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US - A - 3 844 361
US - A - 3 922 173
US - A - 3 953 335
US - A - 3 953 336
US - A - 3 989 630
US - A - 4 003 838

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The present invention relates to thixotropic solutions of cellulose ethers. Aqueous solutions of cellulose ethers e.g. hydroxyl ethyl cellulose, are used for many purposes and are for example used as bore hole fluids in the oil industry. Therefore they may be used in fracturing fluids and in drill muds. For these purposes aqueous solutions of cellulose ethers are used which have pseudo plastic viscosity properties i.e. their viscosity decreases as the shear applied to them is increased. It would be desirable to impart thixotropic properties to aqueous solutions of cellulose ethers. (Liquids display thixotropy when their viscosity falls when subject to a constant shear and thixotropy is thus a time dependent phenomenon). A thixotropic aqueous solution of a cellulose ether would be better able to support the particles of rock etc produced in the bore hole drilling process so preventing them from settling onto the drill bit.

It is known to use cellulose ether solutions in drilling fluid. US 3 954 628 discloses drilling fluid based on carboxyl methyl cellulose.

US 3 727 687 discloses that it may be useful to gel aqueous solutions of cellulose ethers used as drilling fluids and for this purpose uses a water-soluble compound of a polyvalent metal and a water-soluble reducing agent. The polyvalent metal compounds specifically disclosed are chromium and manganese compounds and the reducing compounds mentioned include sulphur compounds such as hydrosulphite and ferrous chloride. The use of manganese and chromium compounds is undesirable for toxicity reasons. They are expensive and the need to provide an additional reducing agent will increase the expense still further.

Further, US 3 922 173 discloses an aqueous gel which may be made from hydroxyl ethyl cellulose and may be cross linked by the addition of various metal ions including iron (III). However there is no disclosure of the production of thixotropic materials. There is no disclosure of the importance of treating a cellulose ether simultaneously with a water soluble ferric compound and a water soluble alkali."

US 3 804 174 discloses a cementing composition for use in oil and gas wells. The composition contains a cellulose ether, cement, and a polyvalent metal salt which may be a salt of zirconium, lead, chromium, ferric iron, hafnium and lanthanum. The use of ferric chloride is mentioned but it is preferred to use zirconium oxychloride. Compositions containing cement can be used in various special situations in drilling oil and gas wells. They cannot be used as standard drilling fluids or 'muds' because they will in due course set and become solid.

It is desirable to be able to prepare aqueous solutions of cellulose ethers which do not contain cement, and which can therefore be used in the preparation of drilling muds, but which have thixotropic properties. It is also desirable to be able to avoid the use of toxic and/or expensive materials.

Ferric chloride when added alone to hydroxyl ethyl cellulose does not impart satisfactory thixotropic properties.

According to a further aspect of the present invention a process for producing a non-hydraulic thixotropic aqueous liquid comprises mixing together an aqueous solution of hydrated cellulose ether and a water soluble ferric salt with a water soluble alkali, the quantities of ferric salt and alkali being sufficient to give an alkaline solution and to make said liquid thixotropic in the absence of a hydraulic substance.

It is particularly preferred that the ferric hydroxide is formed in situ in the aqueous solution of the cellulose ether.

The present invention is concerned with non-hydraulic thixotropic aqueous liquid i.e. liquids which do not form a crystalline lattice structure exhibiting a degree of mechanical stability and/or physical strength by reaction of water at ambient temperature with a hydraulic substance. Examples of hydraulic substances are gypsum, calcium, sulphate hemihydrate (plaster of paris), pulverised fuel, ash, and hydraulic cements e.g. Portland cement. If the composition of the present invention is to be non-hydraulic any hydraulic substances present must not be present in an effective amount i.e. in an amount sufficient to give hydraulic properties.

The thixotropic solution is prepared using a cellulose ether in hydrated form. When a cellulose ether is mixed with water there is initially no increase in viscosity. After a certain time known as the "hydration time", the viscosity starts to increase as the cellulose ether becomes hydrated. The cellulose ether is used in the present invention after this hydration step has taken place.

