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(54) **PROCESS FOR PRODUCING OPTICALLY BRIGHTENED PAPER**

VERFAHREN ZUR HERSTELLUNG VON OPTISCH AUFGEHELLTEM PAPIER

PROCÉDÉ DE PRODUCTION DE PAPIER OPTIQUEMENT ÉCLAIRCI

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US-A- 5 064 570 US-B1- 6 387 296

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Description

[0001] The present invention relates to a process for the production of optically brightened paper by treating the pulp suspension with an optically brightened filler composition.

[0002] A high degree of brightness is a desirable property of paper and cardboard articles. The most important raw material of the papermaking industry is pulp, which naturally absorbs blue light and therefore is yellowish in color and imparts a dull appearance to the paper. Optical brighteners are used in the papermaking industry to compensate for the absorption of blue light by absorbing UV-light with a maximum wavelength of 350-380nm and converting it into visible blue light with a maximum wavelength of 440nm.

[0003] Optical brighteners of the triazinylaminostilbene type have been used almost exclusively to brighten paper either by application to pulp or to the paper surface. It is well-known however that the lightfastness of brighteners of this type is no better than poor to moderate, or 1 to approximately 3 on the "Blue Wool Scale". (See "Optische Aufheller - neuere Erkenntnisse zu Eigenschaften und Verhalten im Papier" by F. Müller, D. Loewe and B. Hunke in Wochenblatt für Papierfabrikation 1991, 6, pages 191-203.) There is therefore a demand to protect optically brightened papers from yellowing in light.

[0004] In order to provide optically brightened papers of high lightfastness, it is generally recognized that brighteners other than those of the triazinylaminostilbene type must be used; in particular, brighteners typically used for the optical brightening of textiles, such as those of the benzoxazole, naphthalimide, triazolylcoumarin or triazinylpyrene types. Such brighteners are however typically much more expensive, and can only be applied with difficulty to either pulp or to the paper surface.

[0005] EP-A-801 700 overcomes some of these problems by describing the use of optically brightened polyacrylonitrile powder to prepare white coating slips for paper. Preferred optical brighteners are those typically used to provide a high lightfastness on textiles, for example of the triazolylcoumarin or benzoxazole type. Papers prepared using such coating slips show excellent whitening effects with high lightfastness. There is no suggestion however that this approach could be used to prepare optically brightened papers by a more economic pulp application.

[0006] The economic use of textile brighteners to prepare optically brightened papers is therefore a difficult problem to which a satisfactory solution has not yet been found.

[0007] Surprisingly, it has now been found that by treating a pulp suspension with a filler composition comprising finely divided optically brightened plastic fibres, an optically brightened paper of high lightfastness is obtained in an economic manner.

[0008] Therefore an object of the instant invention is a process for optical brightening of paper wherein a filler composition comprising optically brightened plastic fibres is added to the pulp suspension.

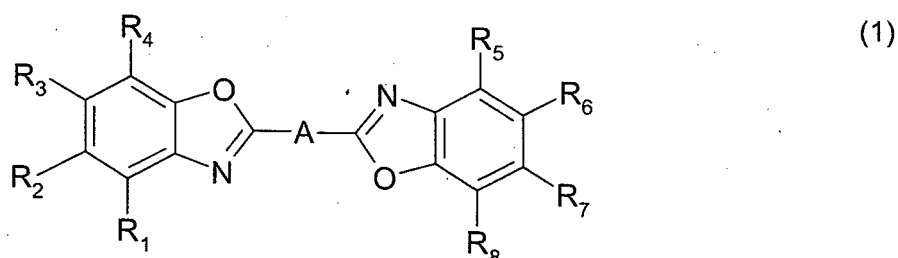
[0009] Said fibres preferably can be made from polyester, polyethylene, polypropylene or polyamide. Most preferably the fibres are made from polyester.

[0010] The fibres have a fineness between 1 and 10 dtex and are cut to a length of between 0.1 and 1 mm, preferably they have a fineness between 1 and 2 dtex and a length between 0.2 and 0.6mm.

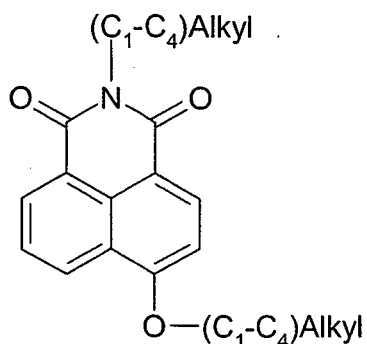
[0011] The preparation of polyester fibres is well-known and is described, for example, in "Handbook of Fiber Chemistry" by Menachem Lewin published in 1998 by Marcel Dekker, page 18.

[0012] The production of optically brightened polyester is equally well-known and is described, for example, in GB 835,898 and EP-A-1 379 585.

