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54 **Electrically conducting fibres and method of making same.**

57 An electrically conducting acrylic or modacrylic fibre is impregnated with 1 to 30 wt. % of copper sulfide, e.g. digenite.

A two-step method of making these fibres comprises subjecting the fibres to a first heat-treatment in a bath containing a copper compound and a reducing agent to adsorb monovalent copper ions into the fibre, and subjecting the fibre to a second heat-treatment in the presence of a sulfur-containing compound to convert said adsorbed monovalent copper ions to copper sulfide.

An alternative one-step method comprises subjecting the fibre to heat-treatment in a bath which contains a copper ion compound, a reducing agent which is capable of reducing copper ions to monovalent ions, and a sulfur-containing compound to convert monovalent copper ions to copper sulfide.

The electrically conducting fibres have superior conductivity, which is not lost in repeated washing, can be dyed readily with cationic dyes without loss of electrical conductivity and possess the touch and other physical characteristics of the starting acrylic or modacrylic fibres.

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ELECTRICALLY CONDUCTING FIBRES AND METHOD OF MAKING SAME

This invention relates to electrically conducting acrylic and modacrylic fibres and to methods of making them.

- Numerous methods for imparting electrical conductivity to synthetic polymeric fibres are known. For example, one method for imparting electrical conductivity to polymeric fibres involves plating a metal onto the surface of the fibre. However, this method requires etching of the surface of the fibre prior to plating so as to obtain satisfactory adhesion, and then involves sensitising and activating the fibre prior to plating. In addition, the resulting electrically conducting fibre differs greatly from the starting fibre in softness, flexibility and smoothness.
- 15 In another prior art process, a metal is kneaded into a polymer. The polymer is then spun into a yarn. However, this process suffers from problems such as clogging of the nozzle with metallic particles during spinning. In addition, unless the metal content of the fibres is kept relatively low, the electrically conducting fibre obtained by this prior method has inferior mechanical properties compared to the starting fibre.
- 20

In a third known process, metallic powder is deposited in the pores of a polymeric fibre. This method usually requires an extremely porous fibre and intricate process steps.

- 5 U.S. Patents 3,014,818 and 4,122,143 disclose the production of electrically conductive fibres by reducing a copper compound to metallic copper. In U.S. Patent 3,014,818, an electrically conductive fibrous material is produced by soaking the fibres, such as cotton or acrylic fibres, in  
10 a bath comprising a reducible salt of nickel, cobalt, copper or iron; the fibre is then subjected to a reducing treatment to obtain free metal particles which are dispersed through the interior of the fibre. Sodium borohydride and hydroxylamine are disclosed as satisfactory reducing agents.  
15 In U.S. Patent 4,122,143, cured products are obtained by reducing copper simultaneously with the curing of a resin; the method does not give electrical conductivity to an already existing fibre.

In the latter two known processes, electrical conductivity  
20 is obtained by the presence of metallic copper in the polymeric material. However, it is well-known that acrylic or modacrylic fibres have a strong affinity for monovalent copper ions; it is believed that this results from coordinate bonding between the cyano groups in the fibre  
25 and the monovalent copper ions. The adsorption of monovalent copper ions into acrylic or modacrylic fibres turns the fibres yellowish. However, as determined e.g. by measurements of electrical resistance, the fibres themselves do not possess any electrical conductivity.

- 30 Electrically conducting fibres having superior conductivity which is not lost in repeated washings are obtained without the need for special pretreatment of the fibres by means of this invention.

The electrically conductive fibres of the present invention comprise acrylic or modacrylic fibres, which have been impregnated with a copper sulfide such as cupric or cuprous sulfide or digenite.

- 5 Acrylic fibres are made from a synthetic linear polymer that consists of not less than 85% (by mass) of acrylonitrile units (-CH- $\overset{\text{CN}}{\underset{|}{\text{C}}}$ -CH-) or acrylonitrile copolymers; modacrylic fibres contain not less than 35% of said units or copolymers. The term "fibre" or "acrylic fibre" is used hereinafter  
10 to refer to acrylic and modacrylic fibres.

