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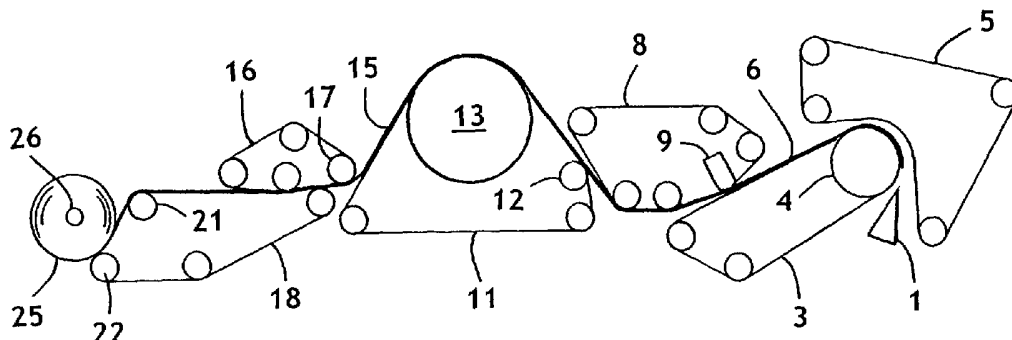
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[Continued on next page]

(54) Title: SOFT ABSORBENT TISSUE CONTAINING DERIVITIZED AMINO-FUNCTIONAL POLYSILOXANES



(57) Abstract: A tissue product having improved hand feel and good wettability is produced by printing onto one or both sides of the tissue an aqueous emulsion containing a derivitized amino-functional polysiloxane. The derivitized amino-functional polysiloxane structure has one or more pendant groups containing an amine derivative.



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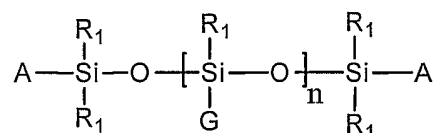
SOFT ABSORBENT TISSUE CONTAINING DERIVITIZED AMINO-FUNCTIONAL POLYSILOXANES

Background of the Invention

In the field of soft tissues, such as facial tissue and bath tissue, it is well known that the application of polysiloxanes to the surface of the tissue can impart an improved surface feel to the tissue. However, polysiloxanes are also known to impart hydrophobicity to the treated tissue. Hence, it is difficult to find a proper balance between softness and wettability, both of which are desirable attributes for tissue, particularly bath tissue.

Summary of the Invention

It has now been discovered that the wettability of a tissue can be improved with minimal negative impact on the surface feel of the tissue by treating one or both outer surfaces of the tissue with a particular group of derivitized amino-functional polysiloxanes. More specifically, suitable polysiloxane structures have one or more pendant groups which contain an amine derivative. A general structure is as follows:



wherein:

"A" is selected from the group consisting of hydroxy; C₁-C₆ alkyl or C₁-C₆ alkoxy radical, which can be straight chain, branched or cyclic, unsubstituted or substituted;

R₁ = a C₁-C₆ alkyl radical, which can be straight chain, branched or cyclic;

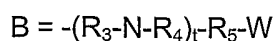
G = (R₁)_m + (B)_p + (D)_q with R₁, B and D distributed in random or block fashion;

m = 20-100,000;

p = 1-5,000;

q = 0-5,000;

m + p + q = n;



wherein

$t = 0$ or 1 ;

5 R_3 = a C_2 - C_8 alkylene diradical, which can be straight chain or branched, substituted or unsubstituted;

R_4 = a hydrogen or C_1 - C_8 alkyl radical, which can be straight chain or branched, substituted or unsubstituted or a R_6 ;

R_5 = a C_2 - C_8 alkylene diradical, which can be straight chain or branched, substituted or unsubstituted;

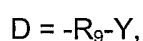
10 $W = -N-R_6R_7$

wherein

R_6 = a radical of hydrogen or COR_8 ;

R_7 = a radical of a hydrogen or COR_8 ;

15 R_8 = a C_1 - C_{10} alkyl radical, which can be straight chain, branched or cyclic, substituted or unsubstituted;



wherein

R_9 = a C_2 - C_6 alkylene diradical;

$Y = -NR_{10}R_{11}$, $-OSO_3R_{12}$, or $-[N^+R_{12}R_{12}SO_2PhR_{13}]I^-$

20 wherein

Ph = a phenyl radical;

R_{10} = hydrogen, C_1 - C_8 alkyl, $-COOR_{15}$, or $-CONR_{16}R_{17}$ radical;

R_{11} = hydrogen, C_1 - C_8 alkyl, $COOR_{15}$, or $-CONR_{16}R_{17}$ radical;

25 R_{12} = C_1 - C_8 alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

R_{13} = C_1 - C_{24} alkyl radical;

R_{15} = C_1 - C_8 alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

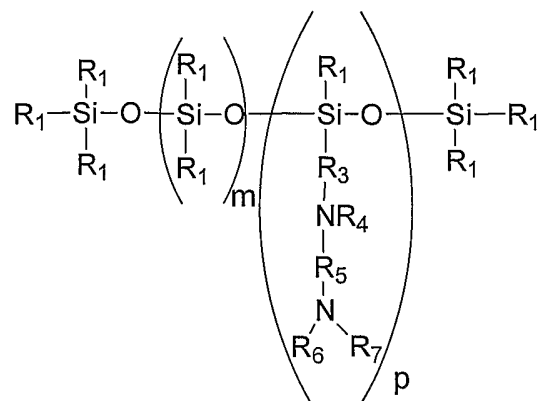
30 R_{16} = C_1 - C_8 alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

R_{17} = C_1 - C_8 alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched; and

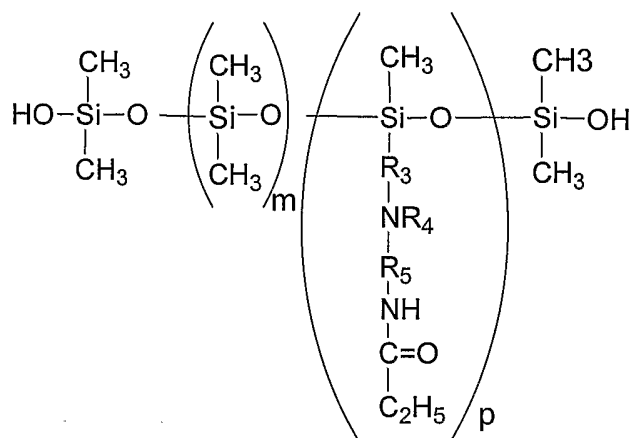
I = a halide or sulfate ion.

