

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>4</sup> : <b>B29C 61/00, C08L 71/00</b>		<b>A1</b>	(11) International Publication Number: <b>WO 86/ 04542</b>
			(43) International Publication Date: 14 August 1986 (14.08.86)
<p>(21) International Application Number: PCT/GB86/00066</p> <p>(22) International Filing Date: 6 February 1986 (06.02.86)</p> <p>(31) Priority Application Number: 699,102</p> <p>(32) Priority Date: 7 February 1985 (07.02.85)</p> <p>(33) Priority Country: US</p> <p>(71) Applicant (for MG only): RAYCHEM LIMITED [GB/GB]; Rolls House, 7 Rolls Buildings, Fetter Lane, London EC4 1NL (GB).</p> <p>(71) Applicant (for all designated States except MG): RAYCHEM CORPORATION [US/US]; 300 Constitution Drive, Menlo Park, CA 94025 (US).</p> <p>(72) Inventors: RAMSEY, Edward, Matthew ; 2425 Delaware Avenue, Redwood City, CA 94061 (US). ROWLANDS, Ceinwen, Delia ; 6 Abingdon Court Lane, Cricklade, Wiltshire (GB). SCHOTT, Brian, Edward ;</p>		<p>37249 Greenpoint Street, Neward, CA 94560 (US). SIDEN, Dennis, Carl ; 9 Vista Verde Way, Portola Valley, CA 94025 (US).</p> <p>(74) Agent: JAY, A., W.; Raychem Limited, Intellectual Property Law Department, Faraday Road, Dorcan, Swindon, Wiltshire (GB).</p> <p>(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), MG, NL (European patent), SE (European patent).</p> <p><b>Published</b>  <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
(54) Title: HEAT RECOVERABLE AUTOMOTIVE RETAINING MEMBERS			
(57) Abstract			
<p>Heat recoverable automotive retaining members prepared from semi-crystalline polymers having a glass transition temperature, T<sub>g</sub>, above about 25°C exhibit unexpectedly high recovery stress under certain conditions and can withstand conditions encountered in automotive use, e.g. retaining hoses, etc., in place in high temperature engine enclosures of vehicles.</p>			

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GA	Gabon	MR	Mauritania
AU	Australia	GB	United Kingdom	MW	Malawi
BB	Barbados	HU	Hungary	NL	Netherlands
BE	Belgium	IT	Italy	NO	Norway
BG	Bulgaria	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	LI	Liechtenstein	SN	Senegal
CH	Switzerland	LK	Sri Lanka	SU	Soviet Union
CM	Cameroon	LU	Luxembourg	TD	Chad
DE	Germany, Federal Republic of	MC	Monaco	TG	Togo
DK	Denmark	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali		
FR	France				

HEAT RECOVERABLE AUTOMOTIVE RETAINING MEMBERS

This invention relates to automotive retaining members capable of replacing known metal "Jubilee" hose clips and the like with considerable advantages in terms of weight and installation costs. The "Jubilee"-type retaining members have hitherto been regarded as virtually unparalleled in their ability to withstand the stresses of automotive service, especially in the high temperatures of the engine enclosures of vehicles.

The invention provides an automotive retaining member comprising a dimensionally heat recoverable semi-crystalline material having a glass transition temperature,  $T_g$ , above about  $25^{\circ}\text{C}$ , said member having a recovery stress of above about  $1100 \times (E-1)^{0.5}$  pounds per square inch, wherein  $E$  is the unresolved recovery ratio.

The invention thus provides, contrary to expectation, polymeric retaining members, preferably in the form of rings, and preferably comprising polyester or polyamide material, which have surprisingly high resistance to the conditions encountered in automotive service, even in the relatively higher temperature environments in and around the engine enclosure of a vehicle. The retaining members of this invention may thus replace metal clips (or clamps) for holding resiliently deformable articles, especially hoses or other hollow tubular articles, in contact with substantially non-resilient substrates, part of which, for example, may be gripped by an aperture of the hose or other resilient article. Fibers of the polymeric material may be used

instead of continuous polymer to form the retaining member, if desired.

A dimensionally heat recoverable article is an article the dimensional configuration of which may be made substantially to change when subjected to heat treatment. Usually these articles recover towards an original shape from which they have previously been deformed but the term "heat-recoverable", as used herein, also includes an article which, on heating, adopts a new configuration, even if it has not been previously deformed.

In their most common form, such articles comprise a heat-shrinkable sleeve made from a polymeric material exhibiting the property of elastic or plastic memory as described, for example, in U.S. Patents 2,027,962; 3,086,242 and 3,597,372. As is made clear in, for example, U.S. Patent 2,027,962, the original dimensionally heat-stable form may be a transient form in a continuous process in which, for example, an extruded tube is expanded, whilst hot, to a dimensionally heat-unstable form but, in other applications, a preformed dimensionally heat-stable article is deformed to a dimensionally heat-unstable form in a separate stage.

Typically, such articles are prepared from polymers that are capable of being cross-linked, for example, polyethylene, polybutene-1, poly 4-methyl pentene and fluorinated polyolefins for example, ethylene-trifluorochloroethylene

copolymers, ethylenetetrafluoroethylene copolymers, and vinylidene fluoride polymers, especially polyvinylidene fluoride, and blends thereof, for example, the fluorinated olefin blends as described and claimed in British Patent No. 1,120,131, and the like.

In the production of heat recoverable articles, from cross-linkable polymers, the polymer material may be cross-linked at any stage in the production of the article that will enhance the desired dimensional recoverability. One manner of producing a heat-recoverable article comprises shaping the polymeric material into the desired heat-stable form, subsequently cross-linking the polymeric material, heating the article to a temperature above the crystalline melting point or, for amorphous materials the softening point, as the case may be, of the polymer, deforming the article and cooling the article whilst in the deformed state so that the deformed state of the article is heat-unstable, whereafter application of heat will cause the article to assume its original heat-stable shape.

Heat recoverable articles from cross-linkable crystalline polymers can be prepared by deforming the uncrosslinked polymer below the crystalline melting point and without cross-linking, cooling the deformed article. Subsequent heating of the article to the deformation temperature causes the article to recover toward the undeformed configuration but it does so with a relatively low recovery stress. As a result such recoverable articles are generally unsuitable

for use as mechanical devices, such as couplings, where a high recovery stress is required. Further, the use of such devices requires not only a high recovery stress but that the high stress be maintained after the device has been recovered against the substrate and subsequently cooled to ambient temperature. Heat recoverable devices disclosed in the art do not meet this requirement.

It has been unexpectedly discovered that dimensionally heat-recoverable retaining members of semi-crystalline polymers having a glass transition temperature above about 25°C, preferably above 120°C, exhibit exceptionally high recovery stress under certain conditions, which recovery stress is subsequently retained and in some instances increased, and the members can withstand conditions encountered in automotive use, as aforementioned.

Another aspect of this invention comprises a method of producing the dimensionally heat-recoverable automotive retaining members comprising

- a) heating a shaped article of a semi-crystalline polymer having a glass transition temperature ( $T_g$ ) above 25°C to a temperature above the  $T_g$  of the polymer;
- b) deforming the article; and
- c) cooling the article while maintaining the article

in the deformed state, thereby producing an article which, when heated to a temperature between  $T_g$  and the crystalline melting temperature,  $T_m$ , of the polymer, recovers with a recovery stress above about  $1100 \times (E-1)^{0.5}$  pounds per square inch, wherein  $E$  is the unresolved recovery ratio and substantially retains such stress on cooling of the article to a temperature below  $T_g$ .

These and other features, aspects and advantages of the present invention will become better understood with reference to the appended claims, the following description and accompanying drawings, where:

FIG. 1 is a graph of the peak values of unresolved recovery stress divided by the expansion stress vs. the difference between the recovery and expansion temperatures for 4 materials useful for preparing articles of the invention and for one material (lowest curve) incapable of providing articles of the present invention;

FIG. 2 is a graph of the unresolved recovery stress after 1 minute at the recovery temperature divided by the expansion stress vs. the difference between the recovery and expansion temperatures for 4 materials useful for preparing articles of the invention and for one material (lowest curve) incapable of providing articles of the present invention;

FIG. 3 is a graph of the unresolved recovery stress vs. the unresolved recovery ratio for 4 materials useful for preparing articles of the present invention and for 2 materials (lowest 2 curves) incapable of providing articles of the present invention; and

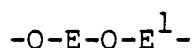
FIG. 4 is a graph of the unresolved recovery stress vs. percentage recovery for 4 materials useful for preparing articles of the present invention and for 1 material (PE) incapable of providing articles of the present invention.

