Jan. 4, 1972 KAZUMASA YAMAMOTO ET AL 3,632,526

HEAT-SENSITIVE HIGH MOLECULAR WEIGHT RESISTORS

Filed July 29, 1968 3 Sheets-Sheet 1

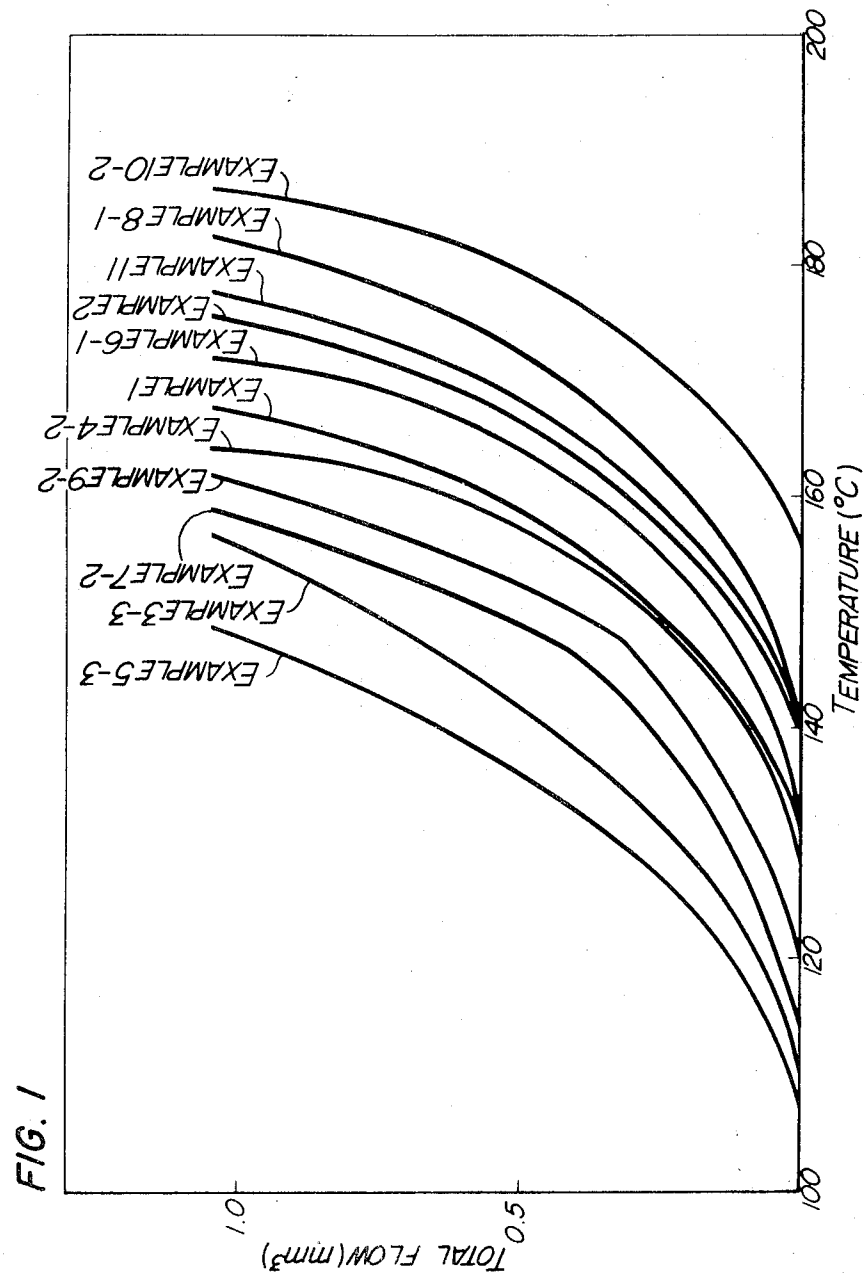


FIG. 1

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HEAT-SENSITIVE HIGH MOLECULAR WEIGHT RESISTORS

Filed July 29, 1968 3 Sheets-Sheet 2

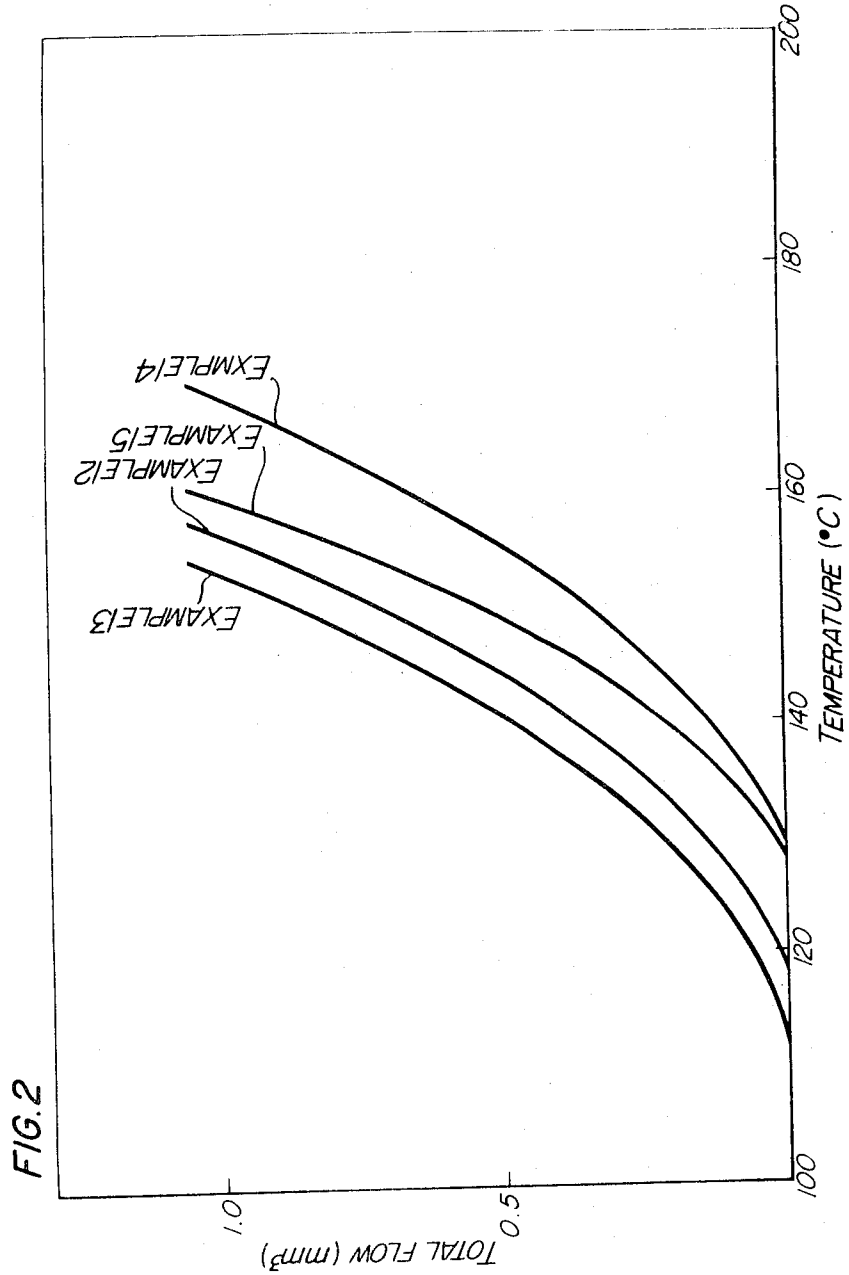


FIG. 2

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HEAT-SENSITIVE HIGH MOLECULAR WEIGHT RESISTORS

Filed July 29, 1968 3 Sheets-Sheet 3

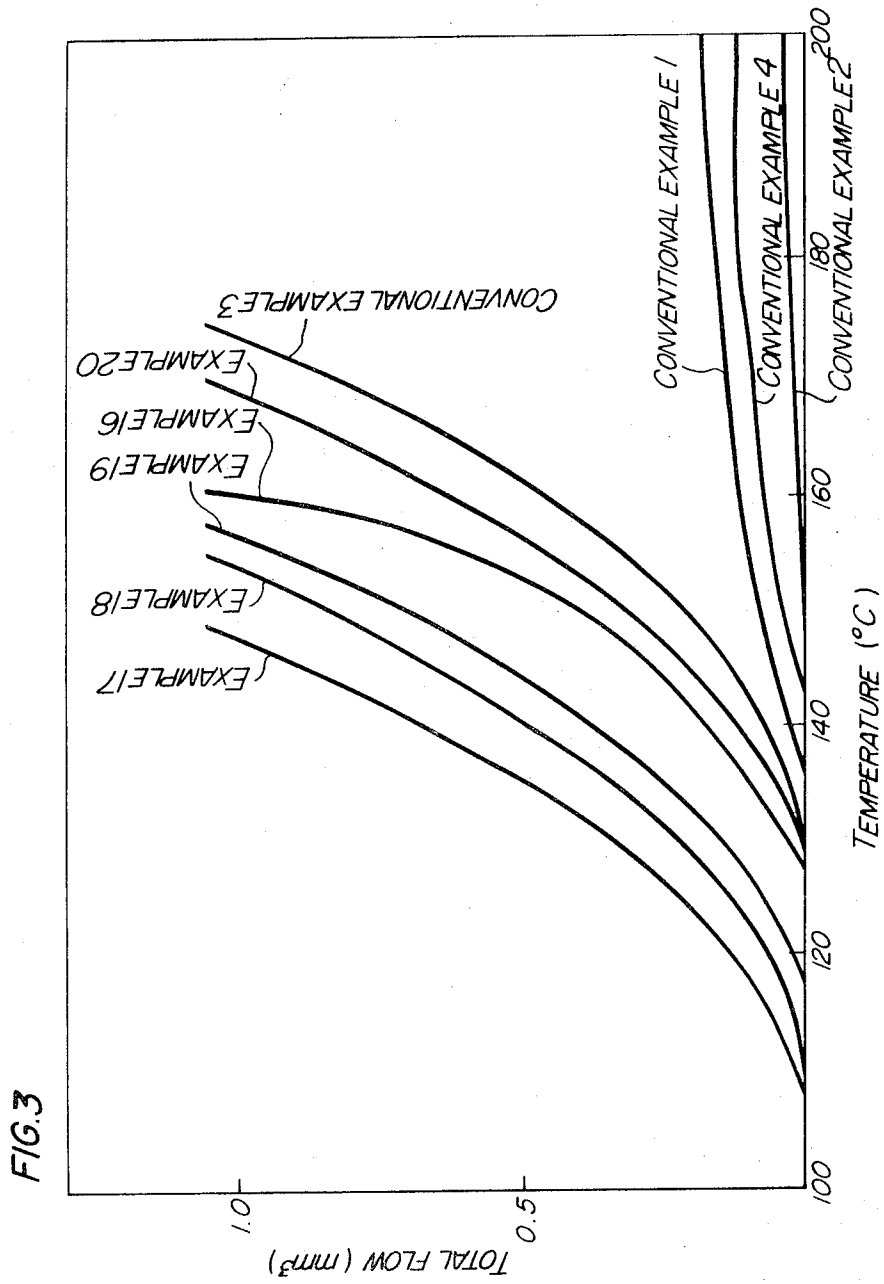


FIG. 3

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HEAT-SENSITIVE HIGH MOLECULAR WEIGHT RESISTORS

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Int. Cl. H01b *1/00*; C08d *9/08*; C08f *3/60*

U.S. Cl. 252—500 2 Claims

ABSTRACT OF THE DISCLOSURE

Heat-sensitive high molecular weight resistors (plastic thermistors) capable of providing electric conductivity due to charge transfer bonds which are comparable in moldability and flexibility to the plastics of general use and are electronic conductive. The resistors are best suitable as heat-sensitive resistors for controlling the temperatures of electric blankets, and are reduced in resistance value to ⅓–¼ per temperature variation of 10° C. Within the temperature range of −30° to +120° C. They can withstand heat resistance test at 120° C. for 300 hours.

This invention relates to heat-sensitive high molecular weight resistors which are not only electronic conductive but also comparable in moldability and flexibility to the plastics of general use.

As temperature-detecting processes for the detection or control of temperatures, there have heretofore been employed processes of detecting temperatures according to variations in resistance values of metal wire resistors or metal oxide thermistors, or according to variations in thermoelectromotive force of thermocouples, or according to variations in geometrical shape of bimetal. These processes are excellent for local temperature detection, but suffer from such fatal drawbacks that for the detection of average temperature in a definite atmosphere, a plurality of elements are required to be used, and that they are low in variation ratio of signals towards temperature variations.

