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(54) **Production of metallic material.**

(57) A process and apparatus for the production of metallic material as filaments, fibre or particulates, whereby the material in molten form is extruded and the extrudate is transiently destabilised to form an unstable state which is subsequently stabilised by solidification. Preferably the destabilising force and extrusion pressure are created by centrifugal force, the molten material being contained in a rotatable reservoir having peripheral extrusion orifices. Fibre produced according to the invention is suitable for electromagnetic shielding.

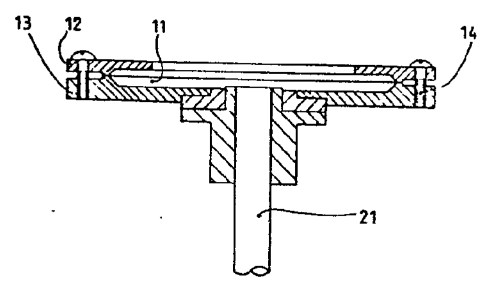

FIG.1.

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PRODUCTION OF METALLIC MATERIAL

This invention relates to the production of metallic material and in particular to the production of metallic fibres having a cross-sectional diameter less than about 50 microns.

Metallic fibres having a cross-sectional diameter of less than about 50 microns, preferably less than about 25 microns, are particularly useful for the shielding of electronic components from electromagnetic radiation, particularly in the frequency range 100kHz to 1GHz. Electronic components, by which is meant microcomputers and the like, are being used in ever increasing numbers in the control systems of for example aircraft, missiles and land transport vehicles, both civil and military, and in hospital equipment and other areas, and failure of such components due to interference by ambient electromagnetic radiation is recognised as being a potentially catastrophic hazard. The hazard is increasing dramatically not only because of the increasing usage of electronic components in control systems but also because there is an increasing level of ambient electromagnetic radiation from sources such as radio and television transmitters, radar installations, industrial equipment, for example electronic arc-welding equipment, and domestic equipment such as home computers. Shielding involves either protection of a component from external radiation or prevention of emission of radiation generated by the shielded component from contributing to the ambient radiation.

Various ways have been proposed for shielding electronic components, which are frequently contained in an electromagnetic radiation-transparent plastics housing, from ambient electromagnetic radiation by treatment of the housing with conductive paints, metallisation by vacuum deposition techniques or arc/flame spraying, application of metal foils, and reduction of silver nitrate, for example. However, each of these has its own particular disadvantages and none has provided a practical, commercially-attractive solution. Addition of a conductive filter to the plastics material had also been proposed but the high metal loadings required (typically 10-40% by weight) have a detrimental effect on other properties of the material, and also raise the overall cost to commercially-unacceptable levels.

One proposal which appears to be highly efficient is the incoporation of fine conducting fibres such as stainless steel fibres into a polymer matrix. The resulting composite material is subsequently formed into housings for electronic and other electromagnetic radiation-sensitive components. It is believed that the fibres used should be ductile and as fine as possible to obtain the lowest possible metal loading commensurate with the maintenance of conductance. However, hitherto it has not proved possible economically to produce fibres of sufficient fineness, that is, below about 50 microns cross-sectional diameter, preferably below about 25 microns and even more preferably below about 10 microns, in an essentially single-stage operation. Techniques which have been considered include free flight melt spinning, crucible or pendant drop melt extraction, drawing of glass sheathed wire, and gas fibrulation of a molten tube, but all of these require the product to be cut into individual fibres in a separate stage. For reasons of economics it is preferred to use a technique that produces material suitable for cutting into fibres direct from the molten state, but diameter is difficult to control and anyway is too large, being generally about 50-100 microns, whereas traditional drawing down to reduce the diameter to that required for electromagnetic shielding results in an unacceptable increase in production costs. It is also believed that working of this nature causes a degree of embrittlement or work hardening which renders the achievement of conductance in a polymer matrix more difficult. Furthermore, stainless steel fibres result in an overall grey colouration in the polymer which is cosmetically unacceptable in certain applications.

We have now found that metallic materials may be processed direct from the molten state to form filaments, fibres or particulates, and that such products may have a diameter or minimum dimension of 50 microns or less by a process which involves extrusion of the melt to form a transiently unstable state which is subsequently stabilised by solidification.

According to the present invention, therefore, a process for the production of metallic material comprises extrusion of molten metallic material through an orifice to forma transiently unstable state, and stabilisation of the unstable state by solidification.

