Activator for pulp bleaching

A process for the bleaching of cellulosic fibres comprising the steps of (a) providing a water supply; (b) adding hydrogen peroxide to the stabilised water supply to form a hydrogen peroxide solution; (c) adjusting the pH of the hydrogen peroxide solution by adding alkali; mixing the pH adjusted solution resulting from step (c) to allow complete formation of perhydroxyl ion; (e) adding a carboxylic acid anhydride compound to the solution resulting from step (d); (f) mixing the solution resulting from step (e) to allow complete formation of percarboxylic acid to give a dilute solution of percarboxylic acid; and (g) contacting the solution with a suspension of cellulosic fibres.
Description

This invention relates to a process for generating a dilute solution of percarboxylic acid which is subsequently used to bleach wood or non wood pulp. More specifically, in this process the bleaching solution is formed by reaction of hydrogen peroxide with a carboxylic acid anhydride compound which behaves as a bleach activator.

Wood and non wood pulp are valuable raw materials in the paper industry and it is desirable that a high degree of whiteness is obtainable. Oxygen based bleaching is used for pulp bleaching because of its environmental benefits and oxidising power. Hydrogen peroxide is increasingly being used in oxygen based pulp bleaching.

Hydrogen peroxide, however, suffers from some performance disadvantages which become particularly important when an existing pulp bleaching sequence is being converted to operate with hydrogen peroxide. One major problem is the fact that the degree of whiteness may be reduced compared with the use of chlorine based bleaches which significantly reduces the value of the pulp.

In order to overcome these problems work has gone into developing an alternative bleaching solution. It is proposed in various patent applications to react at least part of the hydrogen peroxide with a bleach activator thereby generating a peroxycarboxylic acid based oxygen bleaching species in situ. Bleach activators contain a good leaving group such that on mixing with hydrogen peroxide, reaction takes place to give peracid species which are more effective bleaching agents than hydrogen peroxide itself.

EP-A-0670929 describes a method for bleaching lignocellulose containing pulp in which equilibrium peracid is generated by reacting acetic acid and hydrogen peroxide. It also suggests that in situ peracid can be generated by reaction of acetic anhydride with hydrogen peroxide directly in the bleaching stage although the equilibrium peracid is preferred and is what is used in the examples of this application. EP-A-0670928 describes an is used in the examples of this application. EP-A-0670928 describes an identical method. However, whilst equilibrium peracid improves the bleaching it also introduces problems of handling and dosing, peracid in the pulp plant.

Further examples such as EP456032 describe the use of tetraacetylethlenediamine (TAED) as the bleach activator. Whilst this produces a very effective bleaching solution, generation of such a solution in certain circumstances may not prove to be economical for all mills. It would therefore be desirable to develop a process by which peracid can be generated in a good yield by reacting hydrogen peroxide with a more cost effective bleach activator, thus ensuring that it is more cost effective than the method of the prior art which uses TAED. A bleach activator suitable for solving this problem is acetic anhydride. Whilst the use of acetic anhydride as a bleach activator to produce peracetic acid is well documented, surprisingly better performance can be delivered using peracetic acid generated from acetic anhydride as compared to preformed peracetic acid. Furthermore there is yet to be developed a simple and inexpensive process by which good yields of peracid can be produced.

According to the present invention there is provided a process for the bleaching of cellulosic fibres comprising the steps of;

- a) treating a fresh water supply with a chelating agent to give a stabilised water supply;
- b) adding hydrogen peroxide to the stabilised water supply to form a hydrogen peroxide solution;
- c) adjusting the pH of the hydrogen peroxide solution by adding alkali;
- d) mixing the pH adjusted solution resulting from step (c) to allow complete formation of perhydroxyl ion;
- e) adding a carboxylic acid anhydride compound to the solution resulting from step (d);
- f) mixing the solution resulting from step (e) to allow complete formation of percarboxylic acid to give a dilute solution of percarboxylic acid; and
- g) contacting the percarboxylic acid solution with a suspension of cellulosic fibres.

It is preferable that the water used in step a) is of a temperature between 5°C-100°C, preferably between 10°C-50°C and more preferably between 15°C-30°C. At cooler temperatures the generation of the percarboxylic acid may be inhibited whilst at higher temperatures, although the generation would be rapid, it is anticipated that degradation of the percarboxylic acid species would be promoted.