In order to overcome said drawbacks, heat sensitive high molecular weight resistors, which are freely moldable into the form of lines or sheets, have recently been developed and are applied, in practice, to security mechanisms for electric blankets, electric carpets and the like. As heat-sensitive high molecular weight substances usable for said purposes, there are high polymer compositions prepared by adding a small amount of surface active agent to such a matrix as plastisized polyvinyl chloride which detect temperatures according to variation in resistivity of resistance temperature characteristics thereof, and nylon, polyehylene and the like which detect temperatures according to variation in resistivity due to degradation of dielectric breakdown strength thereof at elevated temperatures. A drawback common to these resistors, however, is that since the electroconductive mechanisms thereof are ionic conductive, it is difficult to detect temperatures if direct current is applied thereto.

It is an object of the present invention to provide novel heat-sensitive high molecular weight resistors (plastic thermistors) which are excellent in moldability, flexibility and mechanical properties and which are usable by application of direct current.

The heat-sensitive high molecular weight resistors of the present invention are thermistors which do not cause polarization even when direct current is applied thereto and are stable in electric resistivity even at elevated temperatures. Further, the present resistors are comparable in moldability and flexibility to the plastics of general use. Accordingly, when molded into lines, they are usable for the temperature detection of heat-sensitive heating electric wires of electric blankets, carpets and the like, and for the temperature detection of fire detectors and air-conditioners. Further, when molded into the form of sheets, they are usable for the temperature detection of floor heaters, spherical surfaces of hot rollers and the like. Thus, the resistors of the present invention are expected to find limitless industrial uses for temperature detection. Further, they are high in temperature detection sensitivity and hence are excellent plastic thermistors prominent in moldability and flexibility.

PRIOR ARTS

A comparison in detection sensitivity between the plastic thermistors of the present invention and metal wire resistors, thermocouples and metal oxide thermistors which have heretofore been used as temperature detection elements is as shown in Table 1.

TABLE 1.—SENSITIVITY OF TEMPERATURE DETECTION MATERIALS

Temperature detection material	Signal	Polarity	Variation ratio/° C. (ratio/° C.)
Iron-constantan thermocouple	Thermoelectromotive force.	+	6.6×10^{-2}
Chromal-alumel thermocouple	do	+	6.1×10^{-2}
Nickel wire resistor	Resistance	+	1.6×10^{-2}
Platinum wire resistor	do	+	1.4×10^{-1}
Ceramic thermistor	do	−	$4.0\times10^{-2}\sim8.0\times10^{-2}$
Plastic thermistor	do	−	1.0×10

Thus, the present plastic thermistor has a sensitivity of 10–200 times the sensitivity of the conventional temperature detection elements. Although the present plastic thermistors are usable at such limited temperatures ranging from −30° C. to +120° C., they show high detection sensitivity at temperatures within said range. The conventional temperature detection elements cannot be subjected to any further processing than the primary processing and, moreover, are low in flexibility. Accordingly, they are limited in shape. In contrast thereto, the present plastic thermistors are same in moldability and flexibility as the thermoplastics of general use, e.g. plastisized polyvinyl chloride, and hence can be processed into optional shapes. Further, the conventional thermocouples and thermistors are small in detection portion and are low in heat capacity, and hence display prominent effects for local temperature detection. However, the plastic thermistors of the present invention have a volume resistivity at 30° C. of $5.8\times10^{3}\sim3.1\times10^{12}$

(Ω cm.), and hence are usable with broad electrode surfaces. The present plastic thermistors display great characteristics for temperature detection broader in surface area or space than the conventional local temperature detection, and they have been invented for the above purpose.

For example, when applied as heat-sensitive heaters of electric blankets, the plastic thermistors make possible such temperature detection means that not only the average temperature but also any local unusual temperature increase within the blankets can be detected. As mentioned previously, the plastic thermistors are moldable and hence can be processed into any such shapes as lines, ribbons and sheets. Accordingly, they can be used in most effective shapes for the purposes of appliances, which require temperature detection. When applied to electric blankets, the present plastic thermistors having such epoch-making characteristics will drive out the temperature control systems using bimetals which have heretofore been employed.

Electronic conductive polymers comparable in processability, mechanical properties and flexibility to the thermoplastics of general use have not been invented yet. However, several attempts for the manufacture of moldable and flexible thermistors have been made as explained below.

(1) An attempt in which a good conductor for electricity such as a metal powder or carbon black is dispersed in a high molecular weight substance to impart electric conductivity thereto by inter-particle contact. When the amount of conductor added, according to the above process, is more than a certain amount, there is obtained a thermistor which is substantially identical in resistance value and temperature coefficient of thermistor with the added conductor. If the amount added is made smaller, a thermistor high in resistance value and in temperature coefficient of thermistor is obtained, but the resistance value is unstable and is low in reproductivity. Particularly at elevated temperatures, the inter-particle contact becomes unstable due to molecular movement.

(2) An attempt in which, onto the surface of carbon black, a monomer such as styrene, ethyl acrylate or the like is graft-copolymerized to cover the surfaces of carbon particles with a polymer, thereby providing processability. This process can give a thermistor low in resistance and in temperature coefficient of thermistor, but is not suitable for mass production.

(3) An attempt in which a surface active agent is kneaded with and dispersed in an insulating high molecular weight material. This process can give a thermistor which is ionic conductive and which is high both in resistance value and in temperature coefficient of thermistor. This thermistor is utilized as a heat-sensitive high molecular weight resistor.

Usable as the surface active agent are stearyl dimethyl benzyl ammonium chloride, cetyl dimethyl benzyl ammonium chloride, N-lauryl imidazolium bromide, tetrabutyl ammonium picrate, etc.

Usable as the insulating high molecular weight material are polyamide, polyethylene, butadiene-acrylonitrile copolymer, polyvinyl chloride, etc.

Thermistors of this type have such drawbacks that since they are ionic conductive, they cannot be used unless alternating current is applied, and that they become unstable when continuously used for a long period of time.

(4) An attempt in which a charge transfer complex, which is an organic semiconductor, is polymerized to provide moldability.

A charge transfer polymer comprising poly-2-vinyl pyridine as a donor and tetracyanoparaquinodimethane (TCNQ) as an acceptor has a volume resistivity of 1.0×10^3 Ω cm. and a temperature coefficient of thermistor of 2,000° K., but is low in mechanical strength and flexibility, and hence is not put into practical use at present.

CONSTRUCTION

The plastic thermistors of the present invention are high molecular weight semiconductors comprising high polymers having high polymer portions which provide moldability and flexibility and charge transfer bonds which provide electric conductivity. They have a volume resistivity of at least 10^2 Ω cm. and a temperature coefficient of thermistor of at least 1,000° K. Constructions of the present plastic thermistors and processes for the production thereof are detailed below with reference to examples.