35 Representative species within the foregoing general structure include the following wherein the foregoing definitions apply:

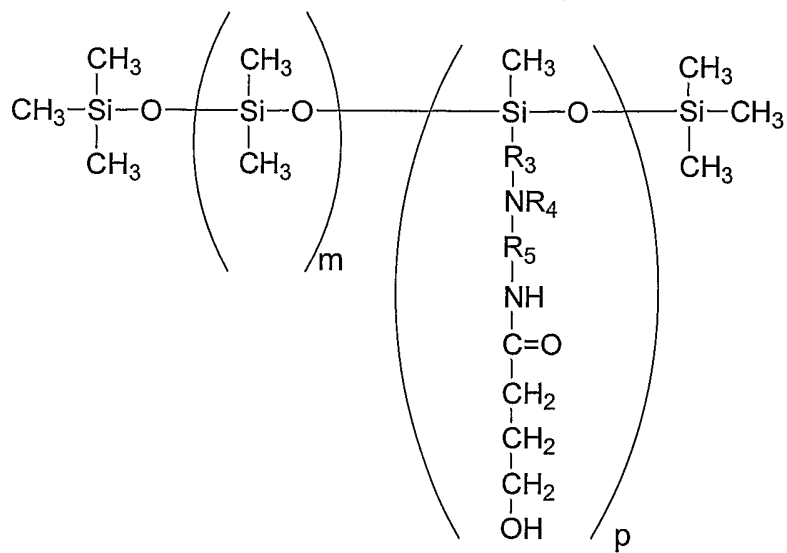
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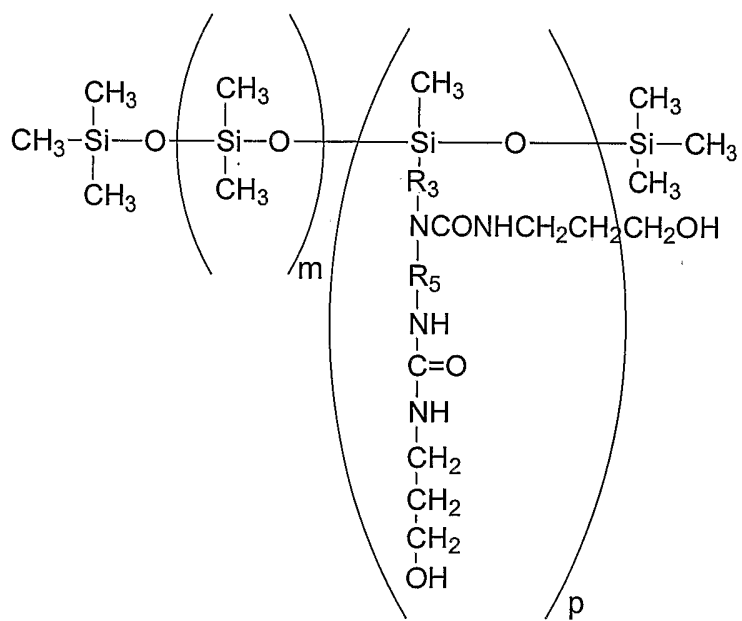
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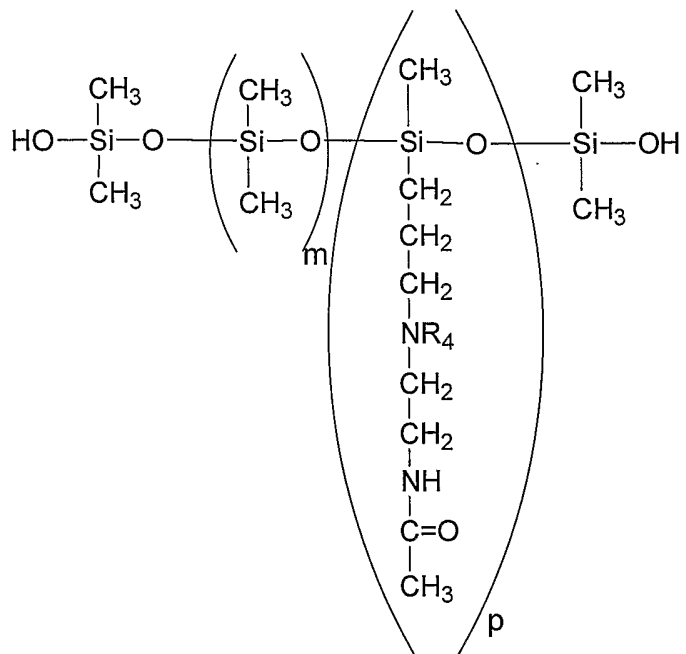
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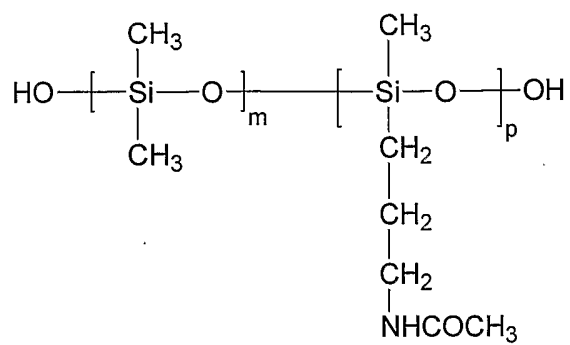
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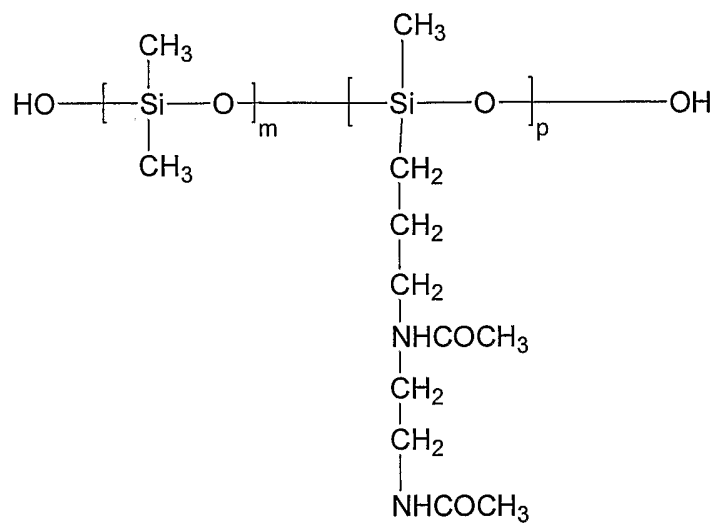
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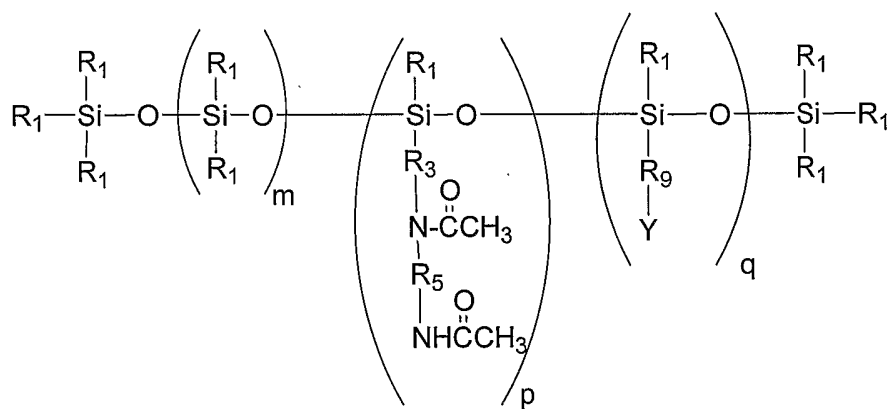
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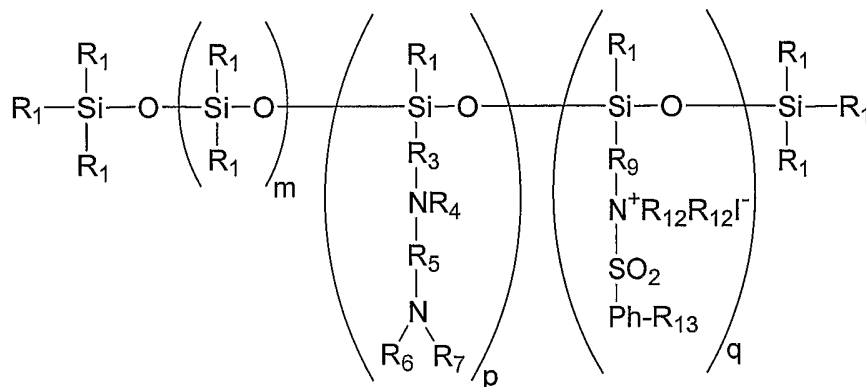
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The derivitized amino-functional polydimethylsiloxanes described above can be applied to the tissue web alone or in conjunction with other chemicals, such as bonders or debonders. They can be applied to the tissue web, particularly an uncreped throughdried web, by spraying or printing. Rotogravure printing of an aqueous emulsion is particularly effective. Add-on amounts can be from about 0.5 to about 15 dry weight percent, based on the weight of the tissue, more specifically from about 1 to about 10 dry weight percent, still more specifically from about 1 to about 5 weight percent, still more specifically from about 2 to about 5 weight percent. The distribution of the deposits of the derivitized amino-functional polydimethylsiloxanes is substantially uniform over the printed surface of the tissue, even though the surface of the tissue, such as in the case of uncreped throughdried tissues, may be highly textured and three-dimensional.