#### Detailed Description of the Invention

The heat-recoverable articles of this invention are prepared using a semi-crystalline polymer having a glass transition temperature,  $T_g$ , above about 25°C. Preferably the polymer used to make the article has a  $T_g$  above about 100°C, more preferably above 120°C, and most preferably above about 150°C. The polymer used should be a polymer having crystalline melting temperature of above about 150°C, preferably above about 180°C and most preferably above about 290°C. Such polymers include for example, polyamides, such as polycaprolactam, nylon 6, and poly(11-iminoundecanoyl), nylon 11, crystalline polyesters, such as crystalline polyethylene terephthalate, polybutylene terephthalate and the like, other crystalline or crystallizable aromatic polymers, such as polyphenylene sulfide and polyaryl ethers, in particular polyaryl ether ketones. Blends of these polymers with each other and/or with other polymers can also be utilized.

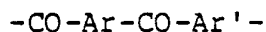
Semi-crystalline polyaryl ether ketones are particularly preferred polymers for the preparation of heat recoverable articles of this invention. Such polymers typically have a glass transition temperature in the range of between about 140°C to about 250°C and a crystalline melting temperature between about 270°C and 450°C.

Polyaryl ether ketones comprise repeat units of the formula:



wherein E and E<sup>1</sup> are aromatic radicals at least one of which is a polynuclear aromatic moiety having two aromatic nuclei joined by a ketone group, the other of E and E<sup>1</sup> is an aromatic moiety containing at least one aromatic ring. The polymer can contain other polynuclear moieties joined by other functional groups such as sulfone, sulfide, alkylene, etc.

Poly(aryl ether ketones) suitable for use in this invention have the repeat units of the formula:

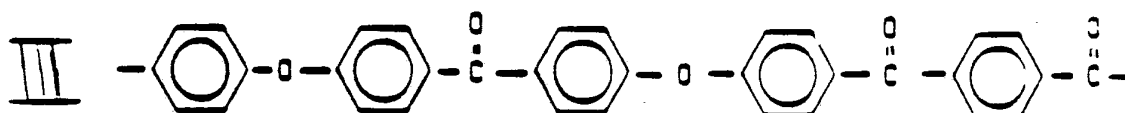
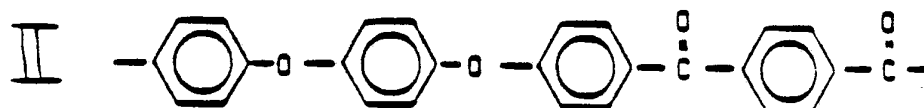
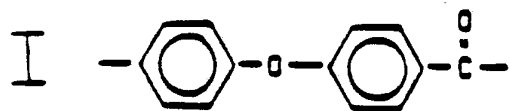


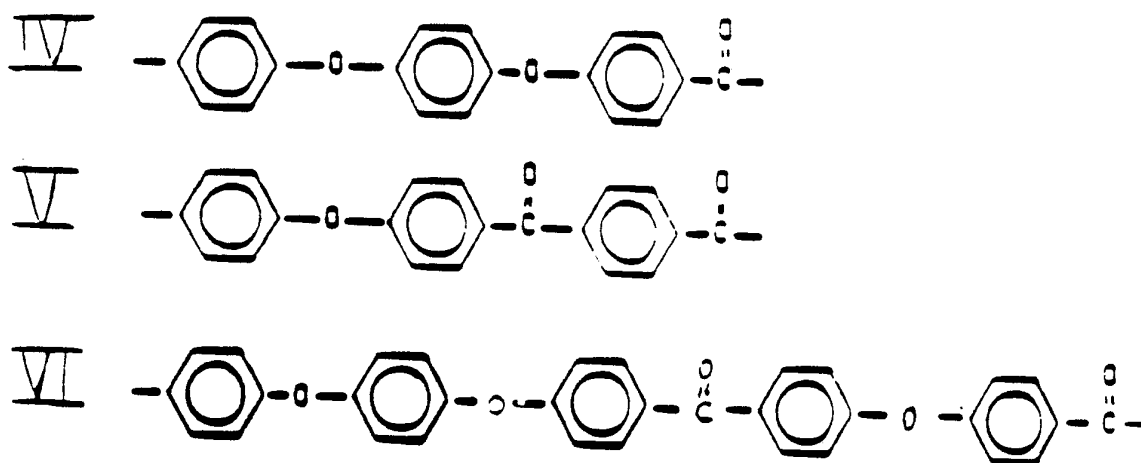
wherein Ar and Ar' are aromatic moieties at least one of which contains a diaryl ether linkage forming part of the polymer backbone and wherein both Ar and Ar' are covalently linked to the carbonyl groups through aromatic carbon atoms.

Preferably, Ar and Ar' are independently selected from substituted and unsubstituted phenylene and substituted and unsubstituted polynuclear aromatic moieties. The term polynuclear aromatic moieties is used to mean aromatic moieties containing at least two aromatic rings. The rings can be fused, joined by a direct bond or by a linking group. Such linking groups include for example, carbonyl, ether sulfone, sulfide, amide, imide, azo, alkylene, perfluoroalkylene and the like. As mentioned above, at least one of Ar and Ar' contains a diaryl ether linkage.

The phenylene and polynuclear aromatic moieties can contain substituents on the aromatic rings. These substituents should not inhibit or otherwise interfere with the polymerization reaction to any significant extent. Such substituents include, for example, phenyl, halogen, nitro, cyano, alkyl, 2-alkynyl and the like.

Poly(aryl ether ketones) having the following repeat units (the simplest repeat unit being designated for a given polymer) are preferred:





Poly(aryl ether ketones) can be prepared by known methods of synthesis. Preferred poly(aryl ether ketones) can be prepared by Friedel-Crafts polymerization of a monomer system comprising:

- I) (i) phosgene or an aromatic diacid dihalide together with
- (ii) a polynuclear aromatic comonomer comprising:
  - (a)  $\text{H-Ar-O-Ar-H}$
  - (b)  $\text{H-(Ar-O)}_n\text{-Ar-H}$   
wherein  $n$  is 2 or 3
  - (c)  $\text{H-Ar-O-Ar-(CO-Ar-O-Ar)}_m\text{-H}$   
wherein  $m$  is 1, 2 or 3

or

- II) an acid halide of the formula:  
$$\text{H-Ar}''\text{-O-}[(\text{Ar}''\text{-CO})_p\text{-(Ar}''\text{-O})_q(\text{Ar}''\text{-CO})_r]_k\text{-Ar}''\text{-CO-Z}$$
wherein Z is halogen, k is 0, 1 or 2, p is 1 or 2, q is 0, 1 or 2 and r is 0, 1 or 2;