Chelating agent is added to the water in step a) prior to the addition of further components and is advantageous as it ensures that any trace metals which may be present in the supply are removed. Such trace metals could potentially promote the decomposition of hydrogen peroxide. A mixing step is preferably included to maximise the chelation of the trace metals.

Preferably the chelating agent is an aqueous phosphonic acid based chelating agent. Examples of suitable phosphonic acid based chelating agents are polyamino methylene phosphonic acids such as based on ethylene diamine or diethylenetriamine. Commercially available compounds of this type include Dequest SPE9505, Dequest 20605, Dequest 2066, Dequest 2066A manufactured by Solutia and Versenate PS manufactured by DOW. In a preferred embodiment the chelating agent is Dequest SPE 9505 and/or Dequest 2066. An aqueous phosphonic acid based
chelating agent has been found to work best under the conditions of the method of the present invention.

[0012] Preferably the amount of chelating agent, eg phosphonic acid based agent, added to the water is 0.1-0.4wt%, more preferably 0.125-0.3%wt and most preferably 0.15-0.25%wt.

[0013] Preferably the amount of hydrogen peroxide added in step b), based on a 50% solution, is a value in the range 0.5-6wt%, more preferably in the range 1.5-4.0wt% and most preferably in the range 1.75-2.5wt%.

[0014] It is desirable that the addition of hydrogen peroxide is followed by an in line mixing step. This mixing step is often required because the water and hydrogen peroxide are transferred separately from their holding containers to the vessel in which the reaction proceeds. It is therefore beneficial to include a mixing step to ensure that a uniform solution is obtained.

[0015] The alkali is added in step c) in an amount to raise the pH of the solution from a value in the range 6-7 to a value in the range 10.5-11.5. It is important that this alkali addition occurs prior to step (d). This is because rendering the hydrogen peroxide solution of step b) alkaline promotes the formation of perhydroxyl ion with which the carboxylic acid anhydride compound preferentially reacts instead of water. If step c) was not included, the carboxylic acid anhydride compound would hydrolyse thus reducing the amount of percarboxylic acid eventually formed. Suitable alkalis include potassium hydroxide, calcium hydroxide, magnesium hydroxide and sodium hydroxide. Preferably the alkali is sodium hydroxide. It is important to raise the pH of the solution because it is at alkaline pHs that formation of the perhydroxyl ion is promoted. Sodium hydroxide is available as a 30w/w% or 50w/w% solution. Suitable amounts were determined by monitoring the pH. Preferably the amount of sodium hydroxide added based on a 50% solution is a value in the range 0.2-3wt%, more preferably in the range 0.4-1.5wt% and most preferably in the range 0.5-1wt%.

[0016] Following the addition of the alkali, there is a further mixing step (step d)). The duration of this step is preferably at least one minute. This is important to optimise the extent of formation of the perhydroxyl ion in the subsequent steps. At present, a specific method for directly analysing whether complete formation of the perhydroxyl ion has taken place is not available. However, it is possible to obtain an indication of the extent of perhydroxyl ion formation by analysing the percentage conversion of the carboxylic acid anhydride compound to percarboxylic acid. A low percentage conversion rate may indicate incomplete formation of the perhydroxyl ion. If sufficient time is not allowed for this mixing step and the carboxylic acid anhydride compound is added prematurely then it would preferentially undergo a hydrolysis reaction with water resulting in a low percarboxylic acid generation.

[0017] After sufficient mixing in step d) has taken place, the carboxylic acid anhydride compound is added (step e)). Preferably the carboxylic acid anhydride compound added in step e) is selected from one or more of the group consisting of acetic anhydride, maleic anhydride, succinic anhydride, phthalic anhydride, maleic anhydride, benzoic anhydride and propanoic anhydride. Preferably the amount of carboxylic acid anhydride compound added is in the range 0.02 - 0.6mol%, more preferably in the range 0.05 - 0.3mol% and most preferably in the range 0.075 - 0.15mol% and this addition is followed by a further important mixing step (step f)). This mixing step should be allowed to occur for at least 10 minutes. This is to maximise generation of the percarboxylic acid species. It is, however, possible to accelerate the generation of the percarboxylic acid species by using amounts of alkali at the higher end of the ranges mentioned above prior to the carboxylic acid anhydride addition.

