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METHOD OF BLEACHING AND PROCESS FOR PREPARING LIQUORS THEREFOR

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This invention relates to improvements in the bleaching of fibrous materials especially cellulosic fibrous material derived from wood.

This application is a continuation in part of our co-pending applications Serial No. 449,245, filed March 2, 1921, which has matured into Patent No. 1,768,819, Serial No. 544,322, filed March 16, 1922, which has matured into Patent No. 1,768,820 and Serial Nos. 481,146 and 481,147, filed June 28, 1921.

In the common methods of bleaching pulp with chlorine or chlorine-bearing compounds such as bleaching powder, the bleaching treatment tends to injure or weaken the fibres. So also, wood pulp bleached with chlorine-bearing compounds sometimes has a natural wood tint, rendering it inferior for the better qualities of product, and its ash content may be increased by the bleaching operation, particularly when bleaching powder is used.

We have found that manganates as well as permanganates can be successfully and advantageously employed in the bleaching process of the present invention, as for example, in conjunction with chlorine or/and hypochlorite. The manganates are usually less efficient than the permanganates; and we regard the use of permanganates as more advantageous than the use of manganates for bleaching fibrous material, e. g., pulp. Permanganates can be produced from manganates by oxidation with suitable agents; and this production of permanganates and their subsequent use according to the present invention can advantageously be combined. For example, sodium manganate, admixed with an excess of alkali (such as sodium hydroxide), may be treated with chlorine to oxidize the sodium manganate to sodium permanganate and to form typochlorite with the excess alkali; and the resulting mixture can then be utilized as a composite bleaching or oxidizing agent, as hereinafter more fully described.

The permanganates which we consider particularly advantageous are sodium permanganate and alkaline earth metal permanganate, such as calcium permanganate. Potassium permanganate has a limited solubility, as compared with sodium permanganate, and we have found that its solution is more stable, so that in many instances it is less advantageous for use as a bleaching agent. With sodium permanganate, to explain, stronger solutions can readily be prepared and only a relatively small or moderate amount of the solution need be added to the material to be bleached to obtain the desired bleaching effect.

The permanganates can be used in either acid, neutral or alkaline solution, and with some materials we have found it desirable to use a neutral or an alkaline liquor.

We have found that the bleaching action of manganates or permanganates upon the material can be accelerated by increasing the temperature within a limited degree, by more intense agitation, etc., and this is desirable for the purpose of control in bleaching certain materials, particularly where acid is not present for example, the material may be heated up to 30 deg. C., or to any suitable temperature, up to boiling, but it is one advantage of the process that it can be carried out expeditiously with but moderate heating, thus reducing the liability of injuring the fibrous materials so treated.

The bleaching liquor can advantageously be prepared in the form of a strong stock solution and added in predetermined amounts to the fibrous material to be bleached. The fibres may be mixed with and distributed throughout a sufficient amount of water to constitute an aqueous suspension of fibrous material. When adding a strong solution containing manganate or permanganate to the material to be bleached, we find it advantageous to gradually introduce the solution into a mixture of fibrous material and water while the latter is being circulated or agitated, thus avoiding the presence of a large excess of the bleach liquor in contact with any one portion of the material to be bleached and minimizing the possibility of the local production of oxycellulose. For example, the strong solution may be sprinkled or sprayed or atomized into the mixture.

After the manganate or permanganate has acted upon the material, the material can then be directly treated with sulfur dioxide

or solution of sulfurous acid, a bi-sulfite, or a sulfite and acid; or it can with advantage be separated from its accompanying liquor to a greater or less extent before the sulfurous treatment, for example, by washing the material so that a fair portion of the original liquor is replaced by water, and then treating the fibrous material with sulfurous material after such washing operation.

The amount of sulfur dioxide or other sulfurous material required for removing from the fibrous material, the brown material (if any) produced by action of a manganate or permanganate, may vary somewhat with the amount of maganate or permanganate consumed. Ordinarily, only a small amount of sulfurous material is required to form a soluble manganese compound and bring the fibrous material to a white color, after a sufficient amount of bleaching material has been consumed, but sufficient should be used to insure dissolving all undissolved manganese compounds, if any.

We have found that sodium manganate or permanganate is less stable than potassium manganate or permanganate respectively, and when used for bleaching give up oxygen more readily, and we have found that these manganates and permanganates, nevertheless, can readily bleach without unduly injuring the fibrous material.

When bleaching pulp which is to remain in the wet form until used in the manufacture of paper, colorless or white manganese salts may be left with the wet pulp. They may then combine with the alkaline size if any is used. However, such salts may be removed from such pulp, and, if the pulp is to be dried, care should be taken to remove objectionable compounds by washing the bleached pulp after the bleaching operation.