(1) Electronic conductive polymer-type thermistors

Thermistors of this type are plastic thermistors which are composed of high molecular weight charge transfer complexes formed from a processable, moldable and flexible high molecular weight electron donor and a high molecular weight electron acceptor, or which are composed of charge transfer complexes formed from an electron donor and an electron acceptor, either one of said donor and acceptor being a processable, moldable and flexible high molecular weight substance and the other being a low molecular weight substance. When the kinds and proportions of electron donor monomers and electron acceptor monomers in the constituents of charge transfer complexes are varied, it is possible to obtain electronic conductive plastic thermistors having optional volume resistivity and temperature coefficient of thermistor.

As the high molecular weight electron donor, there is used a binary or ternary copolymer of an electron donor monomer, e.g. 2-vinylpyridine (2VP), 4-vinylpyridine (4VP), 1-vinyl-2-methylimidazole (1V2MI), N-vinylcarbazole (NVCA), N-vinylthiocarbazole (NVSCA) or N-vinylpyrrolidone (NVPy), with any of monomers capable of providing processability, moldability and flexibility, e.g. styrene (St.), methyl acrylate (MA), methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA), ethylhexyl acrylate (EHA), acrylonitrile (AN), vinyl acetate (VAc and octylvinyl ether (OVE), or a homopolymer of said electron donor monomer.

The high molecular weight electron acceptor is a homopolymer of a monomer having properties as an electron acceptor, such as for example, trinitrostyrene, dinitrostyrene, phthalic anhydride, or maleic anhydride, or is a binary or ternary copolymer comprising, as the first component, the above-mentioned monomer and, as the second and/or third components, such monomers capable of providing processability, moldability and flexibility as exemplified in the case of the electron donor. As the low molecular weight electron donor, there is used p-phenylenediamine, diphenylamine, perylene or 1-naphthylamine, and as the low molecular weight electron acceptor, there is used chloranil, bromanil, tetracyanoethylene, tetracyano-p-quinodimethane, hexacyanobutadiene, hexachlorobutadiene or tetracyanobutadiene.

Examples 1 and 2, described later, show complexes comprising high molecular weight electron donors and high molecular weight electron acceptors; Examples 3 to 10 show complexes comprising high molecular weight electron donors and low molecular weight electron acceptors; and Example 11 shows a complex comprising a low molecular weight electron donor and a high molecular weight electron acceptor.

(2) Blend-type electroconductive high molecular weight compositions

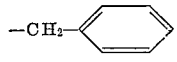
Compositions of this type are such that, noticing the electric conductivity of charge transfer complexes, processability, moldability, mechanical strength and flexibility are intended to be provided chiefly by matrix polymers. In the case of the compositions of this type, it is necessary that the complexes should have been molecularly dis-

persed in the matrixes in order to attain favorable electrical properties (volume resistivity and temperature coefficient of thermistor) and, particularly, stability in electric resistivity at elevated temperatures. As the source for providing electric conductivity, therefore, there is used a high molecular weight or low molecular weight charge transfer complex which is favorable in compatibility with an insulating high polymer to be used as the matrix.

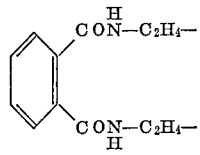
The charge transfer complex may be any of those in which either one or both of the donor and acceptor are high molecular weight polymers. Usable as such charge transfer complex are:

(i) (Ethyl acrylate-styrene-2-vinylpyridine)-TCNE complex.
(ii) (2-ethylhexyl acrylate-styrene-2-vinylpyridine)-TCNQ complex.
(iii) (Styrene-N-vinylcarbazole)-(styrene-trinitrostyrene) complex.
(iv) p-Phenylenediamine-(styrene-trinitrostyrene) complex.

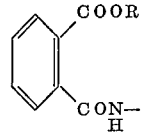
As the low molecular weight charge transfer complex, there is used one having in the molecule at least one group capable of increasing compatibility with a matrix polymer, such as for example, an alkyl group $-C_nH_{2n+1}$ (n=1, 2, 3, . . . 40), a benzyl group



a phthalodiamide ethyl group



a monoester phthaloyl group



R=CH_3, C_2H_5 . . . $C_{40}H_{81}$), a fatty acid amide group R'—CONH— (R'=CH_3, C_2H_5 . . . $C_{40}H_{81}$), an alkylenedicarbonyl group —CO—R—CO, an alkylenedioxy group —O—R—O or a hydroxy alkylenecarbonyl group HO—R—CO—. For the preparation of the blends, said charge transfer complexes are molecularly dispersed in high molecular weight matrixes.

Usable as such high molecular weight matrixes are polyvinyl chloride, polystyrene, ethylene-ethyl acrylate copolymers, ethylene-vinyl acetate copolymers, styrene-butadiene copolymers, acrylonitrile-methyl methacrylate copolymers, styrene-2-ethylhexyl acrylatebutyl acrylate copolymers, and urethane. When these high molecular weight matrixes are blended with the charge transfer complexes, plastic thermistors excellent in moldability and flexibility can be produced. For uses where more precise molding is required, they may be blended with styrene-butadiene-acrylonitrile copolymers (ABS resins) or with epoxy resins. Detailed production procedures are described in the examples. Examples 12–15 show compositions containing high molecular weight charge transfer complexes, and Examples 15–21 show compositions containing low molecular weight charge transfer complexes.

EXAMPLE 1

Charge transfer complex comprising 2-vinylpyridine-styrene copolymer as donor and maleic anhydride-styrene copolymer as acceptor

(a) Synthesis of 2-vinylpyridine-styrene copolymer: To 100 g. of toluene are added 20 g. of vacuum distilled 2-vinylpyridine, 80 g. of styrene and 0.5 g. of azobisisobutyronitrile as a polymerization initiator. The mixture is refluxed for 4 hours to effect polymerization. The reaction liquid is added dropwise to 5 l. of methanol, and the resulting precipitate is recovered by filtration and is repeatedly subjected to thorough water-washing. Subsequently, the precipitate is dried under reduced pressure to obtain a 2-vinylpyridine-styrene copolymer containing 23% of 2-vinylpyridine.