[0018] Preferably the carboxylic acid anhydride compound comprises acetic anhydride. Acetic anhydride has a flash point of 54°C and as such is classified as flammable. A compound is classified as flammable where it has a flashpoint in the range of 21°C-55°C. This means that the modification of old mill equipment, although minor, will require consideration of the Dangerous Substances and Explosive Atmosphere Regulations (DSEAR). Flammability rating also has an impact on zone classification on manufacturing plants. In order to further minimise the minor modifications required, the applicants have investigated increasing the flash point of acetic anhydride by mixing with a further carboxylic acid anhydride with a higher flashpoint. For example, maleic anhydride has a flash point of 102°C. Samples of 80:20 and 50:50 acetic anhydride: maleic anhydride solutions were prepared and it was found that in both cases the flash point was increased, to 60°C and 65°C respectively, meaning that the solutions would not be classified as flammable. Further testing also surprisingly showed that these solutions were as effective as a bleach activator as a solution of acetic anhydride only.

[0019] Thus in one embodiment of the present invention, the flashpoint of acetic anhydride is modified by addition of a carboxylic acid anhydride with a higher flashpoint to form a mixture which has a flash point of 55.1°C or higher such that it is not classified as flammable. Preferably a mixture which has a flash point of 60°C or higher is formed. Preferably the amount of carboxylic acid anhydride with a higher flashpoint added is such that the resulting mixture has a ratio of acetic anhydride to carboxylic acid anhydride with a higher flashpoint greater than 50:50 but less than or equal to 80:20. Preferably the carboxylic acid anhydride with a higher flashpoint is maleic anhydride. A 50:50 mixture of acetic anhydride: maleic anhydride is not commercially practical as, upon cooling, the maleic anhydride precipitates out of the solution. Preferably the ratio of acetic anhydride to maleic anhydride is 80:20. Preferably the mixture consists of the acetic anhydride and further carboxylic acid anhydride with a higher flashpoint only.

[0020] The mixture of acetic anhydride and carboxylic acid anhydride with a higher flashpoint can then be used as the carboxylic acid anhydride compound in the method for bleaching cellulosic fibres of the invention.
It is anticipated however, that the mixture of acetic anhydride and carboxylic acid anhydride with a higher flash point may be useful in various applications not just limited to the bleaching of cellulosic fibres. The method of increasing the flash point of acetic anhydride by mixing with a carboxylic acid anhydride with a higher flashpoint and the mixture itself form a second aspect of the invention.

The molar ratio of carboxylic acid anhydride compound to hydrogen peroxide added is preferably in the range 1:1 to 1:10, preferably 1:1.5 to 1:6, more preferably 1:2 to 1:4. Most preferably the molar ratio is about 1:3. In terms of the number of moles added, it is preferable that more hydrogen peroxide is required than carboxylic acid anhydride compound in order to drive the reaction to form perhydroxyl ion.

The resultant dilute percarboxylic acid solution formed in step f) will have a pH of approximately 5. Depending on the mill conditions, it may be necessary to increase the solution pH to suit the bleaching conditions required in the final step of the process, step g).

Typically a conversion of carboxylic acid anhydride compound to percarboxylic acid of 90-95% is obtained. Preferably the resultant solution contains percarboxylic acid in a concentration range of 0.1-10%, more preferably 0.25-5% and most preferably 0.5-2%.

The final step (step g)) of the process is to contact the dilute percarboxylic acid solution with a cellulosic fibre suspension e.g formed from pulp. The pulp may be any sort of pulp, including chemical and mechanical pulp and mixture thereof, including recycled material. Wood and non wood fibres can be bleached using this process. The product may be used directly to form paper or board or may be fully or partially dewatered to form a pulp intermediate for eventual paper or board manufacture.

The following examples give an indication of how effective this process is and demonstrate the high yield of percarboxylic acid which can be expected to be generated.