- The greater the quantity of copper ions present adsorbed by the fibre, the better the electrical conductivity of the product fibres. However, if the copper ion content is too high the physical properties, such as fibre strength  
15 and color, are affected. On the other hand, satisfactory electrical conductivity properties cannot be obtained at very low copper ion contents. The preferred amount of monovalent copper ions adsorbed by the fibre is from 1 to 30% by weight (expressed in terms of the weight of metallic  
20 copper) based upon the initial weight of the fibre.

- In one embodiment of the process of the present invention for making these fibres, an acrylic fibre or modacrylic fibre is first heat-treated in a bath containing monovalent copper ions and a reducing agent so that the fibre adsorbs  
25 the monovalent copper ions; the fibre is then heat-treated with a sulfur-containing compound to convert the adsorbed monovalent copper ions into a copper sulfide. This is a two-step process.

- No special pretreatment of the fibres is needed. The  
30 touch and other physical characteristics of the starting acrylic or modacrylic fibre is preserved in the process of the present invention; the electrically conductive fibres of the invention have superior electrical conductivity and

washability and can be dyed by cationic dyes.

In the first stage of this process of the present invention, the fibres are heat-treated in a bath containing a compound providing monovalent copper ion and a reducing agent, so  
5 that monovalent copper ions are adsorbed by the fibres. The bath can optionally contain, for adjusting the pH of the bath to preferably 1.5 to 2.0, an acid or an acid salt such as sulfuric acid, hydrochloric acid or a salt thereof.

Suitable copper compounds which provide monovalent copper  
10 ions for adsorption on the fibres are cupric salts, such as cupric sulfate, chloride, nitrate or acetate and chelate compounds of copper. Suitable reducing agents for inclusion in the bath are metallic copper, hydroxylamine, ferrous sulfate, ammonium vanadate, sodium hyphosphite, glucose and furfural.

15 The bath temperature is preferably in the range from 90°C to 110°C so as to efficiently adsorb the monovalent copper ions and to maintain the strength of the fibres. At temperatures below 90°C, it takes many hours to complete adsorption. At temperatures over 110°C, the strength of  
20 the fibres drops.

In the first stage of this process of the present invention, the acrylic fibres having adsorbed monovalent copper ions become yellowish but do not possess any electrical conductivity. Electrical conductivity is imparted to the  
25 fibres in the second stage, wherein the fibres having adsorbed monovalent copper ions are preferably first thoroughly scoured or washed with water and the washed fibres are heat-treated in a liquid or gas which comprises a sulfur-containing compound which is capable of reacting  
30 with the adsorbed monovalent copper ions to produce a copper sulfide. The copper sulfide is adsorbed into the fibres, thereby imparting excellent electrical conductivity properties to the

fibres. The weight percentage of the copper sulfide in the electrically conducting fibre expressed in terms of the weight of metallic copper is preferably also 1% to 30% based upon the initial weight of the fibre.

5 Suitable sulfur-containing compounds for converting the monovalent copper ions into adsorbed copper sulfide are sodium sulfide, sulfur dioxide, sodium hydrogen sulfite, sodium pyrosulfite, sulfurous acid, dithionous acid, sodium dithionite, sodium thiosulfate, thiourea dioxide,  
10 hydrogen sulfide, sodium formaldehyde sulfoxylate and zinc formaldehyde sulfoxylate and mixtures thereof. The liquid which contains the sulfur-containing compounds is generally water, and for adjusting the pH values to preferably 5.5 to 6 can include an acid or an acid salt such as sulfuric  
15 acid, sodium acetate or hydrochloric acid.

The heat-treatment temperature in the second state of this process of the present invention is preferably more than 50°C. Heat-treatment temperatures below 50°C do result in the production of a copper sulfide and impart electrical  
20 conductivity to the fibres, but many hours are needed to accomplish this at these low temperatures. Suitably, the heat-treating in the second stage of the process of the present invention is at a temperature from 50°C to 105°C for about 1 hour and can be carried out in a gaseous  
25 sulfur-containing compound, such as sulfur dioxide.

In a second embodiment of the process of the invention an acrylic or modacrylic fibre is heat-treated in a bath containing (i) divalent copper ions, (ii) a reducing agent capable of reducing said copper ions to monovalent ions, and  
30 (iii) a compound having the ability to release sulfur atoms and/or sulfur ions. This one-step process is simple to perform.

