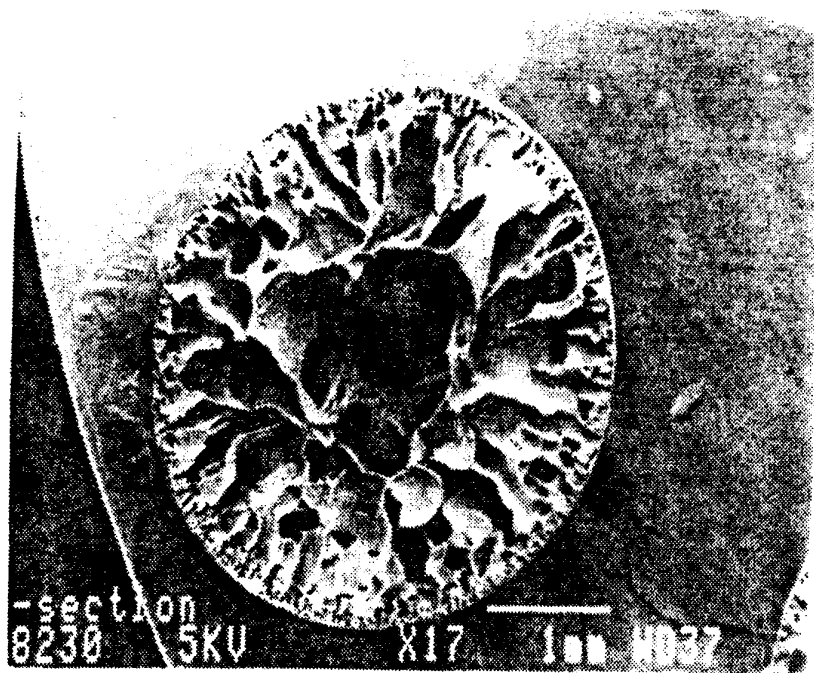




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US91/09169 <b>(22) International Filing Date:</b> 17 December 1991 (17.12.91)  <b>(30) Priority data:</b> 631,269 20 December 1990 (20.12.90) US  <b>(71) Applicant:</b> E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).  <b>(72) Inventors:</b> FIGULY, Garret, Daniel ; 18 Drummond Drive, Wilmington, DE 19808 (US). SHIH, Hsiang ; 727 Foxdale Road, Wilmington, DE 19803-1603 (US). SMITH, Linda, Hayes ; 103 Beaver Court East, Bear, DE 19701 (US).		<b>(74) Agents:</b> SCHWARTZ, Sol et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

**(54) Title:** MICROPOROUS ELASTIC SEGMENTED POLYURETHANE SHAPED STRUCTURE

**(57) Abstract**

Solutions of segmented polyurethanes are coagulated to form shaped structures comprising a substantially continuous pore-free sheath surrounding a cellular core.

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<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

TitleMicroporous Elastic Segmented Polyurethane  
Shaped StructureBackground of the Invention

5 Elastic segmented polyurethane filaments are well known for their resistance to hydrolysis and other desirable properties such as stretch, recovery and power. These properties make the filaments invaluable for swim suits and other end-use applications. The present  
10 invention provides the elastic segmented polyurethane in a novel form which lends itself to a broad spectrum of new uses.

Drawings

Fig. 1 is a scanning electron micrograph (SEM) of a  
15 cross-section view at 17X magnification of a shaped structure (a bead) of the invention.

Fig. 2 is an SEM of a surface view of a bead of the invention at 17X magnification showing a substantially continuous sheath encapsulating the bead.

20 Fig. 3 is an SEM of a surface view of a bead of the invention at 5000X magnification.

Fig. 4 is a view of a partial cross-section by SEM of a bead at 100X magnification showing a portion of the skin of the bead from which thickness may be readily  
25 measured.

Summary of the Invention

This invention provides shaped structures consisting essentially of microporous elastic segmented polyurethane having a void content of from 60 to 90% encapsulated by a  
30 substantially continuous sheath having a thickness of less than about 3 microns and having essentially no pores visible at the surface at a magnification of 5000 X. The shaped structures may be substantially spherical having a diameter of from about 1 mm. to about 4 mm. or can be  
35 filamentary in form of denier from 60 to 1800, in which

event only the cut ends will lack the sheath material. Also encompassed by this invention is the method for preparing the shaped structures. The products can be employed as insulation, as carriers for the slow release  
5 of imbibed substances, cushioning materials, absorbents for organic solvent spills, etc.