Description of the Figures

Figure 1 shows the percarboxylic acid release profile of formulations 1-5 as detailed in Example 1;
Figure 2 shows the pH profile of formulations 1-5 as detailed in Example 1;
Figure 3 shows the brownstock delignification of soft wood pulp using a 0.5% peracetic acid charge from anhydride sources formulations 1-5 in terms of Kappa as detailed in example 2;
Figure 4 shows the brownstock delignification of soft wood pulp using a 0.5% peracetic acid charge from anhydride source formulations 1-5 in terms of ISO brightness as detailed in Example 2;
Figure 5 shows the storage chest bleaching of fully bleached pulp using peracetic acid from formulations 1-5 measured in terms of ISO brightness as detailed in Example 3; and
Figure 6 shows the recycled fibre (80:20 Newssprint:MOW) bleaching using peracetic acid from formulations 1-5 measured in terms of ISO Brightness as detailed in Example 4.
Figure 7 shows a comparison of preformed and acetic anhydride derived peracetic acid on bleaching brownstock pulp.
Figure 8 shows a comparison of preformed and acetic anhydride derived peracetic acid on bleaching 80:20 Newsprint: MOW recycled furnish.

Examples

In order to compare the bleaching ability of the acetic anhydride derived peracetic acid solutions with those derived from TAED as are commonly used in the art, various formulations were prepared. It was also the case that formulations containing an acetic anhydride/maleic anhydride solution were tested.

The formulations prepared are as detailed below:
Each of the formulations were prepared according to the method of the present invention. More specifically, fresh water at a temperature in the range from 15-30°C was treated with 0.2wt% of Dequest 2066. 2wt% of a 50% hydrogen peroxide solution was added to the stabilised water supply the pH of the resulting hydrogen peroxide solution was adjusted to a pH in the range from 10.5 to 11.5 by the addition of 0.75wt% of a 50% solution of sodium hydroxide. The mixture was then mixed for a period of 1 minute to allow complete formation of the perhydroxyl ion. The bleach activator was added to this mixed solution in the amounts shown above respectively and the solution was mixed to allow complete formation of peracetic acid to give a dilute solution of peracetic acid.

Example 1

Peracid release/pH profile

The peracid release profile for each of formulations 1-5 was determined by taking measurements between 2 and 145 minutes. The solution temperatures were maintained at 25°C. pH profiles were also attained during the process. The results of the peracid release profile are shown in Table 1 and Figure 1. The pH profiles attained are illustrated in Table 2 and Figure 2.
<table>
<thead>
<tr>
<th>Time mins</th>
<th>Formulation 1</th>
<th>Formulation 2</th>
<th>Formulation 3</th>
<th>Formulation 4</th>
<th>Formulation 5</th>
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<td>145</td>
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Example 2

Brownstock Delignification

[0032] Using formulations 1-5, brownstock delignification was carried out. The experimental conditions and results are summarised in Table 3. In order to determine how effectively the different formulations worked using softwood brownstock pulp, kappa and ISO brightness data was recorded using International Standards, ISO 302-1981 (E) and ISO 3688-1977 respectively. The results are also illustrated graphically in Figures 3 and 4.
<table>
<thead>
<tr>
<th>Stage Conditions / Results</th>
<th>Formulation 1</th>
<th>Formulation 2</th>
<th>Formulation 3</th>
<th>Formulation 4</th>
<th>Formulation 5</th>
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<td>Peracid Charge</td>
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<td>87.7%</td>
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</table>
Example 3

Storage Chest Bleaching

[0033] Using formulations 1-5, a storage chest bleaching study was performed using a fully bleached pulp. Kappa and ISO brightness data was recorded using International Standards, ISO 302-1981 (E) and ISO 3688-1977 respectively. The experimental conditions and results are summarised in Table 3. The results obtained are also illustrated graphically in Figure 5.

Example 4

Recycled Fibre Bleaching Study

[0034] Using formulations 1-5, a recycled fibre bleaching study was carried out using 80:20 Newsprint: MOW grade furnish. ISO brightness data was recorded using International Standards, ISO 302-1981 (E) and ISO 3688-1977 respectively. The experimental conditions and results are summarised in Table 3. The results obtained are also illustrated graphically in Figure 6.