or

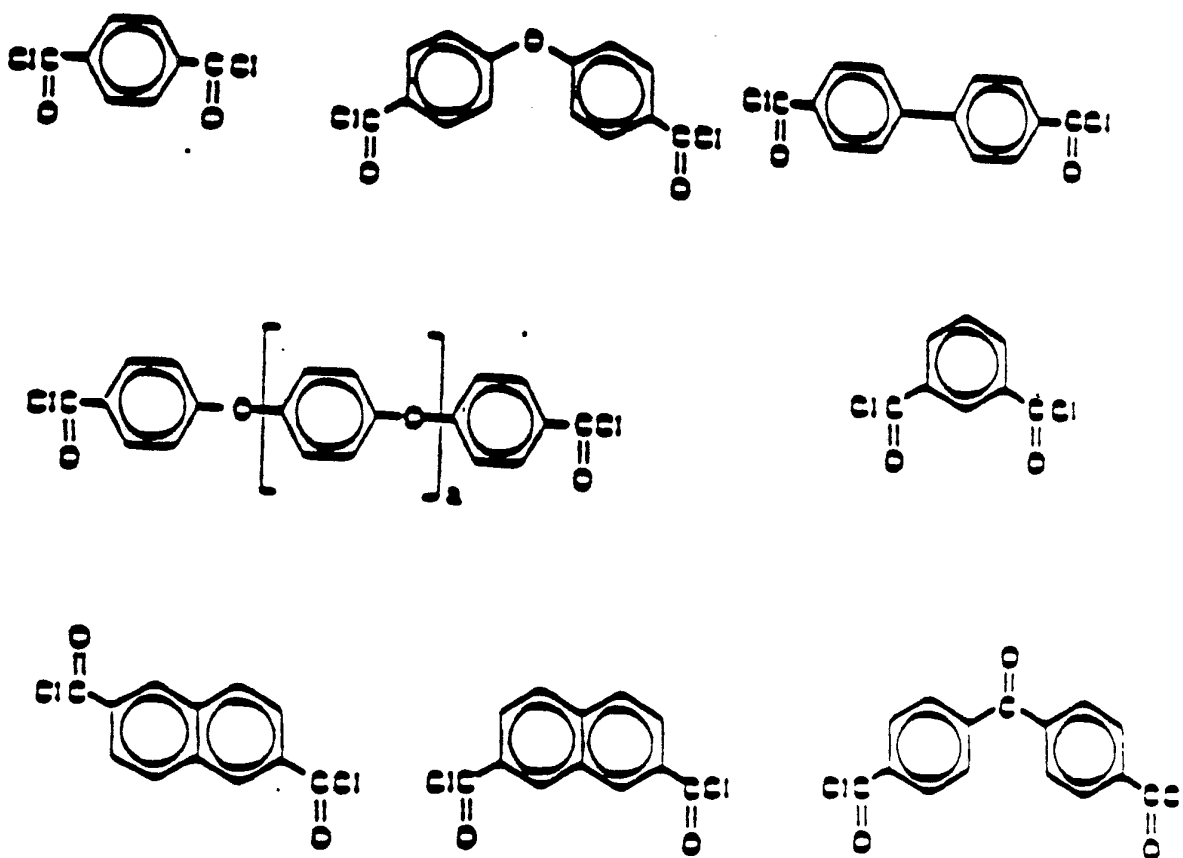
- III) an acid halide of the formula:  
$$\text{H-(Ar}''\text{-O)}_n\text{-Ar}''\text{-Y}$$
wherein n is 2 or 3 and Y is CO-Z or CO-Ar''-CO-Z where Z is halogen;

wherein each Ar'' is independently selected from substituted or unsubstituted phenylene, and substituted or unsubstituted polynuclear aromatic moieties free of ketone carbonyl or ether oxygen groups, in the presence of a reaction medium comprising:

- A) A Lewis acid in an amount of one equivalent per equivalent of carbonyl groups present, plus one equivalent per equivalent of Lewis base, plus an amount effective to act as a catalyst for the polymerization;
- B) a Lewis base in an amount from 0 to about 4 equivalents per equivalent of acid halide groups present in the monomer system;
- C) a non-protic diluent in an amount from 0 to about 98% by weight, based on the weight of the total

reaction mixture.

The aromatic diacid dihalide employed is preferably a dichloride or dibromide. Illustrative diacid dihalides which can be used include, for example



wherein a is 0-4.

Illustrated polynuclear aromatic comonomers which can be used with such diacid dihalides are:

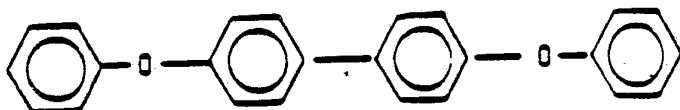
(a)  $\text{H-Ar}''\text{-O-Ar}''\text{-H}$ , which includes for example:



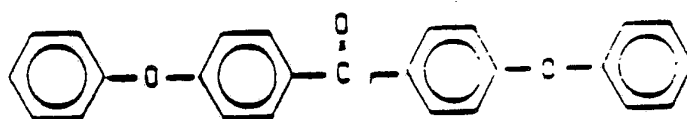
(b)  $\text{H-(Ar}''\text{-O)}_n\text{-Ar}''\text{-H}$ , which include, for example:



and

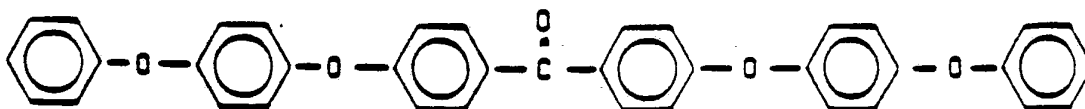


(c)  $\text{H-Ar}''\text{-O-Ar}''\text{-(CO-Ar}''\text{-O-Ar}'')_m\text{-H}$ , which includes, for example:

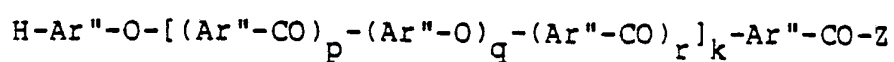


and

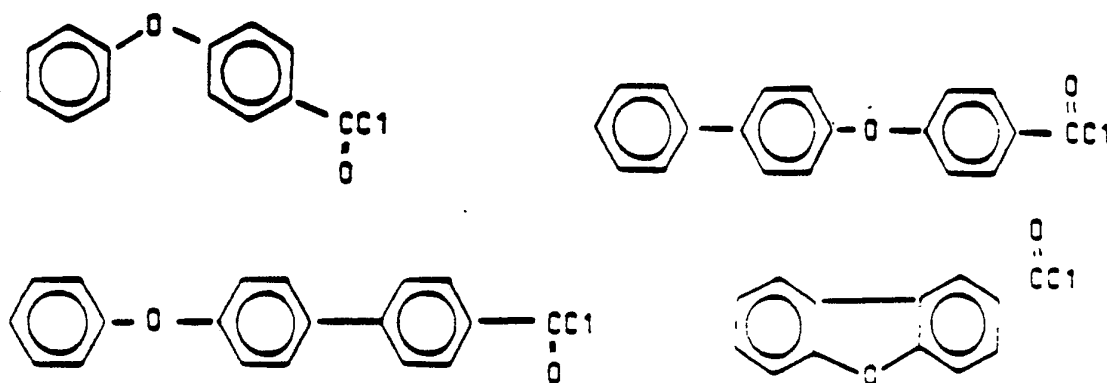
(d)  $\text{H-(Ar}''\text{-O)}_n\text{-Ar}''\text{-CO-Ar}''\text{-(O-Ar}'')_m\text{-H}$  which includes, for example:



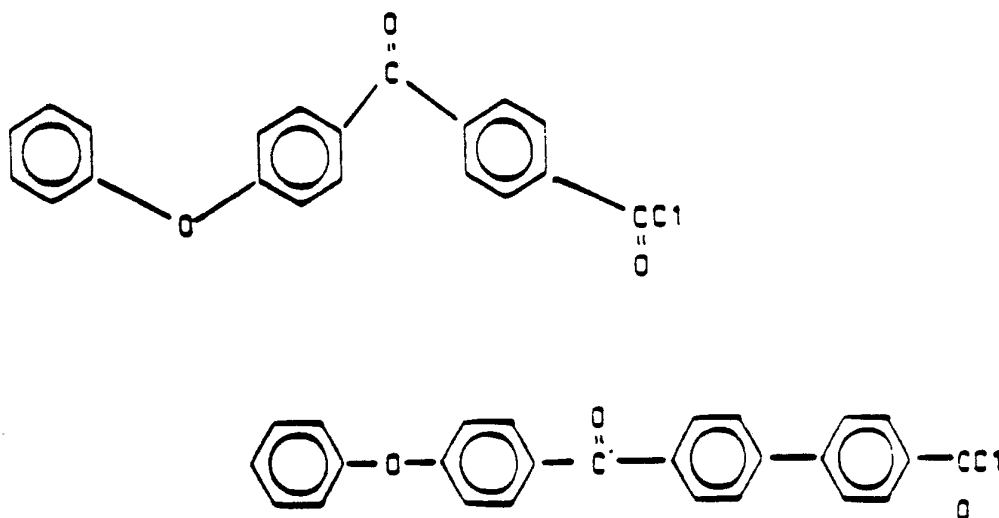
Monomer systems II and III comprise an acid halide.  
(The term acid halide is used herein to refer to a monoacid monohalide.) In monomer system II, the acid halide is of the formula:



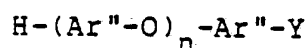
Such monomers include for example, where  $k = 0$



