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(54) **Coated paper product and the method for producing the same**

(57) The present invention relates to a coated paper product and the method for producing the same. High levels of an organic pigment, an inorganic pigment, relatively high levels of a binder, as well as, water are combined to form a coating composition which is applied to a low weight paper web. Then, the coated paper web is

dried and calendered at relatively low calender intensity. A high bulk low weight or ultra-low weight coated paper product results which exhibits optical and printing properties comparable to its heavier counterparts.

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## Description

**[0001]** The present invention relates to a coated paper product that allows a coated light weight, inexpensive paper product to perform favorably when compared to a heavier coated paper product while maintaining the optical, tactile, and printing properties of the heavier coated paper product. Furthermore, this invention relates to the method for producing the same coated paper product.

**[0002]** A method for preparing a coated paper product having improved properties while maintaining high bulk, as disclosed in U.S. Patent No. 6,531,183, involves applying on a surface of a base stock at least one layer of a coating composition comprising a particulate plastic pigment; and, passing the base stock through a multi-nip calender device maintained at relatively low roll temperature and nip pressure. Additionally, U.S. Patent No. 6,387,213, discloses a printing paper having the appearance of uncoated paper and improved printability properties approaching those of coated papers which result from the application of 5-25 lbs. of coating per side, per ream of paper.

**[0003]** The problem addressed by the present invention is achieving good bulk and optical and printing properties while reducing the coat weight and moderating the calendering conditions in a relatively inexpensive ground-wood containing paper.

**[0004]** An aspect of this invention is a coated paper product comprising:

a 16 to 36 lbs per ream uncoated paper web comprising ground wood-containing pulp;  
wherein the paper web is coated on both sides with an aqueous coating composition comprising:

0 to 45 parts inorganic pigment per 100 parts of total pigment on a dry basis,  
55 to 100 parts void-containing polymeric pigment particles per 100 parts of total pigment on a dry basis wherein said void containing particles have a diameter from 0.2 to 5  $\mu\text{m}$  and a void volume of 20 — 80%,  
10 to 50 parts of starch-based or protein-based polymeric binder per 100 parts of total pigment on a dry basis,  
wherein

the dried and calendered coated paper product has 1 to 3 lbs per ream per side of the dried coating composition and has a weight of 18 to 40 lbs per ream, an opacity of not greater than about 90, a gloss from 40 to 85, and a brightness from 70 to 83. As used herein, one ream is equivalent to 3300 ft<sup>2</sup>.

**[0005]** Another aspect of this invention is a method for producing a coated paper product comprising the steps of:

coating a ground wood containing paper web having an uncoated weight of 16 to 36 pounds per ream on at least one side of the ground wood containing paper web with a coating composition comprising:

0 to 45 parts inorganic pigment per 100 parts of total pigment on a dry basis,  
55 to 100 parts void-containing polymeric pigment particles per 100 parts of total pigment on a dry basis wherein said void containing particles have a diameter from 0.2 to about 5  $\mu\text{m}$  and a void volume of 20 — 80%,  
10 to 50 parts of starch-based or protein-based polymeric binder per 100 parts of total pigment on a dry basis, and  
water in an amount greater than 60% of the total aqueous composition,

drying the coating composition on the paper product such that 1 to 3 lbs per ream per side of the dried coating composition remains on the dried coated paper product providing a dried coated paper product having a weight of 18 to 40 lbs per ream, an opacity of not greater than about 90, a gloss from 40 to 85, and a brightness from 70 to 83, and;  
passing the dried coated paper product through a calender device, wherein the calender device comprises at least two rolls and at least one nip.

**[0006]** The combination of 55 to 100 parts of voided polymeric particles per total pigment particles on a dry basis, and 10 to 50 parts of starch-based and/or protein-based binder per volume of total pigment particles on a dry basis combined with the aforementioned calender conditions enables the use of a lower coat weight; and, it enables the manufacture of lightweight and ultra light weight papers which use a greater fiber to coat ratio than is typically used in coated papers. Preferable coated paper product weight ranges from 24-34 lbs per ream.