The Wet Out Time (hereinafter defined) for tissues of this invention can be about 15 seconds or less, more specifically about 10 seconds or less, still more specifically about 6 seconds or less, still more specifically about 5 seconds or less, still more specifically from about 4 to about 8 seconds. As used herein, "Wet Out Time" is related to absorbency and is the time it takes for a given sample to completely wet out when placed in water. More specifically, the Wet Out Time is determined by cutting 20 sheets of the tissue sample into 2.5 inch squares. The number of sheets used in the test is independent of the number of plies per sheet of product. The 20 square sheets are stacked together and stapled at each corner to form a pad. The pad is held close to the surface of a constant temperature distilled water bath (23 +/-2° C.), which is the appropriate size and depth to ensure the saturated specimen does not contact the bottom of the container and the top surface of the water at the same time, and dropped flat onto the water surface,

staple points down. The time taken for the pad to become completely saturated, measured in seconds, is the Wet Out Time for the sample and represents the absorbent rate of the tissue. Increases in the Wet Out Time represent a decrease in absorbent rate.

5 The "Differential Wet Out Time" is the difference between the Wet Out Times of a tissue sample treated with a derivitized amino-functional polydimethylsiloxane and a control tissue sample which has not been treated. The Differential Wet Out Time, for purposes of this invention, can be about 10 seconds or less, more specifically about 5 seconds or less, still more specifically about 3 seconds or less, still more specifically about 2 seconds or less, and still more specifically about 1 second or less.

10 The ratio of the Differential Wet Out Time to the add-on amount of the derivitized amino-functional polydimethylsiloxane can be about 3 seconds per weight percent or less, more specifically about 1 second per weight percent or less, still more specifically about 0.5 second per weight percent or less.

