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(54) **Process for bleaching using peroxo-polyoxometalates for textiles made from mixtures of cellulosic fibers such as: flax-cotton, hemp-cotton**

(57) According to the invention, the process consists of bleaching textile materials from mixtures of cellulosic fibre, such as: (flax-cotton, hemp-cotton) until achieving a whiteness degree of 70-80%, which is carried out in two stages: in the first stage, the materials are treated in aqueous solution containing peroxo-POM catalysts $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ in the presence of ionic surfactant and $H_2O_2$, at the temperature of 70-90° C for 60-90 minutes, while in the second stage the material treated in the first stage is suspended in a solution containing 1,5-7 g NaOH, 0,2-1,3 g $Na_2SiO_3$ and 0,8-3,2 g $H_2O_2$, for 1-1.5 hours at the temperature of 70-80°C, after which it is washed with cold water until it reaches neutral pH, and then it is air-dried.

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## Description

### Field of the invention

**[0001]** The present invention refers to a process for bleaching using peroxo-polyoxometalates for textiles (fibers, cloth and t-shirts) from mixtures of cellulosic fibers such as: flax-cotton, hemp-cotton.

**[0002]** For the textile industry, bleaching materials made from mixtures of cellulosic fibers such as: flax-cotton, hemp-cotton, presents great interest due to the fact that the different chemical composition of each component of the fibrous mix requires different bleaching conditions and methods.

**[0003]** The problem raised by bleaching these materials is the bleaching networks which must answer to the requirements of each component without depolymerising the cellulose, the most important component of this type of fibre.

**[0004]** Cellulose is a polysaccharide which forms the walls of the fibre's basic cells, together with lignin, various hemicelluloses etc. Unlike cotton fibers, which have a very low lignin and other non-cellulosic component content, the other types of fibers which compose these mixes, such as flax and hemp have a yellowish-grey appearance, especially due to the high lignin and hemicelluloses content, as well as other impurities (dust etc.).

**[0005]** Obtaining materials with a high degree of whiteness from the fibrous mixes mentioned above is done in several successive steps, during which lignin and hemicelluloses are gradually removed using large amounts of chemical reagents, at high temperatures and pressures (Geier J., Holzforschung 1982, 36, 55, Brage C. , Erickson T. and Gierer J., 1991 Sing R.P., 1979).

**[0006]** The principle for achieving the bleaching operation of cotton materials is based on the destruction, through oxidation reactions, of the >C=C< double bonds (the natural pigment chromophore), whose $\pi$ electrons are responsible for the color effect [ M.Pustianu, M.S.Bucur, Finisarea produselor textile, Vol.1, Albitorie, Editura Universit□at□ tii "Aurel Vlaicu" Arad 2004, ISBN 973-8363-60-8, pg.27]. In this case, bleaching may be done using NaOH, $H_2O_2$ (40% vol.) and $Na_2SiO_3$($40^0$Be). In the case of materials made from flax or hemp, classic bleaching is done using sodium hypochlorite, sodium hydroxide and hydrogen peroxide [M.Pustianu, M.S.Bucur, Finisarea produselor textile, Vol.1, Albitorie, Editura Universit□ tii "Aurel Vlaicu" Arad 2004, ISBN 973-8363-60-8, pg.49] or in repeated cycles after a boiling phase, using sodium carbonate, pyrosulphite, sodium hydroxide (in the case of flax materials) and using sodium carbonate, pyrosulphite and sodium silicate (in the case of hemp materials) followed by the bleaching phase, using hypochlorite, sulphuric acid and pyrosulphite. In order to obtain a higher degree of whiteness, the bleaching process is repeated [E. Bucurenci, N Boitor, C□ă□l□ă□auza finisorului de bumbac, in □i cânep□ă□, Centrul de documentare si publicatii tehnice al ministerului Industriei u□□ soare, 1973, pg, 75-77]. The disadvantages of obtaining a higher whiteness for these materials consist in the reduction of the cellulose polymerizing degree.

**[0007]** The oxidation products which result from these known processes are chlorinated aromatic compounds, which, after the alkaline extraction stage end up in wash waters (Boman B. and Frostell B., 1988, Sun Z.J. and Argyropoulos D.S., 1966, Smook G.A., 1982). The secondary products are known for their toxic and carcinogenic effects, and raise serious pollution issues.

### Backround of the invention

**[0008]** Over the last years, intense systematic research has been carried out in order to elaborate non-polluting technologies for obtaining materials from natural fibers, with a high degree of whiteness ( Sedelnik N., 1999, Grundersby P., 1997 Call H.P. and Muckle J., 1997, Sekar N., 2001, Vitelli M.L., Arbo G. and Montecatim A., 1956 Szmenowicz B.L., Tanska B and Sapieja A., 2004). Thus, new technologies have been elaborated for bleaching natural fibers, which are initially pre-treated using various enzymes and mediators. Laccase and xylanase are used as enzymes, and 1-hydroxybenzotriazole (HOBT), tetraacetylethylenediamine (TAED) and 2,2 azinobis (ABTS) as mediators.