It is one advantage of the present invention that the bleaching agents, when alkali metal compounds are used, are readily soluble so that the bleached and washed fibrous material is relatively low in ash as well of good white color and excellent texture. The bleaching process, moreover, is one which can be carried out at a moderate or relatively low temperature.

As above stated, the permanganate which may be used in the present invention, may advantageously be produced from manganate. Alkali metal manganates are commonly made by fusion methods which leave an excess of alkali, such as sodium oxide or hydroxide, with the manganate, when good yields are obtained. Instead of neutralizing this excess of alkali with an acid, we have found that it is advantageous to leave it with the manganate, and then treat the mixture of manganate and excess alkali in solution, or in suspension in part, with chlorine, either after or before adding the mixture to the fibrous material to be bleached. Chlorine will act upon the manganate to form permanganate and it will also act upon the excess alkali to form hypochlorite, so that if enough chlorine be added there will be produced a composite solution containing both permanganate and hypochlorite.

When such a composite bleaching solution is admixed with the pulp or other material to be bleached, or when the composite bleaching solution is produced in admixture with the pulp or other material (as hereinafter described), the hypochlorite, especially when present in relatively large amount in alkaline solution, appears to act through the permanganate perhaps by reoxidizing any manganate (if any) formed by reduction of permanganate in presence of organic matter and reconverting it into permanganate, although we do not desire to limit ourselves by any such explanation if other chemical action takes place when such a composite bleach liquor is used. The hypochlorite, in such composite bleach liquor, appears to act in a different and more advantageous manner than when used alone, while the action of the permanganate is supplemented by the action of the hypochlorite so that a lesser amount of permanganate need be used than if the permanganate alone were relied upon.

In so far as we have been able to ascertain, such a composite bleaching agent containing sodium permanganate and sodium hypochlorite and its use are new in the art; and we claim such composite bleaching agent as our invention or discovery, as well as the method of bleaching in which such composite agent is employed, and also the method of preparing such composite agent. Owing to its characteristic composition and properties, this composite agent can also be advantageously used for other purposes than bleaching, e. g., as a disinfectant, deodorant, germicide, for water purification, sewage treatment, cleaning purposes, etc.

The composite bleaching agent may be directly made in solution at the time and place of use. For example, if sodium manganate is made by a fusion method and contains an excess of soda, this material can be shipped in a solid state to a laundry, textile factory, pulp mill, paper mill, etc., and there dissolved in water, and the solution treated with gaseous chlorine sufficient to oxidize the manganate to permanganate and produce hypochlorite by reaction upon excess soda. This resulting solution can then be added directly to the pulp or other material to be bleached, preferably after clarification, if needed. If the manganate or permanganate contains less than a desired amount of excess alkali, suitable alkali or alkaline compounds can be added before the treatment with chlorine, and the composite solution will be obtained.

Instead of producing the composite solution containing permanganate and hypo-

chlorite and subsequently adding this solution to the pulp or other material to be bleached, the manganate or permanganate and excess alkali or other suitable compound can be added to and mixed with the pulp or other material to be bleached and the chlorine then introduced, for example, in the form of a chlorine solution or preferably in gaseous form, care being taken to secure good distribution and absorption of the chlorine.

The composite bleaching liquors employed in a single stage bleaching treatment, or in a multiple stage treatment in which liquor is or is not removed from the resulting fibrous material between two successive stages, may range in its ratio of manganate or permanganate to hypochlorite, for example, from about 3 parts of sodium permanganate, or its chemical equivalent, to about ¼ part more or less of such permanganate, and from about ¼ part of sodium hypochlorite, or its chemical equivalent in other suitable hypochlorite such as calcium hypochlorite, to about 15 parts to 20 parts, more or less, of sodium hypochlorite (or its equivalent as stated). Such amounts of such bleaching reagents may be employed on about 100 parts (air-dry weight) of the pulp such as chemical pulp derived from wood. Suitable ratios of such reagents intermediate to such proportions may be used, in each case employing such an amount of bleaching material as is required to effect the desired degree of bleaching, although a moderate excess over such needed amount may be used. This may facilitate the bleaching treatment. The proportions of permanganate and hypochlorite in the composite bleach solution can be varied and regulated, for example, by varying and regulating the amount of free alkali in admixture with the manganate which is to be treated with chlorine. So also, a composite bleach solution of regulated permanganate and hypochlorite content can be made by dissolving known amounts of separately produced permanganate and hypochlorite. Such solutions can be produced prior to the addition of the composite bleaching solution to the pulp or other material to be bleached, or the mixture may be produced, for example, in the pulp by separately adding the permanganate and hypochlorite solutions thereto, with appropriate agitation of the pulp to bring about uniformity of distribution of the reacting materials. The regulation of the proportions of permanganate and hypochlorite makes possible the regulation of the bleaching operation in a simple and advantageous manner, as will be readily appreciated.