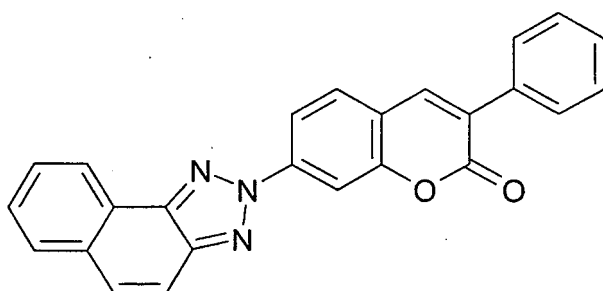
[0013] For the purpose of the present invention, the fibres are preferably optically brightened with compounds of formulae (1) to (4)



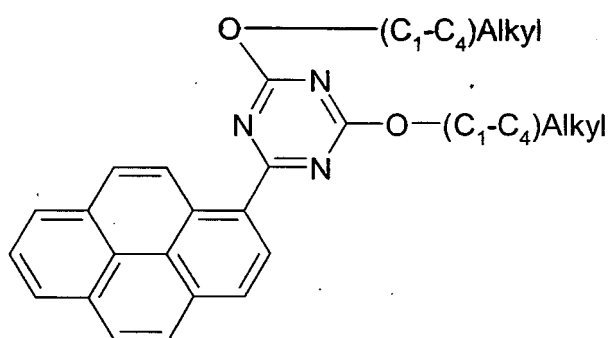
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(4)



where in formula (1)

45 R_1 to R_8 independently of one another are hydrogen, C_1 - C_{20} -alkyl or groups of the formula $-COOR_9$, where R_9 is hydrogen, C_1 - C_{20} -alkyl or phenyl, or R_1 to R_8 are a group of the formula $-SO_2R_{10}$, where R_{10} is hydrogen, C_1 - C_{10} -alkyl or C_1 - C_{10} -hydroxyalkyl, and A is stilbene, naphthalene, phenylene, thiophenylene or biphenylene, or mixtures of said compounds.

50 **[0014]** More preferred optical brighteners are compounds of formula (1) where R_1 to R_8 independently of one another are hydrogen or C_1 - C_4 -alkyl, and A is stilbene, naphthalene, phenylene, thiophenylene or biphenylene.

[0015] Most preferred optical brighteners are compounds of formula (1) where R_1 to R_8 independently of one another are hydrogen or methyl, and A is stilbene.

[0016] The optically brightened plastic fibre contains between 10 and 500 ppm optical brightener, preferably between 20 and 250 ppm.

55 **[0017]** The pulp may be any conventional pulp used to produce paper, for example stone groundwood pulp, thermo-mechanical pulp, chemithermomechanical pulp, semichemical pulp, sulphite pulp or kraft pulp, or a mixture of these.

[0018] In general the pulp suspension is treated with 2 to 60%, preferably 10 to 40% by weight, based on weight of dry pulp, of the instant filler composition.

[0019] The filler composition may be added to the pulp suspension either in dry form or, preferably, in the form of an aqueous dispersion. It may be useful to add a dispersing agent, particularly suitable dispersing agents being of the type described in EP-A-964 015. Finally, the paper is formed on a wire screen of a conventional paper machine, pressed and dried.

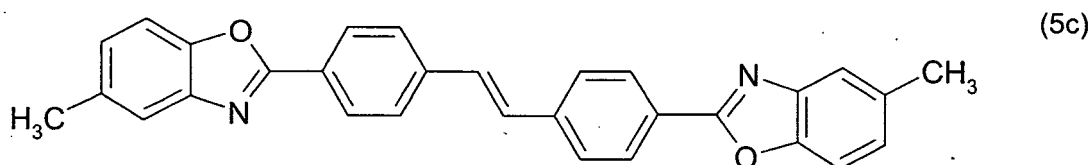
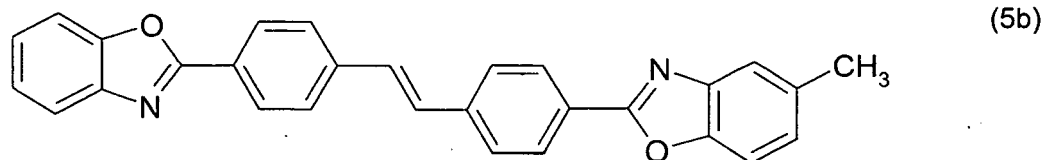
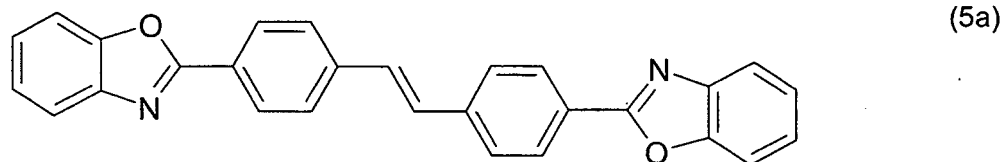
[0020] The present invention also provides an optically brightened paper produced according to the instant process and which comprises 2 to 60%, preferably 10 to 40% by weight, based on weight of dry pulp, of the filler composition of the instant invention.