#### Detailed Description of the Invention

The elastic shaped structures of this invention are manufactured from fiber-forming, long chain, synthetic  
10 polymer comprised of at least 85% of a segmented polyurethane. Preferably the segmented polyurethane is one based on polyether or polyester. Such polymers are prepared by well-known methods such as those described in U.S. 4,296,174 and in EPO Application No. 343,985  
15 published on November 29, 1989.

To obtain the products of this invention, a solution of the polyurethane is first prepared. Suitable solvents include amide solvents, such as dimethylacetamide (DMAc), dimethylformamide (DMF) and N-methylpyrrolidone (NMP).  
20 Suitable solutions have a viscosity of between 125 and 2000 centipoises, preferably from about 500 to 800 centipoises, at room temperature. In practice, polymer is added to the solvent until the desired viscosity is achieved. Generally, from about 8 to 20% by weight of  
25 polymer will result in a suitable viscosity.

The solution is then be introduced as droplets of from about 0.01 to 0.05 cubic centimeters (cc.) into a coagulating bath which solidifies the polymer in the form of small substantially spherical beads having a diameter  
30 of from about 1 to 4 mm. The coagulating bath comprises a liquid that extracts the solvent of the polymer solution but is a non-solvent for the polymer. Water is suitable for this purpose.

Alternatively, the polymer solution may be spun  
35 through a spinneret directly into the coagulating bath

and withdrawn therefrom as filament. Still other shaped structures can be obtained by agitation of the coagulating bath as the stream of polymer solution is introduced into the coagulating bath.

5 In the case of beads, essentially the entire surface comprises a nonporous sheath having a thickness of less than about 3 microns (see Figs. 2 and 4) By "nonporous" is meant that essentially no pores are visible at the surface in a scanning electron micrograph at a  
10 magnification of 5000 X (see Fig. 3). A pore is defined as a passage through the sheath to a void beneath the sheath. Such passages, if present, would be visible in cross-section under a microscope. At times, the sheath may be crenulated or in collapsed form giving the  
15 appearance of one or more pores, but the absence of pores can be confirmed by examining a cross-section of the sphere through the suspect zone. If the sheath is intact, no passageway to the voids below will be observed.

20 The material under the sheath is in the form of cells or voids (see Fig. 1) left by extraction of the polymer solvent. A measure of the void content is obtained by density measurement as described below.

When in the form of filaments, the product of the  
25 invention has a sheath similar to that present in the beads which will of course be absent at the filament ends where lengths of filament ends have been cut. Filaments having a denier of from 60 to 1800 have been made although filaments of substantially greater denier could  
30 be prepared if desired.

In a typical procedure, the beads may be prepared as follows:

A 10% solution of a segmented polyurethane in dimethylacetamide (DMAc) is prepared. A particularly  
35 preferred polyurethane is comprised of polytetramethylene

ether glycol of molecular weight between 600 and 5000, preferably between 1500 and 2500, end-capped with methylene diphenylene diisocyanate and chain extended with aliphatic diamine. Droplets of about 0.04 cc. are released from about 45 cm. above through a non-coagulating zone, e.g., air, and into a container of water (depth about 30 cm.) at 25°C. Coagulation takes place almost immediately upon contact with the water and substantially spherical beads form which are collected from the bottom of the container.

As the droplets of solution enter the coagulation bath, solidification of the polymer of the droplet begins. Large droplets will, of course, produce large beads. Droplet size will also influence porosity of the final product because of the effect of the time it takes to extract solvent from the droplet. The distance between the point the droplet is released to the surface of the coagulation bath as well as the force with which it contacts the bath will affect the shape of the final bead. Distances of from 20 to 60 cm. have given satisfactory results.

The coagulated beads are then separated from the coagulation bath, washed to ensure substantially complete removal of DMAc and subjected to drying. Temperatures and time for drying may vary considerably. Typically, a temperature range of from 25 to 80°C is used, with drying best accomplished by passing heated air over the wet beads.

A technique similar to the above can be employed to prepare filaments, however, the spinneret surface is preferably kept in contact with the water coagulant as in a wet-spinning operation and the coagulated filament is withdrawn from the bath. Freeze-drying of the filament allows best retention of shape.