**[0009]** After the enzymatic pre-treatment phase, other chemical treatment phases follow, especially using NaOH and $H_2O_2$ at high temperatures and pressures (Khristova P., Tomkinson J., Valchev I. Dimitrov J. and Jones G.L 2002, Kadla J.F., Chang H.M and Jameel H., 1999, Garcia O., Coldon J.F. Vidal T., 2000, P200102804, Garcia O., Camarero S., Colom J.F., Martinez M.J., Monje R., 2003, Camarero S., Garcia O., Vidal T., Colom J.F and del Rio J.C., 2001, Mussing J., Dreyer J., Haring H., and Identhal W.D., 2000).

**[0010]** The disadvantages of these procedures consist in the fact that the cellulose fibre is affected, due to the fact that the oxidation of lignin in a basic medium (with NaOH and $H_2O_2$) is very difficult to control. Furthermore, the use of large quantities of chemicals, high temperatures and pressures causes a decrease in the physical-mechanical parameters of the natural fibers, without achieving a corresponding whiteness.

**[0011]** Recent scientific research in the field of cellulose pulp delignification using compounds from the polyoxometalate class has led to the replacement of chloride compounds in this process, thus achieving the selective oxidation of lignin without significant depolymerisation of the cellulose. The applicability of this class of compounds for bleaching natural fibers such as cotton, flax, hemp, ramie or sisal was proved through a Romanian patent [Sirghie C., Botar A., Dinc□ă N., Cr□ă□ciun G., Dochia M., Patent RO no. 122728 B1 /2007] in which four polyoxometalate compounds were used, as follows: POM 1= $Na_5PMo_{10}V_2O_{40}$, POM 2= $K_5H_4PMo_6V_6O_{40}$, POM 3 =

$K_5H_4PW_6V_6O_{40}$ and POM 4= $H_3PMo_{12}O_{40.}$ These compounds selectively oxidize the lignin in flax, hemp, ramie, sisal fibers and more; their effect is concentrated on the lignin which it breaks and solubilizes. After the alkaline extraction phase, the whiteness degree of the fibers increases.

**[0012]** Later research has led to the development of a special class of polyoxometalates, namely peroxo-polyoxometalates, as catalysts in organic chemistry and biochemistry [Dickmann D.H, pope M.T, Chem Rev. 1994, 94, pg 569-584; Tamasini B., Yeganeh H., React.Funct, Polym 2002, vol 50 pg 101-106, Zhou Z.H., Hou S.Y., Wan H.L J.Chem.Soc.,Dalton Trans, 2004,1393-1399].

**The solution to the technical problem**

**[0013]** The present invention proposes the use of the peroxo-polyoxometalate reaction mechanism in the process of bleaching materials made from cellulose fibre mixes such as flax-cotton, hemp-cotton because peroxo-polyoxometalates are much more reactive than the classic polyoxometalates and therefore selective oxidizing of lignin in flax and hemp fibers will be much more efficient than the current methods. These catalysts, under mild conditions and in the presence of peroxide release oxygen which is the active species in the selective oxidation of lignin in cotton, flax, hemp fibers, components of mixed cellulosic materials. In fact, it is a reaction implying the destruction of the chromophore groups that are part of the aromatic nuclei from lignin, which is responsible for obtaining a higher degree of whiteness.

**[0014]** The problem solved by the invention is the bleaching of materials made from cellulosic fibre mixes such as: flax-cotton, hemp-cotton by using peroxo-polyoxometalates $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ by creating mild conditions for the selective oxidation of lignin and hemicelluloses from the mixtures mentioned above, without significantly affecting the cellulose in the fibre, but while achieving a higher degree of whiteness.

**[0015]** The technical problem which the invention solves is the application of an oxidation mechanism based on the effect of active oxygen on the chromophore group found in lignin. The peroxo-polyoxometalates $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ are regenerated and reused in the bleaching process by adding peroxide, no toxic compounds appear in the bleaching and catalyst regeneration process, and lignin is finally oxidized in $CO_2$ and water.

**Main presentation of the invention**

**[0016]** The peroxo-polyoxometalate bleaching process $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ for textiles (fibers, cloth and t-shirts) made from mixtures of cellulosic fibers such as: flax-cotton, hemp-cotton, according to the invention, eliminates the disadvantages of existing processes in that the mixed textiles mentioned above are bleached using small amounts of NaOH, $Na_2SiO_3$ and $H_2O_2$ due to the introduction of peroxo-polyoxometalates; the use of hypochlorite, sulphuric acid and pyrosulphite, which pollute waste water, is also eliminated. The process is based on regenerating and reusing the catalysts and thus rendering the process more efficient from an economic point of view and protecting the environment.