In this second method, as the compound (i) providing divalent copper ions, cupric compounds such as cupric sulfate,

chloride, nitrate or acetate or a chelate of copper are used. The reducing agent (ii) can be metallic copper, ferrous sulfate, ammonium vanadate, sodium hypophosphite, hydroxylamine or its sulfate, furfural or glucose. The sulfur-releasing  
 5 compound can be any of the sulfur containing compounds listed above for the first process; the sulfoxylates can be used in the form of Rongalite C ( $\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$ ) or Rongalite Z ( $\text{ZnSO}_2 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$ ); sulfur dioxide or hydrogen sulfide can be used by being bubbled into the bath. Further,  
 10 in order to regulate the pH, acid or salt may be added, e.g. inorganic acid such as sulfuric or hydrochloric acid, organic acid such as citric acid or acetic acid or a combination of acid and salt such as citric acid and disodium hydrogen phosphate.

15 The treatment temperature used in this one-step method is normally  $50^\circ\text{C}$  to  $120^\circ\text{C}$ ; a temperature higher than  $120^\circ\text{C}$  is liable to reduce the fibre strength, although the reaction will be quicker.

An electrically conducting fibre prepared by either process  
 20 is washed thoroughly, e.g. with water, and then dried. Electrically conducting fibres obtained by the processes of the present invention were analyzed by X-ray diffraction techniques for the determination of the crystal structure of the adsorbed copper sulfide. It was thereby ascertained  
 25 from the diffraction lines that the copper sulfide was adsorbed within the fibres in the form of digenite (empirical formula:  $\text{Cu}_9\text{S}_5$ ), cuprous sulfide or cupric sulfide.

The respective interfacial distances in Angstroms of the copper sulfides are:-

30	$\text{CuS}$	$\text{Cu}_9\text{S}_5$	$\text{Cu}_2\text{S}$
	1.89	1.97	1.88
	2.81	2.79	1.97
	3.05	3.21	2.40

In each process, the copper compound and/or reducing agent  
 35 used can be a single compound or a suitable mixture of compounds.

Adsorption of the copper sulfide within the whole fibre results in a fibre which possesses excellent electrical conductivity and washability, and the touch and physical properties of the starting fibre is substantially preserved.

The electrically conducting fibres of the present invention can be dyed, e.g. with cationic dyes. (Electrically conducting fibres produced by the metal plating method cannot be dyed.) Suitably, the electrically conducting fibres of the present invention are dyed in an aqueous solution containing cationic dye at a temperature of about 100°C for about 30 minutes to 1 hour.

An electrically conducting fibre of the present invention can be used for many purposes. It can be used alone or in combination with other fibres to produce woven or knitted fabrics for electric blankets, electrically heated clothing and the like. Excellent control over the electrical properties of knitted or woven goods is obtained by combining in one textile the electrically conductive fibres of the present invention with other non-conductive fibres. For example, a small amount of the electrically conductive fibres of the present invention can be mingled into knitted or woven goods in the form of filament fibres. Also, spun yarns can be produced from mixtures of the electrically conductive fibres of the present invention with other natural or synthetic fibres which are both in the form of staple fibres.

The invention is illustrated but not limited by the following examples in which all percentages and ratios are by weight. The No. 31 mesh has 12 openings per square of side 1 inch (2.54 cm) long. The washing test involves washing the sample in a rotating drum in soapy water for 30 minutes at 50°C.



Example 1

An acrylic fibre of 2 deniers yarn and 51 millimetres in length of cut, marketed as Cashmilon, type FWBR, by Asahi Chemical Industry Co., Ltd. of Japan, was heat-  
5 treated in an aqueous bath containing 30 wt.% of cupric sulfate, 4% of sulfuric acid and 80% of copper net (No. 31, of a 12-mesh) in relation to the weight of the fibre in the bath. The ratio of the fibres to water containing the chemicals was 1:15. The heat-treatment was at a  
10 temperature of 95°C for 60 minutes. Subsequently, the fibres were thoroughly washed in water.

