(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 074 281**
A1

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 82304744.4

(22) Date of filing: 09.09.82

(51) Int. Cl.³: H 01 B 1/24
H 01 C 7/02, H 05 B 3/14

(30) Priority: 09.09.81 US 300709

(43) Date of publication of application: 16.03.83 Bulletin 83/11

(84) Designated Contracting States: AT BE CH DE FR IT LI NL SE

(71) Applicant: RAYCHEM CORPORATION
300 Constitution Drive
Menlo Park California 94025(US)

(72) Inventor: Van Konynenburg, Peter
739 Coastland Drive
Palo Alto California, 94303(US)

(72) Inventor: Au, Andrew
34801 Potomac River Place
Fremont California, 94536(US)

(74) Representative: Jay, Anthony William et al,
RAYCHEM Limited Faraday Road Dorcan
Swindon Wiltshire(GB)

(54) **Conductive polymer composition.**

(57) Conductive polymer compositions based on polyvinylidene fluoride have improved properties when the polyvinylidene fluoride has a very regular structure characterized by a low head-to-head content in the repeating units. The improved properties include improved electrical stability when contacted by organic fluids and/or when maintained at elevated temperatures in air. Such compositions are particularly useful in the form of self-limiting heaters, e.g. for heating diesel fuel.

EP 0 074 281 A1

COMPLETE DOCUMENT

This invention relates to conductive polymer compositions and devices comprising them.

Conductive polymer compositions, and devices comprising them, are known or are described in copending patent applications. Reference may be made for example to U.S. Patents Nos. 2,978,665, 3,243,753, 3,351,882, 3,571,777, 3,793,716, 3,823,217, 3,861,029, 4,017,715, 4,177,376, 4,188,276, 4,237,441, 4,238,812, 4,242,573, 4,246,468, 4,255,698, 4,272,471 and 4,276,466; U. K. Patent No. 1,534,715; J. Applied Polymer Science 19, 813-815 (1975), Klason and Kubat; Polymer Engineering and Science 18, 649-653 (1978) Narkis et al; and German OLS Nos. 2,634,999, 2,755,077, 2,746,602, 2,755,076, 2,821,799, 2,949,173 and 3,030,799; European Published Patent Applications Nos. 0,026,571, 0,028,142, 0,030,479, 0,038,713, 0,038,714, 0,038,715, 0,038,716, 0,038,717 and 0,038,718; and the copending applications corresponding to U.S. Serial Nos. 150,909, and 254,352 and U.K. Applications Nos. 2,075,992A, 2,080,834A, 8209923, 8217000, 8216999 and 8216997. The disclosure of each of the patents, publications and applications referred to above is incorporated herein by reference.

Electrical devices containing conductive polymers generally (though not invariably) comprise an outer jacket, usually of insulating material, to protect the conductive polymer from damage by the surrounding environment. However, if no protective jacket is used, or if the jacket is permeable to harmful species in the environment, or if the conditions of use are such that the jacket may become damaged, it is necessary or desirable to select a conductive polymer which is not damaged (or which deteriorates at an acceptably low rate) when exposed to the surrounding environment. Exposure of conductive polymers to organic fluids generally results in an increase in resistivity; exposure to air, especially at elevated temperatures between room temperature and 35°C below the melting point generally results in a decrease in resistivity both at the elevated temperature and at room temperature (a phenomenon known in the art as "resistance relaxation").

We have discovered that conductive polymer compositions which are based on polyvinylidene fluoride exhibit substantially improved stability if the polyvinylidene fluoride has a very regular structure which can be characterized by a low head-to-head content in the repeating units. Polyvinylidene fluoride is made up of repeating units of formula $-CH_2CF_2-$, which can be arranged head-to-tail (i.e. $-CH_2CF_2-CH_2CF_2-$) or head-to-head (i.e. $-CH_2CF_2-CF_2CH_2-$), and we have found that the lower the head-to-head content, the greater the stability of the resistivity of the composition when exposed to organic fluids and/or when exposed to air at elevated temperature. Previously known conductive polymer compositions based on polyvinylidene fluoride have made use of polyvinylidene fluoride of relatively high head-to-head content, namely at least 5.2% and generally higher, which are easier to process than the polymers used in the present invention.

