes substantially delignified cellulose fibers which have been isolated from wood chips or any kind of vegetable raw material by chemical digestion. Similarly, the term "semi-chemical cellulose" denotes fibers derived from any kind of vegetable raw material and which are partially delignified and thereafter separated by chemical means. As has been indicated above, the present invention has been especially devised to enable effective and economic treatment of such chemical and semi-chemical cellulose, also straw, i.e. materials characterized by a low lignin content.

I claim:

1. In a process for bleaching chemical or semi-chemical cellulose pulps, the improvement which comprises the step of contacting an aqueous suspension of the pulp, at a temperature within the range of 20°-80° C., with a metallic chlorate selected from the group consisting of the alkali metal chlorates and alkaline earth metal chlorates, in the presence of a vanadium catalyst, said chlorate being present in an amount within the range of 0.2-10% by weight of the pulp, and said suspension containing 1-2 grams acid per litre of suspension.

2. A process according to claim 1, wherein sodium chlorate is used.

3. Process according to claim 1, characterized in that the catalyst comprises vanadium and tin.

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