The washed fibres were again heat-treated in an aqueous solution containing 10 grams of sodium formaldehyde sulfoxylate (Rongalite C,  $\text{NaHSO}_2 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$ ) and 1 millilitre of sulfuric acid  
15 in relation to 1 litre of water, at a temperature of 80°C for 60 minutes. The electrically conducting fibre was dried after being washed in water for a second time. It had an olive-grey colour and contained 12.3% of copper sulfide in relation to the weight of the starting fibre.  
20 Its electrical resistivity was 0.085 ohm.centimetre. The crystal structure of this electrically conducting fibre was analyzed by X-ray diffraction; the line of diffraction (interfacial distance: 1.97Å, 3.21Å, 2.79Å) was of digenite (empirical formula:  $\text{Cu}_9\text{S}_5$ ).

25 When this electrically conducting fibre was subjected ten times to the repeated washing test according to Japanese Industrial Standard L-1045, A-2, its electrical resistivity was 0.090 ohm.centimetre and its washability was excellent.

30 This electrically conducting fibre was treated in an aqueous solution containing 2% of Sumiacryl Brilliant Red N-4G (cationic dye, made by Sumitomo Chemical Industry Co., Ltd., Japan) in relation to the fibre weight at a

temperature of 100°C for 30 minutes. It was excellently dyed a dark-red colour without deterioration of its conductivity.

Example 2

- 5     Example 1 was repeated except that Rongalite Z ( $\text{ZnSO}_2 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$ ) was used in place of Rongalite C. There was likewise obtained an electrically conducting fibre of the same nature as the fibre obtained in Example 1.

Example 3

- 10    A modacrylic fibre of 2 deniers yarn and 51 millimetres in length of cut, marketed as Kanekalon S made by Kanegafuchi Chemical Co., Ltd., Japan, was heat-treated in a bath containing 30% of cupric sulfate and 15% of hydroxylamine sulfate in relation to the weight of fibre in the bath.
- 15    The ratio of the fibres to the water containing the chemicals was 1:15. The heat-treatment was at a temperature of 100°C for 90 minutes. The fibres were then thoroughly washed in water.

- The washed fibres were again heat-treated in an aqueous
- 20    solution containing 10 grams of dithionous acid and 2 grams of sodium acetate per litre of water, at a temperature of 90°C for 60 minutes. The electrically conducting fibre obtained after being thoroughly washed in water and dried had an olive-grey colour and contained 10.8% of copper
- 25    sulfide in relation to the weight of the starting fibre. Its electrical resistivity was 0.86 ohm-centimetre.

When this electrically conducting fibre was subjected ten times to the repeated washing test as in Example 1, deterioration of its conductivity was scarcely perceived.

Further, this electrically conducting fibre was treated in an aqueous solution containing 2% of Diacryl Brilliant Blue H<sub>2</sub>R-N (cationic dye, made by Mitsubishi Chemical Industry Co., Ltd., Japan) in relation to the fibre weight at a temperature of 100°C for 60 minutes. The electrically conducting fibre was excellently dyed a dark-blue colour.

Examples 4-7

The procedure of Example 3 was repeated except that instead of dithionous acid, either sodium dithionite, sodium thiosulfate, sodium hydrogen sulfite or sodium pyrosulfite was used. In each case, there was obtained an electrically conducting fibre of the same nature as the fibre obtained in Example 3.

Example 8

An acrylic fibre of 3 deniers yarn and 102 millimetres in length of cut, marketed as Toraylon type T-106, made by Toray Industry, Inc., Japan, was heat-treated in a bath containing 40% of cupric chloride and 20% of hydroxylamine sulfate in relation to the weight of fibre in the bath. The ratio of fibres to water containing the chemicals was 1:15. The heat-treatment was at a temperature of 100°C for 60 minutes. Subsequently, the fibres were thoroughly washed in water.

The washed fibres were again heat-treated in an aqueous solution containing 15 grams of sodium sulfide and 4 millilitres of sulfuric acid per litre of water, at a temperature of 90°C for 60 minutes. The electrically conducting fibre obtained after being thoroughly washed in water and dried had an olive-grey color and contained 15.1% by weight copper sulfide in relation to the weight of the starting fibre. Its electrical resistivity was 0.060 ohm.centimetre.

When this electrically conducting fibre was subjected to the repeated washing test in as Example 1, deterioration of its conductivity was negligible.