**[0007]** Additionally, the combination of 55 to 100 part of voided polymeric particles per total pigment particles on a dry basis, and 10 to 50 parts of starch-based and/or protein-based binder per volume of total pigment particles on a dry basis combined with the aforementioned calender conditions provides for a strong paper at a given weight, which in turn provides for better runnability/ productivity on the paper machine, as well as, in subsequent printing operations than heavier counterparts. Less compression of the lighter coated paper than conventional heavier paper and retention of bulk and stiffness are some of the additional attributes achieved by using this combination. Furthermore, the optical,

tactile, and printing properties of the coated paper product may be maintained at a level comparable to coated paper products having a higher initial base weight.

**[0008]** Following the application of this coating composition in the amount specified, gloss (measured according to TAPPI 75° test procedure), opacity (measured according to TAPPI test procedure T425-OM-91), and brightness (measured according to TAPPI test procedure T452-OM-92) were calculated. A coated paper product with comparable properties to a paper coated with no voided polymeric pigment and at least double the coat weight resulted. Preferable ranges for opacity and gloss are 85-90 and 50-55 respectively.

**[0009]** In the coating of the present invention, there are included voided polymeric pigment particles, hereinafter particles, with a particle size ranging from approximately 0.2 to 5.0 microns, preferably 0.3 to 2.0 microns and void volumes ranging from approximately 20 to 80%, preferably 40-70%. These particles have a density in the range of 0.4 - 1.0g/cc, preferably 0.4 - 0.6 g/cc. Additionally, these particles include a single hollow core or void, or multiple voids within each particle; the voids may be spherical or irregular in shape and the voided areas may be isolated or connected. These particles may have an appearance of being sponge-like. The surface of these particles may range from smooth and unbroken to rough and perforated. Such particles are disclosed in, for example, the following patents: US 4,427,836; US 5,036,109; US 5,157,084; US 5,216,044; US 5,409,776; US 5,494,971; US 5,521,253; US 5,527,613; US 5,989,630; US 6,020,435; US 6,139,961; and US 6,673,451. Additionally, these particles may be cross-linked and charged; examples of cross-linked charged particles are disclosed in US 6,624,272.

**[0010]** Other polymeric pigment particles, including but not limited to, solid polystyrene bead particles such as DOW711 and DOW722, both made by Dow Chemical Company (Midland, Mich.); solid polymethylmethacrylate bead particles; polymer particles with a morphology (particles comprising at least one polymer core phase containing at least one void, at least one polymer shell phase at least partially surrounding the core, and at least one channel connecting the void in the core to the exterior of the particle) and composition defined in U.S. Pat. No. 5,510,422 and European Published Patent Application No. 0 842 992 A2; and any polymer particles with a glass transition temperature greater than 40° C may be used in the present invention.

**[0011]** Furthermore, mineral pigments may also be included in the present invention. Suitable mineral pigments include but are not limited to ground and precipitated calcium carbonate, kaolin, calcined kaolin, delaminated and structured kaolin clay, titanium dioxide, aluminum silicate, magnesium silicate, magnesium carbonate, amorphous silica, zinc oxide, zinc hydroxide, aluminum oxide, aluminum hydroxide, talc, satin white, barium sulfate and calcium silicate.

**[0012]** Suitable starch-based and protein-based polymeric binders of the present invention include but are not limited to, caseins, starch and wheat flours, gelatin and alginates, cellulose, hydroxyethylcellulose, methylcellulose, and carboxymethylcellulose as modified natural products, dextrans, ethylated starch (including ethylated corn starch), lignin, and the like. Starches which are obtainable by reacting natural, cationic, anionic and/or amphoteric starch with synthetic cationic polymers are used as dry strength agents. The natural starches used may be, for example, corn starch, potato starch, wheat starch, rice starch, tapioca starch, sago starch, sorghum starch, cassava starch, pea starch, rye starch or mixtures of the stated natural starches. Other suitable starches are ryemeal and other meals. Protein-containing starches from rye, wheat and leguminous plants are also suitable. Those natural starches which have an amylopectin content of at least 95% by weight are also suitable for the cationic modification with polymers. Starches containing at least 99% by weight of amylopectin are preferred. Such starches can be obtained, for example, by starch fractionation of conventional natural starches or by cultivation measures from plants which produce virtually pure amylopectin starch. Starches having an amylopectin content of at least 95, preferably at least 99%, by weight, are commercially available. They are offered, for example, as waxy corn starch, waxy potato starch or waxy wheat starch. The natural starches can be modified either alone or as a mixture with cationic polymers.

