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| (51) International Patent Classification ⁵ : C08G 69/28, 69/48, 69/20 C08G 69/04 | A1 | (11) International Publication Number: WO 90/04614 (43) International Publication Date: 3 May 1990 (03.05.90) |
| (21) International Application Number: PCT/US89/03464 (22) International Filing Date: 17 August 1989 (17.08.89) (30) Priority data: 262,936 20 October 1988 (20.10.88) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: WHELAND, Robert, Clayton ; 510 Twaddell Mill Road, Wilmington, DE 19807 (US). (74) Agents: HAMBY, William, H. et al.; E.I. du Pont de Nemours and Company, 1007 Market Street, Wilmington, DE 19898 (US). | | (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), SU. Published <i>With international search report.</i> |
| (54) Title: PROCESS FOR INCREASING THE MOLECULAR WEIGHT OF A POLYAMIDE (57) Abstract Process for increasing the molecular weight of a polyamide using substituted phenylphosphonic or phenylphosphinic acids as catalyst. | | |

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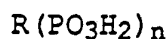
TITLEPROCESS FOR INCREASING THE MOLECULAR WEIGHT
OF A POLYAMIDE

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BACKGROUND OF THE INVENTION

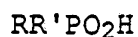
10 This invention relates to increasing the molecular weight of a polyamide by using a designated catalyst.

U.S. 3,763,113 describes a process for the amidation of nylon 66 using as catalysts phosphonic acids of the formula:



15 wherein n is 1, 2 or 3, and R is a mono-, di-, or trivalent organic radical depending on the value of n. Example 10 shows the use of a weakly activating substituent (p-PO₃H₂C₆H₄-). The results, however, as
20 stated in the patent clearly show that this example gives results which are only slightly better than phenylphosphonic acid as measured by the relative viscosity of the final product. There is no
25 indication from the Examples that moderate or strongly activating groups would have a significant effect on the rate of reaction.

U.S. 3,365,428 describes a process for the amidation of nylons using as catalysts phosphinic acids of the formula:



30 wherein R is an aryl or alkaryl radical, and R' is hydrogen or an alkyl, aralkyl, aryl or alkaryl radical. Example 8 shows the use of the weakly activating substituents CH₃- and C₆H₅-; as stated in
35 this Example, the results as obtained are similar to the results obtained using a similar amount of phenylphosphinic acid. There is no indication from

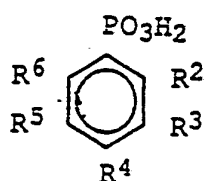
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the Examples that moderate or strongly activating groups would have a significant effect on the rate of reaction.

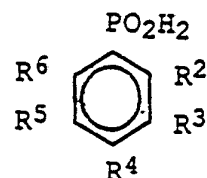
Thus a need still exists for catalysts which will effect the rate of reaction for increasing molecular weight. Greater throughput, or for the same reaction time, production of a higher molecular weight material would result in a higher strength material.

BRIEF SUMMARY OF THE INVENTION

According to this invention there has been discovered an improved process for increasing the molecular weight of a polyamide, consisting essentially of heating the polyamide in the presence of a catalyst to effect a desired increase in molecular weight, wherein the improvement is employing, as the catalyst, at least one compound of the formulae A or B:



A



B

wherein R^2 , R^4 , and R^6 are independently selected from the group H, $\text{R}_2\text{N}-$, $\text{RO}-$, $\text{RS}-$, $\text{R}-$, wherein R is $\text{C}_x\text{H}_{2x+1}$ with $x = 1$ to 10, C_6H_5- and $\text{C}_6\text{H}_5\text{CH}_2-$ with the proviso that R^2 , R^4 and R^6 cannot be hydrogen simultaneously and with the further proviso that when only H or R groups are present in the molecule at least one of R^2 or R^6 be R. R^3 and R^5 are independently selected from the group H, $\text{R}_2\text{N}-$, $\text{RO}-$, $\text{RS}-$, $\text{R}-$, wherein R is $\text{C}_x\text{H}_{2x+1}$ with $x = 1$ to 10, C_6H_5- and $\text{C}_6\text{H}_5\text{CH}_2-$.

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These catalysts unexpectedly provide a substantial increase in the rate of amidation as compared to phenylphosphonic or phenylphosphinic acid.