5 Further, this electrically conducting fibre was treated in an aqueous solution containing 4% of Diacryl Navy Blue RL-N (cationic dye, made by Mitsubishi Chemical Industry Co., Ltd., Japan) in relation to the fibre weight, at a temperature of 100°C for 60 minutes. An electrically conducting fibre dyed well in a dark-blue  
10 colour was obtained.

#### Example 9

An acrylic fibre of 2 deniers yarn and 51 millimetres in length of cut, marketed as Cashmilon by Asahi Chemical Industry Co., Ltd., Japan, which had been treated to  
15 adsorb monovalent copper ions through the same treatment as in Example 1, was put into a closed receptacle having a gas inlet. Sulfur dioxide was fed into the receptacle until the pressure in the interior thereon reached 0.5 kg/cm<sup>2</sup> gauge pressure. Then, saturated water vapour at  
20 105°C was fed into the receptacle until the pressure within the receptacle reached 1.0 kg/cm<sup>2</sup> gauge pressure. After the receptacle had been shut tightly, the fibres reacted therein with the sulfur dioxide. They were taken out after cooling, washed thoroughly in water and dried.  
25 The electrically conducting fibre thus obtained had an olive-grey colour. Its electrical resistivity was 0.50 ohm.centimetre.

The electrically conducting fibre was tested for wash-ability and dyeability by cationic dyestuffs. The results  
30 were as good as in the case of Examples 1 to 8.

Example 10

Example 9 was repeated except that hydrogen sulfide was used instead of sulfur dioxide. An electrically conducting fibre of the same nature as the fibre obtained in Example 9  
5 was obtained.

Example 11

An acrylic fibre of 2 deniers yarn and 51 mm in length of cut, Casmilon type FWBR, made by Asahi Chemical Industry Co., Ltd., was first thoroughly scoured, and then heat-  
10 treated in a bath containing 30 wt. % of cupric sulfate, 15 % of sodiumthiosulfate and 15 % of sodium hydrogen sulfite in relation to the weight of the fibre in the bath. The ratio of the fibres to the water containing the chemicals was 1:15. The treatment was for 60 minutes at the temperature  
15 of 75°C, to which temperature the bath had been raised over 30 minutes from the room temperature. The fibres were then washed in water and dried.

The conductive fibre thus obtained has an olive green color, a copper sulfide content of 14.2% and an electrical  
20 resistivity of 0.036 ohm.centimetre. X-ray diffraction analysis showed it to contain cupric or cuprous sulfide or digenite.

After the repeated washing test ten time as in Example 1, its resistivity had increased only slightly to 0.043 ohm.cm.

25 This electrically conducting Cashmilon fibre was also dyed as in Example 1.

Example 12

An acrylic fibre of 3 deniers yarn and 51 mm in length of cut, marketed as Kaneboacryl type BR V0-1, by Kanebo Synthetic

Fibre Co., Ltd., Japan, was heat-treated as in Example 11 but in a bath containing 20 % of cupric sulfate, 10 % of sodium pyrosulfite and 10 % of hydroxylamine sulfate and for 120 minutes at 50°C (reached after 15 minutes).

- 5 The conductive fibre obtained was olive green, contained 13.8 % copper sulfide, had a resistivity of 0.058 ohm.cm, and showed digenite diffraction lines.

After the repeated washing test its resistivity was 0.063 ohm.cm and its washability was good.

- 10 The electrically conducting fibre was treated in an aqueous solution of Diacryl Navy Blue RL-N (cationic dye, made by Mitsubishi Chemical Industry Co., Ltd., Japan), and was dyed brilliantly navy blue without lowering the electric conductivity.

15 Example 13

- A modacrylic fibre as used in Example 3 was treated as in Example 11 but in a bath containing 20 % of cupric sulfate, 80 % of copper net (No. 31, of a 12 mesh), 10 % of sodium thiosulfate and 5 % of sulfuric acid for 60 minutes at 20 100°C (reached after 45 minutes).

The conductive fibre obtained was olive green, contained 9.2 % copper sulfide, had a resistivity of 1.3 ohm.cm and showed digenite diffraction lines.

- After the repeated washing test, its resistivity was 25 1.4 ohm cm and its washability was good.