Examples of cellulose ethers which may be used in the present invention are carboxy ethyl cellulose and, preferably, hydroxyl ethyl cellulose. The viscosity of a solution of cellulose ether depends on the molecular weight of the cellulose ether and on the quantity of cellulose ether present in the solution. It is preferred to use a quantity of any given cellulose ether which is sufficient to give an apparent Fann viscosity (500/21) of at least 20 cps 2.0× 10⁻²Pa.sec in pure aqueous solution i.e. in the absence of salts such as ferric chloride. The Fann viscosity is determined using the Fann viscometer and is a well known test in the oil industry.

The molecular weight of cellulose ethers is
usually indicated by the viscosity of a standard solution under standard conditions rather than by giving molecular weight values. Particularly in the oil industry it is desirable to have solutions with low solids content and it is therefore preferred to use a cellulose ether which has a viscosity of at least 70,000 cps (70 Pa.sec) at 25°C at the shear rate of 1 sec⁻¹ at 2% by weight concentration in pure water. An example of such a material is the grade of Cellosolve (registered trade mark) hydroxy ethyl cellulose known as 100M.

The preferred cellulose ether is hydroxy ethyl cellulose and the preferred hydroxy ethyl cellulose are those in which the degree of substitution i.e. the average number of hydroxyl groups in the cellulose which carry groups derived from ethylene oxide, is preferably in the range 0.8 to 1.2. The molar substitution i.e. the average number of ethylene oxide molecules that have reacted with each anhydro glucose unit in the cellulose is preferably in the range 1.7 to 2.3.

The ferric salt may be for example ferric alum but is preferably ferric chloride. The alkali may for example be ammonium hydroxide, sodium hydroxide or potassium hydroxide; it is preferably sodium hydroxide.

Once the man skilled in the art has been taught how to make thixotropic aqueous solutions of cellulose ethers in accordance with the present invention, the quantities of materials required to give optimum results can be readily determined by simple tests. The quantity of cellulose ether necessary to give good thixotropic properties may depend on the quantity of water soluble ions present in the aqueous solution. Thus greater quantities of cellulose ether may be required in the presence of water soluble salts. However it is a feature of the invention that thixotropic solutions can be obtained in the presence of concentrations of dissolved salts which would have very adverse effect on thixotropic solutions obtained by known techniques.

The quantity of ferric salt is preferably equivalent to at least 0.05% weight of ferric chloride based on weight of total solution and is preferably not more than 0.4% or preferably not more than 0.3% by weight of the total solution. The quantity of alkali present is preferably equivalent to at least 0.5% by weight of sodium hydroxide based on total solution. It is preferably not more than that equivalent to 2% by weight of sodium hydroxide based on the total solution preferably not more 1.5% by weight.

The invention will now be illustrated by reference to the following Examples. In these Examples references are made to Fann viscosity and to gel strength. Fann viscosity is a standard test used in the oil industry and is carried out using a Fann viscometer sold by the Baroid Division of NL Industries Inc. A description of the Fann viscosity determination and gel strength measurements is given in Section 900 of the Baroid Drilling Mud Data Book.

All the experiments were carried out using a hydroxy ethyl cellulose solution prepared from Cellosolve (trade mark) QP-100 MH which is hydroxy ethyl cellulose having a viscosity of around 100,000 cps at 25°C in a 5% solution at a shear rate 1 sec⁻¹ with a degree of substitution of approximately 1 and a molar substitution of approximately 2. The hydroxy ethyl cellulose solutions are all prepared in hydrated form. Solutions of ferric chloride hexahydrate and sodium hydroxide were added to the hydroxy ethyl cellulose solutions to give the concentrations based on total solution given in the Tables. The ferric chloride solution had in the composition FeCl₃·6H₂O 100 grams water 200 grams H₂SO₄ (concentrated) 1 drop

The sodium hydroxide solution used contained 20% sodium hydroxide by weight.