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DETAILED DESCRIPTION OF THE INVENTION

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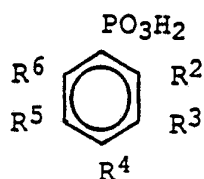
It is known in the art to use phenylphosphonic and phenylphosphinic acids as catalysts for increasing the molecular weight of a polyamide. It has now been unexpectedly found that substitution of the ortho or para hydrogen atoms of the phenylphosphonic or phenylphosphinic acid catalysts with electron releasing (activating) groups increases the relative viscosity several fold, i.e., 3 to 14 fold for the same reaction time.

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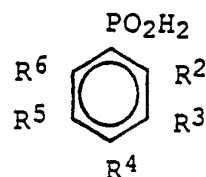
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More specifically the process of the instant invention is an improved process for increasing the molecular weight of a polyamide, comprising heating the polyamide in the presence of a catalyst to effect a desired increase in molecular weight wherein the improvement comprises employing, as the catalyst, at least one compound of the formulae A or B:

30



A



B

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wherein R^2 , R^4 , and R^6 are independently selected from the group H, $\text{R}_2\text{N}-$, $\text{RO}-$, $\text{RS}-$, $\text{R}-$, wherein R is $\text{C}_x\text{H}_{2x+1}$ with $x = 1$ to 10, C_6H_5- and $\text{C}_6\text{H}_5\text{CH}_2-$ with the proviso that R^2 , R^4 and R^6 cannot be hydrogen simultaneously and with the further proviso that when only H or R groups are present in the molecule

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at least one of R^2 or R^6 be R. R^3 and R^5 are independently selected from the group H, R_2N- , $RO-$, $RS-$, R, wherein R is C_xH_{2x+1} with $x = 1$ to 10, C_6H_5- and $C_6H_5CH_2-$.

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Among the preferred compounds are those wherein R^2 and $R^4 = CH_3O-$ and $R^3, R^5,$ and $R^6 = H$; $R^2 = CH_3O-$ and $R^3, R^4, R^5,$ and $R^6 = H$; $R^4 = CH_3O-$ and $R^2, R^3, R^5,$ and $R^6 = H$; R^2 and $R^5 = CH_3-$, and $R^3, R^4,$ and $R^6 = H$.

10

Specific examples of substituted phenylphosphonic and phenylphosphinic acids are selected from 2-methoxyphenylphosphonic acid, 2,4-dimethoxyphenylphosphinic acid, 4-methoxyphenylphosphinic acid, 2,4-dimethoxyphenylphosphonic acid, 2,6-dimethylphenylphosphonic acid, 2-benzyloxyphenylphosphonic acid, 2-methylphenylphosphonic acid, and 4-methoxyphenylphosphonic acid.

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Derivatives of substituted phenylphosphonic or phenylphosphinic acids which are easily hydrolyzed to the parent acid under the conditions of the polymerization reaction, such as the mono or diesters or the mono or diamides, are suitable for the process of this invention.

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The catalysts used in the process of this invention are either available chemicals or chemicals which can be readily produced in accordance with known processes. A preferred process for making the phosphonic acid catalysts comprises photochemically reacting the appropriate halide with an alkyl phosphite (Arbuzov reaction) and hydrolyzing the phosphonite ester so produced (See, for example, J. B. Plum et al., J. Org. Chem., 27, 4711 (1962)). A preferred process for making the phosphinic acid catalysts comprises reacting the appropriate aromatic with phosphorous trichloride in the presence of catalyst and

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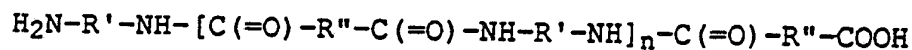
hydrolyzing the aromatic phosphorous dichloride so produced (See, for example, Houben-Weyl, "Methoden Der Organischen Chemie", page 294 and following).

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The polyamides used in the process of this invention are conventional. Polyamides are condensation products that contain recurring amide groups as integral parts of the main polymer chains. Linear polyamides are formed from condensation of bifunctional monomers.