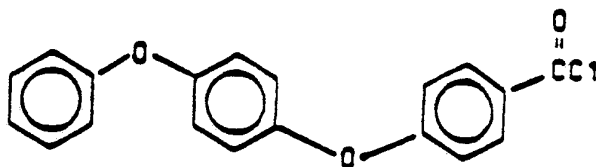
and where  $k = 1$



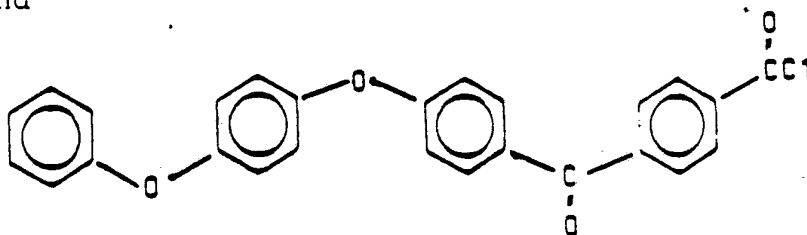
In monomer system III, the acid halide is of the formula



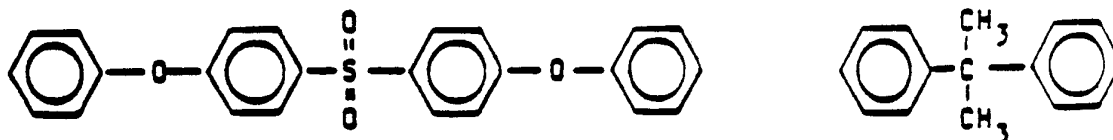
Examples of such acid halides include



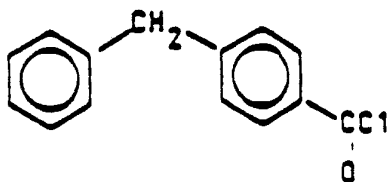
and



It is to be understood that combinations of monomers can be employed. For example, one or more diacid dihalides can be used with one or more polynuclear aromatic comonomers as long as the correct stoichiometry is maintained. Further, one or more acid halides can be included. In addition monomers which contain other linkages such as those specified above, can be employed as long as one or more of the comonomers used contains at least one ether oxygen linkage. Such comonomers include for example:



which can be used as the sole comonomer with an ether containing diacid dihalide or with phosgene or any diacid dihalide when used in addition to a polynuclear aromatic comonomer as defined in I(ii)(a), I(ii)(b), I(ii)(c) or I(ii)(d). Similarly



can be used as a comonomer together with an ether-containing polynuclear aromatic acid halide or as an additional comonomer together with a monomer system as defined in I.

The monomer system can also contain up to about 30 mole % of a comonomer such as a sulfonyl chloride which polymerizes under Friedel-Crafts conditions to provide ketone/sulfone copolymers.

Further details of this process for producing poly(aryl ether ketones) can be found in commonly assigned co-pending U.S. application Serial No. 594,503, filed 31 March 1984, the disclosure of which is incorporated herein by reference.

Other processes for preparing these polymers can be found in U.S. Patent Nos. 3,953,400, 3,956,240, 3,928,295, 4,176,222 and 4,320,224.

The extent to which other functional groups can be present depend on the nature of the particular group. For example, if sulfone groups are present the ratio of sulfone to ketone groups generally should be below about 30:70 as polymers containing a higher sulfone content are generally amorphous and non-crystallizable.

Other semi-crystalline aromatic polymers or polymers which can be rendered semi-crystalline include polyphenylene sulfide, polyphenylene ethers, and the like. Blends of these polymers with each other and with other polymers can be used.

As mentioned above, the polymer used in making the heat recoverable articles of this invention is semi-crystalline polymers or polymers capable of being rendered crystalline, that is are crystallizable. To exhibit the exceptional recovery stress the polymer should have a crystallinity of above about 5%. The degree of crystallinity varies depending on the particular polymer. It is generally desirable that the crystallinity of the polymer used is at a maximum. However, high recovery stresses can be obtained using semi-crystalline polymers with lower crystallinity. The polymer can be treated, for example by annealing, solvent swelling or the like to increase the crystallinity.

The dimensionally heat-recoverable articles of this invention are produced by deforming the polymeric material at a temperature above the glass transition temperature of the polymer but below the melting temperature of the polymer. By the glass transition temperature is meant the temperature which is the approximate midpoint of the temperature range over which a reversible change in the amorphous region of the polymer from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one (see ASTM D883). The crystalline melting temperature of the polymer is the temperature at which the last trace of crystallinity disappears as the temperature of the polymer is raised. The glass transition temperature is designated in the specification and claims of this patent application as  $T_g$  and the crystalline melting temperature as  $T_m$ .

The dimensionally heat-recoverable article is preferably in the form of a ring (not necessarily round) of the polymeric material. Such articles can be produced by conventional techniques such as injection molding, extruding, rotation molding and the like. The article is then rendered dimensionally heat-recoverable by heating the article to a temperature  $T_1$  between  $T_g$  and  $T_m$  of the polymer then deforming the article, for example, expanding it by passing it over a tapered mandrel or the like resulting in a heat shrinkable article, or compressing it by swaging or the like resulting in a heat expandable article. It is to be noted that when a rod shaped or filamentary article is rendered heat-shrinkable along its long axis, it is also rendered radially heat expandable.

The temperature at which the deformation step takes place is preferably about 5°C above  $T_g$  of the polymer. Following the deformation step the article is cooled, for example, to a temperature,  $T_2$ , below the glass transition temperature of the polymer. Generally the article is cooled to ambient temperature.

Another method of producing the article is to take a film of the polymer, the film being produced by extrusion, casting, or the like. The film is then heated to a temperature between  $T_g$  and  $T_m$  of the polymer and stretched. While maintained in the stretched configuration the film is cooled, generally to a temperature below the  $T_g$  of the polymer. The film can then be converted to the dimensionally recoverable ring or tubular article, for example, by wrapping it over a mandrel or by otherwise forming it and securing the ends. The article is then removed. Alternatively, the film can be wrapped around the substrate to be covered. On application of heat to a temperature above  $T_g$  but below  $T_m$  the article recovers with high recovery stress.

Another method of producing a heat-shrinkable article of this invention is to produce a heat-shrinkable fiber of a semi-crystalline aromatic polymer. The fiber can be prepared by conventional spinning techniques, slit film processes and the like. The fiber is heated to a temperature between  $T_g$  and  $T_m$  of the polymer and stretched by conventional fiber stretching techniques. The fiber is cooled,

for example to a temperature below  $T_g$  of the polymer. It is to be understood that the fiber (or film or tape as described above) is in itself a heat-recoverable article within the scope of this invention. To form a ring or tubular article the fiber can be wound around a mandrel and the ends thereof secured. The resulting article is removed from the mandrel. Alternatively, the film can be wrapped around the substrate to be covered. Upon application of heat to a temperature between  $T_g$  and  $T_m$  of the polymer, the article will shrink with a high recovery stress.

The term recovery stress is used herein to mean the recovery stress per unit area exhibited by a heat-recoverable article during constrained or unconstrained recovery. It is generally estimated by measuring the stress necessary to just prevent recovery at the given recovery temperature. Measurement of the recovery stress retention of recovery stress on cooling to room temperature is set forth in more detail hereinafter in the examples.

The term high recovery stress is used herein to mean a recovery stress of at least about  $1100 \times (E-1)^{0.5}$  pounds per square inch (psi), preferably at least about  $1500 \times (E-1)^{0.5}$  psi and most preferably  $2000 \times (E-1)$ , wherein  $E$  is the unresolved recovery ratio. The unresolved recovery ratio,  $E$ , is equal to  $R_r/R_o$  wherein  $R_r$  is the size of the heat recoverable article in a direction of recovery and  $R_o$  is the size of the article in that direction before the article is rendered heat-recoverable.

For the present automotive uses, wherein the item to be retained (e.g. a hose) is usually thicker (e.g. at least twice as thick, often more than three or four times as thick) than the retaining member wall thickness, the ratio E before commencement of any heat recovery is at least 1.5, preferably at least 2, more preferably at least 2-5, and most preferably at least 3.

Orientation of the polymer molecules in the hoop direction of the retaining member (re. "around the ring") is preferable to maximise hoop strength during expansion and gripping force on recovery. In this respect, members made by wrapping and securing suitably oriented fibres or films may be advantageous.

For a heat-shrinkable elongate article, this ratio is the ratio of the length after expansion or during recovery to the original length before expansion. For a thin walled tubular article this ratio is approximately the ratio of the corresponding diameters. For the thick walled tubular article this ratio is given by

$$\frac{(r_o^2 - (x^2 - 1)r_i^2)^{0.5} - r_i}{(r_o - xr_i)}$$

where  $x$  is the ratio of the internal diameter of the heat-recoverable article to the diameter ( $r_i$ ) of the original article before being rendered heat-recoverable and  $r_o$  is the external diameter of the heat recoverable article.