When the pulp or other material to be bleached has been treated with the composite bleaching agent, it can be subsequently treated with sulfur dioxide or other suitable reagent in the manner above described. By washing the pulp or other material to be bleached, after the manganate or permanganate and hypochlorite treatment, the pulp, etc., can be freed from the greater part of the compounds in solution, prior to the sulfur dioxide or other treatment for dissolving a manganese compound. Instead of using sulfur dioxide for converting a compound of manganese into a soluble form, other agents which convert such compound into colorless and soluble compounds can be similarly used. Acid alone can be used for this purpose, such as hydrochloric acid or sulfuric acid, but a considerable amount of such acid will be required unless the action is carried out or finished at an elevated temperature, or allowed to stand for considerable time, and the fibres may be injured thereby. The treatment with sulfur dioxide or sulfurous acid has the advantage that it takes place readily and quickly at ordinary temperature.

While we have described the invention more particularly in connection with the bleaching of pulp, e. g., pulp derived from wood, for which it is particularly advantageous, yet it will be understood that the invention is also applicable to the bleaching of other fibrous materials, such as cotton, silk, linen, wool, etc., in a similar manner, as well as paper pulp stocks recovered through deinking processes, etc., and we include the bleaching of such materials within the more comprehensive claims appended hereto. Among the advantages of the process of the present invention is the uniformity of the bleaching action and the desirable condition in which the fibres are left. The fibres, for example, of cotton, silk, pulp, etc., are thus in a form well adapted for subsequent treatment, e. g., for uniform dyeing, etc.

We have found that pulps obtained, for example, by the soda, sulfate or sulfite process, so called, or modification thereof, are not only given a white color, but retain their white color much better and longer, when bleached according to the present invention with a manganate or a permanganate than when bleached in a single stage by chlorine or a hypochlorite, according to the common methods of bleaching, i. e., without the use of a manganate or permanganate. By this process we have been able to obtain a bleached cellulose product, derived from wood, which substantially retains its whiteness when subjected to a temperature of 100° C. for a period of seventy-two hours in the presence of air. This advantage of increased permanence of the whiteness of the bleached pulp is a characteristic advantage of the present invention.

It is a further advantage of the present invention that it makes possible the satisfactory bleaching of wood pulp cellulose produced by what is commonly known as the short-time or quick-cook method, that is, by carrying out the cook with cooking liquors of va-

rious degrees of strength or of concentration, at various pressures and temperatures and for various periods of time, and terminating the cook without carrying it to completion. Such pulp, produced by the short-time or quick-cook method, so-called, cannot be easily bleached by ordinary bleaching methods, and such treatment usually gives a bleached product of inferior quality. We have found, however, that such pulp, which heretofore would be considered under-cooked and not easy to bleach by common bleaching methods, can advantageously be bleached by the process of the present invention and brought to a good white color with less injury to the fibres than with methods of bleaching heretofore commonly used. The present invention makes possible therefore the production of a satisfactory bleached pulp from under-cooked stock, thus avoiding the necessity in many cases of continuing the cooking operation for the normal period of time, etc. The cutting down of the time of the cooking operation makes possible an increase in the number of digestions which can be carried out in a given apparatus, and correspondingly increases the producing capacity of the digesters over the usual practice in the art. We accordingly include and claim as a part of our invention the production and bleaching of such under-cooked pulp by treating such pulp in the improved manner herein described.

In addition to the bleaching of under-cooked pulps, the process of the present invention is also of particular value for the bleaching of chemical pulps from wood which are relatively difficult to bleach by common bleaching methods and enables a superior bleached pulp to be obtained therefrom, of good white color.

There are large supplies of forest products, etc., which, due to their inherent composition and properties, have been unsuited to the production of high grade cellulose material by the processes heretofore commonly practiced. We have found that many such materials can advantageously be treated for the production of pulp or cellulose materials by the use of a cooking liquor containing an alkali metal sulfite, with or without a lesser amount of other digesting reagent, as more fully described in companion applications. The bleaching process of the present invention is of special value in conjunction with such a cooking process, and gives a high grade white pulp from cellulose material. In this way cellulosic products such as wood, bagasse, reeds, grasses, bamboo, corn stalks, straws, etc., which are not commonly considered suitable for the production of high grade pulp or cellulose material can be converted into white products of relatively high grade. We therefore, have increased the available supply of raw materials available for the production of relatively high grade pulp or cellulose products. Even when such products are subjected to the usual methods of cooking, the pulp obtained can be satisfactorily subjected to the bleaching process of the present invention to give a bleached pulp of high grade and whiter in color than is obtained with the usual bleaching processes, i. e., employing bleaching powder in the customary manner and amounts.