In its first aspect, the present invention provides a conductive polymer composition which comprises (a) polyvinylidene fluoride having a head-to-head content of less than

5.0%, preferably less than 4.5%, particularly less than 4.0%, and (b) a particulate conductive filler, especially carbon black, dispersed in the polyvinylidene fluoride. The composition preferably exhibits PTC behavior.

In its second aspect, the invention provides an electrical device which comprises a conductive polymer element composed of a conductive polymer composition as defined above and at least one electrode in electrical contact with said element, for example, at least two electrodes which can be connected to a source of electrical power and which when so connected cause current to flow through the conductive polymer element. Preferred devices are self-limiting heaters, e.g. flexible strip heaters, in which the conductive polymer composition exhibits PTC behavior. Such heaters are particularly useful for heating liquids in which the heater is immersed, especially diesel fuel (see U.K. applications Nos. 8216999 and 8216997.

In a third aspect, the invention provides a method of heating a liquid, particularly an organic liquid, especially diesel fuel, which comprises passing current through a self-limiting heater as defined above which is immersed in the liquid.

In a fourth aspect the invention provides a fuel feedthrough and heating assembly which can be positioned and connected between a fuel filter and a fuel tank of a fuel supply system to provide means for heating fuel which is being pumped through a fuel line from the fuel tank to the fuel filter, said feedthrough and heating assembly comprising

(A) a feedthrough comprising (i) a fuel conduit having at one end thereof a fuel line connector for connecting the feedthrough to a fuel line and at the other end thereof a fuel filter connector for connecting the feedthrough to a fuel filter; and (ii) a neck portion which protrudes from the fuel conduit between the ends thereof and which comprises a chamber;

(B) a flexible self-limiting strip heater as defined above which preferably comprises a fuel-resistant insulating jacket, one end of the strip heater being within the chamber of the neck portion, and the strip heater passing through the fuel line connector and protruding from the fuel conduit;

(C) insulated electrical leads connected to the electrodes of the heater, the connections lying within the chamber of the neck portion;

(D) a fuel-resistant, water-resistant and insulating composition which encapsulates (i) the connections between the electrodes and the leads, (ii) the insulation at the ends of the connected electrical leads and (iii) the insulating jacket at the end of the connected heater; and

(E) a fuel-resistant gasket which prevents fuel which is being pumped through the fuel conduit from exiting through the neck portion.

Polyvinylidene fluorides suitable for use in this invention are commercially available. The head-to-head content of a polyvinylidene fluoride can be measured by those skilled in the art. We have found that the measured head-to-head contents of different samples of a polymer sold under a particular trade name can differ substantially. In general, the presently available polyvinylidene fluorides made by suspension polymerization (rather than emulsion polymerization) have lower head-to-head contents. The number average molecular weight of the polymer is generally at least 5,000, eg. 7,000 to 15,000.

The polyvinylidene fluoride is preferably a homopolymer of vinylidene fluoride, but the presence of small quantities of comonomers, (preferably less than 15%, particularly less than 5% by weight), eg. tetrafluoroethylene, hexafluoropropylene and ethylene, is not excluded. The polyvinylidene fluoride is preferably the sole crystalline polymer in the composition, but other crystalline polymers, eg. other crystalline fluoropolymers, may also be present. The composition may contain relatively small amounts (preferably less than 35%, especially less than 20%, particularly less than 10%, by volume) of one or more elastomeric polymers, particularly solvent-resistant fluorine-containing elastomers and acrylic elastomers, which are usually added primarily to improve the flexibility and elongation of the composition.

The particulate conductive filler preferably comprises carbon black, and often consists essentially of carbon black. Choice of the carbon black will influence the resistivity/temperature characteristics of the composition. Compositions exhibiting PTC behavior are preferred for many devices of the invention, especially self-limiting heaters, and for these a carbon black having a ratio of surface area (m^2/g) to particle size (mu) of 0.03 to 6.0 is preferred. For other uses, compositions exhibiting ZTC or NTC behavior may be preferred. The amount of conductive filler used will depend upon the desired resistivity of the composition. For flexible strip heaters which are to be used for heating diesel fuel and powered by a 12 volt battery, we prefer a PTC composition whose resistivity at 25°C is less than 200 ohm.cm eg. about 10 to about 100 ohm.cm. In such compositions the amount of carbon black may for example be 16 to 25% by weight.