Some of the solutions were prepared using fresh water the results are given in Tables 1 and 2. Other solutions were prepared using sea water or sea water plus 5% by weight KCl. The results are given in Table 3.
<table>
<thead>
<tr>
<th>QP-100MH Concentration kg/m³</th>
<th>FeCl₃·6H₂O 50% Conc. % (on total solution)</th>
<th>NaOH % (on total solution)</th>
<th>Fann Viscosity (Pa·sec × 10⁻³)</th>
<th>Gel Strength (kg/m² ft²) after shearing 5 mins. at 100,000 sec⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>600 (After shearing)</td>
</tr>
<tr>
<td>4.3</td>
<td>0.4</td>
<td>0.56</td>
<td>72</td>
<td>37</td>
</tr>
<tr>
<td>4.3</td>
<td>0.8</td>
<td>0.56</td>
<td>80</td>
<td>44</td>
</tr>
<tr>
<td>4.3*</td>
<td>1.2</td>
<td>0.56</td>
<td>62</td>
<td>38</td>
</tr>
<tr>
<td>5.7</td>
<td>0.4</td>
<td>0.56</td>
<td>135</td>
<td>65</td>
</tr>
<tr>
<td>5.7</td>
<td>0.8</td>
<td>0.56</td>
<td>&gt;150</td>
<td>82</td>
</tr>
<tr>
<td>5.7</td>
<td>1.2</td>
<td>0.56</td>
<td>115</td>
<td>75</td>
</tr>
</tbody>
</table>

* After 1 week
* After 1 month

¹ = minutes
² = seconds

TABLE 1B (Table 1 with results given in SI units)

PROPERTIES OF QP-100MH/FERRIC CHLORIDE FRESH WATER SOLUTIONS
<table>
<thead>
<tr>
<th>Compound</th>
<th>QP–100MH Concentration (kg/m³)</th>
<th>FeCl₃·6H₂O 50% Concent. % (on total solution)</th>
<th>NaOH 50% (on total solution)</th>
<th>T°C</th>
<th>pH</th>
<th>Fann Viscosity 300 (Pa·sec·x·10⁻²)</th>
<th>Fann Viscosity 600 (Pa·sec·x·10⁻²)</th>
<th>AV</th>
<th>Gel Strength (kg/m² ft²)</th>
<th>API Water Loss (ml/30 mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.3</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>12.8</td>
<td>138</td>
<td>195</td>
<td>97</td>
<td>1.464</td>
<td>0.781</td>
</tr>
<tr>
<td>2</td>
<td>4.3</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>12.8</td>
<td>43</td>
<td>59</td>
<td>30</td>
<td>0.878</td>
<td>0.195</td>
</tr>
<tr>
<td>3</td>
<td>4.3(A)</td>
<td>0.8</td>
<td>0.56</td>
<td>50</td>
<td>12.7</td>
<td>103</td>
<td>140</td>
<td>70</td>
<td>0.830</td>
<td>0.439</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>0.8</td>
<td>0.56</td>
<td>96</td>
<td>12.5</td>
<td>27</td>
<td>41</td>
<td>20</td>
<td>0.195</td>
<td>0.146</td>
</tr>
<tr>
<td>5</td>
<td>4.3</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>6.2</td>
<td>108</td>
<td>148</td>
<td>74</td>
<td>0.878</td>
<td>0.732</td>
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<tr>
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<td>0.8</td>
<td>0.56</td>
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<td>3.0</td>
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<td>65</td>
<td>32</td>
<td>0.195</td>
<td>0.195</td>
</tr>
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<td>7</td>
<td>5.7</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>12.5</td>
<td>180</td>
<td>90</td>
<td>68</td>
<td>1.366</td>
<td>0.683</td>
</tr>
<tr>
<td>8</td>
<td>5.7(A)</td>
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<td>0.56</td>
<td>22</td>
<td>13.0</td>
<td>230</td>
<td>300</td>
<td>150</td>
<td>2.440</td>
<td>1.513</td>
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<td>0.56</td>
<td>50</td>
<td>13.0</td>
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<td>107</td>
<td>53</td>
<td>2.830</td>
<td>0.732</td>
</tr>
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<td>0.56</td>
<td>95</td>
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<td>290</td>
<td>145</td>
<td>0.634</td>
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<td>3.57</td>
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<td>0.56</td>
<td>22</td>
<td>8.0</td>
<td>80</td>
<td>106</td>
<td>53</td>
<td>0.732</td>
<td>0.439</td>
</tr>
<tr>
<td>12***</td>
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<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>13.0</td>
<td>240</td>
<td>300</td>
<td>150</td>
<td>2.586</td>
<td>2.001</td>
</tr>
<tr>
<td>12</td>
<td>5.7(A)</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>13.0</td>
<td>109</td>
<td>130</td>
<td>75</td>
<td>2.196</td>
<td>0.976</td>
</tr>
</tbody>
</table>

* After aging for 24 hours.