15 Tissue sheets useful for purposes of this invention can be creped or uncreped. Such tissue sheets can be used for facial tissues, bath tissues or towels. They can have one, two, three or more plies. The basis weight of the tissue product can be from about 25 to about 50 grams per square meter. If used for bath tissue, a single ply tissue having a basis weight of from about 30-40 grams per square meter is particularly suitable.

20 Brief Description of the Drawings

Figure 1 is a schematic diagram of an uncreped throughdried process for making bath tissue in accordance with this invention.

25 Figure 2 is a schematic diagram of the post-manufacturing method of handling the uncreped throughdried web and the rotogravure coating process used to apply the derivitized amino-functional polydimethylsiloxane emulsion in accordance with this invention.

Detailed Description of the Drawings

30 Referring to Figure 1, shown is a schematic flow diagram of a throughdrying process for making uncreped throughdried tissue sheets. Shown is the headbox 1 which deposits an aqueous suspension of papermaking fibers onto an inner forming fabric 3 as it traverses the forming roll 4. Outer forming fabric 5 serves to contain the web while it passes over the forming roll and sheds some of the water. The wet web 6 is then transferred from the inner forming fabric to a wet end transfer fabric 8 with the aid of a vacuum transfer shoe 9. This transfer is preferably carried out with the transfer fabric

35

traveling at a slower speed than the forming fabric (rush transfer) to impart stretch into the final tissue sheet. The wet web is then transferred to the throughdrying fabric 11 with the assistance of a vacuum transfer roll 12. The throughdrying fabric carries the web over the throughdryer 13, which blows hot air through the web to dry it while preserving bulk.

5 There can be more than one throughdryer in series (not shown), depending on the speed and the dryer capacity. The dried tissue sheet 15 is then transferred to a first dry end transfer fabric 16 with the aid of vacuum transfer roll 17. The tissue sheet shortly after transfer is sandwiched between the first dry end transfer fabric and the transfer belt 18 to positively control the sheet path. The air permeability of the transfer belt is lower than that
10 of the first dry end transfer fabric, causing the sheet to naturally adhere to the transfer belt. At the point of separation, the sheet follows the transfer belt due to vacuum action. Suitable low air permeability fabrics for use as transfer belts include, without limitation, COFPA Mononap NP 50 dryer felt (air permeability of about 50 cubic feet per minute per square foot) and Asten 960C (impermeable to air). The transfer belt passes over two
15 winding drums 21 and 22 before returning to pick up the dried tissue sheet again. The sheet is transferred to the parent roll 25 at a point between the two winding drums. The parent roll is wound onto a reel spool 26, which is driven by a center drive motor.

Particularly suitable methods of producing uncreped throughdried basesheets for purposes of this invention are described in U.S. 6,017,417 issued January 25, 2000 to
20 Wendt et al. and U.S. 5,944,273 issued August 31, 1999 to Lin et al., both of which are herein incorporated by reference.

Figure 2 illustrates a suitable method for applying the derivitized amino-functional polydimethylsiloxane to the tissue basesheet. Shown is the parent roll 25 being unwound and passed through two calender nips between calender rolls 30a and 31a and 30b and
25 31b. The calendered web is then passed to the rotogravure coating station comprising a first closed doctor chamber 33 containing the hydrophilically-modified amino-functional polydimethylsiloxane emulsion to be applied to a first side of the web, a first engraved steel gravure roll 34, a first rubber backing roll 35, a second rubber backing roll 36, a second engraved steel gravure roll 37 and a second closed doctor chamber 38 containing
30 the derivitized amino-functional polydimethylsiloxane emulsion to be applied to the second side of the web. If both sides of the web are to be treated, the two emulsions can be the same or different. The calendered web passes through a fixed-gap nip between the two rubber backing rolls where the derivitized amino-functional polydimethylsiloxane emulsion is applied to the web. The treated web is then passed to the rewinder where the web is
35 wound onto logs 40 and slit into rolls of bath tissue.

Examples

Example 1

In order to further illustrate this invention, an uncreped throughdried tissue was
5 produced using the methods described in Figures 1 and 2 and treated with a derivitized
amino-functional polydimethylsiloxane as set forth in structure 7 described herein above.

More specifically, a single-ply, three-layered uncreped throughdried bath tissue was
made using eucalyptus fibers for the outer layers and softwood fibers for the inner layer.
Prior to pulping, a quaternary ammonium softening agent (C-6027 from Goldschmidt
10 Corp.) was added at a dosage of 4.1 kg/Mton of active chemical per metric ton of fiber to
the eucalyptus furnish. After allowing 20 minutes of mixing time, the slurry was dewatered
using a belt press to approximately 32% consistency. The filtrate from the dewatering
process was either sewerred or used as pulper make-up water for subsequent fiber
batches but not sent forward in the stock preparation or tissue-making process. The
15 thickened pulp containing the debonder was subsequently re-dispersed in water and used
as the outer layer furnishes in the tissue-making process.

The softwood fibers were pulped for 30 minutes at 4 percent consistency and diluted
to 3.2 percent consistency after pulping, while the debonded eucalyptus fibers were
diluted to 2 percent consistency. The overall layered sheet weight was split
20 30%/40%/30% among the eucalyptus/refined softwood/ eucalyptus layers. The center
layer was refined to levels required to achieve target strength values, while the outer
layers provided the surface softness and bulk. Parex 631NC was added to the center
layer at 2-4 kilograms per tonne of pulp based on the center layer.

A three layer headbox was used to form the wet web with the refined northern
25 softwood kraft stock in the two center layers of the headbox to produce a single center
layer for the three-layered product described. Turbulence-generating inserts recessed
about 3 inches (75 millimeters) from the slice and layer dividers extending about 1 inch
(25.4 millimeters) beyond the slice were employed. The net slice opening was about 0.9
inch (23 millimeters) and water flows in all four headbox layers were comparable. The
30 consistency of the stock fed to the headbox was about 0.09 weight percent.