The high recovery stress is exhibited by articles of this invention when the article is constrained from complete recovery, that is, is prevented from recovering to its original dimensions. Generally, the high recovery stress is exhibited when the article is recovered less than 25%, based on the dimension of the deformed article. Preferably the article is prevented by the substrate against which it is recovered from recovery of more than about 20% and particularly more than about 15%, based on the dimension of the deformed article.

The articles of this invention are typically used by recovering the article against a substrate. The article, for example can be used to grip a hose around a pipe over

which the end of the hose is fitted. It can also be used to grip a flexible, preferably corrugated, protective housing around moving parts such as steering gear to be protected from dust and/or to retain lubricants.

The following Examples illustrate the recovery stress characteristics obtainable in materials suitable for making the automotive retaining members of this invention.

#### Example 1

Poly(oxy-p-phenylenecarbonyl-p-phenylene) (Stilan), poly(oxy-p-phenyleneoxy-p-phenylenecarbonyl-p-phenylene) (PEEK), polyethylene terephthalate (PET), poly(11-iminoundecanoyl) (nylon 11) and polyethylene (PE) were extruded as tape of about the same thickness (0.03 in.), width (1.5 in.) and melt draw ratio under the conditions described in Table 1. Tapes of the first four polymers, which have glass transition temperatures above 25°C, were cut into 5 in. X 1/4 in. strips with the long dimension in the extrusion direction and then annealed for the times stated in Table 1 to ensure each polymer was at a significant level of crystallinity. Strips of each polymer were mounted in the jaws of an Instron Tensile Tester and equilibrated for 3 minutes at a temperature 100°C above the Tg of the polymer in a preheated oven before being stretched at a jaw separation speed of 5 in. per minute to give a pre-determined expansion. For the polyarylene ether ketones this expansion was 100%. Nylon 11 and crystalline PET

undergo necking and drawing at the expansion temperatures selected so these polymers were drawn to their natural draw ratios (that is, to the extent that the entire strip between the jaws had necked). As soon as the desired elongation had been attained, the drawing was stopped and the drawn strip was quenched by placing two pieces of damp sponge in contact with either side of the strip and then removed from the Instron Tensile Tester.

Specimens about 3 in. long were cut from the center of the stretched samples and their cross-sectional areas measured. The specimens were placed in thermally insulated clips of such dimensions that only the ends of the samples projected out, which ends were clamped in an Instron Tensile tester jaws mounted inside the oven which was maintained at the appropriate recovery temperature. The insulating clip was then removed allowing the specimen to rapidly warm up to the oven temperature. The recovery stress exerted by the specimen was measured at its peak value and also after one, two and five minutes after removal of the insulating clip. The values of the true expansion stress at the selected expansion ratio and of the recovery stress at various temperatures above the  $T_g$  but below the  $T_m$  and at the above mentioned times after the specimens were placed in the oven are shown in Table 2.

In figures 1 and 2 the ratio of the recovery stress to the original expansion stress has been plotted as a function of the difference between the temperature of expansion and

of recovery. Figure 1 shows the peak values of this ratio and figure 2 the values obtained one minute after the specimens were positioned in the oven. This ratio represents the fraction of the expansion stress that is available at these recovery temperatures and at that expansion ratio. These figures also show the fraction of the expansion stress that is expressed on exposure to the recovery temperature for polyethylene rendered heat recoverable according to the teachings of the prior art as described in Example 2.

#### Example 2

This example illustrates the teachings of the prior art regarding heat recoverable articles and is outside the scope of the instant invention. The polyethylene tape described in Table 1 was rendered heat recoverable at a temperature of 85°C by the natural draw technique described above (we have found that drawing at 85°C yields heat recoverable articles with the highest recovery stresses). The recovery stress exerted by the polyethylene when maintained at temperatures between 40 and 100°C was at a maximum value of 850 psi at 85°C. A polyethylene strip expanded at 85°C which after cooling to room temperature had an expansion of 100% was heated to 85°C whilst clamped in the jaws of the Instron tester. On cooling down to room temperature the stress was found to increase 9% that is to 930 psi. In another embodiment taught by the prior art, polyethylene terephthalate amorphous tape extruded as described in example 1 was stretched at 100°C this being the maximum temperature that

we found could be used without crystallization of the amorphous tape during the drawing. The heat recoverable polyethylene terephthalate when tested as described in example 1 achieved a maximum recovery stress of 677 psi at 100°C recovery temperature after having previously been expanded 555%. In another embodiment outside the scope of this invention a strip of crystalline Stilan was placed in the jaws of an Instron Tensile Tester and elongated at room temperature. We found that the strip necked non-uniformly and broke at a low elongation well before the strip had completely drawn.

#### Example 3

Strips of crystalline tapes prepared and annealed as described in example 1 were expanded 100% at a temperature 50°C above the Tg of each polymer, cooled to room temperature and specimens cut from the expanded strips were heated to a temperature 50°C above their Tg while clamped in the jaws of an Instron Tensile tester. Table 3 shows the values of the recovery stress obtained after 1 minute of exposure to the hot oven.

#### Example 4

Strips of crystalline tapes prepared and annealed as described in example 1 were expanded to various degrees at a temperature 100°C above the Tg of each polymer and cooled to room temperature. Specimens cut from the expanded strips

were then heated to the temperature of expansion while clamped in the jaws of an Instron Tensile tester. Table 4 shows the peak recovery stressss generated within the first five minutes of exposure to the hot oven. Figure 3 shows the peak recovery stress for these specimens plotted as a function of unresolved recovery. The lowest two curves in Figure 3 show the peak recovery stresses observed with materials incapable of use in the present invention (see Table 4, amorphous PET and PE).

#### Example 5

The expanded specimens of Example 3 were heated to  $T_g + 50^\circ\text{C}$  and allowed to shrink to varying degrees, the recovery stress being measured as a function of the degree of recovery. Table 5 shows the values obtained; the variation of shrinkage stress with percent recovery is plotted in figure 4. The recoverable articles of the instant invention exhibit significant recovery stressss after shrinkages of as much as 16% based on the expanded dimensions.

#### Example 6

The expanded specimens of Example 1 were reheated to their expansion temperature while clamped in the jaws of an Instron Tensile tester then cooled to room temperature in the way described in Example 1, the percentage change in stress on cooling to room temperature being recorded. The results obtained are given in Table 6 and show that heat

recoverable articles of the instant invention retain a substantial proportion of or even increase the force which they exert on any substrate they are recovered onto on cooling.

#### Example 7

Tubular rings of engineering thermoplastics useful in this invention were injection molded using the conditions stated in Table 7, annealed as necessary to develop substantial crystallinity and preheated in an oven for ten minutes at  $T_g + 50^\circ\text{C}$ . The preheated rings were removed from the oven and expanded over a mandrel (similarly preheated) as rapidly as possible and quenched in water, then removed from the mandrel. The mandrel size was chosen so that each expanded ring had a diameter twice that of the unexpanded rings after removal from the mandrel. The expanded rings were recovered over tinned copper braid placed on mandrels of varying size so that the braid extended beyond the end of each mandrel. The braid used is typical of that used to electrically shield signal cables used in electronic equipment. The temperature of recovery was the same as that used to expand each ring. Each assembly was allowed to cool to room temperature. The free end of the braid was clamped in one jaw of the Instron Tensile tester and the mandrel in the other. The jaws were separated at a rate of 0.2 in. per minute. The peak force required to pull off the braid is given in table 8. Table 8 also shows the force required to pull of a polyethylene (Marlex 6003) ring expanded at  $85^\circ\text{C}$

as taught by the prior art. Table 8 shows that considerably greater force was required to pull of the heat recoverable rings of the instant invention than that required to remove the rings made following a teaching of the prior art.

Example 8

Annealed crystalline rings of Stilan were expanded onto a mandrel at room temperature. In every instance the rings expanded non-uniformly and broke at an elongation of about 30%.