** Started with a 2.0 lbs/bbl thixotropic solution which was then diluted with water to an AV of 46 cps (100 grams solution + 60 grams H₂O).

*** Fresh water plus 5% KCl.

AV Apparent viscosity

A Solution subjected to 5 minutes shear at 100,000 sec⁻¹.

minutes * seconds
TABLE 3B  (Table 3 with results given in SI units)

PROPERTIES OF QP–100MH/FERRIC CHLORIDE SEA WATER AND SEA WATER PLUS KCI SOLUTIONS

<table>
<thead>
<tr>
<th>Compound</th>
<th>QP–100MH Concentration (kg/m³)</th>
<th>FeCl₃·6H₂O 50% Concent. % (on total solution)</th>
<th>NaOH % (on total solution)</th>
<th>T°C</th>
<th>pH</th>
<th>300 (Pa·sec × 10⁻²)</th>
<th>600</th>
<th>AV</th>
<th>Gel Strength (kg/m² ft²)</th>
<th>API Water Loss (ml/30 mins.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>4.3</td>
<td>0.56</td>
<td>22</td>
<td>12.8</td>
<td>57</td>
<td>82</td>
<td>41</td>
<td>0.732</td>
<td>0.293</td>
<td>0.44</td>
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<tr>
<td>13</td>
<td>4.3(A)</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
<td>12.8</td>
<td>34</td>
<td>49</td>
<td>24</td>
<td>0.195</td>
<td>0.146</td>
</tr>
<tr>
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<td>0.56</td>
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<td>0.56</td>
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<td>13.0</td>
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<td>80</td>
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<td>0.439</td>
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</tr>
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<td>15</td>
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<td>90</td>
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<td>0.927</td>
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<tr>
<td>15</td>
<td>7.1(A)</td>
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<td>0.56</td>
<td>22</td>
<td></td>
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<td>60</td>
<td>0.830</td>
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</tr>
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<td>12.7</td>
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<td>80</td>
<td>40</td>
<td>0.781</td>
<td>0.244</td>
</tr>
<tr>
<td>16*</td>
<td>4.3(A)</td>
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<td>0.56</td>
<td>22</td>
<td>12.7</td>
<td>35</td>
<td>50</td>
<td>25</td>
<td>0.195</td>
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</tr>
<tr>
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<td>0.8</td>
<td>0.56</td>
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<td></td>
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<td>52</td>
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<tr>
<td>17*</td>
<td>5.7(A)</td>
<td>0.8</td>
<td>0.56</td>
<td>22</td>
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<td>94</td>
<td>120</td>
<td>60</td>
<td>0.830</td>
<td>0.586</td>
</tr>
</tbody>
</table>

* Sea water plus 5% KCI
A Solution subjected to 5 minutes shear at 100,000 sec⁻¹.
AV Apparent viscosity
¹ minutes
² seconds
Claims

1. A process for producing a non-hydraulic thixotropic aqueous liquid which comprises mixing together an aqueous solution of a hydrated cellulose ether and a water-soluble ferric salt with a water-soluble alkali, the quantities of ferric salt and alkali being sufficient to give an alkaline solution and to make said liquid thixotropic in the absence of a hydraulic substance.

2. A process according to Claim 1 wherein the cellulose ether is a hydroxyethyl cellulose.

3. A process according to either Claim 1 or 2 wherein the quantity and molecular weight of the cellulose ether used are sufficient to give an apparent Fann viscosity (600/2) of at least 2 x 10^-3 Pa. sec in pure aqueous solution.

4. A process according to any one of Claims 1 to 3 wherein the cellulose ether has a viscosity of at least 70 Pa. sec at 24°C at a shear rate of 1 sec^-1 at 2% by weight concentration in pure water.

5. A process according to any one of Claims 1 to 4 wherein the cellulose ether is a hydroxyethyl cellulose with a degree of substitution in the range 0.8 to 1.2.

6. A process according to Claim 5 wherein the average number of ethylene oxide molecules that have reacted with each anhydroglucose unit in the cellulose is in the range 1.7 to 2.3.

7. A process according to any one of Claims 1 to 6 wherein the ferric salt is ferric chloride.

8. A process according to any one of Claims 1 to 7 wherein the alkali is sodium hydroxide.

9. A process according to any one of Claims 1 to 8 wherein the quantity of ferric salt is equivalent to at least 0.05% weight and not more than 0.4% by weight based on the weight of total solution.