### Tests and Measurement Procedures

Sheath thickness - Scanning electron micrographs of the beads at magnifications of 100X to 5000X show a continuous skin or sheath at the surface with virtually  
5 no pores or openings to the interior. The beads can be cut in half and viewed in cross-section. AT 100-3000X, the sheath thickness can be conveniently measured.

The samples are prepared for measurement as follows:

For the surface view, the bead sample was mounted  
10 directly onto an aluminum stub with double-face tape. The cross-section of the bead was obtained by submerging it in liquid nitrogen and cutting it with a razor blade. The sectioned bead was then mounted on an aluminum stub with double-faced tape. A drop of carbon paint was  
15 applied to the samples, which were then sputter-coated with gold/palladium.

A scanning electron microscope (SEM) that was used in obtaining the micrographs was a JEOL 840. The images were acquired from secondary electrons. The accelerating  
20 voltage was 5 KV. Micrographs were taken at various magnifications.

Void content - The shaped structures, e.g., beads, have numerous voids. The void content is calculated by the equation

$$25 \quad \text{Voids} = \left[ 1 - \left( \frac{\text{bead density}}{\text{bulk polymer density}} \right) \right] \times 100\%$$

Bead density is determined by dividing its mass by its volume. Assuming a spherical bead, the volume will be  
4/3 X

30  $\pi r^3$  where  $r$  is the measured radius (as with a micrometer). The bulk polymer density, if not known, may be readily measured by techniques known in the art.

Viscosity - Measured in centipoises using a Brookfield Viscometer.

ExamplesExample 1

This example illustrates the preparation of microporous elastic segmented polyurethane beads of the invention.

A homogeneous solution was prepared of DMAc and the polyurethane described in Example 1 of U.S. Patent No. 4,296,174 (Col. 5 and 6) namely, a polyurethane comprising a polytetramethylene ether glycol of molecular weight about 1800, end-capped with methylene diphenylene diisocyanate and chain extended with a mixture of aliphatic diamines, except that the ethylene diamine/1,3-cyclohexylenediamine ratio was 90/10 and the capping ratio was 1.62. The solution had a viscosity of 583 centipoise at room temperature as measured by a Brookfield Viscometer. The solution was loaded into a 500 ml pressure equalizing dropping funnel which was placed at least 18 inches above the surface of ~10 liters of distilled water contained in a 14 liter bucket. Into the center of the bucket of water was placed a double helical agitator connected to an air motor. The agitator was kept moving at a medium to high rate. The dropping funnel was placed over the outer perimeter of moving water, and the solution was dripped into the water at a rate which did not exceed 1 drop per second. The resulting droplets were initially quite gel-like; however, within 15 minutes they would become opaque white and elastic. The droplets were agitated until all of the solution was used (5-8 hours). They were then isolated and put into a bucket of agitated fresh water. This process was repeated hourly for at least 4 hours. Often the beads were washed overnight (without changing water). After the beads were thoroughly washed they were drained and excess water was pressed out. They were then loaded into aluminum pans. The beads were then placed into a



vacuum oven at 60-80°C for 4-7 days. During this time the beads were occasionally agitated. The resulting dry beads were non-tacky, well separated, uniform spheres approximately 2-4 mm in diameter. Approximate yield was  
5 30-40g per batch (~750 ml in volume).

Scanning electron micrographs of a sampling of the beads were made. They were found to have continuous skins less than 3 microns thick. Essentially no pores were visible at the surface of the beads at 5000X  
10 magnification. The beads had a void content in the range of 60 to 90%.

#### Example 2

This example illustrates the preparation of a microporous elastic segmented urethane fiber with reduced  
15 density using the invention described herein.

A 15% solids spinning solution in DMAc (about 1000 centipoises) was used. The polymer employed is the same as in Example 1. The solution was charged into a wet spinning cell which is equipped with a gear-driven piston  
20 on one end to force the solution out of the spinneret at a rate of 2.82 ml per minute. The single-hole spinneret having a length and diameter dimension of 0.015 inch X 0.015 inch, was totally immersed in coagulant water bath. The bath was controlled at 9.5°C degree, and the solution  
25 was maintained at room temperature. The extruded filament was immediately coagulated and remained immersed for a distance of 36 inches before withdrawing and winding on bobbin at a speed of 15 meters per minute.