[0021] The optically brightened paper may also contain other additives commonly employed in the papermaking industry. Examples of such additives include sizing agents (for example, rosin, starch, alkyl ketene dimer, alkenyl succinic anhydride), wet strength resins (for example, poly-aminoamide-epichlorohydrin resins), retention- and drainage aids (for example, poly-aluminium chloride, polydiallyldimethylammonium chloride), and shading dyes.

[0022] The following example further serves to illustrate the invention. All parts and all percentages are by weight, unless indicated to the contrary.

EXAMPLE

[0023] 5 parts polyester fibres of fineness 1.7 dtex made by known methods, containing 0.014% of a mixture of optical brighteners of structures 5a-c in an approximate ratio of 30:50:20, and cut to 0.5 mm, are stirred with 0.025 parts dispersing agent (Cartaspers® PSM, commercially available from Clariant) and 1000 parts water for 5 minutes to form a 0.5% dispersion of optically brightened fibres.



[0024] x parts of the 0.5% dispersion of optically brightened fibres are then added to (1000-x) parts of a stirred 0.5% aqueous suspension of a 50:50 mixture of bleached birch and spruce wood pulps beaten to a Schopper-Riegler freeness of 35°. A paper sheet is then made by drawing the dispersed suspension through a wire mesh. After being pressed and dried, the optically brightened paper contains between 5% (x = 50) and 30% (x = 300) optically brightened polyester fibres, equivalent to an optical brightener content of between 7 ppm and 42 ppm.

[0025] Each paper sheet is measured for R457 Brightness on a calibrated Minolta 3270D spectrophotometer.

[0026] Accelerated ageing experiments are conducted by exposing the papers in a Xenotest apparatus. R457 Brightness measurements are made at intervals of 70, 140 and 280 hours. The results are shown below in tabular (Table 1) and graphical (Fig 1) forms.

TABLE 1

% Brightened fibres in paper	R457 Brightness before exposure	R457 Brightness after 70h	R457 Brightness after 140h	R457 Brightness after 280h
0	82.6	83.6	84.3	85.9
5	84.0	85.0	85.3	86.3
10	86.1	86.6	86.6	88.0
15	88.0	88.6	88.6	89.3
20	89.0	89.5	89.3	90.1
25	91.0	91.6	91.3	91.7
30	91.4	92.0	91.8	92.3

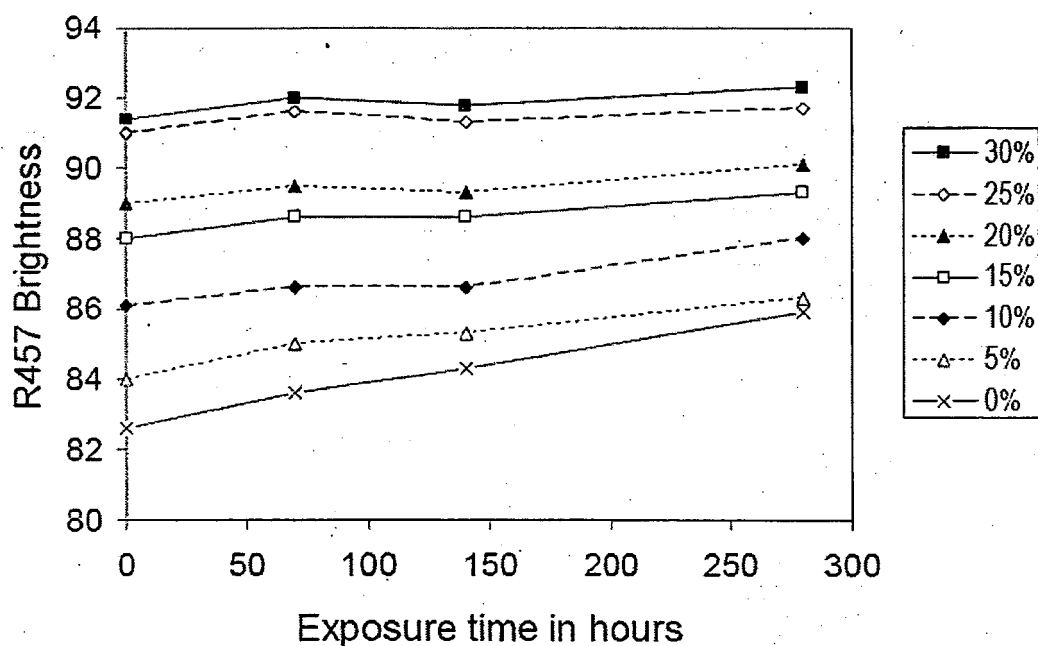


Fig 1: Effect of exposure to light over 280 hours on R457 Brightness of papers containing 5-30% optically brightened polyester fibres.

[0027] It is clear from the results that the present invention provides an optically brightened paper of high lightfastness, with the additional advantage that a surprisingly low concentration (7-42 ppm) of optical brightener is required to achieve a high degree of brightness.