In addition to one or more conductive fillers, the compositions may also comprise other conventional additives, such as non-conductive fillers (including flame retardants), antioxidants and crosslinking agents (or residues thereof if the composition has been cross-linked).

The compositions of the invention are preferably cross-linked (particularly by irradiation), since this has been found to enhance their resistance to organic solvents.

Preparation of the compositions of the invention can be carried out in conventional fashion. Often it will be convenient to melt-extrude the composition directly into a water bath (which may be heated), and using this technique subsequent annealing is often not required.

The invention is illustrated by the following Examples, in which Examples 1, 2, 3, 7, 12 and 13 are Comparative Examples not in accordance with the invention.

EXAMPLE 1

The ingredients listed for Composition A in Table 1 below were mixed in a Banbury mixer. The mixture was dumped, placed on a steam-heated mill and extruded into a water bath through a 3.5 inch (8.9 cm) extruder fitted with a pelletizing die. The extrudate was chopped into pellets which were dried for 16 hours at 80°C.

The ingredients listed for Composition B in Table 1 were mixed and pelletized in the same way as for Composition A.

83% by weight of the Composition A pellets and 17% by weight of the Composition B pellets were tumble blended and dried at 110°C. The composition of the resulting Final Blend is shown in Table 1. Using a 1.5 inch (3.8 cm) diameter extruder fitted with a crosshead die having an orifice 0.4 inch (1.0 cm) x 0.1 inch (0.3 cm), the blend was melt-extruded over a pair of pre-heated 14 AWG (1.85 mm diameter) 19/27 nickel-coated copper wires with a center-to-center separation of 0.25 inch (0.64 cm).m. The extrudate was passed immediately through a bath of water at room temperature, air-dried, and then irradiated to a dosage of 10 Mrad. The conductive polymer had a resistivity of about 50 ohm.cm at 25°C.

TABLE 1

	Composition B			Composition A			Final Blend	
	Wt(g)	Wt%	Vol%	Wt(g)	Wt%	Vol%	Wt%	Vol%
Kynar 460	16,798	72	72.6	16,339	70	70.6	71.7	72.3
Furnex N765	4,433	19	18.7	4,901	21	20.7	19.3	19.0
Viton AHV	1,400	6	5.9	1,400	6	5.9	6.0	5.9
Omya-BSH	467	2	1.3	467	2	1.3	2.0	1.3
TAIC	233	1	1.5	233	1	1.5	1.0	1.5

Kynar 460 is polyvinylidene fluoride available from Pennwalt and having a head-to-head content of about 5.5%.

Furnex N765 is a carbon black available from Columbia Chemical having a particle size of about 60 millimicrons, a surface area of about 32 m^2/g and a DBP value of about 112 $cm^3/100$ g.

Viton AHV is a copolymer of hexafluoropropylene and polyvinylidene fluoride manufactured by du Pont.

Omya-BSH is calcium carbonate available from Omya Inc.

TAIC is triallyl isocyanurate, a radiation cross-linking agent.

EXAMPLES 2-6

The ingredients listed for Examples 2 to 6 in Table 2 below were mixed in a Banbury mixer. The mixture was dumped, granulated and dried for 72 hours at 75°C under vacuum. Using a 0.75 inch (1.9 cm) single screw extruder fitted with a cross-head die having an orifice 0.3 inch (0.76 cm) x 0.1 inch (0.3 cm), the blend was melt-extruded over a pair of pre-heated 18 AWG (1.2 mm diameter) 19/27 nickel-coated copper wires with a center-to-center separation of 0.25 inch (0.64cm). The extrudate was passed immediately through a bath of water at room temperature, air-dried, and then irradiated to a dosage of 10 Mrad.

EXAMPLES 7-15

The ingredients shown for Examples 7-15 in Table 2 were mixed in a Banbury mixer, dumped and then granulated. The granulated materials were molded into slabs of thicknesses of 0.030" (0.076 cm) to 0.036" (.091 cm) by compression molding at 200°C for three minutes.