Table 1

Polymer	<u>Stilan</u>	<u>PEEK</u>	<u>PET</u>	<u>Nylon-11</u>	<u>Nylon-6</u>	<u>PE</u>
Tradename						Marlex 6003
Extruder						
Size						
Temperature Profile:						
Zone 1	360	338	220	230		150°C
Zone 2	360	350	240	250		175°C
Zone 3	372	382	260	270		175°C
Zone 4	382	382	260	290		200°C
Die 1	382	388°C				
Die 2	400	388°C				
Clamp	382	388°C				
Screw type	1	1	2	2		2
RPM	25	10	45	75		100
Head	3000	1800	N/A	N/A	N/A	N/A
Pressure						
Throat	On	On	N/A	N/A	N/A	N/A
water						
Roller	177	177	38	65		93°C
Temperature						
Roller Speed	N/A	4 FPM	N/A	N/A	N/A	N/A
Annealing (°C)	250	250	125	100	0	N/A
Conditions (hrs)	4	4	0.5	1	hours	N/A
Expansion	Tg+100	Tg+100	Tg+100	Tg+100	Tg+100	
Temperature	265	245	175	155	150	85°C
Expansion	2:1	2:1	2.95:1	2.95:1	2:1	2:1

(1) Die dimensions were 2 in. X 0,065 in.

(2) Screw type 1 was a linear low density polyethylene screw.  
Screw type 2 was a low density polyethylene screw.

(3) Nylon 6 was in the form of injection-molded dumbbells,  
ASTM D638 Type IV. For injection molding conditions  
see Table 7.

TABLE 2 Recovery Stress Versus Recovery Temperature

<u>Recovery Temp.</u>	<u>Time</u>	<u>Stilan</u>	<u>PEEK</u>	<u>PET</u>	<u>Nylon 11</u>	<u>Nylon 6</u>
TE-80	1m		6,853	1,211	882	
	2m		6,906	1,288	882	
	5m		7,022	1,355	882	
TE-50	1m	4,537	8,400	3,012	1,491	
	2m	4,578	8,476	3,019	1,469	
	5m	4,603	8,535	3,019	1,413	801
TE-40	1m					
	2m					
	5m					
TE-20	1m	4,741	9,278	3,303	2,175	
	2m	4,741	9,351	3,303	2,126	
	5m	4,741	9,207	3,303	2,056	
TE*	Peak	4,628	9,349	3,383	2,475	
	1m	4,476	9,301	2,975	2,406	
	2m	4,349	9,233	2,924	2,207	
	5m	4,214	9,099	2,848	2,121	1,981
TE+20	Peak	4,674	9,358	3,328	2,646	
	1m	3,710	8,559	1,788	1,212	
	2m	3,621	8,369	1,749	1,057	
	5m	3,451	8,094	1,696	1,003	
TE+50	Peak	4,406	8,875	2,817		
	1m	2,514	6,496	370		
	2m	2,408	6,279	358		
	5m	2,236	5,920	332		198
Expansion Stress		6,104	15,188	5,254	3,266	

\* TE = Expansion temperature

TABLE 3 Recovery Stress After Expansion at T<sub>g</sub> + 50°C

	<u>Expansion</u>		<u>Recovery</u>	<u>Recovery</u>
	<u>Temp. (°C)</u>	<u>Ratio</u>	<u>Temp. (°C)</u>	<u>Stress (psi)</u>
Stilan	215	100%	215	5,653
PEEK	195	100%	195	10,332
PET	125	100%	125	1,933
Nylon 11	105	100%	105	2,039

TABLE 4 Recovery Stress And Expansion

<u>Polymer</u>	<u>Expansion</u>		<u>Recovery</u>	<u>Recovery</u>
	<u>Temp. (°C)</u>	<u>Elongation</u>	<u>Temp. (°C)</u>	<u>Stress (psi)</u>
Stilan	265	100%	265	5,214
	265	166%	265	9,531
PEEK	245	100%	245	8,465
	245	135%	245	10,000
PET	175	225%	175	2,019
	175	285%	175	4,426
	175	350%	175	5,063
Nylon 11	155	195%	175	2,696
	155	220%	175	3,967
	155	280%	175	5,417
	155	350%	175	7,854
PE	85	100%	85	846
	85	370%	85	956
	85	880%	85	2,191
Amorphous	100	100%	100	27
PET	100	260%	100	211
	100	380%	100	385
	100	555%	100	677

TABLE 5 Recovery Stress Versus Percent Shrinkage

<u>Percent Shrink</u>	<u>Recovery Stress (psi)</u>				
	<u>Stilan</u>	<u>PEEK</u>	<u>PET</u>	<u>Nylon 11</u>	<u>PE</u>
0	5,506	10,174	1,794	2,074	887
5	3,472	6,108	1,285	1,220	710
10	2,166	3,062	733	725	556
15	1,209	1,212	307	55	
20	433	128	0	0	208

TABLE 6 Change in Recovery Stress on Cooling to Room Temperature

	<u>Expansion</u>		<u>Recovery</u> <u>Temperature</u>	<u>Changes in</u> <u>Stress on</u> <u>Cooling</u>
	<u>Temperature</u>	<u>Elongation</u>		
Stilan	265°C	100%	265°C	+13%
PEEK	245°C	100%	245°C	+16%
PET	175°C	200%	175°C	+27%
Nylon 11	155°C	195%	155°C	-75%
Nylon 6	150°C	150%	150°C	-20%

Table 7Molding Conditions

	<u>Stilan</u>	<u>PEEK</u>	<u>PET</u>	<u>Nylon 11</u>	<u>PE</u>	<u>Nylon 6</u>
Barrel Temperatures (°C)						
Rear	380°C	370°C	250°C	190°C	140°C	240°C
Front	395°C	380°C	260°C	200°C	145°C	260°C
Mold Temperatures (°C)						
Sprue Side	200°C	165°C	*cold	*cold	*cold	45°C
Ejector Side	200°C	165°C	*cold	*cold	*cold	45°C
Cycle Times (seconds)						
Injection	21	21	22	22	22	10
Mold Close	51	51	52	52	52	30
Mold Close	04	04	04	04	04	03
Injection Pressure (psi)	1200	1200	1200	1200	1200	800

\*Cold-No mold heating used

TABLE 8 Pull-Off Force - Pound/Inch Width

<u>Mandrel Size</u>	<u>0.375</u>	<u>0.395</u>	<u>0.415</u>	<u>0.435</u>	<u>0.455</u>	<u>0.475</u>
Stilan	289	382	484	623	725+	*
PEEK	277	369	469	642	738+	*
Pet	115	198	265	399	525	691
Nylon 11	57	86	112	164	233	346
PE (Marlex 6003)	11	21	66	83	108	148

Results are an average of three samples.

\* Braid tore before pulling off for all three samples.

+ Braid tore before pulling off for 1 sample for PEEK and  
2 samples for Stilan.

We Claim:

1. An automotive retaining member comprising dimensionally heat-recoverable semi-crystalline polymer material having a glass transition temperature,  $T_g$ , above about  $25^{\circ}\text{C}$ , said member having a recovery stress of above about  $1100 \times (E-1)^{0.5}$  pounds per square inch, wherein E is the unresolved recovery ratio.

2. A member in accordance with Claim 1 wherein the said polymer is poly(oxy-p-phenylenecarbonyl-p-phenylene).

3. A member according to Claim 1 wherein the said polymer is a polyester or a polyamide.

4. A member in accordance with Claim 1 in the form of a retaining ring.

5. A member in accordance with Claim 1 or 4 comprising fibers of the said polymeric material.

6. A member according to Claim 1 or 4 dimensionally recovered about a resiliently deformable article so as to retain the article in contact with a substantially non-resilient article in a vehicle.

7. A member according to Claim 6 wherein the deformable article is a hose or other hollow tubular article, an aperture of which is gripped by the retaining member about part of the non-resilient article.

8. An article according to Claim 6 in use inside the engine enclosure of a vehicle.

9. A method of producing a member according to Claim 1 comprising

- a) heating a shaped article of a semi-crystalline polymer having a glass transition temperature,  $T_g$ , above  $25^{\circ}\text{C}$  to a temperature above the  $T_g$  of the polymer;
- b) deforming the article; and
- c) cooling the article while maintaining the article in the deformed state, thereby producing an article which, when heated to a temperature between  $T_g$  and the crystalline melting temperature,  $T_m$ , of the polymer, recovers with a recovery stress above about  $1100 \times (E-1)^{0.5}$  pounds per square inch, wherein  $E$  is the unresolved recovery ratio, and substantially retains such stress on cooling of the article to ambient temperature.