The wound filament was left on bobbin and soaked in  
30 water overnight. Freeze drying was found the most effective method of removing water and any solvent from the fiber while preserving the porous structure. Such dried filament can be rewound with minimum fiber sticking.

The fiber has a density of 0.181 g/cc, versus a density of 0.975 g/cc for a solid polymer fiber. SEM of the porous fiber exhibited a non-porous skin with highly voided interior.

5        While the above examples illustrate shaped structures of pure microporous elastic segmented polyurethane, it will be apparent to those skilled in the art that dyes, pigments and other additives may be incorporated in minor amounts in the polymer solution  
10 prior to producing the droplets or prior to spinning to the extent they are compatible with or soluble in the solvent. Also, structures of polymer blends may be prepared by dissolving other polymers in the polyurethane solution before formation of the shaped structures. In  
15 general, these other polymers, such as poly(m-phenylene isophthalamide) are added in minor amounts to not adversely affect the utility of the structure while imparting other desired qualities.

## CLAIMS

1. A substantially spherical bead consisting essentially of microporous elastic segmented polyurethane having a void content of from 60 to 90% and encapsulated  
5 by a substantially continuous sheath having a thickness of less than about 3 microns and having essentially no pores visible at the surface at a magnification of 5000 X.
2. A filament having a denier of from 60-1800,  
10 essentially of microporous elastic segmented polyurethane having a void content of from 60 to 90% and encapsulated by a substantially continuous sheath having a thickness of less than about 3 microns and having essentially no  
15 pores visible at the surface at a magnification of 5000 X.
3. The shaped structure of Claims 1 or 2 wherein the polyurethane is comprised of polytetramethylene ether glycol of molecular weight between 600 and 5000, end-capped with methylene diphenylene diisocyanate and chain  
20 extended with aliphatic diamine.
4. The shaped structure of Claims 1, 2, or 3 wherein the polyurethane is comprised of polytetramethylene ether glycol of molecular weight about 1800, end-capped with methylene diphenylene diisocyanate  
25 and chain-extended with 90/10 ratio of ethylene diamine/1,3-cyclohexylenediamine and with a capping ratio of the diisocyanate to glycol of 1.62.
5. A process for preparing shaped structures according to Claim 1 comprising, forming a solution of a  
30 segmented polyurethane in an amide solvent, said solution having a viscosity between 125 and 2000 centipoises at room temperature, introducing droplets thereof into a coagulation bath and withdrawing the resulting shaped structures from the bath.

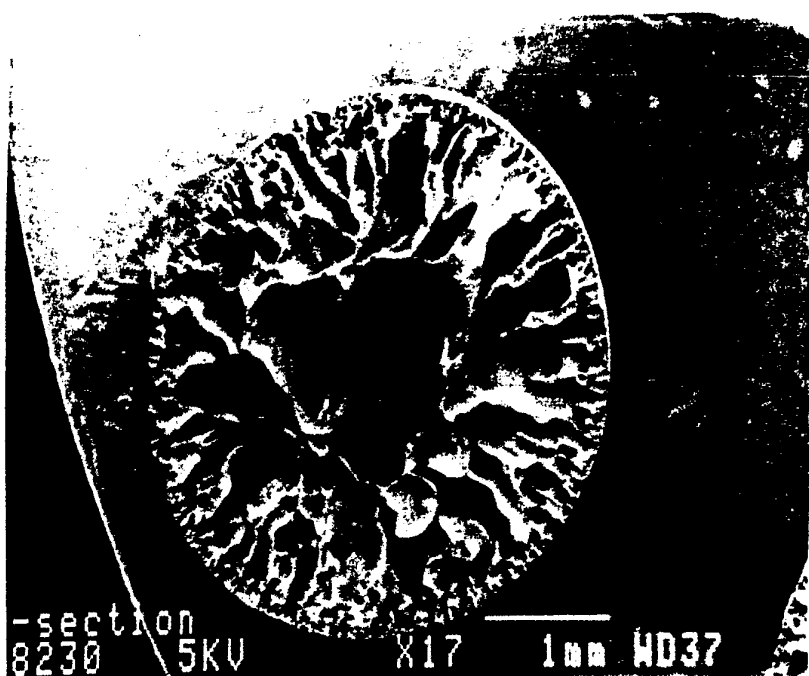
6. A process according to Claim 5 wherein the coagulation bath is water.