Conclusions

[0035] The results obtained from the experiments performed clearly demonstrate that performance similar to that achieved using a PeroxyBoost (RTM) TAED bleach activator can be obtained by using acetic anhydride as required by the present invention. It has further been shown that adding maleic anhydride to the acetic anhydride to form a stabilised acetic anhydride/maleic anhydride solution does not affect the peracid release.

[0036] Furthermore, the bleaching studies demonstrated that bleaching with peracetic acid derived from acetic anhydride provides similar results. The results when using a mixture of peracetic acid and permaleic acid or just permaleic acid alone are also similar. Therefore, surprisingly, the introduction of permaleic acid does not affect the bleaching ability of peracetic acid.

[0037] In a set of further examples, the bleaching ability of the acetic anhydride derived peracetic acid solution was compared with the bleaching ability of a preformed peracetic acid. More specifically, bleaching formulation 4 was compared to a preformed commercially available peracetic acid (supplied by Aldrich), hereinafter referred to as formulation 6.

[0038] Using the peracetic acid solutions, brown stock delignification and recycled bleaching studies were performed using brown stock and 80:20 Newsprint: MOW pulps respectively. The studies were performed using a 0.1 %, 0.25% and 0.5% charge of peracetic acid (based on 100% peracetic acid) respectively at a temperature of 70°C and with a retention time of 120 minutes. Formulation 4 was used at a pH in the range 8-8.5 and formulation 6 was used at a pH of 5 which represents the normal conditions under which it is used.

[0039] ISO brightness data was recorded using International Standard ISO 3688-1977. The results are shown graphically in Figures 7 and 8.

[0040] The data shows that a superior bleaching performance is achieved using acetic anhydride derived peracetic acid as compared to preformed peracetic acid.

Flash Point Analysis

[0041] The flashpoints of various neat carboxylic acid anhydride compounds are illustrated in Table 4.

[0042] Samples of acetic anhydride, maleic anhydride, 80:20 acetic anhydride: maleic anhydride and 50:50 acetic anhydride: maleic anhydride were prepared. The flash points of these solutions were determined using the Pensky Martens closed cup test. The results obtained are summarised in Table 5.

<table>
<thead>
<tr>
<th>Carboxylic acid anhydride</th>
<th>Flashpoint (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic anhydride</td>
<td>54</td>
</tr>
<tr>
<td>Benzoic anhydride</td>
<td>110</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>102</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
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</table>
Freezing Point Assessment

[0043] The freezing point of acetic and maleic anhydride mixtures was assessed. Acetic: maleic anhydride solutions with a total weight of 100g, in the ratios 80:20, 50:50 and 20:80 respectively were prepared. The samples were contained in a lidded glass storage jar and then stored for 2 days at -17°C. The results are detailed in Table 5.

![Table 5](image)

<table>
<thead>
<tr>
<th>Bleach Activator</th>
<th>Flash Point (°C)</th>
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<tbody>
<tr>
<td>Acetic anhydride</td>
<td>54°C</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>102°C</td>
</tr>
<tr>
<td>80:20 acetic: maleic anhydride mix</td>
<td>60°C</td>
</tr>
<tr>
<td>50:50 acetic: maleic anhydride mix</td>
<td>65°C</td>
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[0044] This assessment showed that in order to be suitable, from a commercial point of view, as a liquid activator, a ratio of acetic: maleic anhydride of greater than 50:50 is required.

Claims

1. A process for the bleaching of cellulosic fibres comprising the steps of:

   (a) treating a fresh water supply with chelating agent to give a stabilised water supply;
   (b) adding hydrogen peroxide to the stabilised water supply to form a hydrogen peroxide solution;
   (c) adjusting the pH of the hydrogen peroxide solution by adding alkali;
   (d) mixing the pH adjusted solution resulting from step (c) to allow complete formation of perhydroxyl ion;
   (e) adding a carboxylic acid anhydride compound to the solution resulting from step (d);
   (f) mixing the solution resulting from step (e) to allow complete formation of percarboxylic acid to give a dilute solution of percarboxylic acid; and
   (g) contacting the solution of peracid with a suspension of cellulosic fibres.