COMPARATIVE EXAMPLES

Comparative Example 1: Brightened polyester fibres

[0028] A paper sheet is made as in the Example, containing 25% (x = 250) optically brightened polyester fibres.

Comparative Example 2: Unbrightened pulp

[0029] A paper sheet is made as in the Example, but without the addition of optically brightened polyester fibres.

Comparative Example 3: Unbrightened polyester fibres

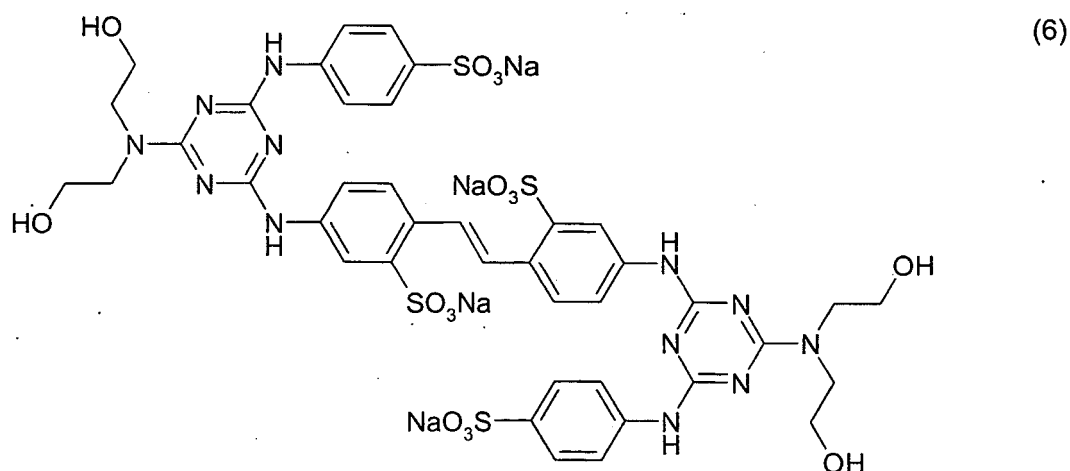
[0030] A paper sheet is made as in the Example, but containing 25% (x = 250) unbrightened polyester fibres in place of the optically brightened polyester fibres.

Comparative Example 4: Unbrightened polyester fibres and optical brightener (5a-c)

[0031] A paper sheet is made as in the Example, but containing 25% (x = 250) unbrightened polyester fibres and - added separately to the 1000 parts of 0.5% aqueous suspension of fibres - 0.000175 parts of a mixture of optical brighteners of structures (5a-c) in an approximate ratio of 30:50:20, all in place of the optically brightened polyester fibres.

Comparative Example 5: Unbrightened polyester fibres and optical brightener (6)

[0032]



[0033] A paper sheet is made as in the Example, but containing 25% (x = 250) unbrightened polyester fibres and - added separately to the 1000 parts of 0.5% aqueous suspension of fibres - 0.004 parts of an optical brightener of structure (6), all in place of the optically brightened polyester fibres.

[0034] Accelerated ageing experiments are conducted as in the Example. The results are shown below in tabular (Table 2) and graphical (Fig 2) forms.

TABLE 2

Comparative Example	R457 Brightness before exposure	R457 Brightness after 70h	R457 Brightness after 140h	R457 Brightness after 280h
1	92.1	93.0	92.9	92.7
2	83.8	85.6	86.5	87.5
3	85.3	87.0	87.7	88.5
4	85.5	87.1	87.8	88.4
5	97.5	90.5	88.7	87.5