The direct product of the process is preferably in the form of fibres, although filamentary material or particulates may be produced by varying the conditions.

The rate of solidification can be influenced inter alia by the temperature of the ambient atmosphere and of the melt and may determine the structural nature, that is the degree and type of crystallinity, as well as the physical form of the product. The structural nature in turn influences the electrical conductivity and other properties of the product.

By "molten" we mean to include slurries of solid material in a molten continuous phase, as well as materials in the 100% molten condition. Metals when in the molten state have very low viscosities, typically substantially less than 10 poise, for example 1.5 poise. At these low viscosities, the dominant intrinsic force acting on an extruded quantity of molten metal is surface tension. Surface tension tends to form the extrudate into a sphere and this form, in the absence of other forces, is regarded as the natural stable state. According to the invention, this state is transiently de-stabilised to form an unstable, preferably fibrous, state which is then stabilised by solidification. De-stabilisation is achieved by applying a pulling force to the extrudate in addition to the pushing force exerted on the molten material to cause extrusion, and maintaining said pulling force until stabilisation by solidification is effected. Conveniently, both the pushing extrusion force and the pulling de-stabilisation force comprise centrifugal force. Thus the molten metallic material may be contained in a rotatable reservoir equipped at the periphery thereof with one or more extrusion orifices. Rotation of the reservoir sets up a centrifugal force in the melt which at a certain angular velocity, depending on the quantity of material in the reservoir, is sufficient to overcome surface tension forces across the mouth of the orifice to initiate extrusion; maintenance of this force causes continued extrusion. The extrudate issues from the orifices initially radially and is subject to a marginally higher centrifugal force compared with that acting within the orifice because of the higher velocity; this constitutes the pulling force which destabilises the extrudate and forms an unstable, preferably fibrous, state. The velocity and hence the centrifugal pulling force increase with increasing fibre length thus continuing the destabilising force on the molten extrudate until stabilisation takes place by solidification.

By "metallic" in this specification we mean to include metals and alloys and other materials whose viscosity behaviour in the molten state is similar to that of molten metals and which are therefore susceptible of being processed according to the invention. We believe that any metallic material is susceptible of being so processed provided that, in the case of the higher-melting materials, a sufficiently high temperature can be sustained under extrusion conditions.

The process according to the invention is distinguished from melt spinning of high-viscosity materials, for example oxide glasses, in that, for the spinning of high-viscosity materials, the orifices are relatively large and surface tension acts to reduce the diameter of the molten fibre. This is a process known as "necking down" but, in contradistinction to the case with low viscosity materials, there is no tendency towards the formation of spheres. Thus the molten high-viscosity material, although filamentary, is at all times in a stable state, the stability arising from the combination of surface tension and viscosity forces.

The maximum size of the extrusion orifice in the process according to the present invention is dictated mainly by the surface tension of the molten material, in that surface tension forces should act to prevent issue of the material except under extrusion conditions. However, the preferred maximum orifice size to produce fibres or other products in a fine state is 150 microns, with sizes of 50 microns or below or even 10 microns or below being particularly preferred for the production of very fine products.

Fibres formed according to the process of the invention are preferably formed as an integral part of the extrusion process, that is, by the extrudate breaking by being subjected to shear or bending forces or by the applied pulling force exceeding the tensile strength of the extrudate, or by a combination of both. Fibres may be formed for example either by the pulling force exceeding the tensile strength of the extrudate, and/or by air resistance or an applied draught creating shear forces.

The invention is particularly suitable for the production of metallic fibres, filaments or particulates having a diameter of about 50 microns or less, preferably 25 microns or even 10 microns or less. We have found that such small diameter products may be successfully formed without blocking of the orifices, although for extrusion of materials which tend to react with the ambient atmosphere it is preferred to carry out the process in an inert or reducing atmosphere. Furthermore, the temperature of the ambient atmosphere may be controlled in order to influence the rate of solidification. By altering the process parameters, the invention may be used to produce particulates, for example spheroids or ellipsoids, which are the result of the process operating at or near limiting parameters such that surface tension forces are dominant. Under these circumstances, extruded material is emitted from the extrusion orifices as droplets which may approach or attain the natural stable state in flight before stabilisation by solidification. Alternatively, the invention may be used to produce filaments, that is, fibres of long and indefinite length.