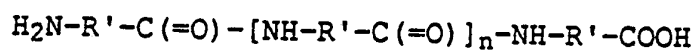
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Typical structural formulas of linear polyamides may be represented as



or

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where R' and R'' are linear or branched alkylene groups containing from 2 to 12 carbon atoms; R'' may also be aromatic groups such as phenylene or naphthalylene and n represents the degree of polymerization or the number of recurring groups in the polymer chain. The value of n for a given polyamide such as nylon-6,6 should be such that the molecular weight is about 15,000 (40 RV).

20

Preferred polyamides are nylons, including but not limited to nylon-6 and nylon-6,6. These and the other nylons known in the field are well described as to structure and manufacture, and for further reference, attention is invited to the patent and general literature, for example, the Kirk-Othmer Encyclopedia of Chemical Technology, 3rd edition, John Wiley and Sons, under the headings "Polyamide Fibers", and "Polyamide Plastics", as well as the Encyclopedia of Textiles, Fibers and Non-Woven Fabrics, John Wiley and Sons, Inc., 1984, pages 347-380, relating to polyamide fibers. For the purposes of the present invention, nylon-6,6 is the most preferred species.

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The temperature range for the melting point of the polyamides to be used in the process of this invention is about 80-360°C. The catalysts of this invention are preferably used at or above the melting temperature of the polyamide, the upper limit being generally dictated by the decomposition temperature of the polymer. In the case of nylon-6,6, the operating temperature is about 265-300°C, preferably 270-295°C.

Conversely, the catalysts can also be employed below the melting temperature of the polymer, preferably at least 15°C below the melting point to avoid working with a hard to handle, sticky mass. For example, since nylon-6,6 melts at 260°C, the preferred operating temperature for employing the catalyst below the melting point is 170-245°C.

The reaction time is sufficient to obtain the desired increase in molecular weight. For nylon-6,6 the increase in molecular weight which is desired is usually measured by the change in relative viscosity and can range from 10 to 600. This represents a change in molecular weight of from about 15,000 to about 45,000. The preferred reaction time being generally about 1 to 60 minutes for the liquid phase reaction. For the solid stage reaction the preferred reaction time being generally >15 minutes. Likewise, the amount of phosphonic and/or phosphinic catalysts employed in the reaction is sufficient to obtain a catalytic effect, the preferred concentration of phosphonic or phosphinic acid, for example, being about ≥ 0.1 gram moles of catalyst per million grams of polyamide. Finally, the reaction is conducted preferably in the absence of air, for example, in the presence of an inert gas such as nitrogen, helium or argon.

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In the following Examples, all temperatures are set forth uncorrected in degrees Celsius and unless otherwise indicated, all parts and percentages are by weight.

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Both the catalysts of this invention and comparative catalysts are tested in a thin film polymerizer. This is an apparatus for conducting small scale nylon polymerizations under controlled conditions of temperature, water vapor pressure, and reaction time; in principal all the factors necessary for the determination of amidation kinetics. Essentially, a low molecular weight nylon sample is melted under its equilibrium steam pressure, the steam pressure is reduced, and the reaction quenched before a new equilibrium is attained. By relative viscosity analysis one can then determine how fast the sample approached the new equilibrium and thus amidation kinetics and catalytic factors. An important feature of the thin film polymerizer is that the nylon samples are melted in broad cups, allowing the melt to spread out as a pool 2 mm deep that can respond rapidly to changes in steam pressure.

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EXAMPLES

General Procedure for Determining Increase in Relative Viscosity

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Six cups, each containing 1 gram of powdered nylon containing the catalyst are placed in a stainless steel sample chamber with 5 ml of water. The nylon samples are melted and brought to reaction temperature as rapidly as possible by dropping the reaction chamber into a preheated 280° sand bath. The water begins to evaporate creating a steam atmosphere inside the reaction vessel. A check valve on the reaction vessel maintains a constant steam pressure of 780 mm. When the internal reactor temperature nears 280°,

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temperature control for the sand bath is switched to a thermocouple inside the reactor. A total of 45-60 minutes is required to attain a stable operating temperature of $280 \pm 1^\circ$. As soon as the reaction vessel stabilizes at $280 \pm 1^\circ$ the steam pressure is reduced from 780 mm to 100 mm to initiate polymerization. The polymerization is allowed to proceed for the indicated time and is then quenched by rapid cooling. The polymer is chopped to a coarse powder and its relative viscosity is determined in an 8.5% by weight solution of 6,6-nylon in 90% formic acid (balance H_2O) at 25° .