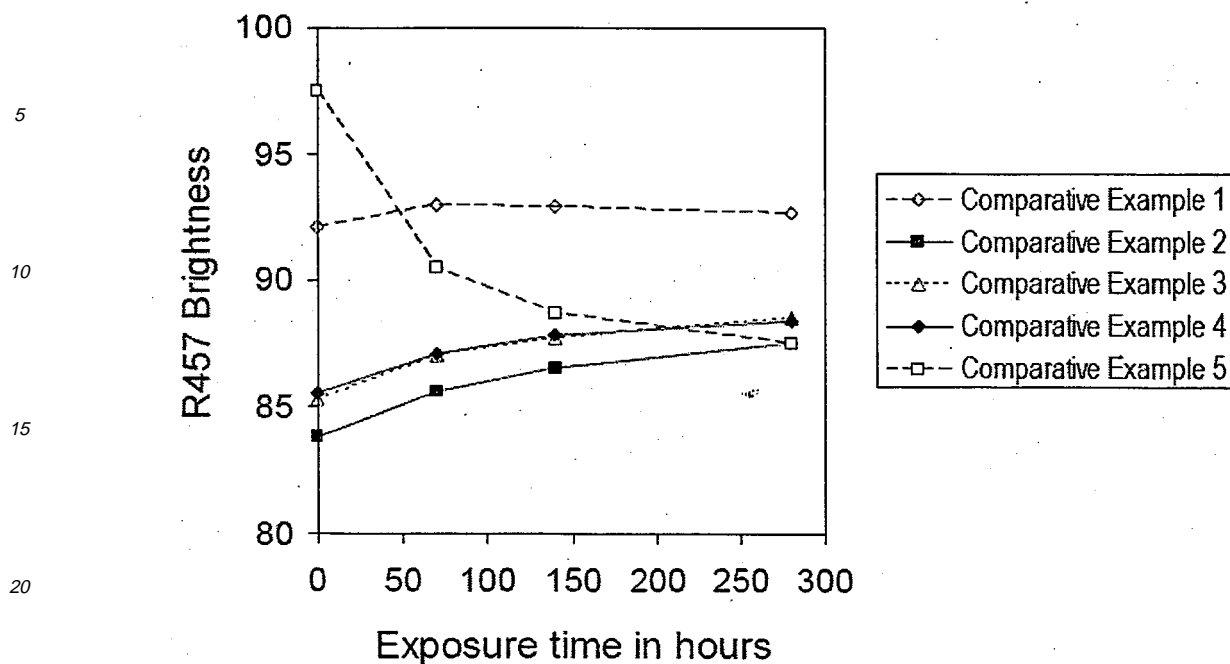


Fig 2: Effect of exposure to light over 280 hours on R457 Brightness of papers.

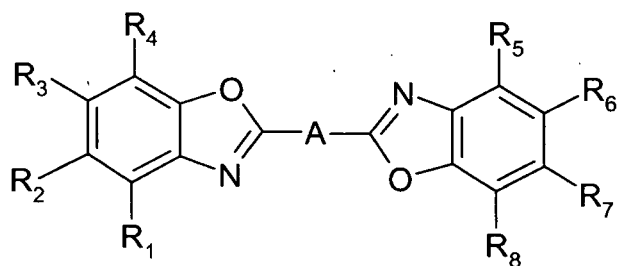
[0035] The Comparative Examples demonstrate the advantage of the invention in providing a bright paper with excellent lightfastness.

[0036] It is clear that the addition of optically brightened polyester fibres (Comparative Example 1) gives a much brighter paper than does the addition of unbrightened polyester fibres (Comparative Example 3). It is equally clear that the optical brightener must be incorporated into the polyester fibre, rather than added separately (Comparative Example 4). Whereas the separate addition of an optical brightener (6) of the triazinylaminostilbene type gives a particularly bright paper, the lightfastness of said paper is poor (Comparative Example 5).

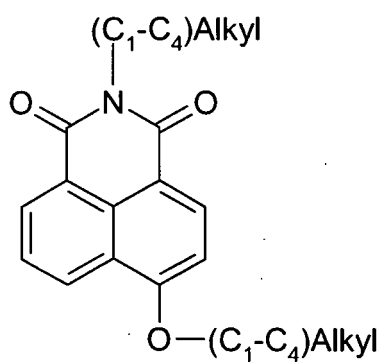
Claims

1. Process for optical brightening of paper wherein a filler composition comprising optically brightened plastic fibres is added to the pulp suspension.
2. Process according to claim 1 wherein the fibres are made from polyester, polyethylene, polypropylene or polyamide.
3. Process according to claim 2 wherein the fibres are made from polyester.
4. Process according to claim 3 wherein the fibres have a fineness between 1 and 10 dtex and are cut to a length of between 0.1 and 1 mm.
5. Process according to claim 4 wherein the fibres have a fineness between 1 and 2 dtex and are cut to a length of between 0.2 and 0.6 mm.
6. Process according to any of the preceding claims wherein the fibres are optically brightened with compounds of formulae (1) to (4)

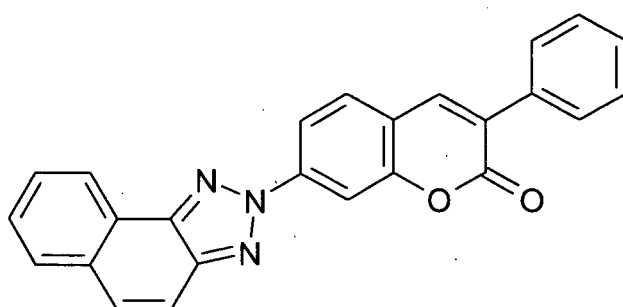
(1)



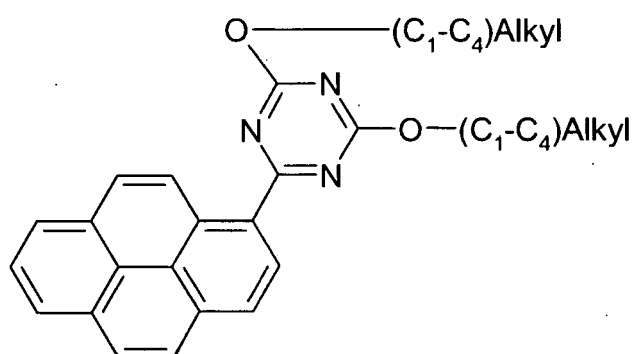
(2)



(3)



(4)



and where in formula (1)

R_1 to R_8 independently of one another are hydrogen, C_1-C_{20} -alkyl or groups of the formula $-COOR_9$,

R₉ is hydrogen, C₁-C₂₀-alkyl or phenyl, or
R₁ to R₈ are a group of the formula -SO₂R₁₀, where
R₁₀ is hydrogen, C₁-C₁₀-alkyl or C₁-C₁₀-hydroxyalkyl, and
A is stilbene, naphthalene, phenylene, thiophenylene or biphenylene,

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or mixtures of said compounds.