For the purposes of electromagnetic shielding, the aspect ratio (length/diameter) of fibre is of importance because, for a given conductivity level, the metal loading required may be reduced with fibres of high aspect ratio. The diameter of fibres produced according to the process of the invention is readily controllable by selecting the appropriate extrusion orifice diameter. The length of the fibres is controllable, within limits set by air resistance and other external influences, by the angular velocity, in that for a given extrusion temperature and for all angular velocities greater than the minimum velocity required for extrusion to take place (called the "critical" angular velocity), the fibre length decreases with increasing velocity. Thus the aspect ratio may readily be controlled. For purposes of electromagnetic shielding, in which the minimum quantity of metallic material is required commensurate with the need to retain electrical conductance, the aspect ratio should be greater than 10:1, preferably greater than 50:1. The desirable maximum fibre length, on the other hand, is determined by the processing conditions of incorporating the material into a polymer matrix, since these conditions may cause breakage of long fibres, depending on their ductility. It is considered that for fibres of normal ductility the longest practicable fibre length is approximately 1 cm in the matrix, although fibres of exceptionally high ductility may undergo elongation during polymer processing. For an aspect ratio of 100:1, the diameter required for a 1 cm fibre would be 100 microns and this is readily achievable by the process according to the invention. However, because diameters of 50 microns or less, or even 25 microns or less, are also realisable, the fibre length may be reduced to 2.5 mm or less while still retaining an aspect ratio of 100:1, or alternatively the fibre length may be held at 1 cm to provide an aspect ratio of 400:1. Aspect ratios in the range 50 to 500:1 are preferred, although aspect ratios up to about 3,000:1 may be realisable using the process according to the invention. Above this aspect ratio, we regard the product as being filamentary, that is to say, in the form of continuous fibres or strands of indefinite length.

Accordingly, the present invention also provides filaments fibres and particulates of metallic material when produced by the process according to the invention, in particular particulates and filaments having a diameter of 50 microns or less, preferably 25 microns or less, and fibres having an aspect ratio in the range 10:1 to 3,000:1, preferably 50:1 to 500:1.

Fibres according to the invention may optionally be coated or treated before being incorporated into plastics or other materials to provide a material suitable for electromagnetic shielding. Thermoplastic plastics materials are preferred. Alternatively, the fibres may be incorporated into other binders or matrices for electromagnetic shielding or other purposes, particularly where it is desired to provide a continuous electrically conductive path therethrough. Plastics or other materials containing fibre according to the invention may be pigmented or otherwise coloured without the presence of the fibre creating undue influence on the pigmentation or colouration. Fibre produced according to the invention is ductile, that is,not embrittled or work hardened, and is thus eminently suitable for satisfactory incorporation into plastics or other materials without breakage of the fibre. Furthermore the use of ductile fibre causes less damage to equipment, for example moulds, used to process the material. To provide a continuous electrically conductive path, it is not essential for there to be a continuous metal path where the fibres defining the path are in physical contact with each other; a degree of proximity is acceptable particularly where the fibres form a segregated network within the plastics or other material. By "segregated network" is meant a semi-ordered arrangement of fibres, being neither randomly orientated nor highly aligned, and in this condition the metal loading may be reduced to a minimum. Metal loadings of or below about 1% by volume are adequate with fibre having a diameter below about 25 microns, for example 15 microns, in a segregated network within a plastics or other material, and lower levels are adequate with smaller diameter or higher aspect ratio fibre.

Accordingly, the invention also provides a composite material suitable for electromagnetic shielding and comprising fibre according to the invention incorporated in a binder or matrix, especially a plastics material. Such composite materials are preferably for structural use although may be for coating use. Preferably, the fibres form a segregated network within the binder or matrix.

In a further aspect, the invention provides apparatus for the production of metallic material, the apparatus comprising means for extrusion of molten metallic material through an orifice, whereby the extrudate is formed into a transiently unstable state which is subsequently stabilised by solidification. Preferably, the material so produced is in the form of fibre, although it may be filamentary or particulate.

The extrusion means preferably comprises a rotatable reservoir for holding a quantity of molten metallic material and equipped at the periphery thereof with one or more extrusion orifices, which may be of 150 microns or less diameter, more preferably 50 microns or less or even 10 microns or less. In use, extrusion proceeds under centrifugal force set up in the molten metallic material by rotation of the reservoir and the unstable state is formed by a pulling force inherent in the extrudate and also derived from centrifugal force. Optionally, heater elements, thermocouples or other temperature measuring devices and the like may be carried by the reservoir. The apparatus or parts thereof are preferably insulated or otherwise adapted to minimise heat losses.