1/4

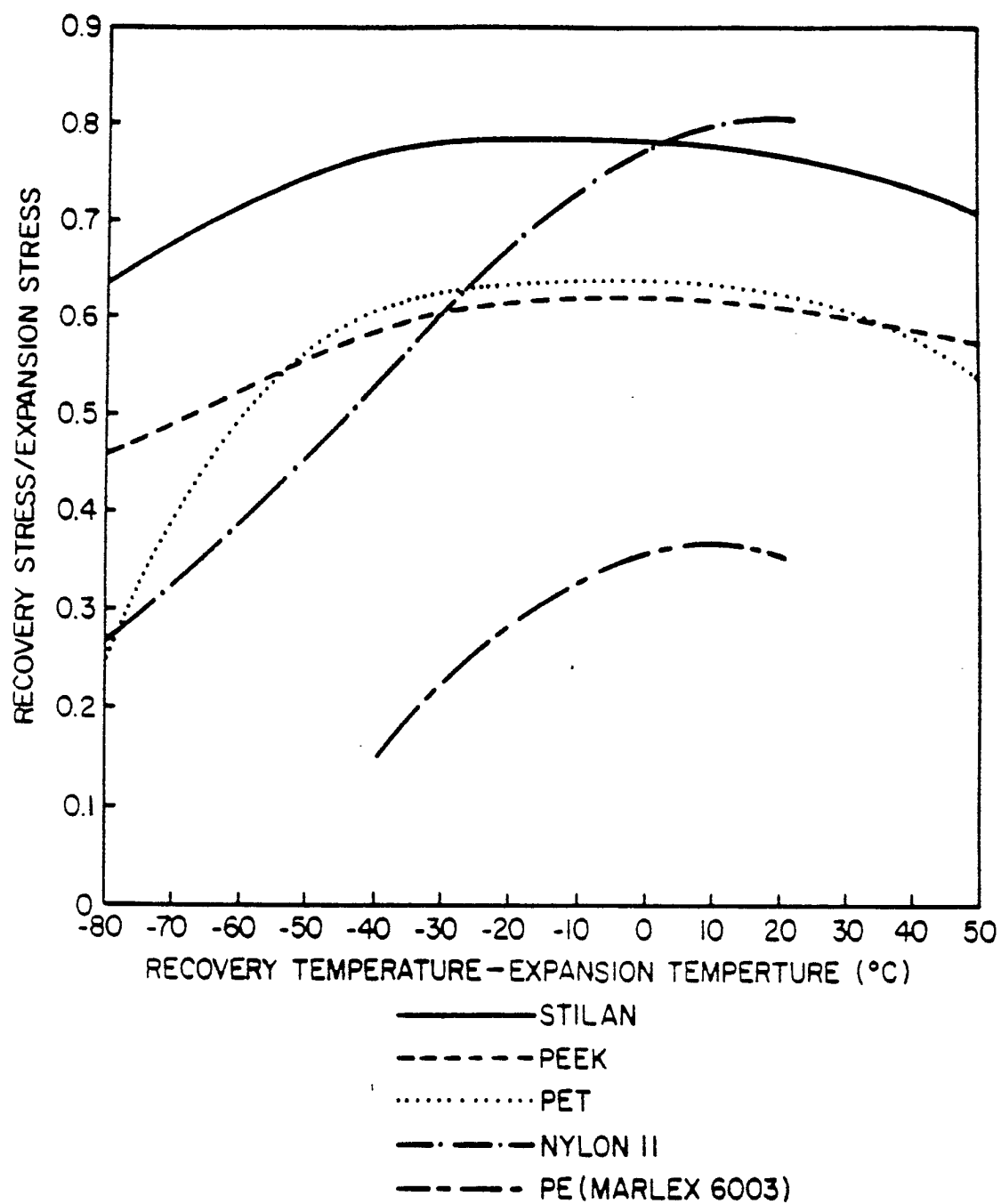


FIG.1.

2/4

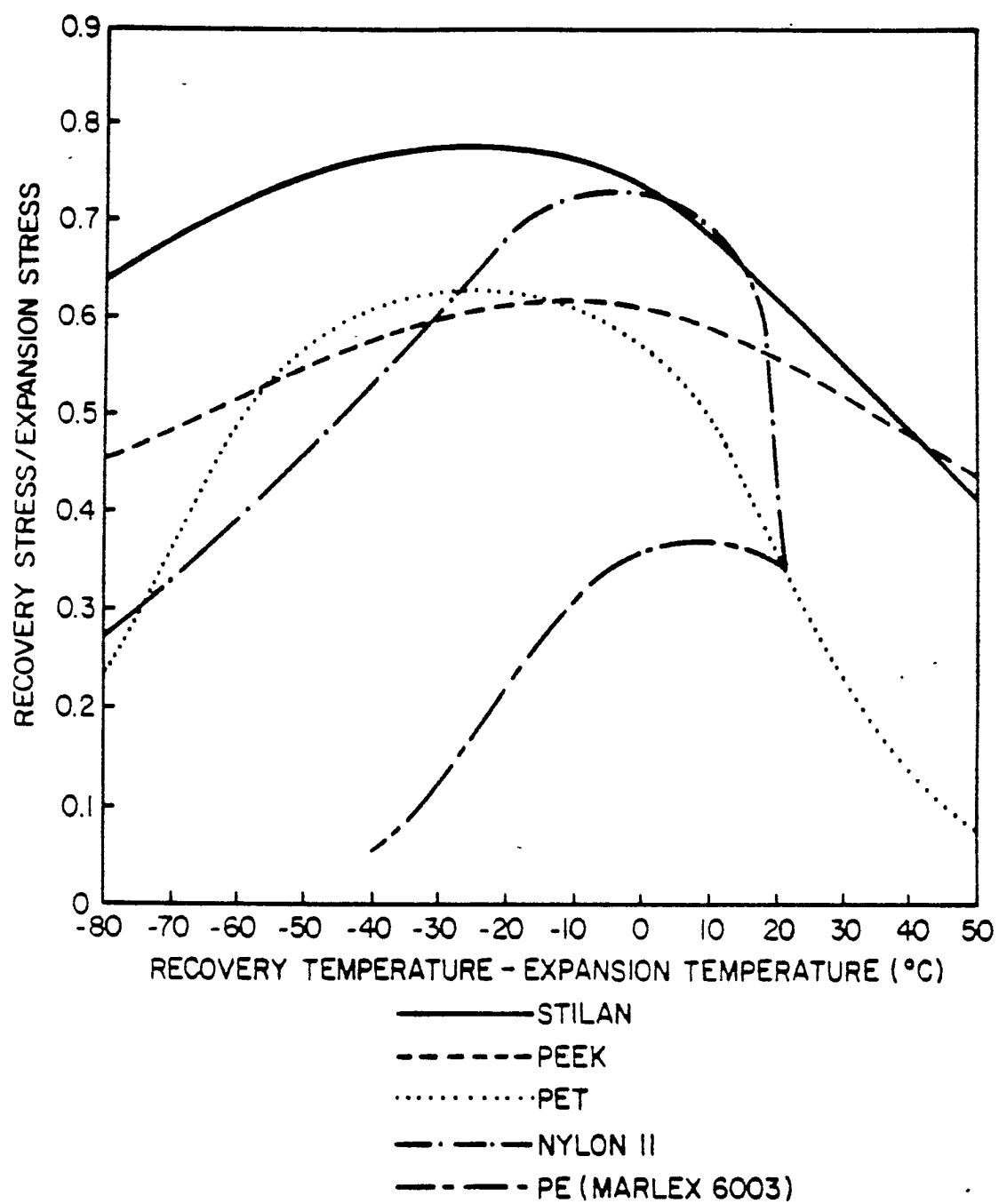


FIG.2.