7. A process according to Claim 5 wherein the solution viscosity is from about 500 to 800 centipoises.

5        8. A process for preparing the shaped structure of Claim 2 comprising forming a solution of a segmented polyurethane in an amide solvent, said solution having a viscosity between 125 and 2000 centipoises at room temperature, extruding the solution directly into a  
10 coagulated bath and withdrawing coagulated filament from the bath.

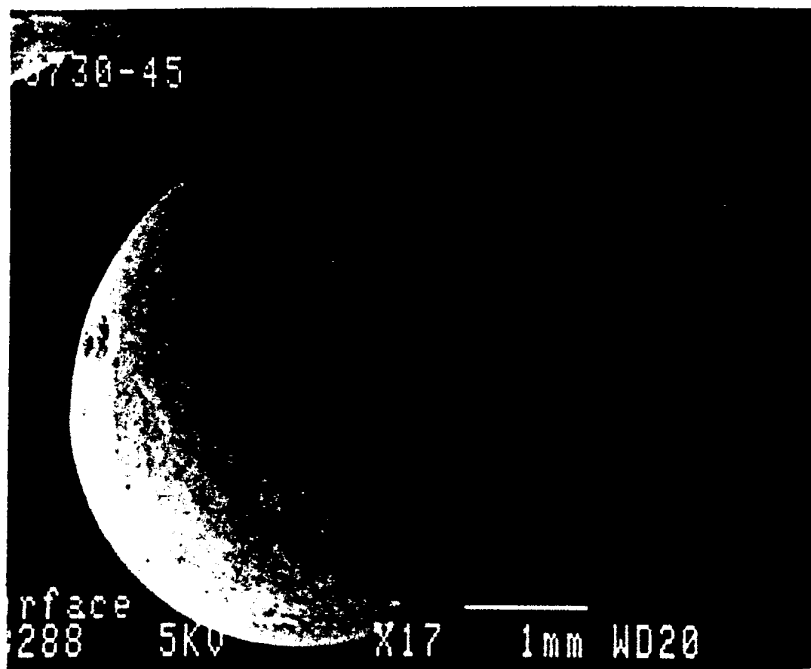
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FIG. 1



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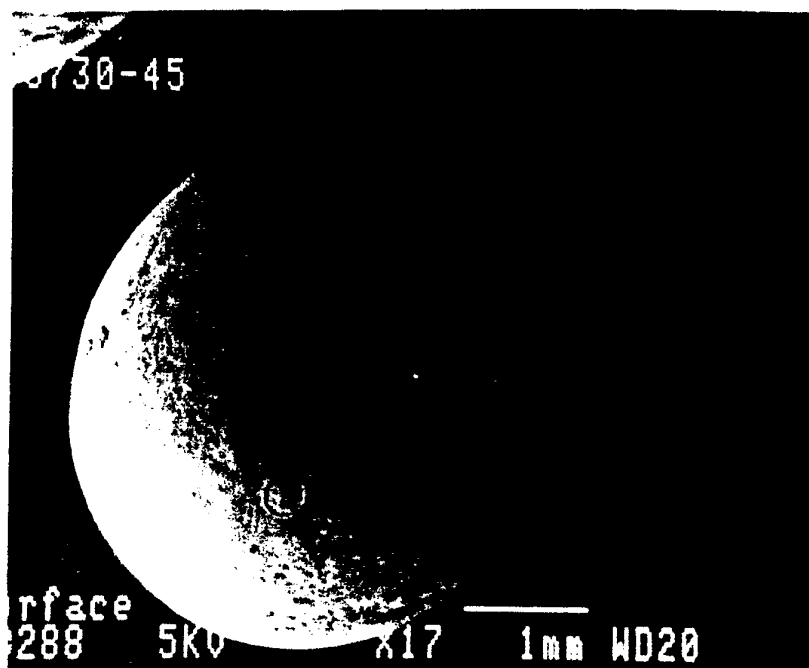
FIG.2



