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⑰ **Heating Diesel fuel.**

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EP-A-0 068 688
DE-A-1 805 906
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㉓ Proprietor: **RAYCHEM CORPORATION (a**
Delaware corporation)
300 Constitution Drive
Menlo Park, California 94025 (US)

㉔ Inventor: **Van Konynenburg, Peter**
739 Coastland Drive
Palo Alto California, 94303 (US)
Inventor: **Au, Andrew**
34801 Potomac River Place
Fremont California, 94536 (US)

㉕ Representative: **Jay, Anthony William et al**
Raychem Limited Intellectual Property Law
Department Faraday Road
Dorcan Swindon Wiltshire (GB)

The file contains technical information
submitted after the application was filed and
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Description

This invention relates to a method of heating diesel fuel using a conductive polymer composition.

Conductive polymer compositions, and devices comprising them, are known or are described in
 5 copending patent applications. Reference may be made for example to U.S. Patents Nos. 2,978,665,
 3,243,753, 3,351,777, 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
 10 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, 0,038,718, 0,040,537, and 0,045,630.

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
 15 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
 20 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 of 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
 25 up of repeating units of formula $\text{—CH}_2\text{CF}_2\text{—}$, which can be arranged head-to-tail (i.e. $\text{—CH}_2\text{CF}_2\text{—CH}_2\text{CF}_2\text{—}$),
 or head-to-head (i.e. $\text{—CH}_2\text{CF}_2\text{—CF}_2\text{CH}_2\text{—}$), 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,
 30 namely at least 5.2% and generally higher, which are easier to process than the polymers used in the
 method of the present invention.

In accordance with the present invention, there is provided a method of heating diesel fuel which
 comprises passing current through a self-regulating heater that has no outer protective jacket, which heater

- (i) is immersed in diesel fuel, and
- 35 (ii) is composed of a conductive polymer composition which
 - (a) comprises a particulate conductive filler dispersed in polyvinylidene fluoride which has a
 head-to-head content of less than 5%,
 - (b) exhibits PTC behaviour, and
 - (c) is in direct contact with the diesel fuel.

40 Preferably, the polyvinylidene fluoride has a head-to-head content of less than 4%.

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
 45 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, e.g. 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), e.g.
 tetrafluoroethylene, hexafluoropropylene and ethylene, is not excluded. The polyvinylidene fluoride is
 50 preferably the sole crystalline polymer in the composition, but other crystalline polymers, e.g. 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.

55 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, and a carbon black having a ratio of surface area (m^2/g) to particle size (nanometers) of 0.03 to
 6.0 is preferred. The amount of conductive filler used will depend upon the desired resistivity of the
 composition. For flexible strip heaters which are to be powered by a 12 volt battery for heating diesel fuel,
 60 we prefer a PTC composition whose resistivity at 25°C is less than 200 ohm · cm e.g. 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 used in the method of the invention may
 also comprise other conventional additives, such as non-conductive fillers (including flame retardants),
 65 antioxidants and crosslinking agents (or residues thereof if the composition has been cross-linked).

The compositions used in the method 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 used in the method of the invention can be carried out in a 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 compositions of Comparative Examples not used in the method of 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) × 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). 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			Composition C 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 nm, a surface area of about 32 m²/g and a DBP value of about 112 cm³/100 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.

*Trade Mark

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) × 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 (0.64 cm). 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" (0.091 cm) by compression molding at 200°C for three minutes.

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 a 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 availabgx from Cities Services Co., Columbian Division having a particle size of about 60 nm, a surface area of about 32 m²/g and a DBP (dibutylphthalate) value of about 90 cm³/100 g. The dibutylphthalate is an oil used in a standard test to determine the structure of carbon black.

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 nm, a surface area of about 224 m²/g and a DBP value of about 178 cm³/100 g.

