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(54) **AN IMPROVED PEROXIDE BLEACHING METHOD.**

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Description

The bleaching of wood pulp with peroxides is an established technique in the manufacture of bleached pulp grades, hydrogen peroxides being the by far the most common reagent used for such purposes. In a large number of patents and reports various details of this technique and its numerous ramifications are described.

Combinations of hydrogen peroxide with certain organic acids stand out as an especially efficient form of the peroxide bleaching technique. The treatment is carried out within the acid range of the pH-scale, facilitating the formation of peroxyacids which are the active chemical species in the bleaching process. Contrary to this, the common way, of bleaching with peroxides is carried out using slightly alkaline conditions enhancing the formation of peroxide anions HO_2^- which are the active ionic species. Higher alkalinities are to be avoided since hydrogen peroxide then decomposes to oxygen.

The purpose of the present disclosure is to describe a simple method to enhance the bleaching efficiency of hydrogen peroxide by adding certain inexpensive organic acids to the bleaching solution. The acids in question are formic, acetic, lactic, maleic acid and phtalic acid; they can be used separately or in various combinations. Contrary to similar mixtures of hydrogen peroxide with such acids which have been proposed to increase the efficiency of the bleaching process, cf. for instance Austrian Patent 203.454, the mixtures of the present disclosure are being used within the alkaline range of the pH-scale and not on its acid side. This alkalinity of the treating solution is the main characteristic feature of the present invention relating to peroxide bleaching process in the presence of the organic acids enumerated above, i.e. formic, acetic, lactic, maleic acid and phtalic acid or mixtures thereof.

Disclosures similar to those of the Austrian Patent 203.454, relating to the use of hydrogen peroxide containing certain organic acids at acidic conditions, can also be found in a number of other patents, cf. for instance US 2.720.441, FR 1.565.397, Japan 77.120.104. It is therefore even more surprising that a significant enhancement of the bleaching efficiency of hydrogen peroxide can be attained in the alkaline range of the pH-scale, where such an enhancement normally would not be expected. The increased bleaching efficiency of hydrogen peroxide in the presence of certain organic acids under acidic conditions can be related to the formation of peroxy acids. However, under the conditions specified in the present invention peroxy acids cannot be of any importance since the alkaline environment does not favor recations leading to such peroxy acids.

It has according to the present invention been found that the bleaching efficiency of peroxides can be improved if the bleaching process is carried out in the presence of low concentrations of one or more of the enumerated acids while maintaining the pH-value within the alkaline range 8-13, which pH-range is provided by the addition of an alkali metal hydroxide, such as sodium hydroxide or potassium hydroxide.

When using peroxide and alkali metal hydroxide for bleaching of pulp with the addition of low concentrations of the enumerated acids a considerably improved bleaching is attained as compared to bleaching carried out with peroxide and the alkali metal hydroxide without the use of said acids.

US-A-3,193,445 discloses a two-step process for bleaching cellulosic materials, e.g. wood pulp, whereby in a first step bleaching takes place using hydrogen peroxide at an alkaline pH and in a second step a carboxylic acid anhydride is added to reduce the content of hydrogen peroxide remaining in the reaction medium.

The method according to the present invention allows bleaching with lower acid and peroxide concentrations than when using common peroxy acid methods while still obtaining the same bleaching effect.

Furthermore by using the method according to the present invention problems associated with the use of common peroxide stabilizers are avoided. Among these primarily silicates may be mentioned which when utilizing bleaching processes based on such methods in a technical scale may give rise to undesirable deposits (scaling).

Another surprising finding according to the present invention is the fact that potassium hydroxide gives a significantly higher brightness of the bleached material than does sodium hydroxide. The difference amounted to 2-8 SCAN brightness units.

The enhancement of the bleaching efficiency of hydrogen peroxide by the acids listed above, using KOH to adjust the pH-value, will now be illustrated by some examples. The experiments were carried out with unbleached mechanical pulp (pine). The chemicals (peroxide and acid) were added simultaneously to a 2% suspension of the pulp in water, whereafter the pH-value was immediately adjusted to 9-10 by KOH at 60 °C, 1 h stirring. After completing the treatment, the pulp was formed into laboratory sheets using standardized procedures (SCAN C11:75). The measurement of brightness was carried out according to SCAN C11:75, the brightness being expressed in ISO-units. The brightness value of the unbleached pulp was 57-60.

The invention is illustrated by means of the following examples.

Example 1

A bleaching mixture containing 4% H_2O_2, 1% acetic acid, and 1% formic acid (based on the weight of the quantity of pulp present in the system) gave after bleaching carried out as described above a brightness of 78%, the brightness gain being 18 units.