0074281

Table 2

Ex. No.	2C	3C	4	5	6	7C	8	9	10	11	12C	13C	14	15
Ingredients														
Kynar 450	77					90					88			
Kynar 460		77										89		
Solef 1010			74				88.5	88						
KF 1100				74					89.5					88.5
KF 1000					77									
Dyflor 2000M										89.5			88.5	
Statex G	21	21	24	24	21									
Vulcan XC72						8	9.5	10	8.5	8.5	10	9	9.5	9.5
Omya BSH	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Resistivity (ohm-cm) at 25°C						3.1×10^4	1.6×10^4	1800	1850	2000	288	298	200	134

Kynar 450 is polyvinylidene fluoride available from Pennwalt and having a head-to-head content in the range 5.5 to 6.3.

Solef 1010 is a polyvinylidene fluoride available from Solvay et cie of Belgium, and having a head-to head content of 4.1%.

KF1000 and KF1100 are polyvinylidene fluorides available from Kureha Chemical Industry Co. of Japan, and having a head-to-head content of 3.5 to 3.8%.

Statex G is a carbon black available from Cities Services Co., Columbian Division having a particle size of about 60 millimicrons, a surface area of about 32 m^2/g and a DBP value of about 90 $cm^3/100$ g.

Dyflor 2000 M is a polyvinylidene fluoride available from Kay-Fries, Inc., member of Dynamit Nobel Chemikalien of Federal Republic of Germany and having a head-to-head content of about 4.4-4.9.

Vulcan XC-72 is a carbon black available from Cabot Co., having a particle size of about 30 millimicrons, a surface area of about 224 m^2/g and a DBP value of about 178 $cm^3/100$ g.

TESTS FOR STABILITY IN ORGANIC SOLVENTS

The extrudates obtained in Examples 1 and 4 were compared by the following tests. Samples 2 inch (5.1 cm) long were cut from the extrudates. The samples were immersed in various solvents at 25°C and the resistance of the samples was measured at intervals. The solvents used, and their solubility parameters, were

Solvent	Solubility Parameter $(cal/cm^3)^{0.5}$
Toluene	8.9
Methylethylketone (MEK)	9.3
Acetone	9.9
o - dichlorobenzene	10.0
Acetic Anhydride	10.3
Pyridine	10.7
Dimethylacetamide (DMAC)	10.8
Dimethylsulphoxide(DMSO)	12.0
Dimethylformamide (DMF)	12.1
Ethanol	12.7

The results for Examples 1 and 4 are shown in Figures 1 and 2 respectively of the accompanying drawings, where the ratio of the resistance at a given time (R_f) to the initial resistance (R_i) is plotted against time. The greater stability of the composition of the invention (Example 4, shown in Figure 2) is apparent.

The extrudates obtained in Examples 1 to 6 were compared in the following way. Samples 2 inch (5.1 cm) long were cut from the extrudates and were immersed in various test liquids maintained at 160° F (71°C). The test liquids are listed below and include diesel fuel and various commercially available additives for diesel fuel alone and mixed with diesel fuel. At intervals, the samples were removed, cooled to 25°C and dried, and their resistance measured. Table 3 shows the value of the ratio R_f/R_i for the different samples at various times. The additives tested, and their main ingredients, were as follows:

B12	Toluene, methanol, acetone, naphthalenic mineral oil and ethylene glycol monobutylether.
Fire Prep 100	Naphthalenic oil and partly oxidised aliphatic hydrocarbon
Sta-Lube	Naphthalenic mineral oil
Redline Catalyst	Naphthalenic mineral oil, barium carbonate and other inorganic carbonates, and sulfur-containing material
Wynn's Conditioner	Naphthalenic mineral oil/and isopropanol
Gumout	Naphthalenic mineral oil, non-aromatic ester and aliphatic acid.
Wynn's Anti-Knock	Naphthalenic mineral oil, non-aromatic ester, aliphatic amide, and aliphatic acid.
FPPF	Ethyl cellulose, ethylene glycol monobutylether, and oxidised hydrocarbons.