(b) Synthesis of maleic anhydride-styrene copolymer: To 100 g. of toluene are added 80 g. of vacuum distilled styrene, 20 g. of maleic anhydride and 0.3 g. of benzoyl peroxide as a polymerization initiator. The mixture is refluxed for 3 hours with stirring to effect polymerization. The reaction liquid is added dropwise to 5 l. of methanol, and the resulting precipitate is recovered by filtration and is repeatedly subjected to thorough water-washing. Subsequently, the precipitate is dried under reduced pressure to obtain a maleic anhydride-styrene copolymer containing 21% of maleic anhydride.

(c) Synthesis of charge transfer complex: The two copolymers (a) and (b) are individually formed into 10% toluene solutions and are mixed together in equivalent amounts, whereby the mixture immediately becomes brown. The mixture is then refluxed for about 1 hour to form a brown precipitate. The thus formed precipitate is water-washed and vacuum-dried to obtain a high molecular weight charge transfer complex comprising the 2-vinylpyridine-styrene copolymer and the maleic anhydride-styrene copolymer. This complex is shaped into the form of a 1 mm. thick sheet and is cut to a size of 50 x 50 x 1 mm. to prepare a test piece for electric resistance measurement.

EXAMPLE 2

Charge transfer complex comprising N-vinylcarbazole-styrene copolymer as donor and polytetracyanobutadiene as acceptor

(a) Synthesis of N-vinylcarbazole-styrene copolymer: To 100 g. of xylene are added 80 g. of vacuum-distilled styrene, 20 g. of N-vinylcarbazole and 0.2 g. of azobisisobutyronitrile as a polymerization initiator. The mixture is refluxed for 3 hours with stirring to effect polymerization. The reaction liquid is added dropwise to 5 l. of methanol, and the resulting precipitate is recovered by filtration and is repeatedly subjected to thorough water-washing. Subsequently, the precipitate is dried under reduced pressure to obtain an N-vinylcarbazole-styrene copolymer containing 20% of N-vinylcarbazole.

(b) Preparation of polytetracyanobutadiene: 50 g. of 1,2,3,4-tetracyanobutadiene is dissolved in 100 g. of acetonitrile. To the solution, 0.1 g. of benzoyl peroxide as a polymerization initiator is added, and the mixture is refluxed for 2 hours with stirring to effect polymerization. The reaction liquid is added dropwise to a 5% NaCl solution, and the resulting precipitate is recovered by filtration, is repeatedly subjected to thorough water-washing, and is then dried under reduced pressure to obtain polytetracyanobutadiene.

(c) Synthesis of charge transfer complex: The two polymers (a) and (b) are individually formed into 10% acetonitrile solutions and are mixed together in equivalent amounts, whereby the mixture immediately becomes brown. The mixture is then refluxed for 2 hours to form a brown precipitate. The thus formed precipitate is water-washed and vacuum dried to obtain a high molecular weight charge transfer complex comprising the N-vinylcarbazolestyrene copolymer and the polytetracyanobutadiene. This complex is shaped to a sheet with a size of 50 x 50 x 1 mm. to prepare a test piece for electric resistance measurement.

TABLE 2

Number	Donor	Acceptor	Donor/acceptor	φ 30° C. (Ω cm.)	β 30°-60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
1-1	2VP:St 20:80	MAn:St 20:80	1:1	8.0×10^{9}	9,000	1.3
2-1	NVCA:St 20:80	PTCNB 100	1:1	8.5×10^{9}	8,300	1.2

EXAMPLE 3

Charge transfer complexes comprising styrene-2-vinylpyridine copolymers and tetracyanoquinodimethane (TCNQ)

(a) Synthesis of styrene-2-vinylpyridine copolymers: The copolymers are synthesized in the same manner as in Example 1(a), except that the amounts of 2-vinylpyridine are varied to 1, 5, 10, 25 and 50%.

(b) Synthesis of charge transfer complexes: Each of the 5 copolymers synthesized in (a) is formed into a toluene solution, is quaternarized with 1.5 times the mole of said copolymer of hydriodic acid, is washed with water to remove liberated iodine (I_2) and is dried under reduced pressure. The thus treated copolymer is formed into a 10% acetone solution. On the other hand, LiTCNQ is formed into a 10% acetone solution. To the copolymer solution, the LiTCNQ solution is added so that the amount of LiTCNQ becomes 1.5 times the mole of vinylpyridine. The mixture is thoroughly stirred and is reacted at 60° C. for 1 hour to form a complex of each copolymer and TCNQ. The complex is thoroughly washed with water until no green color due to flame reaction of chlorine has been observed. The complexes prepared in the above manner are subjected to electrodialysis and are then vacuum dried to obtain high molecular weight charge transfer complexes.

TABLE 3

Number	Donor polymer 2VP:St	Acceptor	VP/TCNQ (molar ratio)	φ 30° C. (Ω cm.)	β 30°-60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
3-1	1:99	LiTCNQ	1:1	1.0×10^{11}	9,500	1.1
3-2	5:95	LiTCNQ	1:1	2.7×10^{10}	8,300	1.2
3-3	10:90	LiTCNQ	1:1	1.0×10^{9}	5,100	1.2
3-4	25:75	LiTCNQ	1:1	1.7×10^{8}	2,900	1.3
3-5	50:50	LiTCNQ	1:1	7.3×10^{3}	1,500	1.3

EXAMPLE 4

Charge transfer complexes comprising styrene-4-vinylpyridine copolymers and tetracyanoethylene (TCNE)

The charge transfer complexes are synthesized in the same manner as in Example 3. The composition ratio of each copolymer is represented by weight percent.

TABLE 4

No.	Donor polymer 4VP:St	Acceptor	VP/TCNE (molar ratio)	φ 30° C. (Ω cm.)	β 30°-60° C. (° K.)	$\Delta\varphi$ 100° C: 1,000 hr.
4-1	1:99	TCNE	1:1	5.4×10^{11}	11,000	1.0
4-2	5:95	TCNE	1:1	1.3×10^{10}	9,800	1.1
4-3	10:90	TCNE	1:1	5.0×10^{8}	5,000	1.0
4-4	25:75	TCNE	1:1	8.9×10^{5}	2,800	1.1
4-5	50:50	TCNE	1:1	5.8×10^{3}	1,600	1.1

EXAMPLE 5

Charge transfer complexes of methyl acrylate-styrene-2-vinylpyridine copolymers and chloranil

The copolymerization of methyl acrylate, styrene and 2-vinylpyridine is effected in toluene solution in the presence of 0.2% of azobisisobutyronitrile as a polymerization initiator. The composition ratio of each ternary copolymer is represented by weight percent. The synthesis of the charge transfer complexes is carried out in the same manner as in Example 3.