7. Process according to claim 6 wherein the fibres are optically brightened with a compound of formula (1) wherein

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R₁ to R₈ independently of one another are hydrogen or C₁-C₄-alkyl, and
A is stilbene, naphthalene, phenylene, thiophenylene or biphenylene.

8. Process according to claim 7 wherein

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R₁ to R₈ independently of one another are hydrogen or methyl, and
A is stilbene.

9. Process according to any of claims 2 to 8 wherein the optically brightened plastic fibres contain between 10 and 500 ppm optical brightener.

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10. Process according to claim 9 wherein the optically brightened plastic fibres contain between 20 and 250 ppm optical brightener.

11. Process according to any of the preceding claims wherein 2 to 60 % by weight, based on the weight of the dry pulp, of the optically brightened filler composition is added to the pulp suspension.

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12. Process according to claim 11 wherein 10 to 40 % by weight, based on the weight of the dry pulp, of the optically brightened filler composition is added to the pulp suspension.

13. Process according to claims 11 or 12 wherein the optically brightened filler composition is added to the pulp suspension in the form of an aqueous dispersion.

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14. Optically brightened paper produced by a process according to any of the preceding claims.

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Patentansprüche

1. Verfahren zum optischen Aufhellen von Papier, bei dem man der Stoffsuspension eine optisch aufgehellte Kunststoffasern enthaltende Füllstoffzusammensetzung zusetzt.

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2. Verfahren nach Anspruch 1, bei dem es sich bei den Kunststoffasern um Polyester, Polyethylen, Polypropylen oder Polyamid handelt.

3. Verfahren nach Anspruch 2, bei dem es sich bei den Kunststoffasern um Polyester handelt.

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4. Verfahren nach Anspruch 3, bei dem die Kunststoffasern einen Titer zwischen 1 und 10 dtex und eine Schnittlänge zwischen 0,1 und 1 mm aufweisen.

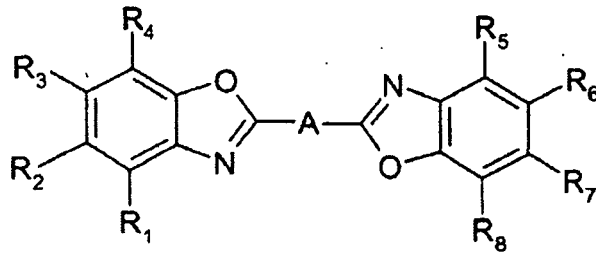
5. Verfahren nach Anspruch 4, bei dem die Kunststoffasern einen Titer zwischen 1 und 2 dtex und eine Schnittlänge zwischen 0,2 und 0,6 mm aufweisen.

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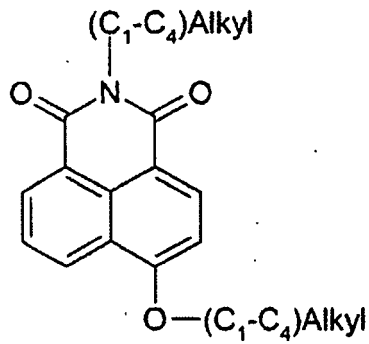
6. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Kunststoffasern mit Verbindungen der Formeln (1) bis (4)

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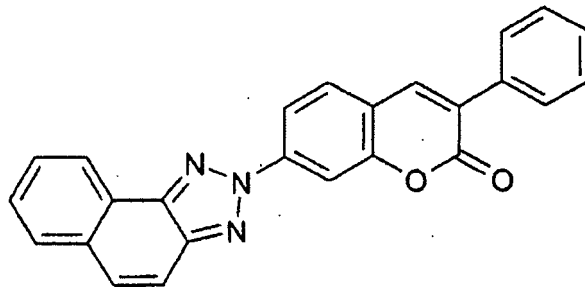
(1)



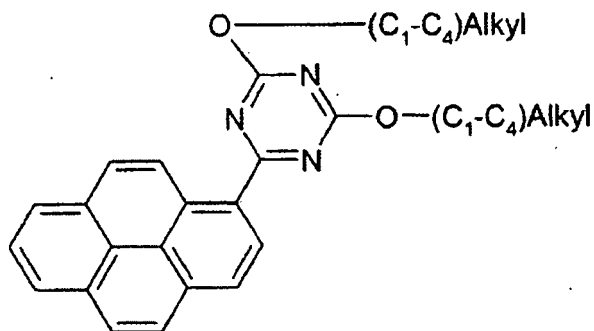
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wobei in Formel (1)