A receptacle preferably surrounds the apparatus to receive solidified product.

Embodiments of the invention will now be described by way of example with reference to the accompanying drawings, of which:

Fig. 1 is a cross section of an extrusion apparatus according to the invention;

Fig. 2 is a plan view on a slightly reduced scale of the apparatus shown in Fig. 1; and

Fig. 3 is an exploded cross section on the line A-A of the apparatus shown in Fig. 2.

Referring to the drawings, apparatus according to the invention is shown generally at 10 and consists of a circular reservoir 11 for holding molten metallic material and defined by upper and lower plates 12 and 13 respectively, each having a central aperture and bolted together by bolts 14 carried in holes 15 which are tapped in plate 13. The aperture in plate 12 constitutes the mouth of the reservoir. Notches 16 are provided in lip 17 of plate 12; these notches form in conjunction with corresponding lip 18 of plate 13 extrusion orifices at the periphery of the reservoir. The notches and orifices (the latter shown at 19 in Fig. 2) are shown oversize in the drawings for the sake of clarity. The assembly of upper and lower plates 12 and 13 is secured by means of bolts (not shown) through holes 20 formed in lower plate 13 to rotatable shaft 21 via suitable bushing means to close the aperture in lower plate 13. The shaft is driven by a suitable motor (not shown). The apparatus as shown in Fig. 1 is contained in a drum to allow a free flight path for the extruded material of approximately 10 cm.

In use, metallic material is introduced into the mouth of the reservoir. The material is either in the molten state or is heated to above its melting temperature by heating elements associated with the reservoir. The reservoir is rotated and the molten material, because of its low viscosity, automatically distributes itself under the influence of centrifugal force evenly around the interior periphery of the reservoir. When the critical angular velocity is reached, extrusion of molten material through the orifices begins. (The critical angular velocity is a function of the surface tension of the molten material, the amount of molten material in the reservoir, the diameter of the orifice and the radius of the reservoir). The extrudate emerging from the orifices is subject to a pulling force also derived from centrifugal force which overcomes the tendency to form a sphere and produces instead an unstable state which is ultimately stabilised by solidification. The unstable state preferably comprises fibres which are cropped from the extrudate under the influence of bending due to atmospheric drag.

A plurality of top plates 12 may be held in stock, each containing notches of a different size from the other plates, to allow for the use of different sizes of extrusion orifice. Optionally, as well as heating elements, the reservoir may be equipped with thermocouples and so on, electrically connected via slip rings mounted around the shaft 21. As examples of alternatives to notches, extrusion orifices of diameter down to about 5 microns may be provided by drilling in stainless steel foil, for example, or by utilising electron microscopy apertures.

We have found that material is produced having a diameter approximately 0.25 to 0.9 times that of the extrusion orifice from which it issues, depending on conditions. The physical form of the material is generally smooth although nodes or other undulations may occur at intervals. These appear to be influenced by the extrusion conditions and are therefore controllable.

In the apparatus described, we have produced the following results for production of tin fibres. The reservoir diameter was 13 cm and the extrusion orifices were 50-75 microns in diameter. At a rotation speed of 800 r.p.m., equivalent to a periphery speed of 600 cm/sec., fibres were formed having a length of 2 to 3 mm and a diameter of 50 microns. At a rotation speed of 1500 r.p.m., equivalent to a periphery speed of 1100 cm/sec., fibres were formed having a length of 25 to 30 mm and a diameter of 30 microns. Using a different top plate to define extrusion orifices of 110 microns in diameter, a rotation speed of 1160 r.p.m. (equivalent to a periphery speed of 800 cm/sec) produced fibres of length 4 to 9 mm and a diameter of 73 microns, whereas a rotation speed of 2180 r.p.m. (equivalent to a periphery speed of 1500 cm/sec) produced fibres of length 2 to 6 mm and a diameter of 66 microns. The temperature as well as the speed influence the length of the fibres and, while we have not measured precise extrusion temperatures, the initial temperature of the melt was 400°C at 1160 r.p.m. and 380°C at 2180°C.