2. The process according to claim 1 in which the fresh water supply is at a temperature in the range 15-30°C.

3. The process according to claim 1, wherein the chelating agent is an aqueous phosphonic acid based.

4. The process according to claim 3, wherein the phosphonic acid based chelating agent is Dequest SPE9505 and/or Dequest 2066.

5. The process according to claim 1, wherein the amount of chelating agent added is in the range 0.1-0.4 wt%.
6. The process according to claim 1, wherein the amount of chelating agent added is in the range from 0.125-0.3wt%.

7. The process according to claim 1, wherein the amount of chelating agent added is in the range 0.15-0.25wt%.

8. A process according to any of the preceding claims wherein the amount of hydrogen peroxide added based on a 50% solution is in the range 0.5-6wt%, more preferably in the range 1.5-4.0wt% and most preferably in the range 1.75-2.5wt%.

9. The process according to any preceding claim wherein the alkali is sodium hydroxide.

10. A process according to any preceding claim wherein the amount of alkali added is in the range 0.2-3wt%, preferably in the range 0.4-1.5wt% and more preferably in the range 0.5-1.0wt%.

11. A process according to any preceding claim wherein the pH is adjusted to a value in the range 10.5-11.5.

12. A process according to any preceding claim in which the duration of the mixing step (d) is at least 1 minute.

13. A process according to any preceding claim in which the amount of carboxylic acid anhydride compound added is in the range 0.02 - 0.6mol%, preferably in the range 0.05 - 0.3mol% and more preferably in the range 0.075 - 0.15mol%.

14. A process according to any preceding in which the duration of the mixing step (f) is up to 10 minutes.

15. The process according to any preceding claim which further comprises an additional pH adjusting step prior to the solution being contacted with the fibrous cellulosic solution.

16. The process according to any preceding claim wherein the carboxylic acid anhydride is selected from one or more of the group consisting of acetic anhydride, maleic anhydride, succinic anhydride, malonic anhydride, benzoic anhydride and propanoic anhydride.

17. The process according to claim 17, wherein the carboxylic acid anhydride compound comprises acetic anhydride.

18. The process of claim 17, wherein the carboxylic anhydride compound additionally comprises a further carboxylic acid anhydride with a higher flashpoint and the acetic anhydride has been premixed with the further carboxylic acid anhydride with a higher flashpoint to form an acetic anhydride/carboxylic acid anhydride mixture with a modified flashpoint of 55.1 °C or above.

19. The process of claim 18 wherein the ratio of acetic anhydride to maleic anhydride in the acetic anhydride/carboxylic acid anhydride mixture with a modified flashpoint is greater than 50:50.

20. The process of claim 18 wherein the ratio of acetic to maleic anhydride with a higher flashpoint in the acetic anhydride/carboxylic acid anhydride mixture with a modified flashpoint is 80:20.

21. The process according to any of claims 19 to 21, wherein the carboxylic acid anhydride with a higher flashpoint is maleic anhydride.

22. A method for increasing the flash point of acetic anhydride to at least 55.1 °C comprising forming a mixture of acetic anhydride and a further carboxylic acid anhydride with a higher flashpoint in order to form a acetic anhydride/carboxylic acid anhydride mixture with a modified flashpoint.

23. The method of claim 22, wherein the acetic anhydride/carboxylic acid anhydride mixture with a modified flashpoint has a ratio of acetic anhydride to carboxylic acid anhydride with a higher flashpoint greater than 50:50.

24. The method according to claim 22, wherein the acetic/carboxylic acid anhydride mixture with a modified flashpoint has a ratio of acetic anhydride to carboxylic acid anhydride with a higher flashpoint of 80:20.

25. The method according to any of claims 22 to 24, wherein the carboxylic acid anhydride with a higher flashpoint is maleic anhydride.
26. A composition comprising acetic anhydride and a further carboxylic acid anhydride with a higher flashpoint, which has a flashpoint of at least 55.1 °C and wherein the ratio of acetic anhydride to carboxylic acid anhydride with a higher flashpoint is greater than 50:50 but less than or equal to 80:20.