The process of the present invention, as above stated, is of more or less general application to the bleaching of fibrous material and fabrics, etc., of a bleachable character and will give whiter bleached materials and with less injury than with any of the common bleaching methods of which we are aware.

While we have described the bleaching process of the present invention as carried out with a manganate or permanganate, or with a composite bleach liquor containing both permanganate and hypochlorite, we do not exclude the use of other bleaching agents, which may be used in conjunction with the manganate or permanganate. For example, chlorine or a hypochlorite may be used to bring about a partial bleaching of the material, and the bleaching operation can then be completed with the manganate or permanganate, and, to the extent that residual chlorine or an active chlorine bearing compound remains when the manganate or permanganate is added, the further bleaching operation may be of a character similar to that when a composite bleach liquor containing permanganate and hypochlorite is added. So also, other bleaching agents may be used in conjunction with the manganate or permanganate, to modify the bleaching operation. Perborates or peroxides, for example, may thus be used.

While we have described the invention more particularly in connection with the use of alkali metal and alkaline earth metal manganates and permanganates, the invention is not limited thereto, but other suitable manganates and permanganates can be used which are capable of exerting a bleaching or oxidizing action, and such manganates or permanganates can be used in conjunction with other agents, e. g., hypochlorites, etc., as hereinbefore described.

When alkali metal manganates or permanganates are employed, they can be produced by any suitable method of production, such as by fusion, electrolytically, etc. One advantageous method of production is by electrolyzing a solution of caustic alkali or alkali metal carbonate, using anodes of ferromanganese or other suitable manganese-bearing material. In preparing the manganate or permanganate solutions in this way, it is advantageous to discontinue the elec-

trolysis before all of the caustic alkali or alkali metal carbonate is converted into manganate or permanganate and to treat the resulting still alkaline solution with suitable chlorine bearing material to form a composite bleaching liquor containing permanganate and hypochlorite in solution.

In the accompanying claims we have used the phrase "a manganate" to include both manganates and permanganates. The term "alkali-forming metal" is intended to include both alkaline earth metals such as calcium, barium or magnesium and alkali metals such as sodium or potassium.

The broad invention described herein as well as other specific inventions described but not claimed herein are claimed in our companion applications and patents Serial No. 449,245, filed March 2, 1921, which has matured into Patent No. 1,768,819, Serial No. 261,696, filed March 14, 1928, which has matured into Patent No. 1,768,821, Serial No. 261,697, filed March 14, 1928, which has matured into Patent No. 1,768,822, and Serial No. 544,322, filed March 16, 1922, which has matured into Patent No. 1,768,820. Other specific inventions for related subject matter are claimed in our application Serial No. 370,726, filed June 13, 1929, which has matured into Patent No. 1,768,823.

We claim:

1. The process of bleaching pulp produced from wood by an incomplete digesting treatment which comprises treating the resulting fibrous material by means of liquor supplied with a manganate and with alkali metal hypochlorite capable of exerting a bleaching action.

2. The process of treating cellulosic-fibrous material to obtain a product relatively high in alpha cellulose, which comprises subjecting wood pulp obtained from wood by a treatment in a liquor containing a sulfite of sodium, said treatment being insufficient to free the fibres from all non-cellulose material, to a treatment with a liquor supplied with a manganate of an alkali forming metal and an alkali metal hypochlorite.

3. The process of treating cellulosic-fibrous material to obtain a product relatively high in alpha cellulose, which comprises subjecting wood pulp obtained from wood by a treatment in a liquor containing a sulfite of sodium, said treatment being insufficient to free the fibres from all non-cellulose material, to a treatment with a liquor supplied with a manganate of an alkali metal and an alkali metal hypochlorite until substantially all the colored non-fibrous organic constituents of the pulp have been rendered substantially colorless or are readily separable from the fibres of the pulp and subsequently treating the resulting fibrous material to render soluble a compound of manganese.

4. The process of bleaching colored fibres of chemical pulp from wood, which comprises preparing a mixture containing such fibres and water, distributing throughout such mixture a solution containing an alkali metal hypochlorite and a permanganate, treating the fibres by means of bleaching materials supplied by the solution until substantially all the colored non-fibrous organic constituents of the pulp have been rendered substantially colorless or readily separable from the fibres, and subsequently treating the resulting fibrous material by means of an acid liquor so as to render soluble a colored manganese compound and thereafter washing the bleached fibres.

5. The process as per claim 4, in which said solution contains an alkali metal permanganate.

6. The process as per claim 4, in which said solution contains sodium permanganate and sodium hypochlorite.

7. The process as per claim 4, in which said solution contains a relatively large amount of hypochlorite and a relatively small amount of permanganate.

In testimony whereof we affix our signatures.

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