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R₁ bis R₈ unabhängig voneinander für Wasserstoff, C₁-C₂₀-Alkyl oder Gruppen der Formel -COOR₉,
 R₉ für Wasserstoff, C₁-C₂₀-Alkyl oder Phenyl stehen oder
 R₁ bis R₈ für eine Gruppe der Formel -SO₂R₁₀ stehen, wobei R₁₀ Wasserstoff, C₁-C₁₀-Alkyl oder C₁-C₁₀-Hy-
 droxyalkyl bedeutet, und

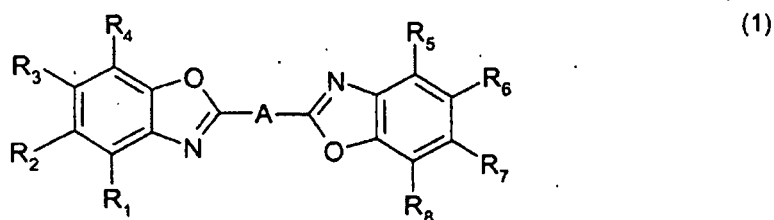
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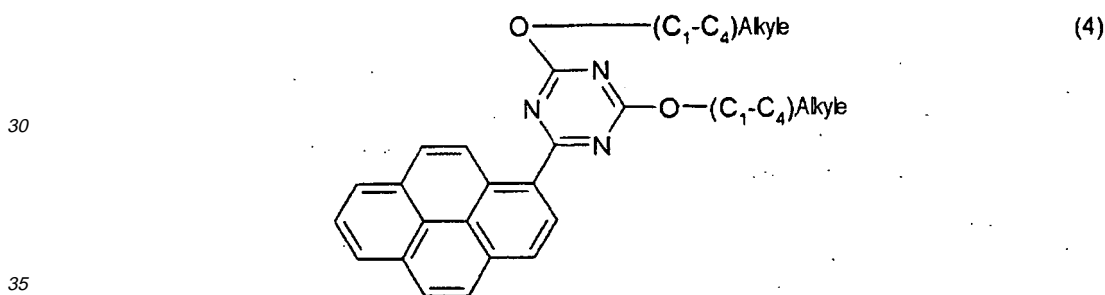
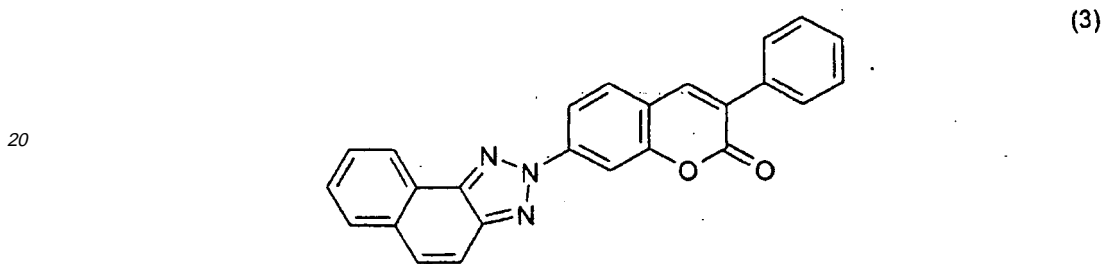
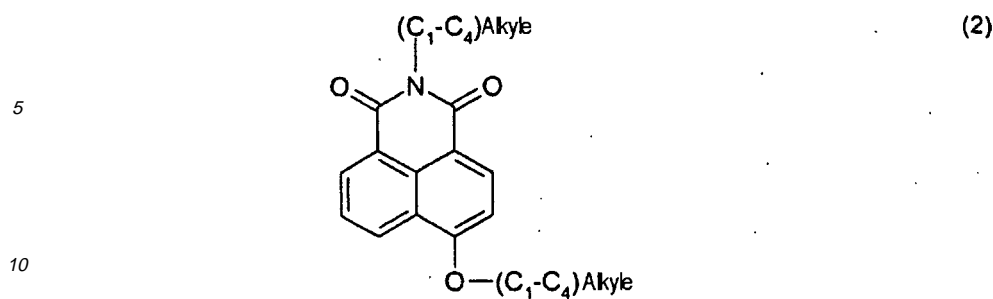
A für Stilben, Naphthalin, Phenylen, Thiophenylen oder Biphenylen steht, oder Mischungen der genannten Verbindungen optisch aufgehellt sind.