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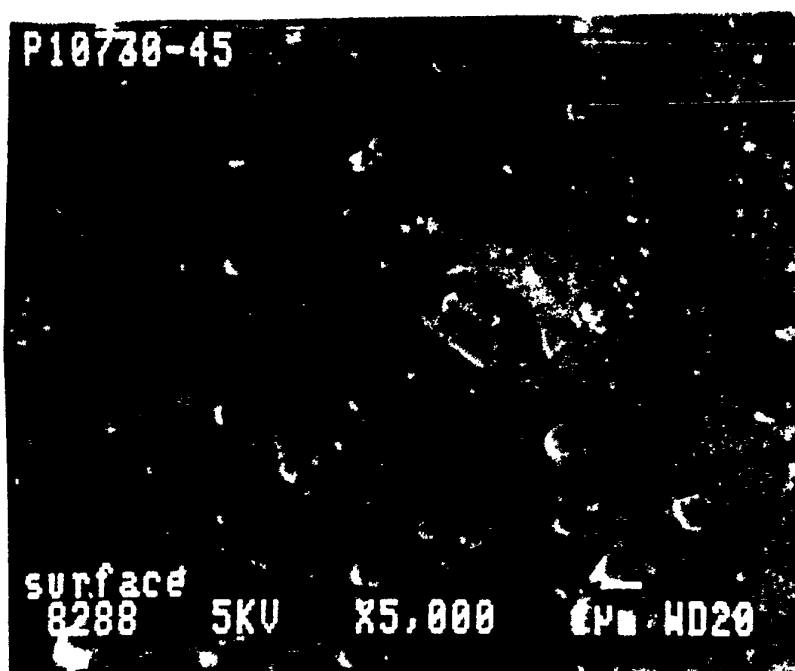
FIG.2



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FIG. 3

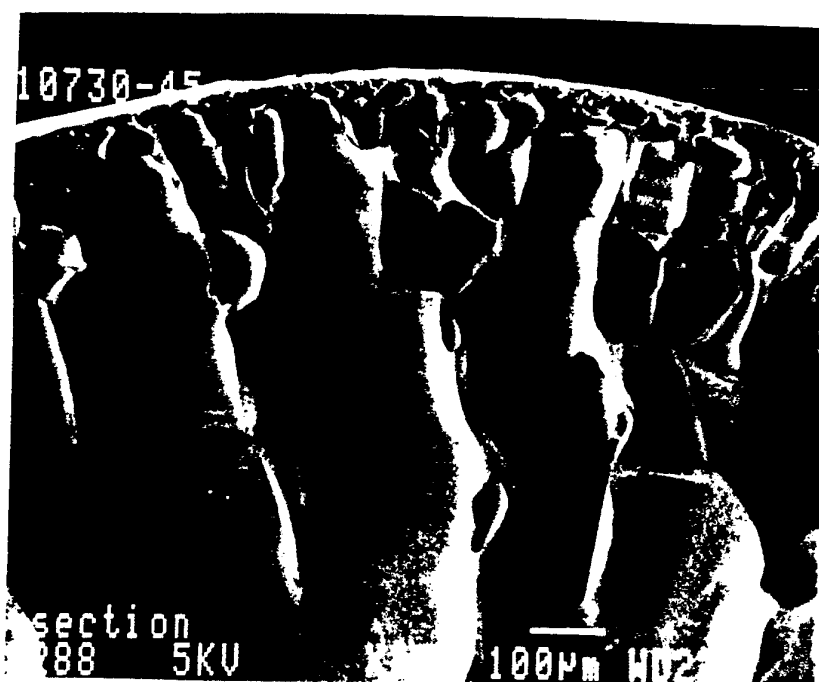


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FIG. 4

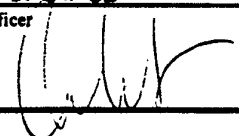


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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/09169

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08J9/28; D01F6/70; //C08J9/28, C08L75:04		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08J ; C08F ; D01F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	EP,A,0 343 985 (DU PONT DE NEMOURS) 29 November 1989 cited in the application	1-8
A	see claims 1-7	1
Y	US,A,4 905 367 (PINCHUK & AL.) 6 March 1990 see claims 1-5,7	2-8
Y	GB,A,939 244 (HOECHST A.G.) 9 October 1963 see page 3, line 60 - line 103; claim 1; example 1	1
<p><sup>10</sup> Special categories of cited documents:</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> <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>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
25 MARCH 1992		28.04.92
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		OU DOT R. 

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. US 9109169  
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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  
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0343985	29-11-89	US-A- 5000899 JP-A- 2019511	19-03-91 23-01-90
US-A-4905367	06-03-90	None	
GB-A-939244		DE-B- 1269357 FR-A- 1242020	