- When this electrically conducting fibre was treated in an aqueous solution of Diacryl Brilliant Blue H<sub>2</sub>R-N (cationic dye, made by Mitsubishi Chemical Industry Co., Ltd., Japan), it was dyed brilliantly dark blue, without 30 lowering the electric conductivity.

Claims:

1. An electrically conducting acrylic or modacrylic fibre, characterised in that the fibre is impregnated with a copper sulfide.
2. An electrically conducting fibre as claimed in Claim 1, wherein the amount of copper sulfide, expressed as metallic copper, is 1% to 30% of the weight of the starting fibre.
3. An electrically conducting fibre as claimed in Claim 1 or 2, wherein said copper sulfide is digenite.
4. An electrically conducting fibre as claimed in Claim 1 or 2, wherein said copper sulfide is cupric sulfide or cuprous sulfide.
5. An electrically conducting fibre as claimed in Claim 1, 2 or 3, which has been dyed with a cationic dye.
6. A method of making an electrically conducting fibre as claimed in Claim 1, 2, 3 or 4, comprising subjecting an acrylic or modacrylic fibre to a first heat-treatment in a bath containing a copper compound and a reducing agent so as to adsorb monovalent copper ions into the fibre, and subjecting the fibre to a second heat-treatment in the presence of a sulfur-containing compound to convert said adsorbed monovalent copper ions to a copper sulfide.
7. A method as claimed in Claim 6, wherein said fibre is washed between the first and second heat-treatments.
8. A method as claimed in Claim 6 or 7, wherein said first heat-treatment is at a temperature of from 90°C to 110°C.

9. A method as claimed in any of Claims 6, 7 or 8, wherein said second heat-treatment is at a temperature of from 50°C to 105°C.

10. A method as claimed in Claim 6, 7, 8 or 9, wherein said second heat-treatment is conducted in a gaseous sulfur-containing compound.

11. A method of making an electrically conducting fibre as claimed in Claim 1, 2, 3 or 4, comprising subjecting an acrylic or modacrylic fibre to heat-treatment in a bath which contains a copper compound, a reducing agent which is capable of reducing copper ions to monovalent ions, and a sulfur-containing compound to convert said monovalent copper ions to a copper sulfide.

12. A method as claimed in Claim 11, wherein said treatment is at a temperature of 50°C to 120°C.

13. A method as claimed in any of Claims 5 to 12, wherein said copper compound is cupric sulfate, cupric chloride, cupric nitrate, cupric acetate or a chelate of copper.

14. A method as claimed in any of Claims 5 to 13, wherein said reducing agent is metallic copper, ferrous sulfate, ammonium vanadate, sodium hypophosphite, hydroxylamine or its sulfate, furfural or glucose.

15. A method as claimed in any of Claims 5 to 14, wherein said sulphur-containing compound is selected from sodium sulfide, sulfur dioxide, sodium formaldehyde sulfoxylate, zinc formaldehyde sulfoxylate, sodium pyrosulfite, sulfurous acid, dithionous acid, sodium dithionate, sodium thiosulfate, thiourea dioxide, hydrogen sulfide and sodium hydrogen sulfite.



16. A method as claimed in any of Claims 5 to 15, wherein the treated fibre is then dyed with a cationic dye.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<p><u>DE - C - 74 056</u> (ODERNHEIMER) + Column 1, lines 1-18; claim + --</p> <p><u>GB - A - 1 372 656</u> (RHONE- POULENC) + Page 1, lines 37-60; page 2, lines 17-26; claims 1-4, 10,12 + --</p> <p><u>DE - B2 - 2 329 484</u> (ASAHI KASEI KOGYO) + Claims 1,5; column 4, lines 51-53 + &amp; GB-A-1 396 072 &amp; US-A-3 958 066 -----</p>	<p>1,4,6, 10,15</p> <p>1,4,13, 15</p> <p>1,4</p>	<p>D 06 M 11/04 C 23 C 17/02 H 01 B 1/10</p> <p>TECHNICAL FIELDS SEARCHED (Int. Cl. 3)</p> <p>D 06 M D 06 Q C 23 C H 01 B</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons</p>
X	The present search report has been drawn up for all claims		&: member of the same patent family, corresponding document
Place of search VIENNA		Date of completion of the search 03-06-1981	Examiner SCHÄFER