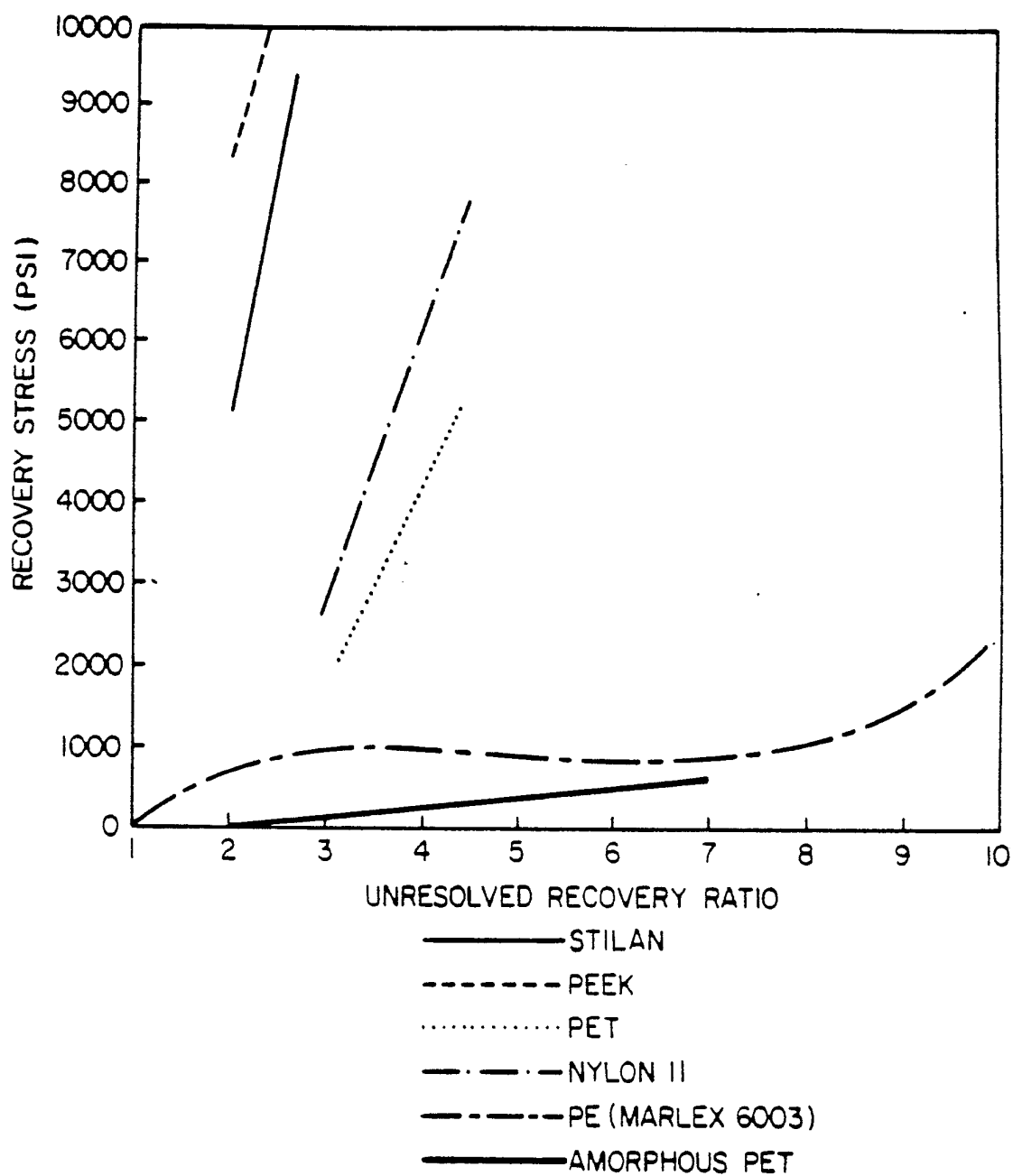


FIG.3.

4/4

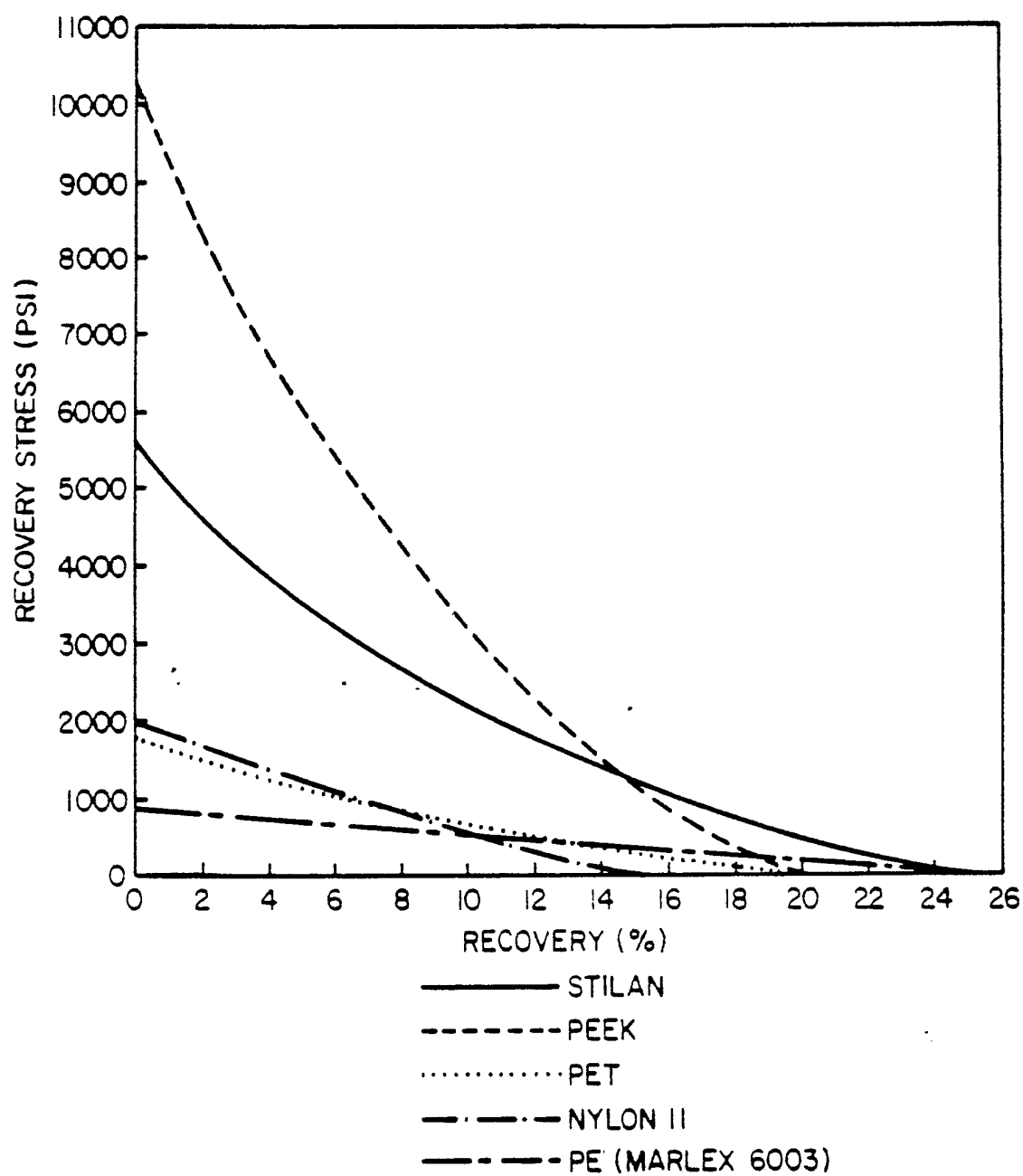
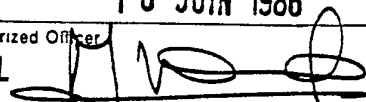


FIG.4.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 86/00066

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : B 29 C 61/00; C 08 L 71/00		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	B 29 C	
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>9</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>
L, P, X	BE, A, 901683 (RAYCHEM) 29 May 1985, see the whole document	1-9
X	FR, A, 2297342 (RAYCHEM) 6 August 1976, see page 3, line 22 - page 4, line 29; claim 1	1-3, 6, 9
P, X	EP, A, 0152279 (RAYCHEM) 21 August 1985, see the whole document	1-6, 9
X	EP, A, 0105775 (SOC. CHIMIQUE DES CHARBON- NAGES) 18 April 1984, see page 5, lines 1-27; claims 1-4, 10, 11	1, 4, 6-9
-----		
<p>* Special categories of cited documents: <sup>10</sup></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	
12th May 1986	10 JUIN 1986	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	M. VAN MOL 	

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON

INTERNATIONAL APPLICATION NO. PCT/GB 86/00066 (SA 12062)

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 28/05/86

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
BE-A- 901683	29/05/85	JP-A- 60181158	14/09/85
FR-A- 2297342	06/08/76	BE-A- 837452	09/07/76
		DE-A- 2600647	02/09/76
		AU-A- 1018276	14/07/77
		GB-A- 1529351	18/10/78
		CA-A- 1031755	23/05/78
		JP-A- 51125457	01/11/76
		AU-B- 524541	23/09/82
EP-A- 0152279	21/08/85	JP-A- 60184712	20/09/85
		AU-A- 3855585	15/08/85
EP-A- 0105775	18/04/84	JP-A- 59053528	28/03/84

For more details about this annex :  
see Official Journal of the European Patent Office, No. 12/82