We have also produced fibres of lead/tin eutectic (i.e. 62% Sn, 38% Pb) by extrusion through 20 micron orifices at an initial temperature of 460°C. At a rotation speed of 1660 r.p.m. equivalent to a periphery speed of 1100 cm/sec., fibres were formed having a length of 1 to 15 mm and a diameter of 18 microns.

Using a laboratory bench apparatus comprising a rotating glass tube with a length (i.e. spinning diameter) of 6 cm and a 20 micron orifice at each end, we have successfully produced zinc fibres having a diameter of 10 to 25 microns and a length of 1.3 cm.

CLAIMS

1. A process for the production of metallic material comprising extrusion of molten metallic material through an orifice to form a transiently unstable state, and stabilisation of the unstable state by solidification.

2. A process according to claim 1 in which the metallic material is produced in the form of fibres.

3. A process according to claim 1 or claim 2 in which the unstable state is achieved by applying a pulling force to the extrudate in addition to the pushing extrusion force.

4. A process according to claim 3 in which the pulling force and the pushing force comprise centrifugal force.

5. Fibres filaments or particulates when produced according to the process as claimed in any of claims 1 to 4.

6. Fibres, filaments or particulates according to claim 5 and having a diameter of 50 microns or less.

7. Fibres according claim 6 having an aspect ratio in the range 10 to 3000:1.

8. Fibres according to claim 7 having an aspect ratio in the range 50 to 500:1.

9. A composite material suitable for electromagnetic shielding and comprising fibre according to claim 7 or claim 8 incorporated in a binder or matrix.

10. A composite material according to claim 9 in which the binder or matrix comprises a plastics material.

11. A composite material according to claim 10 in which the fibres form a segregated network within the plastics material.

12. A composite material according to claim 11, in which the metal loading of fibres is 1% by volume or less, the fibre having a diameter of about 25 microns or less.

13. Apparatus for the production of metallic material, the apparatus comprising means for extrusion of molten metallic material, whereby the extrudate is formed into a transiently unstable state which is subsequently stabilised by solidification.

14. Apparatus according to claim 13 in which the extrusion means comprises a rotatable reservoir for holding a quantity of molten metallic material and equipped at the periphery thereof with one or more extrusion orifices.

15. Apparatus according to claim 14 in which the extrusion orifices are 150 microns or less in diameter.

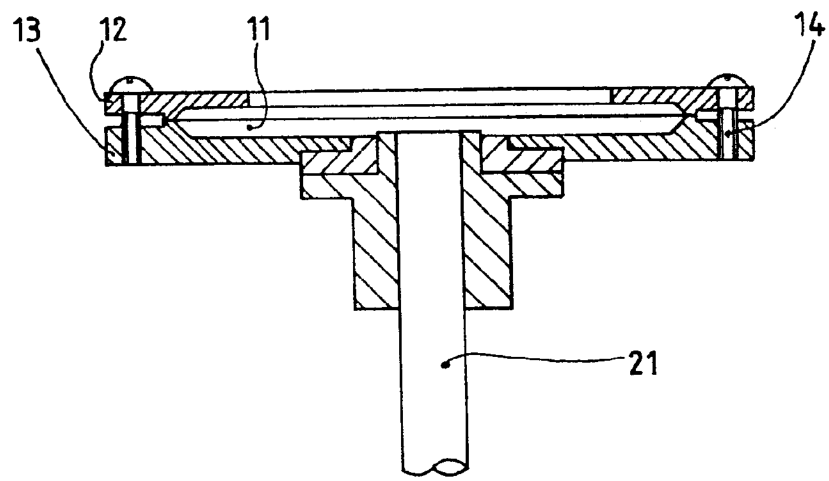

FIG.1.