27. The composition according to claim 26 which consists of acetic anhydride and a further carboxylic acid anhydride only.
# European Search Report

**Application Number:** EP 04 25 3546

## Documents Considered to Be Relevant

<table>
<thead>
<tr>
<th>Category</th>
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<th>Relevant to claim</th>
<th>Classification of the Application (Int.Cl.)</th>
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<tr>
<td>Y</td>
<td>US 3 227 655 A (PRETT KONRAD ET AL) 4 January 1966 (1966-01-04) * column 1, line 15 - line 20 * * examples 1-7 * * claim *</td>
<td>1-2,16, 17</td>
<td>D21C9/16</td>
</tr>
<tr>
<td>Y,D</td>
<td>WO 94/12722 A (EKA NOBEL AB; LINSTEN, MAGNUS; BASTA, JIRI; HAESELLSTROM, ANN-SOFIE) 9 June 1994 (1994-06-09) * page 4, lines 1-18 * * claims 1,4 *</td>
<td>1-27</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>GB 2 304 126 A (* WARWICK INTERNATIONAL GROUP LIMITED) 12 March 1997 (1997-03-12) * page 8, line 20 - page 9, line 6 * * claims 1,4,7 *</td>
<td>1-27</td>
<td></td>
</tr>
</tbody>
</table>

The present search report has been drawn up for all claims.

### Place of search: Munich
### Date of completion of the search: 15 March 2005
### Examiner: Naeslund, P
### ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO. EP 04 25 3546

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-03-2005

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<thead>
<tr>
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<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
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</thead>
<tbody>
<tr>
<td>US 3227655 A</td>
<td>04-01-1966</td>
<td>DE 1158956 B</td>
<td>12-12-1963</td>
</tr>
<tr>
<td></td>
<td>FR 1238246 A</td>
<td></td>
<td>12-08-1960</td>
</tr>
<tr>
<td></td>
<td>GB 901687 A</td>
<td></td>
<td>25-07-1962</td>
</tr>
<tr>
<td></td>
<td>AU 671337 B2</td>
<td></td>
<td>22-08-1996</td>
</tr>
<tr>
<td></td>
<td>AU 5583194 A</td>
<td></td>
<td>22-06-1994</td>
</tr>
<tr>
<td></td>
<td>BR 9307520 A</td>
<td></td>
<td>31-08-1999</td>
</tr>
<tr>
<td></td>
<td>CA 2149664 C</td>
<td></td>
<td>19-09-2000</td>
</tr>
<tr>
<td></td>
<td>CZ 9501328 A3</td>
<td></td>
<td>17-01-1996</td>
</tr>
<tr>
<td></td>
<td>DE 69304342 D1</td>
<td></td>
<td>02-10-1996</td>
</tr>
<tr>
<td></td>
<td>DE 69304342 T2</td>
<td></td>
<td>06-03-1997</td>
</tr>
<tr>
<td></td>
<td>ES 2091121 T3</td>
<td></td>
<td>16-10-1996</td>
</tr>
<tr>
<td></td>
<td>FI 952551 A</td>
<td></td>
<td>24-05-1995</td>
</tr>
<tr>
<td></td>
<td>JP 85090749 T</td>
<td></td>
<td>23-04-1996</td>
</tr>
<tr>
<td></td>
<td>MX 9307413 A1</td>
<td></td>
<td>29-07-1994</td>
</tr>
<tr>
<td></td>
<td>NO 952074 A</td>
<td></td>
<td>26-07-1995</td>
</tr>
<tr>
<td></td>
<td>NZ 258273 A</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>PL 309190 A1</td>
<td></td>
<td>18-09-1995</td>
</tr>
<tr>
<td></td>
<td>RU 2097463 C1</td>
<td></td>
<td>27-11-1997</td>
</tr>
<tr>
<td></td>
<td>WO 9412722 A1</td>
<td></td>
<td>09-06-1994</td>
</tr>
<tr>
<td></td>
<td>ZA 9308751 A</td>
<td></td>
<td>28-06-1994</td>
</tr>
<tr>
<td>GB 2304126 A</td>
<td>12-03-1997</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CA 2041468 A1</td>
<td></td>
<td>26-10-1991</td>
</tr>
<tr>
<td></td>
<td>FI 911963 A</td>
<td></td>
<td>26-10-1991</td>
</tr>
<tr>
<td></td>
<td>NO 911626 A</td>
<td></td>
<td>28-10-1991</td>
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</tbody>
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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82