The resulting three-layered sheet was formed on a twin-wire, suction form roll,
former with the two forming fabrics being a Lindsay 2164 and an Asten 867a fabric. The
speed of the forming fabrics was 11.9 meters per second. The newly-formed web was
then dewatered to a consistency of about 20-27 percent using vacuum suction from below
35 the forming fabric before being transferred to the transfer fabric, which was travelling at
9.1 meters per second (30% rush transfer). The transfer fabric was an Appleton Wire

T807-1. A vacuum shoe pulling about 6-15 inches (150-380 millimeters) of mercury vacuum was used to transfer the web to the transfer fabric.

The web was then transferred to a throughdrying fabric (Lindsay Wire T1205-1). The throughdrying fabric was travelling at a speed of about 9.1 meters per second. The web was carried over a Honeycomb throughdryer operating at a temperature of about 5 350°F. (175°C.) and dried to final dryness of about 94-98 percent consistency. The resulting uncreped tissue sheet was then wound into a parent roll.

The parent roll was then unwound and the web was calendered twice. At the first station the web was calendered between a steel roll and a rubber covered roll having a 4 10 P&J hardness. The calender loading was about 90 pounds per lineal inch (pli). At the second calendering station, the web was calendered between a steel roll and a rubber covered roll having a 40 P&J hardness. The calender loading was about 140 pli. The thickness of the rubber covers was about 0.725 inch (1.84 centimeters).

The calendered single-ply web was then fed into the rubber-rubber nip of the 15 rotogravure coater to apply the derivitized amino-functional polydimethylsiloxane emulsion to both sides of the web. The aqueous emulsion contained 40% of a derivitized amino polydimethylsiloxane, **[which structure?]** 8% surfactant, 0.5% antifoaming agent, 0.2% preservative, and the balance water. The gravure rolls were electronically engraved, chrome over copper rolls supplied by Specialty Systems, Inc., Louisville, Kentucky. The 20 rolls had a line screen of 200 cells per lineal inch and a volume of 6.0 Billion Cubic Microns (BCM) per square inch of roll surface. Typical cell dimensions for this roll were 140 microns in width and 33 microns in depth using a 130 degree engraving stylus. The rubber backing offset applicator rolls were a 75 Shore A durometer cast polyurethane supplied by American Roller Company, Union Grove, Wisconsin. The process was set up 25 to a condition having 0.375 inch interference between the gravure rolls and the rubber backing rolls and 0.003 inch clearance between the facing rubber backing rolls. The simultaneous offset/offset gravure printer was run at a speed of 2000 feet per minute using gravure roll speed adjustment (differential) to meter the polysiloxane emulsion to obtain the desired addition rate. The gravure roll speed differential used for this example 30 was 1000 feet per minute. This process yielded an add-on level of 2.5 weight percent total add-on based on the weight of the tissue. The tissue was then converted into bath tissue rolls. Sheets from the bath tissue rolls had a silky, lotiony hand feel and a Wet Out Time of 5.0 seconds. (Similarly made tissues without the treatment of this invention had a Wet Out Time of about 4.0 seconds.) The ratio of the differential Wet Out Time to the weight 35 percent add-on amount was 0.4.

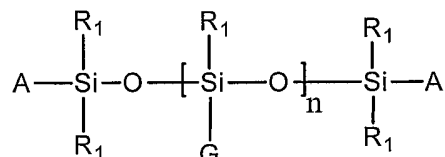
Example 2

An uncreped throughdried tissue is produced similarly as described in Example 1 with the following exceptions: (1) prior to pulping, an amino functionalized polydimethylsiloxane of structure 8 is added to the eucalyptus fibers at a dosage of 0.2 kg/Mton of active chemical per metric ton of fiber; (2) the add-on level of the derivitized amino-functional polydimethylsiloxane is 1.5 weight percent; (3) the structure of the derivitized amino-functional polydimethylsiloxane printed onto the tissue is as set forth in structure (9); and (4) the derivitized amino-functional polydimethylsiloxane constitutes 20 weight percent of the aqueous emulsion used to deliver the derivitized amino-functional polydimethylsiloxane to the tissue. The resulting bath tissue product obtained has a silky, lotiony hand feel and a Wet Out Time of 4.8 seconds.

It will be appreciated that the foregoing examples and discussion is for purposes of illustration only and is not to be construed as limiting the scope of this invention, which is defined by the following claims and all equivalents thereto.

We claim:

1. A tissue having a Wet Out Time of about 15 seconds or less and containing at least about 2 dry weight percent of a hydrophilically-modified amino-functional polysiloxane
 5 having the following structure:



wherein:

“A” is selected from the group consisting of hydroxy; C₁-C₆ alkyl or C₁-C₆ alkoxy radical,
 10 which can be straight chain, branched or cyclic, unsubstituted or substituted;

R₁ = a C₁-C₆ alkyl radical, which can be straight chain, branched or cyclic;

G = (R₁)_m + (B)_p + (D)_q with R₁, B and D distributed in random or block fashion;

m = 20-100,000;

p = 1-5,000;

15 q = 0-5,000;

m + p + q = n; B = -(R₃-N-R₄)_t-R₅-W

wherein

t = 0 or 1;

20 R₃ = a C₂-C₈ alkylene diradical, which can be straight chain or branched, substituted or unsubstituted;

R₄ = a hydrogen or C₁-C₈ alkyl radical, which can be straight chain or branched, substituted or unsubstituted or a R₆;

R₅ = a C₂-C₈ alkylene diradical, which can be straight chain or branched, substituted or unsubstituted;

25 W = -N-R₆R₇-

wherein

R₆ = a radical of hydrogen or COR₈;

R₇ = a radical of a hydrogen or COR₈;

30 R₈ = a C₁-C₁₀ alkyl radical, which can be straight chain, branched or cyclic, substituted or unsubstituted;

D = -R₉-Y,

wherein

R_9 = a C₂-C₆ alkylene diradical;

$Y = -NR_{10}R_{11}, -OSO_3R_{12},$ or $-[N^+R_{12}R_{12}SO_2PhR_{13}]I^-$

wherein

5

Ph = a phenyl radical;