**[0013]** Synthetic polymeric binders are included within the present invention from about 0 to 25 parts of synthetic binder per 100 parts of total pigment on a dry basis, preferably 5 to 25 parts of synthetic binder per 100 parts of total pigment on a dry basis. Suitable synthetic polymeric binders of the present invention include but are not limited to, homopolymers, copolymers or terpolymers such as acrylic and/or methacrylic polymers, polyvinyl acetate, polyvinyl alcohol, styrene-acrylic copolymers, styrene-butadiene copolymers, vinyl acetate-acrylic copolymers, ethylene-vinyl acetate copolymers, vinyl acetate-vinyl versatate copolymers, vinyl acetate-vinyl maleate copolymers, vinyl acetate-vinyl chloride-acrylic terpolymers, ethylene-vinyl acetate-acrylic terpolymers, polyurethane, polyvinyl butyral, structural acrylic polymers, anaerobic, cyanoacrylate polymers, polyvinyl chloride, polyvinylidene chloride, polyethylene, ethylene-vinyl acetate copolymers, polypropylene, ethylene/acrylic acid copolymer, ethylene/methyl acrylate copolymers, irradiated polyethylene, polyamide, polyester, epoxy, phenolic, amino, furan, polyimides, natural rubber, styrene copolymers and terpolymers, non-block, styrenic block copolymers, neoprene, nitrile rubber, butylene, polybutene, ethylene-propylene-diene rubbers, rubber silicone, and animal glue. The polymers or prepolymers may optionally contain up to about 10% by weight of a functional monomer, for example, but not limited to, carboxylic acid, phosphate, sulfate, sulfonate, and amide monomers and combinations thereof, non-functional monomers, and mixtures thereof. The polymeric binders are preferably water-borne latex polymers.

**[0014]** In a preferred embodiment, the synthetic polymeric binders include styrene-acrylate, styrene-butadiene, sty-

rene-butadiene-acrylonitrile, vinyl-acetate, and vinyl-acrylate.

**[0015]** The coating of the present invention contains water in an amount greater than 60% of the total weight of the coating composition. Amounts of water less than 60% may achieve comparable results.

**[0016]** The coating of the present invention may additionally include minor amounts, *i.e.*, less than about 20% by weight, based on the total weight of the coating composition of conventional adhesive additives such as crosslinkers, slip agents, thickeners, bases, optical brighteners, defoamers, dispersing resins, mildewcides, biocides, opacifying pigments, extender pigments, and colorants. These optional ingredients may be added separately or added to the premixes.

**[0017]** The method of the current invention involves coating the base stock by applying the aforementioned coating with a coater and then subsequently drying the coated paper such that 1 to 3 lbs per ream per side, preferably 1.0- 2.5 lbs per ream per side of the dried coating composition remains on the coated paper product.

**[0018]** Suitable coaters include but are not limited to short dwell, roller applicator, jet, metered size press, spray, curtain, and rod. In one embodiment the coater is a short dwell trailing blade coater having a blade of 0.457 mm/45°. In another embodiment the coater is a jet coater.

**[0019]** Suitable drying methods include, but are not limited to, infrared, air-flow, and air-caps or a combination thereof. In one embodiment the coated paper is dried using IR and hot-air dryers to a moisture target of 5%.

**[0020]** The coated paper is then calendered to produce the gloss and smoothness that is required for the final paper product. At constant temperature and pressure the calender intensity is lowered by reducing the number of nips, resulting in a bulkier sheet. Maintaining the number of rolls and nips while lowering the temperature and pressure has the same effect of producing a bulkier sheet. The coated paper web may be calendered on both sides by either two on-line soft nip calenders arranged in series or by using an offline multi-nip super-calender stack to achieve a target gloss of 50-55. Other suitable calenders include, but are not limited to, Jamis, Optiload, extended nip and Shoe used either on-line or off-line. The calendering devices of the present invention are comprised of a series of nips and rolls. The nips are present in quantity in a range of one to eleven. The rolls are present in a quantity in a range of two to twelve. The calendering conditions of the present invention are milder than those typically used for lightweight coated papers.