Table 3

Example No.	1C(C)	2(C)	3(C)	4	5	6
R_i (ohms)	9.3	8.8	2.3	14.1	19.7	10.4
R_f/R_i after 19 hours in						
B12	$23X10^4$	$28X10^4$	$43X10^4$	$3.3X10^4$	133	339
Fire Prep 1000	1.02	1.04	0.96	0.91	0.94	0.92
Sta-Lube	1.09	1.04	1.11	0.94	0.95	0.91
Red-line Catalyst	1.22	1.06	1.33	1.00	0.97	1.05
Wynn's Conditioner	1.39	1.18	1.19	1.13	1.08	1.15
Gumout	1.14	1.10	1.22	1.01	1.01	1.08
Wynn's Anti	1.12	1.04	1.18	0.99	1.00	1.09
R_f/R_i after 110 hours in						
Diesel Fuel	1.03	0.97	1.07	0.93	1.00	0.92
R_f/R_i after 69 hours in						
Diesel Fuel + 7% B12	1.26	1.10	1.67	1.15	1.05	1.12
Diesel Fuel + 7% FPPF	1.32	1.12	1.20	1.08	1.05	1.12
Diesel Fuel + 10% gasoline	1.17	1.05	1.15	1.01	0.99	1.07
R_f/R_i after 275 hours in						
Diesel Fuel	1.09	1.01	1.12	0.95	0.93	1.04
R_f/R_i after 157 hours in						
Diesel fuel + 7% B12	1.66	1.17	2.97	1.37	1.08	1.35
Diesel Fuel + 7% FPPF	1.78	1.30	1.47	1.17	1.14	1.27
Diesel Fuel + 10% gasoline	1.33	1.10	1.28	1.06	1.01	1.16

RESISTANCE RELAXATION TESTS

The compositions of Examples 7-15 were tested by the following tests. Samples 1 inch (2.54cm) by 1.5 inch (3.8 cm) were cut from the molded slabs. Electrodes were formed on each sample by painting a strip 0.25 inch (0.62 cm) wide at each end with a suspension of silver particles (Electrodag 504 available from Acheson Colloids). The samples were annealed for 5 minutes at 200°C, and then cooled. The samples were then placed in an oven at 100°C and their resistances measured at intervals. It was found at the lower the head-to-head content of the polymer, the less its change in resistance.

CLAIMS

1. A conductive polymer composition which comprises a particulate conductive filler dispersed in polyvinylidene fluoride which has a head-to-head content of less than 5.0%, preferably less than 4.5%, particularly less than 4.0%.

2. A composition according to Claim 2 wherein the conductive filler is carbon black.

3. A composition according to Claim 1 or 2 which exhibits PTC behavior.

4. An electrical device which comprises

   (i) a conductive polymer element composed of a composition as claimed in any one of claims 1 to 3; and

   (ii) at least one electrode in electrical contact with the conductive polymer element.

5. A device according to Claim 4 which is a self-regulating heater in which the conductive polymer composition exhibits PTC behavior.

6. A method of heating diesel fuel which comprises passing current through a self-regulating heater as claimed in Claim 5 which is immersed in the diesel fuel.

7. A fuel feedthrough and heating assembly which can be positioned and connected between a fuel filter and a fuel tank of a fuel supply system to provide means for heating fuel which is being pumped through a fuel line from the fuel tank to the fuel filter, said feedthrough and heating assembly comprising

(A) a feedthrough comprising

(i) a fuel conduit having at one end thereof a fuel line connector for connecting the feedthrough to a fuel line and at the other end thereof a fuel filter connector for connecting the feedthrough to a fuel filter; and

(ii) a neck portion which protrudes from the fuel conduit between the ends thereof and which comprises a chamber;

(B) a flexible self-limiting strip heater as claimed in Claim 5 which comprises a fuel-resistant insulating jacket, one end of the strip heater being within the chamber of the neck portion, and the strip heater passing through the fuel line connector and protruding from the fuel conduit;

(C) insulated electrical leads connected to the electrodes of the heater, the connections lying within the chamber of the neck portion; and

(D) a fuel-resistant, water-resistant and insulating composition which encapsulates (i) the connections between the electrodes and the leads and (ii) the insulation at the ends of the connected electrical leads and (iii) the insulating jacket at the end of the heater; and

(E) a fuel-resistant gasket which prevents fuel which is being pumped through the fuel conduit from exiting through the neck portion.