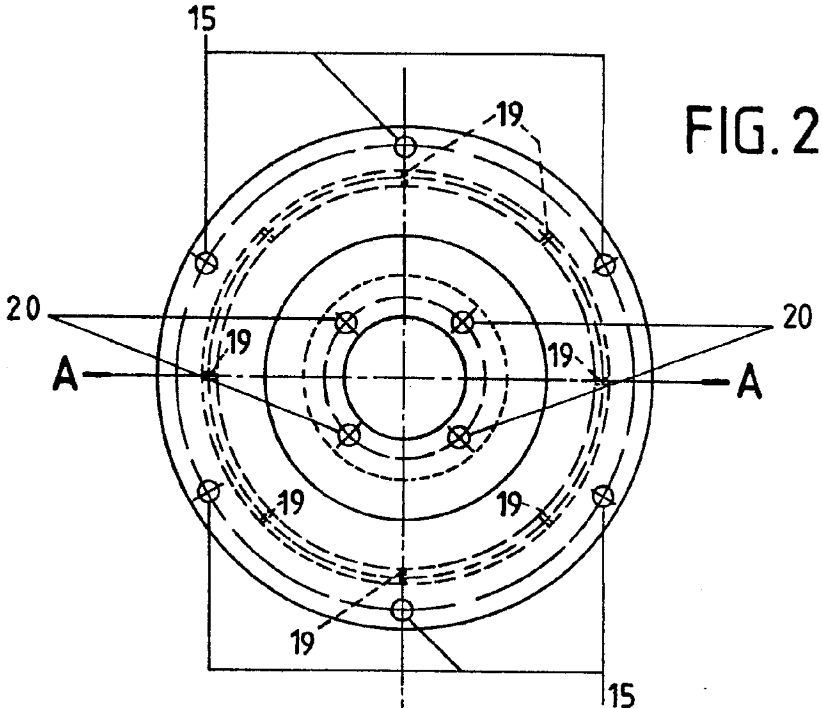

FIG. 2.

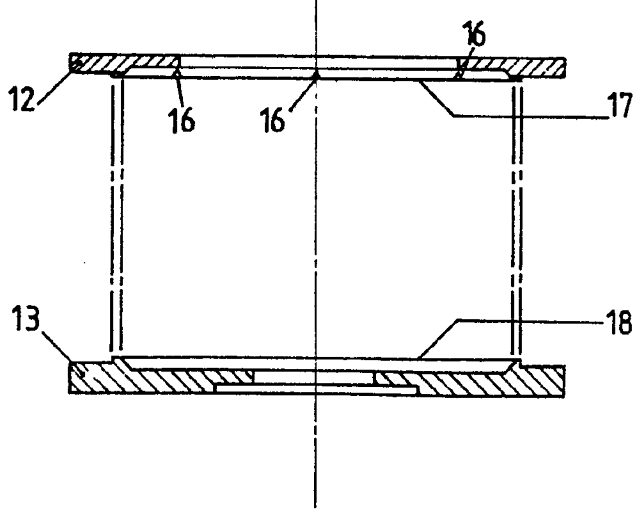

FIG. 3.

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EUROPEAN SEARCH REPORT

0181696

Application number

EP 85 30 7093

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 466 352 (CORBETT) * Column 1, lines 32-48; figure 1; abstract *	1-5,13,14	B 22 D 11/00
Y		6,7,9,10	
A		15	

P,X	PATENTS ABSTRACTS OF JAPAN, vol. 8, no. 227 (M-332) [1664], 18th October 1984; & JP - A - 59 107 752 (KUBOTA TEKKO K.K.) 22-06-1984 * Abstract *	1,3-5,13,14	
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X	US-A-1 592 140 (HORTON & PEAKE) * Page 1, lines 1-7; page 2, lines 73-80 *	1,3-5,13,14	B 22 D

X	US-A-3 960 200 (KAVESH) * Column 1, lines 25-43; column 4, line 23; column 6, line 65 - column 7, line 5 *	1,3	
Y		6	
A		5	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-01-1986	ASHLEY G.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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D : document cited in the application
L : document cited for other reasons
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EUROPEAN SEARCH REPORT

Application number

EP 85 30 7093

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 543 831 (SCHILE) * Abstract; column 1, lines 15-31; column 6, line 66 - column 7, line 4 *	1-3	
A		5	

X	US-A-3 861 452 (MASSOUBRE) * Abstract; column 1, lines 9-12 *	1	

Y	EP-A-0 117 884 (TORAY INDUSTRIES) * Page 3, line 35 - page 4, line 1; page 4, line 28 - page 5, line 8 *	6,7,9, 10	
A		2	TECHNICAL FIELDS SEARCHED (Int. Cl.4)

Y	US-A-2 825 108 (POND) * Column 1, lines 26,27 *	9	

A	US-A-3 658 979 (DUNN et al.) * Column 1, lines 31-57; column 2, line 16; column 5, lines 18-22 *	1,2,9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-01-1986	ASHLEY G.W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
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D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document