TABLE 5

No.	Donor polymer 4VP:St:MA	Acceptor	4VP/chloranil (molar ratio)	φ 30° C. (Ω cm.)	β 30°-60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
5-1	1:49:50	Chloranil	1:1	3.1×10^{12}	14,800	1.0
5-2	5:45:50	...do...	1:1	8.7×10^{10}	10,000	1.0
5-3	10:40:50	...do...	1:1	4.5×10^{9}	8,300	1.1
5-4	25:25:50	...do...	1:1	4.8×10^{7}	7,200	1.0

NOTE.—MA: methyl acrylate.

EXAMPLE 6

Charge transfer complexes of ethyl acrylate-1-vinyl-2-ethylimidazole copolymers and bromanil

The copolymerization of ethyl acrylate-1-vinyl-2-ethylimidazole is effected in toluene solution in the presence of 0.2% of benzoyl peroxide as a polymerization initiator.

The composition ratio of each ternary copolymer is represented by weight percent. The synthesis of the charge transfer complexes is effected in the same manner as in Example 3.

TABLE 6

Number	Donor polymer EA:V2EI	Acceptor	V2EI/bromanil (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
6-1	90:10	Bromanil	1:1	5.0×10^{9}	8,500	1.2
6-2	80:20	do	1:1	3.2×10^{7}	7,400	1.1

EXAMPLE 7

Charge transfer complexes of butyl acrylate-N-vinylcarbazole copolymers and hexacyanobutadiene

The copolymerization of N-vinylcarbazole and butyl acrylate is effected in 50% benzene solution in the presence of 0.2% of azobisisobutyronitrile as a polymerization initiator. The synthesis of the complexes is carried out in the following manner:

N-vinylcarbazole-butyl acrylate, which has been quaternarized with hydriodic acid, is formed into a 10% acetonitrile solution. On the other hand, sodium hexacyanobutadiene is formed into a 10% acetonitrile solution. The two solutions are mixed together so that the molar ratio of hexacyanobutadiene to N-vinyl carbazole becomes 1:1.5. The mixture is refluxed for 2 hours with stirring. Subsequent operations are the same as in Example 3.

TABLE 7

No.	Donor polymer NVCA:BA	Acceptor	NVCA/HCNB (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
7-1	10:90	HCNB	1:1	4.8×10^{8}	8,100	1.3
7-2	20:80	HCNB	1:1	2.1×10^{7}	7,200	1.2

NOTE.—HCNB: hexacyanobutadiene.

EXAMPLE 8

Charge transfer complexes comprising 2-ethylhexyl acrylate-N-vinylpyrrolidone copolymers and hexachlorobutadiene

The copolymerization of 2-ethylhexyl acrylate and N-vinylpyrrolidone is effected in 50% toluene in the presence of 0.2% of benzoyl peroxide as a polymerization initiator. The synthesis of the charge transfer complexes is carried out in the following manner:

A 10% benzene solution of 2-ethylhexyl acrylate-N-vinylpyrrolidone copolymer is mixed with hexachlorobutadiene in an amount equimolar to the amount of N-vinylpyrrolidone. The mixture is refluxed for 3 hours to obtain a brownish black precipitate. Subsequent operations are the same as in Example 3.

TABLE 8

No.	Donor polymer NVPy:2EHA	Acceptor	NVPy/HClB (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. ° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
8-1	10:90	HClB	1:1	8.5×10^{9}	9,500	1.4
8-2	20:80	HClB	1:1	1.0×10^{8}	8,300	1.2

NOTE.—HClB: hexachlorobutadiene.

EXAMPLE 9

Charge transfer complexes comprising acrylonitrilevinyl acetate-N-vinylthiocarbazole copolymers and tetracyanobutadiene

The copolymerization of N-vinylthiocarbazole, vinyl acetate and acrylonitrile is effected in 50% toluene solution in the presence of 0.3% of azobisisobutyronitrile as a polymerization initiator. The synthesis of the charge transfer complexes is carried out in the same manner as in Example 8.

TABLE 9

No.	Donor polymer NVSCA:AN:VAc	Acceptor	NVSCA/TCNB (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
9-1	10:45:45	TCNB	1:1	3.0×10^{9}	8,500	1.2
9-2	20:40:40	TCNB	1:1	1.5×10^{8}	7,500	1.3

NOTE.—TCNB: tetracyanobutadiene.

EXAMPLE 10

Charge transfer complexes comprising 2-vinylpyridine-octylvinyl ether copolymers and tetracyanoethylene

(a) Synthesis of 2 - vinylpyridine - octylvinyl ether copolymers: To 100 g. of each of 10:90 and 20:80 mixed liquids of 2-vinylpyridine and octylvinyl ether, 100 g. of a 1% sodium lauryl sulfate emulsion is added. The resulting mixture is reacted at 50° C. for 4–5 hours in the presence of a catalyst comprising 0.3% (based on the weight of monomers) of potassium perphosphate and 0.1% of sodium acidic sulfite. The reaction product is charged into methanol to form a precipitate, which is then recovered by filtration, washed with water and dried.

(b) Preparation of charge transfer complexes: Each of the 2-vinylpyridine-octylvinyl ether copolymer is formed into a 10% benzene solution. To this solution is added a 5% benzene solution of tetracyanoethylene in an amount equal to the amount of vinylpyridine. The mixture is refluxed for 3 hours to obtain a brown precipitate. Subsequent operations are the same as in Example 3.

TABLE 10

No.	Donor polymer 2VP:OVE	Acceptor	2VP/TCNE (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	Δφ 100° C. 1,000 hr.
10–1	10:90	TCNE	1:1	7.0×10^{8}	7,800	1.2
10–2	20:80	TCNE	1:1	8.5×10^{7}	6,500	1.4

NOTE.—TCNE: tetracyanoethylene.

EXAMPLE 11

Charge transfer complex comprising p-phenylenediamine as donor and trinitrostyrene - styrene copolymer as acceptor

(a) Synthesis of trinitrostyrene-styrene copolymer: 100 g. of a 50:50 mixture of trinitrostyrene and styrene monomer is dissolved in 100 g. of toluene, and the solution is polymerized in the presence of 0.3% (based on the weight of monomer) of azobisisobutyronitrile as a polymerization initiator.

(b) Preparation of charge transfer complex: A 20% benzene solution of p-phenylenediamine is mixed with a 10% benzene solution of trinitrostyrene-styrene copolymer, so that the amount of p-phenylenediamine becomes equimolar to that of the copolymer, whereby a black-brown complex is obtained. Subsequent operations are the same as in Example 3.