**[0021]** In one embodiment, the light weight coated paper product is calendered on both sides simultaneously by two on-line soft-nip calenders arranged in series to achieve a target gloss of 50-55. The soft nip calender rolls are heated to 70-200°C and a pressure load of 100-350 kN/m at each nip is applied to obtain the target gloss.

**[0022]** In another embodiment, the low weight coated paper product is calendered on an offline super-calender using at least 3 nips but no greater than 5 nips at a speed of 500m/min and a temperature from 50-150°C. No pressure is added other than the gravitational load of the rolls.

## Examples

**[0023]** In the following examples, the paper coatings were made and applied at a pilot coater facility. The base stock used in the examples was a ground wood containing paper with a basis weight of 24 lbs/3300 sq. ft. This base stock was coated on two sides (one side at a time) using a short-dwell (blade: 0.457mm/45°) coater at a coating speed of ca. 4000 ft/min. and dried using IR and hot-air dryers to a moisture target of 5%.

### Example 1

Experimental Details:

**[0024]** Example 1 was a control coated paper product having a coating that contains no voided polymeric pigment particles per total pigment volume. The coating was applied to the base stock, a 24 lb ground wood-containing base stock, using a short-dwell (blade coater) at a coating speed of 4000 ft/min, one side at a time, such that the coat weight, as measured by an in-line beta gauge, was 5.5 lbs/ream/side. During the coating operation on the second side, half of the paper web was passed through two in-line soft-nip calender rolls, each set maintained at 170 deg C with nip loads of 350 kN/m, such that a sheet gloss of about 52-53 resulted (measured by in-line gloss meter). At the end of this coating operation, the remaining coated, but uncalendered, half roll was passed through 5 nips of an off-line supercalender stack maintained at 80 deg C with an applied nip load of 150 PSI to obtain sheet gloss of about 51-52 (measured by in-line gloss meter). Soft-nip calendering results are displayed within the table.

### Examples 2-7

Experimental Details:

**[0025]** Examples 2-7 were paper products having a coating that contains between 55 and 100 parts of voided polymeric particles per total pigment volume. The coating was applied, as aforementioned, to the base stock using a short-dwell

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(blade coater) at a coating speed of 4000 ft/min, one side at a time, however, the coat weight of Examples 2-7, measured by an in-line beta gauge, was 2.0 lbs/ream/side. During the coating operation half of the paper web was passed through two in-line soft-nip calender rolls, each set maintained at 90 deg C with nip loads of 125 and 300 kN/m, such that a sheet gloss of about 50-65 was achieved (measured by in-line gloss meter). At the end of this coating operation, the remaining coated, but uncalendered, half roll passed through 3 nips of an off-line supercalender stack maintained at 60 deg C with no applied nip loads (other than the gravitational weight of calender stack) to obtain a sheet gloss from about 50-65 (measured by in-line gloss meter). Soft-Nip calendering results are displayed within the table in examples 2-4, 6, and 7. Supercalendering results are displayed in Example 5.