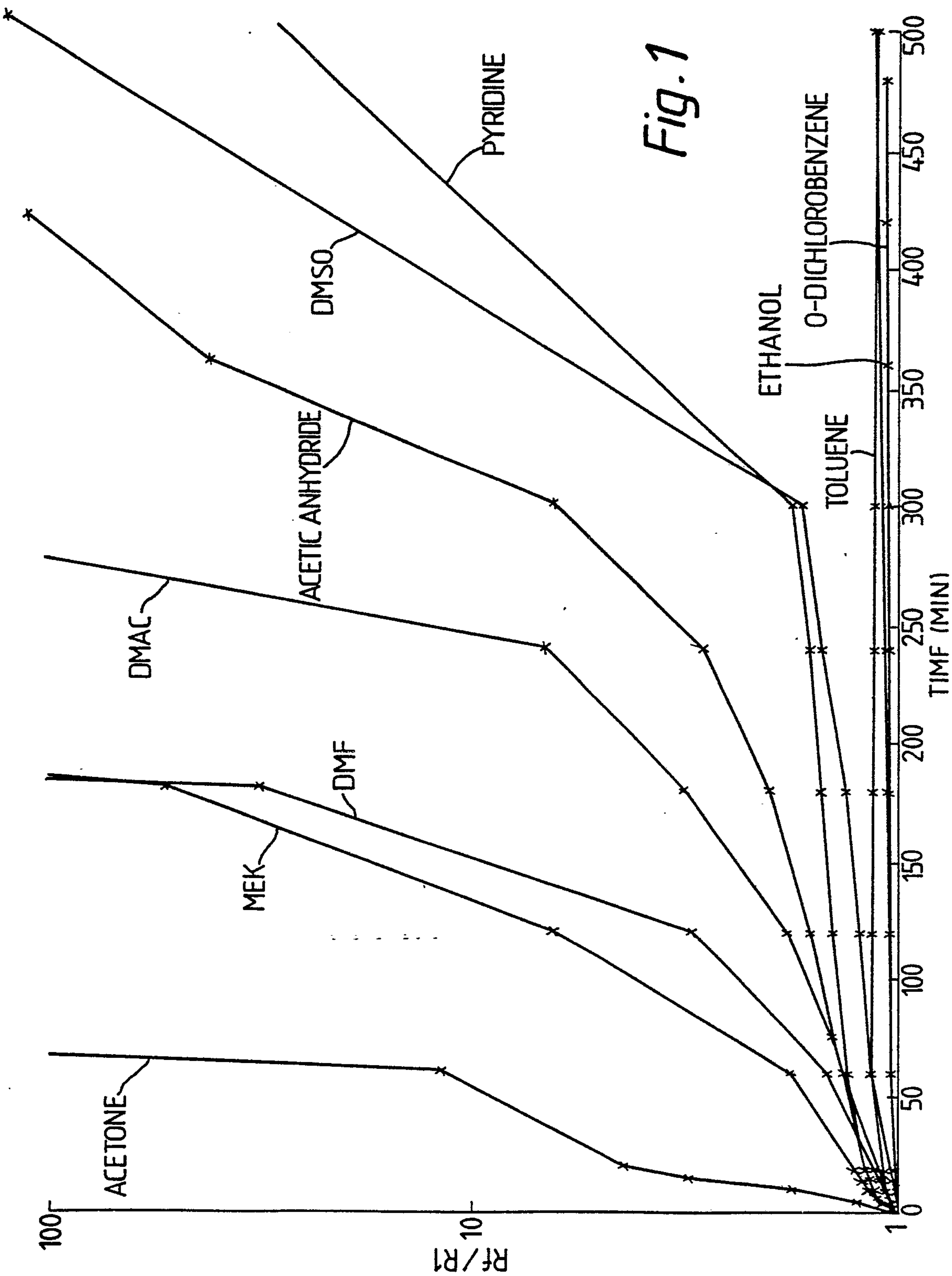
ACETONE
MEK
DMF
DMAC
ACETIC ANHYDRIDE
DMSO
PYRIDINE
ETHANOL
O-DICHLOROBENZENE
TOLUENE
Rf/R1
100
10
1
0
50
100
150
200
250
300
350
400
450
500
TIMF (MIN)