TABLE 11

Number	Donor	Acceptor polymer TNS:St	p-PDA/TNS (molar ratio)	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	Δφ 100° C. 1,000 hr.
11–1	p-PDA	1:1	1:1	2×10^{6}	7,500	1.3

NOTE.—p-PDA: p-phenylenediamine.

EXAMPLE 12

Heat-sensitive high molecular weight resistors (plastic thermistors) comprising (2 - vinylpyridine-ethyl acrylate-styrene copolymer)-(TCNE: tetracyano-ethylene) charge transfer complexes and (ethylene-ethyl acrylaet copolymers)

The 2-vinylpyridine-ethyl acrylate-styrene copolymer of each plastic thermistor is obtained by polymerization in 50% toluene solution in the presence of 0.2% of azobisisobutyronitrile as a polymerization initiator. The copolymer is formed into a 10% acetone solution, and is mixed with a 10% benzene solution of tetracyanoethylene in an amount of 1.5 times the mole of 2-vinylpyridine, whereby the mixture is immediately colored to greenish black. When the mixture is heated at 60° C. for 1 hour, a complex is formed. 20 g. of this complex and an ethylene ethyl acrylate copolymer containing 20% of ethyl acrylate are individually dissolved in 500 cc. of carbon tetrachloride. The resulting two solutions are thoroughly mixed and blended together. The thus obtained blend is dried by means of a rotary evaporator, is shaped into the from of a sheet by means of a hot roll and is cut to a size of 50 x 50 x 1 mm. to prepare test pieces for electric resistance measurement.

EXAMPLE 13

Plastic thermistors comprising (2 - vinylpyridine - 2-ethylhexyl acrylate - styrene copolymer) - (TCNQ) charge transfer complexes and (ethylene-vinyl acetate copolymers)

The 2 - vinylpyridine - 2 - ethylhexyl acrylate-styrene copolymer is obtained by polymerization in 50% toluene solution in the presence of 0.2% of benzoyl peroxide as an initiator. The copolymer is quaternarized with hydriodic acid and is then formed into a 10% acetone solution. This solution is mixed with a 10% acetone solution. of LiTCNQ in an amount of 1.5 times the mole of 2-venylpyridine, and the mixture is heated to obtain a greenish black complex. 20 g. of the complex is kneaded on a hot roll at 130° C. with 20 g. of an ethylene-vinyl acetate copolymer containing 20% of vinyl acetate. The mixture is shaped into the form of a sheet to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 14

Plastic thermistors comprising (N-vinylcarbazole-styrene copolymer)-(trinitrostyrene-styrene copolymer) charge transfer complexes and styrene-butadiene copolymers

The synthesis of each copolymer is effected in the same manner as in Example 2(a) and Example 11(a). 20 g. of an N-vinylcarbazole-styrene copolymer and 23 g. of a trinitrostyrene-styrene copolymer are individually formed into 10% benzene solution. The two solutions are mixed and heated to obtain 31 g. of a greenish brown powder of charge transfer complex. 31 g. of this complex and 15 g. of a styrene-butadiene copolymer are individually formed into 15% toluene solutions, and the two solutions are mixed and heated. Subsequently, the mixture is dried by means of a rotary evaporator and is shaped into the form of a sheet by means of a hot roll to prepare a test piece for the measurement of electrical characteristics.

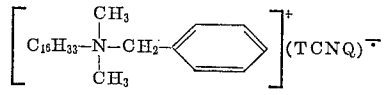
EXAMPLE 15

Plastic thermistors comprising (p-phenylenediamine)-(trinitrostyrene-styrene copolymer) charge transfer complexes and polyvinyl chloride

9 g. of p-phenylenediamine and 20 g. of a trinitrostyrene-styrene copolymer are used to form 22 g. of a brownish purple powder of charge transfer complex. 20 g. of this complex is kneaded by means of a hot roll at 160° C. with 15 g. of polyvinyl chloride, 7 g. of dioctyl phthalate as a plasticizer and 2 g. of tribasic lead sulfate as a stabilizer. The mixture is shaped into the form of a sheet to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 16

Plastic thermistor comprising dimethylcetyl benzyl ammonium tetracyano-p-quinodimethane of the structural formula



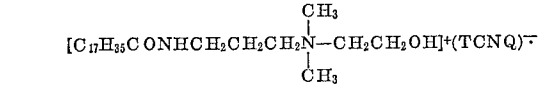
and polyvinyl chloride

degree $\overline{P}=1200$) is thoroughly kneaded with 10 g. of tri-
degree P=1200) is thoroughly kneaded with 10 g. of tribasic lead sulfate and 20 g. of the charge transfer complex dimethylcetyl benzyl ammonium tetracyano-p-quinodimethane. Thereafter, the mixture is charged with 50 g. of pentaerythritol-ester, as a plasticizer and is subjected to dry blending at 60° C. for 30 minutes. Subsequently, the mixture is kneaded for about 10 minutes by means of a roller heated to 170°–180° C., is taken out in the form of a sheet with a thickness of about 1 mm., and is cut to a

size of 50 x 50 x 1 mm. to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 17

Plastic thermistor comprising stearamide-propyl-dimethyl-β-hydroxyethyl-ammonium-tetracyano-p-quinodimethane of the structural formula



and ethylene-ethyl acrylate copolymer

100 g. of an 80:20 ethylene-ethyl acrylate copolymer (trade name: Dow 6129) is kneaded by means of a hot roll at 120° C. while adding little by little to the copolymer 20 g. of the charge transfer complex stearamide-propyl-dimethyl-β-hydroxyethyl-ammonium tetracyano-p-quinodimethane. After the total amount of said complex has been added, the mixture is further kneaded for 15 minutes, is taken out in the form of a sheet with a thickness of 1 mm., and is cut to a size of 50 x 50 x 1 mm. to prepare a test piece for the measurement of electrical characteristics.