EXAMPLES 1-12

The general procedure outlined above was followed using a catalyst concentration of 10 g moles/ 10^6 grams of nylon, 6-6. The reaction time was 5 minutes.

| Example/Catalyst | Increase in RV |
|---------------------------------------|----------------|
| A. Phenylphosphonic Acid | 47 |
| B. Phenylphosphinic Acid | 37 |
| 1. 2,4-dimethoxyphenylphosphinic Acid | 508 |
| 2. 2-methoxyphenylphosphonic Acid | 499 |
| 3. 4-methoxyphenylphosphonic Acid | 464 |
| 4. 2,4-dimethoxyphenylphosphonic Acid | 333 |
| 5. 2,6-dimethylphenylphosphonic Acid | 307 |
| 6. 2-benzyloxyphenylphosphonic Acid | 283 |
| 7. 4-methoxyphenylphosphonic Diamide | 263 |
| 8. 2-methylphenylphosphonic Acid | 260 |
| 9. 4-methoxyphenylphosphonic Acid | 257 |
| 10. 2-methoxyphenyldiethylphosphonate | 255 |
| 11. 2,5-dimethylphenylphosphinic Acid | 146 |
| 12. 2,5-dimethylphenylphosphonic Acid | 132 |

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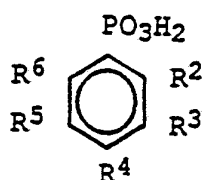
The results clearly show that the phenylphosphonic or phenylphosphinic acids containing electron releasing groups in the ortho or para positions of the phenyl ring are much more reactive amidation catalysts as evidenced by the fact that the increase in RV is 3 to 14 fold higher when compared to the unsubstituted acids.

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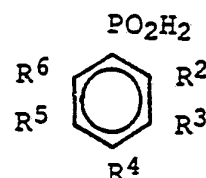
CLAIMS

What is Claimed is:

1. In a process for increasing the molecular weight of a polyamide, consisting essentially of heating the polyamide in the presence of a catalyst to effect a desired increase in molecular weight, wherein the improvement consists essentially of employing, as the catalyst, at least one compound of the formulae selected from A or B:



A



B

20 wherein R^2 , R^4 , and R^6 are independently selected from the group H, R_2N- , $RO-$, $RS-$, or $R-$, wherein R is C_xH_{2x+1} with $x = 1$ to 10, C_6H_5- and $C_6H_5CH_2-$ with the proviso that R^2 , R^4 and R^6 cannot be hydrogen simultaneously and with the further proviso that when only H or R groups are present in the molecule at least one of R^2 or R^6 be R and R^3 and R^5 are independently selected from the group H, R_2N- , $RO-$, $RS-$, or R, wherein R is C_xH_{2x+1} with $x = 1$ to 10, C_6H_5- and $C_6H_5CH_2-$.

30 2. The process of Claim 1 wherein R^2 and $R^4 = CH_3O-$ and R^3 , R^5 , and $R^6 = H$; $R^2 = CH_3O-$ and R^3 , R^4 , R^5 , and $R^6 = H$; $R^4 = CH_3O-$ and R^2 , R^3 , R^5 , and $R^6 = H$; R^2 and $R^5 = CH_3-$, and R^3 , R^4 , and $R^6 = H$.

35 3. The process of Claim 1 wherein the substituted phenylphosphonic and phenylphosphinic acids are selected from 2-methoxyphenylphosphonic acid, 2,4-dimethoxyphenylphosphinic acid, 4-methoxyphenylphosphinic acid, 2,4-

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dimethoxyphenylphosphonic acid, 2,6-
dimethylphenylphosphonic acid, 2-
benzyloxyphenylphosphonic acid, 2-
methylphenylphosphonic acid, and 4-
methoxyphenylphosphonic acid.