| Example→<br>Composition↓                                                                                                                                                | 1    | 2    | 3    | 4     | 5    | 6    | 7    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|------|-------|------|------|------|
| Eng. Clay (Contour 100)                                                                                                                                                 | 87   | 45   |      |       |      |      |      |
| # 2 Coating Clay                                                                                                                                                        |      |      | 25   | 25    |      | 25   |      |
| Calcined Clay (Alphatex)                                                                                                                                                | 10   |      |      |       |      |      |      |
| Delam. Clay                                                                                                                                                             |      |      |      |       | 25   |      |      |
| TiO <sub>2</sub>                                                                                                                                                        | 3    |      |      |       |      |      |      |
| Hollow plastic pigment (AF-1055)                                                                                                                                        |      | 55   | 75   |       | 75   | 75   | 100  |
| Hollow plastic pigment (AF-1353)                                                                                                                                        |      |      |      | 75    |      |      |      |
| Starch (PG 280/270)                                                                                                                                                     | 7    | 17.6 | 24   | 24    | 24   | 36   | 32   |
| Synthetic Latex Binder (GenFlo® 5128)                                                                                                                                   | 9    | 12.1 | 16.5 | 16.5  | 16.5 | 16.5 | 22   |
| Optical Brightner (Blancafor P)                                                                                                                                         | 1    |      | 1    | 1     | 1    | 1    |      |
| Crosslinker (Sequerez 755)                                                                                                                                              | 0.28 | 0.7  | 0.96 | 0.96  | 0.96 | 1.44 | 1.28 |
| Lubricant (Sunkote 455)                                                                                                                                                 | 1    | 1    | 1    | 1     | 1    | 1    | 1    |
| Total Target Coat Weight (lbs/3300 sq. ft.)                                                                                                                             | 11.0 | 4.0  | 4.0  | 4.0   | 4.0  | 4.0  | 3.5  |
| Total solids content (%)                                                                                                                                                | 58   | 38   | 33   | 31 34 | 34   | 33   | 29   |
| BF Viscosity (cP) 100rpm, 35 deg C; (Spindle # 4)                                                                                                                       | 1556 | 2400 | 1294 | 1680  | 1352 | 2516 | 2600 |
| <b>Applications data presented below is for soft-nip calendered samples (except for # 5 which was supercalendered). The opticals were measured from the rough-side.</b> |      |      |      |       |      |      |      |
| Total Measured Ct. wt. (lbs/3300ft <sup>2</sup> )                                                                                                                       | 11.8 | 5.0  | 4.0  | 4.2   | 4.7  | 4.4  | 4.1  |
| 75 deg Gloss                                                                                                                                                            | 51.5 | 55.2 | 55.6 | 65    | 48.9 | 50.7 | 55.6 |
| Opacity                                                                                                                                                                 | 90.7 | 88.3 | 89.5 | 89.4  | 90.2 | 88.9 | 89.3 |
| Brightness                                                                                                                                                              | 73.1 | 75.8 | 73.7 | 75.2  | 74.8 | 73.1 | 76.8 |
| Caliper (mils)                                                                                                                                                          | 2.0  | 2.2  | 2.1  | 2.2   | 2.2  | 2.0  | 2.3  |
| Smoothness (PPS)                                                                                                                                                        | 1.85 | 2.22 | 2.34 | 2.19  | 2.59 | 2.34 | 2.31 |
| Sheet Porosity (mL/min)                                                                                                                                                 | 2.1  | -    | 3.6  | 4.2   | 4.6  | 2.9  | -    |

## Claims

1. A coated paper product comprising:

a 16 to 36 lbs per ream uncoated paper web comprising ground wood-containing pulp;  
wherein the paper web is coated on both sides with an aqueous coating composition comprising:

0 to 45 parts inorganic pigment per 100 parts of total pigment on a dry basis,  
55 to 100 parts void-containing polymeric pigment particles per 100 parts of total pigment on a dry basis  
wherein said void containing particles have a diameter from 0.2 to 5 μm and a void volume of 20 — 80%,

10 to 50 parts of starch-based or protein-based polymeric binder per 100 parts of total pigment on a dry basis, wherein

the dried and calendered coated paper product has 1 to 3 lbs per ream per side of the dried coating composition and has a weight of 18 to 40 lbs per ream, an opacity of not greater than about 90, a gloss from 40 to 85, and a brightness from 70 to 83.

2. The coated paper product of claim 1 further comprising 5 to 25 parts of synthetic binder per 100 parts of total pigment on a dry basis.

3. The coated paper product of claim 2 wherein the void-containing pigment particles comprise a particle size of 0.3-2.0  $\mu\text{m}$ .

4. The coated paper product of claim 3 wherein said void-containing pigment particles comprise a void volume of 40-70%.

5. The coated paper product of claim 4 wherein the paper product has a weight of 24-34 lbs per ream after coating with the composition.