**[0017]** The peroxo-polyoxometalate bleaching process is carried out in 2 phases, as follows: in the first phase, the materials are suspended in an aqueous solution which contains peroxo-polyoxometalate-type catalysts$\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ ionic surfactant and $H_2O_2$. The suspension is heated to 70-90 degrees while being mixed, for 60-90 minutes, after which it is cooled to room temperature. After this time, the suspension is filtered and rinsed with water until a neutral pH is achieved. The filtrate which contains the catalysts is kept for reactivation and later reuse. During the second stage, the material is suspended in a solution containing NaOH, $Na_2SiO_3$ and $H_2O_2$ and is heated to 70-80$^0$C for 60-90 minutes. After cooling, the material is filtered, rinsed with cold water until a neutral pH is achieved and is air-dried at room temperature. Materials thus treated will have a whiteness degree of 70-80% given that the physical-mechanical properties are not damaged and the applied treatment is efficient for both fibre types found in the mixture. This bleaching process may be applied to textiles (fibers, cloth and t-shirts) made from mixtures of cellulosic fibers such as: flax-cotton, hemp-cotton, as well as those made from ramie-cotton or nettle-cotton.

**Presentation of advantages**

**[0018]** The invention presents the following advantages:

- peroxo-polyoxometalates $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ , even in small amounts, in the presence of peroxide, carry out the selective oxidation of lignin, through active oxygen, at an almost neutral pH, without affecting the cellulose in the fibre significantly.
- peroxo-polyoxometalates $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ are recovered after the first bleaching step, are regenerated and reused;
- peroxo-polyoxometalates $\{(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2\}$ used are synthesized and used directly in the aqueous solution due to economic reasons;
- the materials bleached using this process have a higher whiteness degree and maintain their physical-mechanical characteristics.
- The process eliminates the use of chlorinated deriv-

atives which allows for environmental protection. At the end of the bleaching process the lignin is oxidized in $CO_2$ and water.

## Example

**[0019]** An example of invention application follows.

**[0020]** In the first treatment stage, 100g of textile material (cloth) made of a mix of cotton and flax fibers are suspended in 1.2 litres of water which contains: 0.3g catalyst $(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$; 7 ml $H_2O_2$ (30%); 0.1g sodium lauryl sulphate. The reactive mixture is then heated to 70-90$^0$C for an hour. After cooling, the mixture is filtered and the material is washed with a little water. The filtrate which contains the used catalyst is kept for regeneration and reuse. In the second stage, the resulting material is suspended in 1.2 litres of 0.1 N NaOH which contains 2.5 g peroxide and 1 g sodium silicate. The mixture thus obtained is heated to 70-80$^0$C for an hour. After cooling, the material is washed using water until a neutral pH is reached, and is then dried. Depending on the fibrous composition of the material, the whiteness degree will range between 70-80%.

**[0021]** The process according to the invention allows for obtaining a bleached material, with a whiteness degree higher than 70% when the fibrous composition contains a percentage of flax or hemp fibers (over 40%).

## Claims

1. The bleaching procedure for textile materials (fibers, yarns, woven and knitted fabrics) and mixtures of cellulose fibers, such as: flax-cotton, hemp-cotton, according to the invention, it is **characterized by** the fact that it's being accomplished in two phases, in the first take place the material's suspension in a water solution that contains: 0,01-0,03 g/l peroxo-polioxometalate catalysts {$(NH_4)_8[Mo_{10}O_{22}(O_2)_{12}]$}; $Na_2[MoO(O_2)_2(C_2O_4)]$; $MoO(O_2)_2$; $WO(O_2)_2$}, 0,001-0,003 % ionic surfactant and maximum 5% $H_2O_2$ for 60-90 minutes stirred at a temperature of 70-90°C, followed by cooling and water washing until the neutral pH is obtained, and in the second phase the material is suspended for 1-1,5 hours in a solution that contains 1,5-7 g NaOH, 0,2-1,3 g $Na_2SiO_3$ and 0,8-3,2 g $H_2O_2$ at a temperature of 70-80°C followed by washing with cool water until the neutral pH is obtained and drying at room temperature.

2. The procedure according to claim 1, **characterized by** the fact that the materials treated as described above shall have a white degree of 70-80% under the conditions in which the physical-mechanical properties do not deteriorate and the applied treatment is efficient for both types of fibers from the composition of the mixtures.

3. The procedure according to claim 1, **characterized by** the fact that it can be applied to other types of materials, such as: ramie-cotton or nettle-cotton.

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# EUROPEAN SEARCH REPORT

Application Number
EP 13 46 4006

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CATEGORY OF CITED DOCUMENTS

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## ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 13 46 4006

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