4. The process of Claim 1 wherein the
polyamides are selected from
$$\text{H}_2\text{N}-\text{R}'-\text{NH}-[\text{C}(=\text{O})-\text{R}''-\text{C}(=\text{O})-\text{NH}-\text{R}'-\text{NH}]_n-\text{C}(=\text{O})-\text{R}''-\text{COOH}$$

or

$$\text{H}_2\text{N}-\text{R}'-\text{C}(=\text{O})-[\text{NH}-\text{R}'-\text{C}(=\text{O})]_n-\text{NH}-\text{R}'-\text{COOH}$$

where R' and R'' are linear or branched alkylene
groups containing from 2 to 12 carbon atoms; R' may
also be aromatic groups such as phenylene or
naphthalylene and n represents the degree of
polymerization or the number of recurring groups in
the polymer chain.

5. The process of Claim 4 wherein the
polyamide is nylon-6,6.

6. The process of Claim 5 wherein the
nylon-6,6 should have a molecular weight of about
15,000 (40 RV).

7. The process of Claim 4 wherein the
temperature range for the melting point of the
polyamides to be used in the process of this
invention is about 80-360°C.

8. The process of Claim 4 wherein the
reaction time is about 1 to 60 minutes for a liquid
phase reaction.

9. The process of Claim 4 wherein the
reaction time is >15 minutes for a solid state
reaction.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/03464

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 G 69/28, C 08 G 69/48, C 08 G 69/20, C 08 G 69/04 | | | | | | | | | | | |
|--|---|-------------------------------------|--|--|--|---|--|--|---|---|--|
| II. FIELDS SEARCHED <div style="text-align: center; margin-top: 10px;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 30%; border: none;">Classification System</td> <td style="border: none;">Classification Symbols</td> </tr> <tr> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">IPC⁵</td> <td style="border: 1px solid black; padding: 10px; vertical-align: top;">C 08 G</td> </tr> </table> <div style="text-align: center; margin-top: 10px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div> | | | Classification System | Classification Symbols | IPC ⁵ | C 08 G | | | | | |
| Classification System | Classification Symbols | | | | | | | | | | |
| IPC ⁵ | C 08 G | | | | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category ⁹</th> <th style="width: 60%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 30%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 3763113 (H.G. BURROWS et al.) 2 October 1973 cited in the application --</td> <td></td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>US, A, 3365428 (D.W. WUJCIAK) 23 January 1968 cited in the application ----</td> <td></td> </tr> </tbody> </table> | | | Category ⁹ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ | A | US, A, 3763113 (H.G. BURROWS et al.) 2 October 1973 cited in the application -- | | A | US, A, 3365428 (D.W. WUJCIAK) 23 January 1968 cited in the application ---- | |
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| A | US, A, 3763113 (H.G. BURROWS et al.) 2 October 1973 cited in the application -- | | | | | | | | | | |
| A | US, A, 3365428 (D.W. WUJCIAK) 23 January 1968 cited in the application ---- | | | | | | | | | | |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"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</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div> | | | | | | | | | | | |
| IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> Date of the Actual Completion of the International Search <div style="text-align: center; margin-top: 10px;">29th November 1989</div> </td> <td style="width: 50%; border: none;"> Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">13.12.89</div> </td> </tr> <tr> <td style="border: none;"> International Searching Authority <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none;"> Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> <div style="text-align: right; margin-top: 10px;">T.K. WILLIS</div> </div> </td> </tr> </table> | | | Date of the Actual Completion of the International Search <div style="text-align: center; margin-top: 10px;">29th November 1989</div> | Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">13.12.89</div> | International Searching Authority <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> <div style="text-align: right; margin-top: 10px;">T.K. WILLIS</div> </div> | | | | | |
| Date of the Actual Completion of the International Search <div style="text-align: center; margin-top: 10px;">29th November 1989</div> | Date of Mailing of this International Search Report <div style="text-align: center; margin-top: 10px;">13.12.89</div> | | | | | | | | | | |
| International Searching Authority <div style="text-align: center; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center; margin-top: 10px;"> <div style="text-align: right; margin-top: 10px;">T.K. WILLIS</div> </div> | | | | | | | | | | |

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

US 8903464
SA 30740

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 08/12/89
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| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| US-A- 3763113 | 02-10-73 | BE-A- 682538 | 14-12-66 |
| | | CH-A- 471181 | 15-04-69 |
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| | | US-A- 3944518 | 16-03-76 |
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| US-A- 3365428 | | None | |
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