10. A process according to any one of Claims 1 to 9 wherein the quantity of alkali present is equivalent to a quantity of sodium hydroxide in the range 0.5% to 2% by weight of the total solution.

Revendications

1. Procédé de préparation d'un liquide aqueux thixotrope non hydraulique qui comprend le mélange d'une solution aqueuse d'un éther cellulosique hydraté et d'un sel ferrique hydroxosoluble avec une base hydro-soluble, les quantités de sel ferrique et de base étant suffisantes pour qu'elles donnent une solution basique et que le liquide soit thixotrope en l'absence d'une substance hydraulique.

2. Procédé selon la revendication 1, caractérisé en ce que l'éther cellulosique est une hydroxyéthylcellulose.

3. Procédé selon l'une des revendications 1 et 2, caractérisé en ce que la quantité et le poids moléculaire de l'éther cellulosique utilisés suffi-

sent pour que la viscosité apparente Fann (60/2) soit d'au moins 2 x 10^-3 Pa. sec dans une solution aqueuse pure.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que l'éther cellulosique a une viscosité d'au moins 70 Pa.s à 24°C avec un gradient de vitesse de 1 s^-1 à une concentration pondérale de 2% dans l'eau pure.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que l'éther cellulosique est une hydroxyéthylcellulose ayant un degré de substitution compris entre 0.8 et 1.2.

6. Procédé selon la revendication 5, caractérisé en ce que le nombre moyen de molécules d'oxyde d'éthylène qui ont réagi avec chaque molécule anhydroglucose dans la cellulose est compris entre 1.7 et 2.3.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le sel ferrique est le chlorure ferrique.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que la base est l'hydroxyde de sodium.

9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que la quantité de sel ferrique équivaut à au moins 0.05% en poids et ne dépasse pas 0.4% en poids des poids de la solution totale.

10. Procédé selon l'une quelconque des revendications 1 à 9, caractérisé en ce que la quantité de base présente équivaut à une quantité d'hydroxyde de sodium comprise entre 0.5 et 2% du poids de la solution totale.

Patentansprüche

1. Verfahren zur Herstellung einer nicht-hydraulischen thixotropen wässrigen Flüssigkeit durch Zusammensetzung einer wässrigen Lösung eines Hydratisierten Celluloseäthers und eines wasserlöslichen Eisens (III)-Salzes mit einem wasserlöslichen Alkalibasischen, wobei die Mengen an Eisen (III)-Salz und Alkali ausreichend sind, um eine alkalische Lösung zu bilden und die Flüssigkeit thixotrop zu machen in Abwesenheit einer hydraulischen Substanz.

2. Verfahren gemäß Anspruch 1, worin der Celluloseäther eine Hydroxyethylcellulose ist.

3. Verfahren gemäß einem der Ansprüche 1 oder 2 worin die Menge und das Molekularge wicht des verwendeten Celluloseäthers ausreichend sind um eine scheinbare Fann Viskosität (600/2) von mindestens 2 x 10^-2 Pa. sec. in rein wässriger Lösung zu ergeben.


5. Verfahren gemäß einem der Ansprüche 1 bis 4 worin der Celluloseäther eine Hydroxyethylcellulose mit einem Substitutionsgrad im
Bereich von 0,8 bis 1,2 ist.

6. Verfahren gemäß Anspruch 5 worin die Durchschnittszahl von Äthylenoxydmolekülen, die mit jeder Anhydroglucoseseinheit in der Cellulose reagiert haben im Bereich von 1,7 bis 2,3 liegt.

7. Verfahren gemäß einem der Ansprüche 1 bis 6 worin das Eisen (III)-Salz Ferrichlorid ist.

8. Verfahren gemäß einem der Ansprüche 1 bis 7 worin das Alkali Natriumphosphat ist.

9. Verfahren gemäß einem der Ansprüche 1 bis 8 worin die Menge an Eisen (III)-Salz äquivalent zu mindestens 0,05 Gew.-% und nicht mehr als 0,4 Gew.-% bezogen auf das Gewicht der gesamten Lösung beträgt.

10. Verfahren gemäß einem der Ansprüche 1 bis 9 worin die Menge an anwesendem Alkali äquivalent ist einer Menge an Natriumphosphat im Bereich von 0,5 bis 2 Gew.-% der Gesamtlösung.