6. The coated paper product of claim 5 wherein the opacity is 85-90.

7. The coated paper product of claim 6 wherein the gloss is 50-55.

8. A method of producing a coated paper product comprising the steps of coating a ground wood containing paper web having an uncoated weight of 16 to 36 pounds per ream on at least one side of the ground wood containing paper web with a coating composition comprising:

0 to 45 parts inorganic pigment per 100 parts of total pigment on a dry basis,  
55 to 100 parts void-containing polymeric pigment particles per 100 parts of total pigment on a dry basis wherein said void containing particles have a diameter from 0.2 to about 5  $\mu\text{m}$  and a void volume of 20 — 80%,  
10 to 50 parts of starch-based or protein-based polymeric binder per 100 parts of total pigment on a dry basis, and  
water in an amount greater than 60% of the total aqueous composition,

drying the coating composition on the paper product such that 1 to 3 lbs per ream per side of the dried coating composition remains on the dried coated paper product providing a dried coated paper product having a weight of 18 to 40 lbs per ream, an opacity of not greater than about 90, a gloss from 40 to 85, and a brightness from 70 to 83, and;  
passing the dried coated paper product through a calender device, wherein the calender device comprises at least two rolls and at least one nip.

9. The method of claim 8, wherein the coating composition is applied with a short dwell coater at a weight of 1.0 pound per ream per side to 2.5 pounds per ream per side, based on the total dry weight of the coating composition.

10. The method of claim 8, wherein the coating composition is applied with a jet coater at a weight of 1.0 pound per ream per side to 2.5 pounds per ream per side, based on the total dry weight of the coating composition.

11. The method of claim 8 wherein the paper product is calendered by a soft-nip calender device comprising rolls which are arranged in series wherein the device is heated to 70-200°C.

12. The method of claim 8 wherein the paper product is calendered on an off-line super-calender device comprising about 3-5 nips wherein the device is heated to 50-150°C.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 05 25 5115

| DOCUMENTS CONSIDERED TO BE RELEVANT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                                                              |                                                    |                                         |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|-----------------------------------------|
| Category                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    | Citation of document with indication, where appropriate, of relevant passages                                                                                | Relevant to claim                                  | CLASSIFICATION OF THE APPLICATION (IPC) |
| D,X                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | US 6 531 183 B1 (CASON DAVID B ET AL)<br>11 March 2003 (2003-03-11)<br>* column 5, line 39 - column 6, line 27 *<br>* column 6, line 66 - column 7, line 5 * | 1,8                                                | D21H19/42                               |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | * the whole document *<br>-----                                                                                                                              | 2-7,9-12                                           |                                         |
| D,A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         | US 6 387 213 B1 (RUCH THOMAS D)<br>14 May 2002 (2002-05-14)<br>* abstract *                                                                                  | 1-12                                               |                                         |
| Y                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | GB 1 513 047 A (DEGUSSA)<br>7 June 1978 (1978-06-07)<br>* claim 1 *<br>-----                                                                                 | 2-7,9-12                                           |                                         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                              |                                                    | TECHNICAL FIELDS SEARCHED (IPC)         |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                              |                                                    | D21H                                    |
| The present search report has been drawn up for all claims                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |                                                                                                                                                              |                                                    |                                         |
| Place of search<br>Munich                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                                                              | Date of completion of the search<br>2 January 2006 | Examiner<br>Naeslund, P                 |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone<br/>Y : particularly relevant if combined with another document of the same category<br/>A : technological background<br/>O : non-written disclosure<br/>P : intermediate document</p> <p>T : theory or principle underlying the invention<br/>E : earlier patent document, but published on, or after the filing date<br/>D : document cited in the application<br/>L : document cited for other reasons<br/>.....<br/>&amp; : member of the same patent family, corresponding document</p> |                                                                                                                                                              |                                                    |                                         |

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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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  
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02-01-2006

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date      |
|-------------------------------------------|---------------------|----------------------------|--------------------------|
| US 6531183                                | B1                  | 11-03-2003                 | NONE                     |
| US 6387213                                | B1                  | 14-05-2002                 | NONE                     |
| GB 1513047                                | A                   | 07-06-1978                 | BE 834649 A1 20-04-1976  |
|                                           |                     |                            | DE 2449616 A1 22-04-1976 |
|                                           |                     |                            | FI 752622 A 19-04-1976   |
|                                           |                     |                            | FR 2288186 A1 14-05-1976 |
|                                           |                     |                            | IT 1047294 B 10-09-1980  |
|                                           |                     |                            | NL 7512151 A 21-04-1976  |