Fig. 1

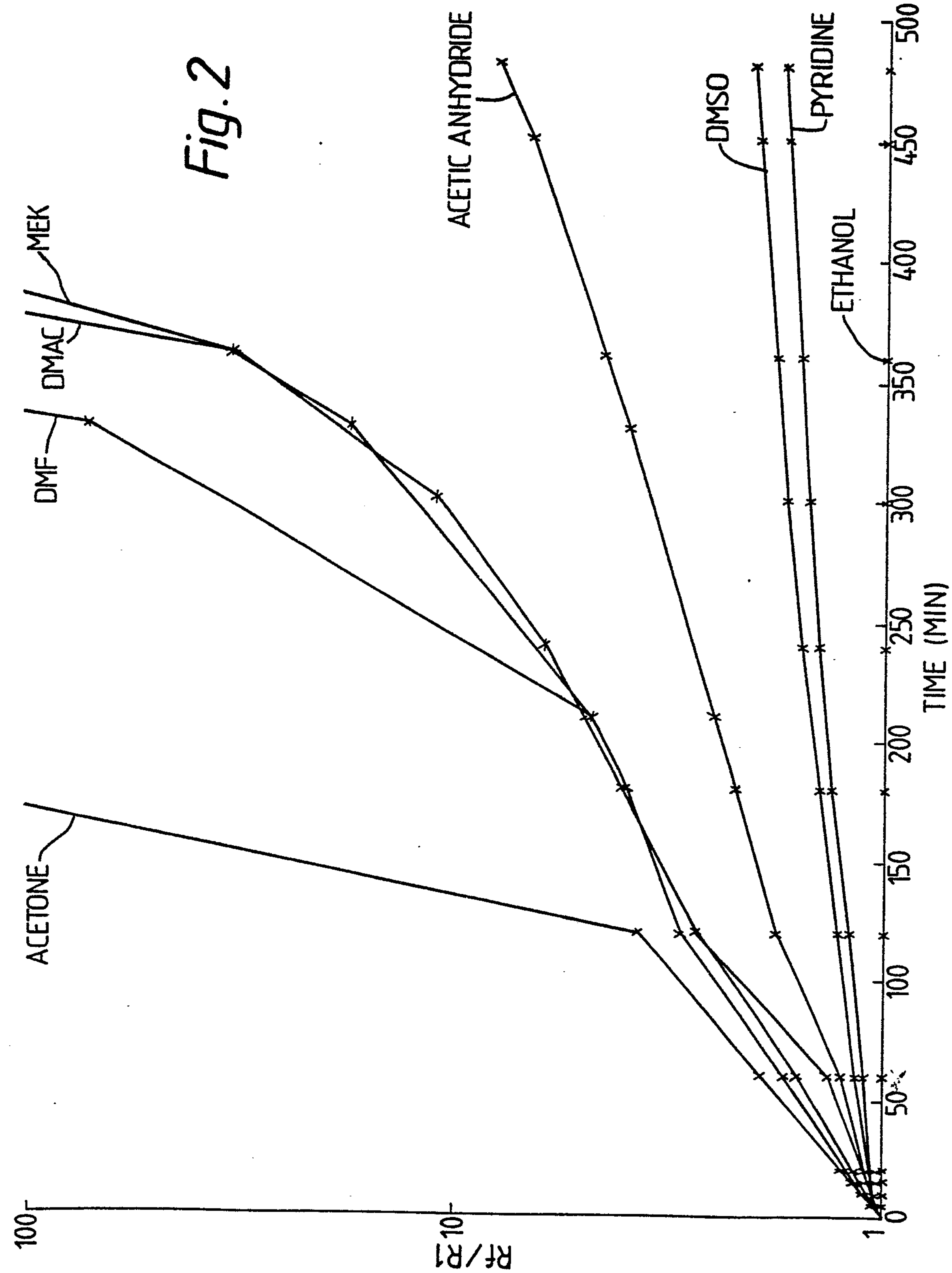
ACETONE
DMF
DMAC
MEK
ACETIC ANHYDRIDE
DMSO
PYRIDINE
ETHANOL
Rf/R1
100
10
1
TIME (MIN)
0
50
100
150
200
250
300
350
400
450
500

Fig. 2

European Patent Office

EUROPEAN SEARCH REPORT

0074281
Application number

EP 82 30 4744

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. ³)
	---		H 01 B 1/24 H 01 C 7/02 H 05 B 3/14
A	DE-A-1 805 906 (PENNSALT CHEMICALS)		

A	FR-A-2 443 123 (RAYCHEM)		

			TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
			H 01 B 1/00 H 01 C 7/00 H 05 B 3/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	25-11-1982	STIENON P.M.E.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document
T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503. 03.82