Example 2

When carrying out the bleaching operation at lower peroxide and acid concentrations, namely 1.5% H_2O_2, 0.75% acetic acid, and 0.75% formic acid a brightness of 72% (gain 15 units) was recorded. Again, the concentration figures are percentages of the amount of pulp used in the reaction. In all other respects, the conditions were similar to those used in Example 1.

Example 3

With a reaction mixture of 4% H_2O_2 and 4% lactic acid a brightness value of 78% was obtained. This value was increased to 81.4 when adding a magnesium compound (0.4% Mg^{2+} = 4% $MgSO_4x7H_2O$). Reducing the peroxide and lactic acid concentrations to 1.5% resulted in a brightness reading of 72% which could be increased to 75 in the presence of 0.4% Mg^{2+} (= 4% $MgsO_4x7H_2O$).

With H_2O_2/maleic acid mixtures similar results were obtained.
With H_2O_2/phtalic acid mixtures similar results were obtained.

The above results have been optimized with regard to the pH-value of the reaction mixture, the pH-value being adjusted using KOH. As already mentioned, the use of NaOH at the same pH resulted in lower brightness values. No optimization was, however, carried out with regard to the pulp concentrations. Using higher pulp concentrations, the brightness gain can be expected to increase by at least 6 units (cf. "The Bleaching of Pulp", L.A. Beeman and J.S. Reichert, Tappi Monograph No. 10, 210 (1953)). The efficiency of the present method thus appears to have been demonstrated with sufficient clarity.

It may be mentioned that experiments where the acid was added to the pulp suspension after the addition of alkali and peroxide produced similar results.

Claims

1. A method for bleaching wood pulp without the use of peroxy acids by means of from 0.1 to 10%, based on the dry weight of the pulp, of hydrogen peroxide wherein an organic acid selected from the group formic acid, acetic acid, lactic acid, maleic acid and phtalic acid or any mixture thereof is added together with such an amount of an alkali hydroxide to the pulp suspension to be bleached as to give a pH-value of the suspension within the alkaline range of from 8.0 to 13.

2. A method according to claim 1, characterized in that the acid is used in an amount of from 0.25 to 10 % based on the dry weight of the pulp.

3. A method according to claim 1 or 2, characterized in that the alkali metal hydroxide used is potassium hydroxide.

4. A method according to any of the preceding claims, characterized in that the alkaline pH-range used is 9-10.

Patentansprüche

1. Verfahren zum Bleichen von Zellstoff ohne Verwendung von Peroxysäuren mit Hilfe von 0,1 bis 10% Wasserstoffperoxid, bezogen auf das Trockengewicht des Zellstoffs, bei dem eine aus der Gruppe Ameisensäure, Essigsäure, Milchsäure, Maleinsäure und Phthalsäure ausgewählte organische Säure oder ein Gemisch hiervon zusammen mit einer solchen Menge eines Alkalihydroxids zu der zu bleichenden Zellstoffsuspension zugegeben wird, um einen pH-Wert der Suspension im alkalischen Bereich von 8,0 bis 13 zu ergeben.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß die Säure in einer Menge von 0,25 bis 10 %, bezogen auf das Trockengewicht des Zellstoffs, verwendet wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß das verwendete Alkalimetallhydroxid Kaliumhydroxid ist.

4. Verfahren nach einem der vorausgehenden Ansprüche**, dadurch gekennzeichnhet**, daß der verwendete alkalische pH-Bereich 9 bis 10 ist.

Revendications

1. Procédé de blanchiment d'une pâte de bois sans l'utilisation de peroxyacides grâce à une quantité de 0,1 à 10 % de peroxyde d'hydrogène, par rapport au poids sec de la pâte, caractérisé en ce qu'on ajoute un acide organique, choisi dans le groupe comprenant les

acides formique, acétique, lactique, maléique et phtalique ou l'un quelconque de leurs mélanges à la suspension de pâte à blanchir, en même temps qu'une quantité d'un hydroxyde alcalin propre à donner une valeur de pH à la suspension, se situant dans l'intervalle alcalin de 8,0 à 13.

2. Procédé suivant la revendication 1, caractérisé en ce qu'on utilise l'acide en une quantité de 0,25 à 10 % par rapport au poids sec de la pâte.

3. Procédé suivant la revendication 1 ou 2, caractérisé en ce que l'hydroxyde de métal alcalin utilisé est l'hydroxyde de potassium.

4. Procédé suivant l'une quelconque des revendications précédentes, caractérisé en ce que l'intervalle de pH alcalin que l'on utilise est de 9-10.