*Trade Mark

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}
10	Toluene	8.9
	Methylethylketone (MEK)	9.3
15	Acetone	9.9
	<i>o</i> -dichlorobenzene	10.0
	Acetic anhydride	10.3
20	Pyridine	10.7
	Dimethylacetamide (DMAC)	10.8
25	Dimethylsulphoxide (DMSO)	12.0
	Dimethylformamide (DMF)	12.1
30	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_t) 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_t/R_i for the different samples at various times. The additives tested, and their main ingredients, were as follows:

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

*Trade Mark

TABLE 3

Example No.	1C(C)	2(C)	3(C)	4	5	6
5 R_f (ohms)	9.3	8.8	2.3	14.1	19.7	10.4
R_f/R_i after 19 hours in B12	23×10^4	28×10^4	43×10^4	3.3×10^4	133	339
10 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
15 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
20 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
25 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
30 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
35 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
40 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 (2.54 cm) 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.

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Claims

1. A method of heating diesel fuel which comprises passing current through a self-regulating heater that has no outer protective jacket, which heater
 - (i) is immersed in diesel fuel, and
 - (ii) is composed of a conductive polymer composition which
 - (a) comprises a particulate conductive filler dispersed in polyvinylidene fluoride which has a head-to-head content of less than 5%,
 - (b) exhibits PTC behaviour, and
 - (c) is in direct contact with the diesel fuel.
2. A method according to claim 1, wherein the polyvinylidene fluoride has a head-to-head content of less than 4%.
3. A method according to claim 1 or 2, wherein the conductive filler is carbon black.
4. A method according to claim 3, wherein the carbon black has a ratio of surface area (meter²/gram) to particle size (nanometer) in the range from 0.03 to 6.0.

Patentansprüche

1. Verfahren zum Erhitzen von Diesel-Treibstoff, welches umfaßt das Durchleiten von Strom durch einen selbstregelnden Erhitzer ohne äußeren Schutzmantel, welcher Erhitzer
- 5 (i) in Diesel-Treibstoff eingetaucht ist, und
(ii) aus einer leitenden Polymerzusammensetzung zusammengesetzt ist, welche
(a) einen feinteiligen leitenden Füllstoff umfaßt, der in Polyvinylidenfluorid dispergiert ist, das einen Kopf-an-Kopf-Gehalt von weniger als 5% aufweist,
(b) PTC-Verhalten aufweist, und
- 10 (c) in direktem Kontakt mit dem Diesel-Treibstoff steht.
2. Verfahren nach Anspruch 1, worin das Polyvinylidenfluorid einen Kopf-an-Kopf-Gehalt von weniger als 4% aufweist.
3. Verfahren nach Anspruch 1 oder 2, worin der leitende Füllstoff Ruß ist.
4. Verfahren nach Anspruch 3, worin der Ruß ein Verhältnis der Oberfläche (m^2/g) zu Teilchengröße
- 15 (nm) im Bereich von 0,03 bis 6,0 aufweist.

Revendications

1. Procédé de chauffage de carburant diesel, lequel comprend le passage d'un courant dans un
- 20 dispositif de chauffage à autorégulation, dépourvu d'enveloppe protectrice externe, lequel dispositif de chauffage
- (I) est immergé dans le carburant diesel, et
(II) est constitué d'une composition de polymère conducteur qui
(a) comprend une charge conductrice particulière dispersée dans du poly(fluorure de vinylidène) ayant
- 25 une teneur en motifs tête-contre-tête inférieure à 5%,
(b) manifeste un comportement de PTC et
(c) est en contact direct avec le carburant diesel.
2. Procédé selon la revendication 1, dans lequel le poly(fluorure de vinylidène) a une teneur en motifs tête-contre-tête inférieure à 4%.
- 30 3. Procédé selon la revendication 1 ou 2, dans lequel la charge conductrice est du noir de carbone.
4. Procédé selon la revendication 3, dans lequel le noir de carbone a un rapport de l'aire spécifique (m^2/g) à la taille de particules (nm) dans la plage de 0,03 à 6,0.

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