- 5 7. Verfahren nach Anspruch 6, bei dem die Kunststoffasern mit einer Verbindung der Formel (1) optisch aufgehellt sind, bei der
R₁ bis R₈ unabhängig voneinander für Wasserstoff oder C₁-C₄-Alkyl und
A für Stilben, Naphthalin, Phenylen, Thiophenylen oder Biphenylen stehen.
- 10 8. Verfahren nach Anspruch 7, bei dem
R₁ bis R₈ unabhängig voneinander für Wasserstoff oder Methyl und
A für Stilben stehen.
- 15 9. Verfahren nach einem der Ansprüche 2 bis 8, bei dem die optisch aufgehellten Kunststoffasern zwischen 10 und 500 ppm an optischem Aufheller enthalten.
- 20 10. Verfahren nach Anspruch 9, bei dem die optisch aufgehellten Kunststoffasern zwischen 20 und 250 ppm an optischem Aufheller enthalten.
- 25 11. Verfahren nach einem der vorhergehenden Ansprüche, bei dem man der Stoffszusammensetzung bezogen auf das Gewicht des Trockenstoffs 2 bis 60 Gew.-% der optisch aufgehellten Füllstoffzusammensetzung zusetzt.
- 30 12. Verfahren nach Anspruch 11, bei dem man der Stoffszusammensetzung bezogen auf das Gewicht des Trockenstoffs 10 bis 40 Gew.-% der optisch aufgehellten Füllstoffzusammensetzung zusetzt.
- 35 13. Verfahren nach Anspruch 11 oder 12, bei dem man die optisch aufgehellte Füllstoffzusammensetzung der Stoffszusammensetzung in Form einer wässrigen Dispersion zusetzt.
- 40 14. Optisch aufgehelltes Papier, hergestellt nach einem Verfahren gemäss einem der vorhergehenden Ansprüche.

Revendications

- 45 1. Procédé pour l'azurage optique de papier, dans lequel une composition de charge comprenant des fibres plastiques optiquement azurées est ajoutée à la suspension de pâte à papier.
- 50 2. Procédé selon la revendication 1, dans lequel les fibres sont composées de polyester, de polyéthylène, de polypropylène ou de polyamide.
- 55 3. Procédé selon la revendication 2, dans lequel les fibres sont composées de polyester.
- 60 4. Procédé selon la revendication 3, dans lequel les fibres présentent une finesse comprise entre 1 et 10 dtex et sont découpées à une longueur comprise entre 0,1 et 1 mm.
- 65 5. Procédé selon la revendication 4, dans lequel les fibres présentent une finesse comprise entre 1 et 2 dtex et sont découpées à une longueur comprise entre 0,2 et 0,6 mm.
- 70 6. Procédé selon l'une quelconque des revendications précédentes, dans lequel les fibres sont optiquement azurées avec des composés de formules (1) à (4).





et où dans la formule (1)

R_1 à R_8 sont, indépendamment les uns des autres, un atome d'hydrogène, un groupe alkyle en C_1-C_{20} ou des groupes de formule $-COOR_9$,

R_9 est un atome d'hydrogène, un groupe alkyle en C_1-C_{20} ou un groupe phényle, ou

R_1 à R_8 sont un groupe de formule $-SO_2R_{10}$, dans laquelle

R_{10} est un atome d'hydrogène, un groupe alkyle en C_1-C_{10} ou un groupe hydroxyalkyle en C_1-C_{10} , et

A est un groupe stilbène, un groupe naphthalène, un groupe phénylène, un groupe thiophénylène ou un groupe biphénylène, ou des mélanges desdits composés.

7. Procédé selon la revendication 6, dans lequel les fibres sont optiquement azurées avec un composé de formule (1), dans laquelle

R_1 à R_8 sont, indépendamment les uns des autres, un atome d'hydrogène ou un groupe alkyle en C_1-C_4 , et

A est un groupe stilbène, un groupe naphthalène, un groupe phénylène, un groupe thiophénylène ou un groupe biphénylène.

8. Procédé selon la revendication 7, dans lequel

R_1 à R_8 sont, indépendamment les uns des autres, un atome d'hydrogène ou un groupe méthyle, et

A est un groupe stilbène.

9. Procédé selon l'une quelconque des revendications 2 à 8, dans lequel les fibres plastiques optiquement azurées contiennent entre 10 et 500 ppm d'azurant optique.

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10. Procédé selon la revendication 9, dans lequel les fibres plastiques optiquement azurées contiennent entre 20 et 250 ppm d'azurant optique.

5 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel de 2 à 60 % en poids, par rapport au poids de la pâte à papier sèche, de la composition de charge optiquement azurée sont ajoutés à la suspension de pâte à papier.

10 12. Procédé selon la revendication 11, dans lequel de 10 à 40 % en poids, par rapport au poids de la pâte à papier sèche, de la composition de charge optiquement azurée sont ajoutés à la suspension de pâte à papier.

13. Procédé selon les revendications 11 ou 12, dans lequel la composition de charge optiquement azurée est ajoutée à la suspension de pâte à papier sous la forme d'une dispersion aqueuse.

15 14. Papier optiquement azuré produit par un procédé selon l'une quelconque des revendications précédentes.

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REFERENCES CITED IN THE DESCRIPTION

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