R_{10} = hydrogen, C₁-C₈ alkyl, -COOR₁₅, or -CONR₁₆R₁₇ radical;

R_{11} = hydrogen, C₁-C₈ alkyl, COOR₁₅, or -CONR₁₆R₁₇ radical;

R_{12} = C₁-C₈ alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

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R_{13} = C₁-C₂₄ alkyl radical;

R_{15} = C₁-C₈ alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

R_{16} = C₁-C₈ alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched;

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R_{17} = C₁-C₈ alkyl radical, which can be aromatic, aliphatic, cyclic, straight chain or branched; and

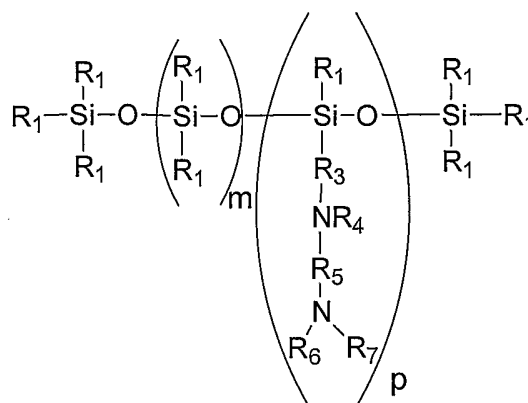
I = a halide or sulfate ion.

2. The tissue of claim 1 wherein the Wet Out Time is about 10 seconds or less.
- 20 3. The tissue of claim 1 wherein the Wet Out Time is about 7 seconds or less.
4. The tissue of claim 1 wherein the Wet Out Time is about 5 seconds or less.
- 25 5. The tissue of claim 1 wherein the Wet Out Time is from about 4 to about 8 seconds.
6. The tissue of claim 1 having from about 0.5 to about 15 dry weight percent of the derivitized amino-functional polysiloxane.
- 30 7. The tissue of claim 1 having from about 1 to about 10 dry weight percent of the derivitized amino-functional polysiloxane.
8. The tissue of claim 1 having from about 1 to about 5 dry weight percent of the derivitized amino-functional polysiloxane.

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9. The tissue of claim 1 having from about 2 to about 5 dry weight percent of the derivitized amino-functional polysiloxane.
10. The tissue of claim 1 wherein the ratio of the Differential Wet Out Time to the add-on
5 amount of the derivitized amino-functional polysiloxane is about 3 seconds per weight percent or less.
11. The tissue of claim 1 wherein the ratio of the Differential Wet Out Time to the add-on
10 amount of the derivitized amino-functional polysiloxane is about 1 second per weight percent or less.
12. The tissue of claim 1 wherein the ratio of the Differential Wet Out Time to the add-on
15 amount of the derivitized amino-functional polysiloxane is about 0.5 second per weight percent or less.
13. The tissue of claim 1 wherein the tissue is an uncreped throughdried tissue.
14. The tissue of claim 1 wherein both sides of the tissue are printed with the same
20 derivitized amino-functional polysiloxane.
15. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane printed on one side of the tissue is different than the derivitized amino-functional polysiloxane printed on the other side of the tissue.
- 25 16. The tissue of claim 1 wherein R_6 and R_7 are independently a COR_8 radical.

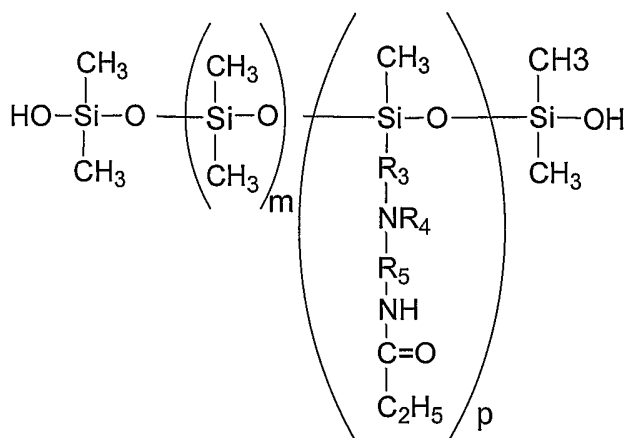
17. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



5

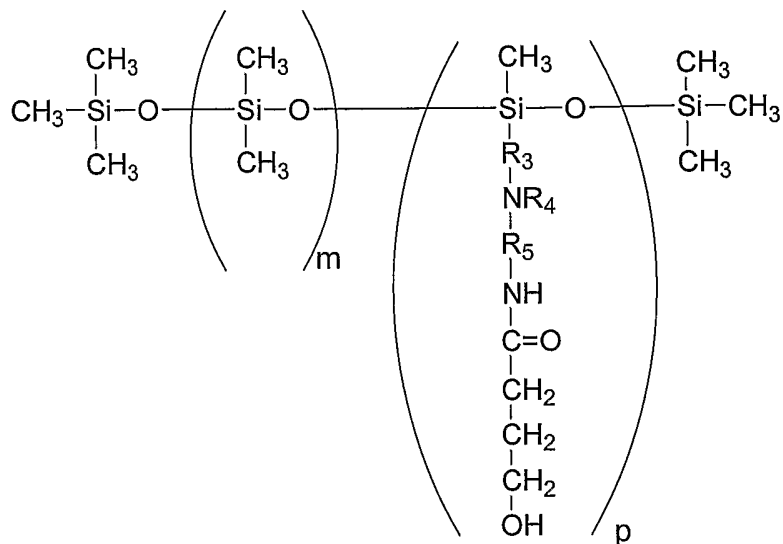
18. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:

10



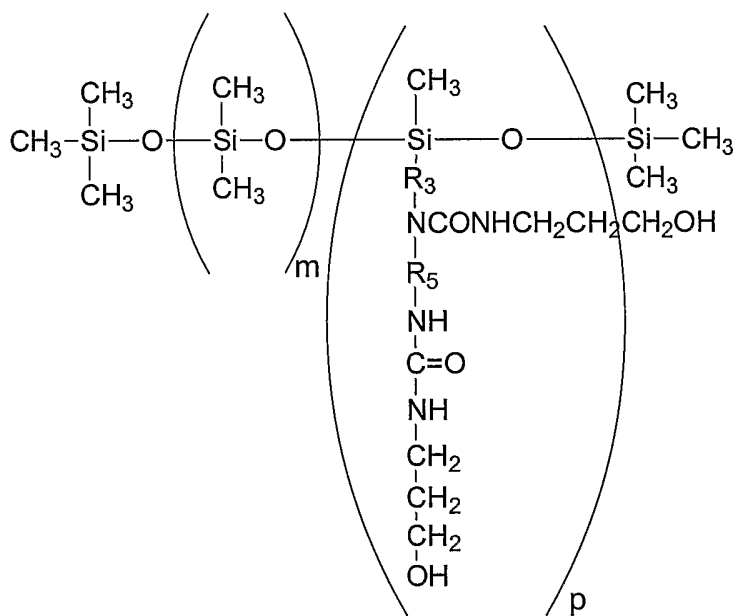
15

19. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



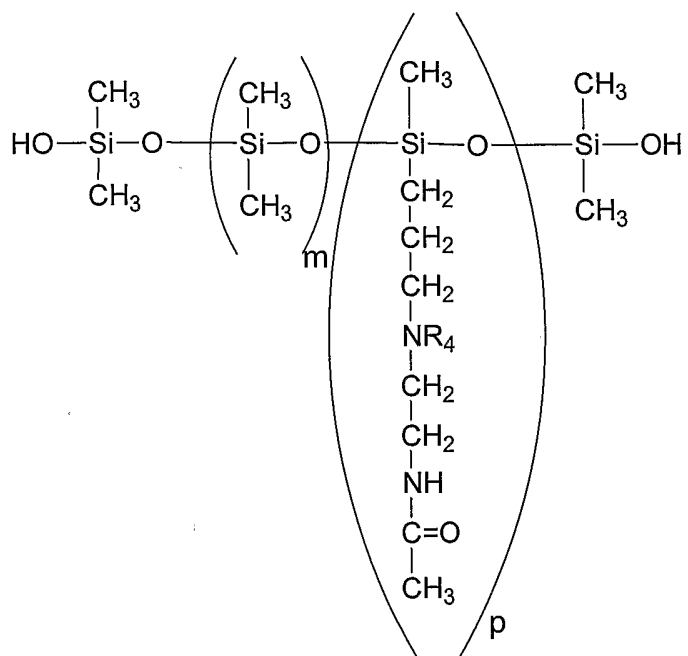
5

20. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:

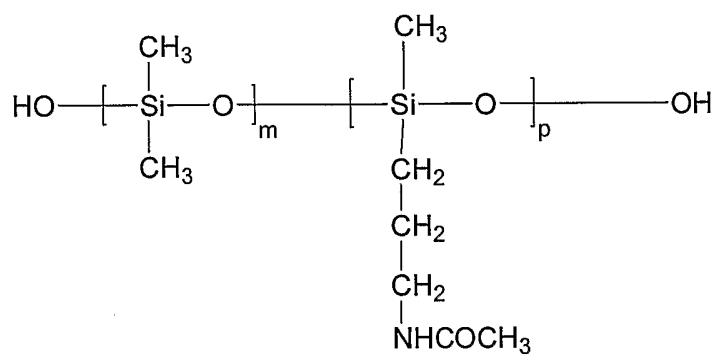


10

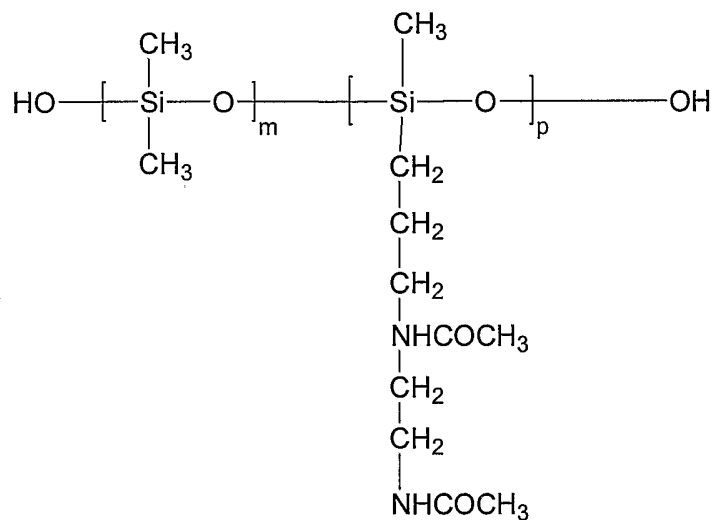
21. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



5 22. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:

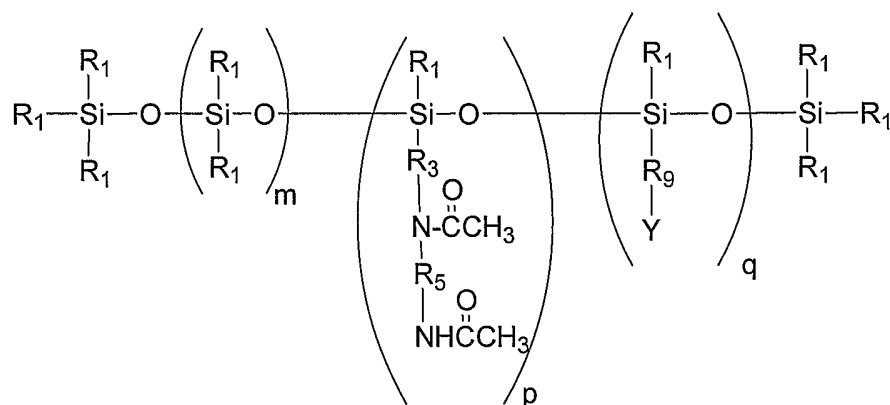


23. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



5

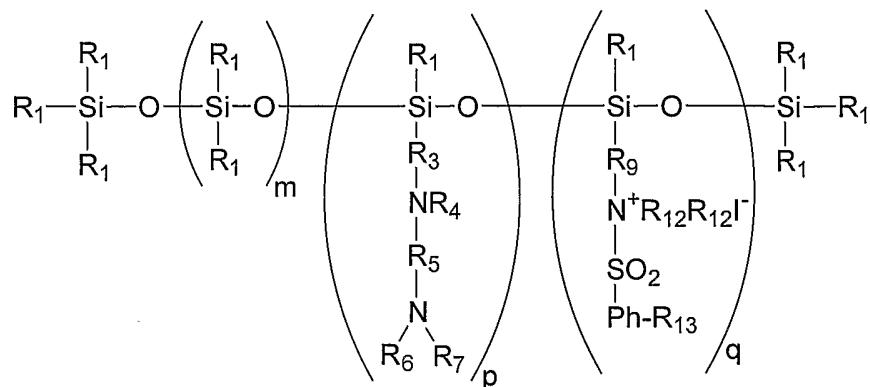
24. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



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25. The tissue of claim 1 wherein the derivitized amino-functional polysiloxane has the following structure:



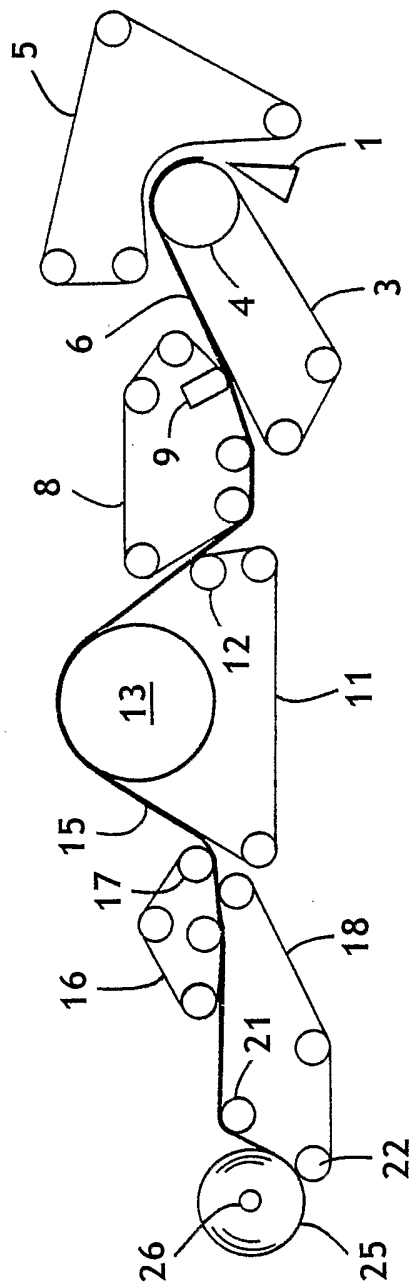


FIG. 1

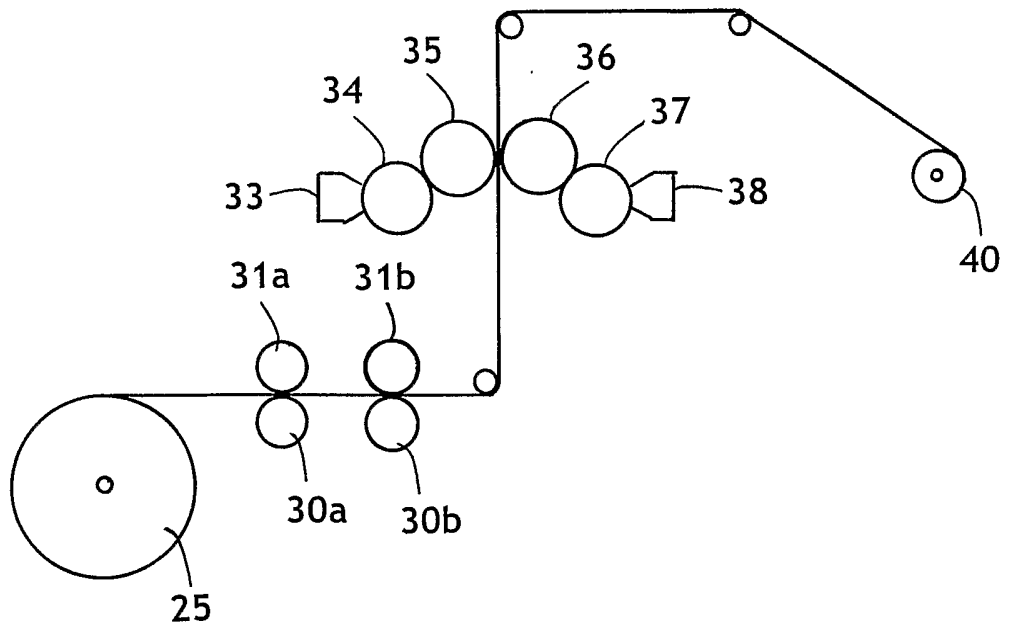


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/12243

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 D21H17/59 D06M15/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 D21H D06M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01 48312 A (KIMBERLY CLARK CO) 5 July 2001 (2001-07-05) page 6, line 10 - line 26 ----	1-25
Y	US 5 538 595 A (TROKHAN PAUL D ET AL) 23 July 1996 (1996-07-23) column 8, line 45 -column 9, line 13 ----	1-25
A	US 6 017 417 A (BURAZIN MARK ALAN ET AL) 25 January 2000 (2000-01-25) the whole document ----	1-25
A	US 5 385 643 A (AMPULSKI ROBERT S) 31 January 1995 (1995-01-31) column 11, line 24 -column 12, line 36 -----	1-25
<input type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
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P document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search <p style="text-align: center; font-size: 1.2em;">7 October 2002</p>	Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">15/10/2002</p>	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center; font-size: 1.2em;">Naeslund, P</p>	

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