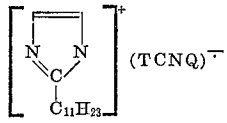
EXAMPLE 18

Plastic thermistor comprising β-hydroxyethyl-2-methyl-imidazolium tetracyanoquinodimethane and ethylene-vinyl acetate copolymer

100 g. of 82:18 ethylene-vinyl acetate copolymer (trade name: Everflex 630) is charged with 0.5 g. of an anti-oxidant ("Ionol" produced by Shell Chemical Co.) and is thoroughly kneaded by means of a hot roll at 130° C., while adding little by little to the copolymer 25 g. of the charge transfer complex β-hydroxyethyl-2-methyl-imidazolium-tetracyano-p-quinodimethane. After completion of the addition of said complex, the mixture is further kneaded for 15 minutes, is taken out in the form of a sheet with a thickness of 1 mm., and is cut to a size of 50 x 50 x 1 mm. to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 19

Plastic thermistor comprising 2-undecylimidazolium tetracyanoquinodimethane of the structural formula



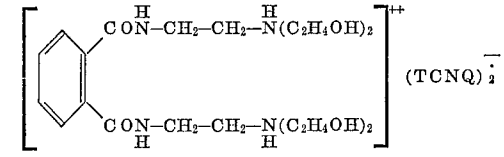
and 40:20:40 styrene-2-ethylhexyl acrylate-butyl acrylate

A 40:20:40 styrene-2-ethylhexyl acrylate-butyl acrylate copolymer is thoroughly kneaded by means of a hot roller at 140° C., while adding little by little to the copolymer 20 g. of the charge transfer complex 2-undecylimidazolium tetracyano-p-quinodimethane. After the total amount of said complex has been added, the mixture is kneaded for 15 minutes, is taken out in the form of a sheet with a thickness of 1 mm., and is cut to a size of 50 x 50 x 1 mm. to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 20

Plastic thermistor comprising di(di-β-hydroxyethylamino-ethyl)-o-phthaldiamide tetracyano-p-quinodimethane and styrene-butadiene-acrylonitrile copolymer (ABS resin)

100 g. of a styrene-butadiene-acrylonitrile copolymer (ABS resin) powder is dry-blended at 60° C. for 30 minutes by means of a ribbon blender with 20 g. of the charge transfer complex of di(di-β-hydroxyethylamino-ethyl)-o-phthaldiamide tetracyano-p-quinodimethane, of the structural formula



which is an electroconductive plasticizer. Subsequently, the blend is injection-molded, by use of a small size injection molding machine, into a metal mold of 50 x 50 x 1 mm., while maintaining the cylinder temperature at 180° C., to prepare a test piece for the measurement of electrical characteristics.

EXAMPLE 21

Plastic thermistor comprising stearamide-propyl dimethyl-β-hydroxyethyl ammonium tetracyano-p-quinodimethane and epoxy resin

To 100 g. of an epoxy resin (Epikote 828) is added with thorough stirring 15 g. of the charge transfer complex stearamide-propyl-dimethyl-hydroxyethyl-ammonium tetracyano-p-quinodimethane, which is an electroconductive curing agent. The mixture is charged into an optional mold for sheet molding and is cured in about 2 hours in a thermostat at 100° C. The resulting sheet is cut to a size of 50 x 50 x 1 mm. to prepare a test piece for the measurement of electrical characteristics.

The characteristics of the plastic thermistors of Examples 12 to 21 are summarized in Table 12.

TABLE 12

Example Number	Charge transfer complex	Matrix polymer	ϕ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
12	(2-vinylpyridine-ethyl acrylatestyrene)·(tetracyano-ethylene).	Ethylene-ethyl acrylate copolymer	8.0×10^{8}	7,500	1.2
13	(2-vinylpyridine-2-ethylhexyl acrylate-styrene)·(tetracyano-p-quinodimethane).	Ethylene-vinyl acetate colpoymer	3.0×10^{8}	7,000	1.1
14	(N-vinylcarbazole-styrene)·(trinitrostyrene-styrene)	Styrene-butadiene copolymer	1.5×10^{9}	9,000	1.3
15	(p-Phenylenediamine)·(trinitrostyrene-styrene)	Polyvinyl chloride	7.5×10^{8}	8,000	1.2
16	Dimethylcetyl benzyl-ammonium tetracyano-p-quinodimethane.	do	3.0×10^{8}	7,500	1.5
17	Stearamide dimethyl hydroxyethyl-ammonium tetracyano-p-quinodimethane.	Ethylene-ethyl acrylate copolymer	5.0×10^{8}	7,000	1.1
18	β-Hydroxyethyl-2-methylimidazolium tetracyano-quinodimethane.	Ethyl-vinyl acetate copolymer	1.1×10^{8}	8,500	1.4
19	2-undecylimidazolium tetracyanoquinodimethane	Styrene-2-ethylhexyl acrylate-butyl acrylate copolymer.	4.0×10^{8}	8,200	1.6
20	Di(di-β-hydroxyethylamino-ethyl)-phthaldi-amide tetracyano-p-quinodimethane.	Styrene-butadiene-acrylonitrile copolymer.	1.5×10^{9}	9,000	1.2
21	Stearamide-propyl-dimethyl-β-hydroxyethyl ammonium tetracyano-p-quinodimethane.	Epoxy resin	2.0×10^{8}	8,000	12.0

Conventional example	Charge transfer complex	Matrix polymer	φ 30° C. (Ω cm.)	β 30°–60° C. (° K.)	$\Delta\varphi$ 100° C. 1,000 hr.
1	Vinylpyridine tetracyanoethylene	None	1.0×10^{3}	1,000	12.0
2	Carbon black	Nitrile-butadiene rubber	2.5×10^{3}	2,000	3.0
3	N-methylquinolinium bromide	Polyvinyl chloride	1.5×10^{9}	10,000	15.0
4	Carbon black	Methyl acrylate graft polymer	3.0×10^{4}	3,000	3.5

EFFECTS

(1) Characteristics of plastic thermistors and methods for the measurement thereof

The electrical charactersitics of the plastic thermistors according to the present invention are set forth in Tables 2–12 in comparison with those of conventional thermistors.

In the table, $\varphi 30°$ C. (Ω cm.) shows a value of volume resistivity at 30° C.; and $\beta 30°$–60° C. (° K.) is an indication of temperature detection sensitivity of plastic thermistor and is represented by the formula

$$\beta=\frac{\ln\frac{\varphi}{\varphi_0}}{\frac{1}{T}-\frac{1}{T_0}} \quad (1)$$

In calculating, according to the above formula, the temperature dependence of volume resistivity at temperatures between 30° C. and 60° C., φ_0 is a volume resistivity value at 30° C.; φ is a volume resistivity value at 60° C.; T_0 is 303° K.; and T is 333° K.

$\Delta\varphi$ 100° C. 1000 hr. shows a variation ratio of volume resistivity values in the case where direct current has been continuously applied in an air atmosphere at 100° C. for 1,000 hours, and is represented by the formula

$$\Delta\varphi \text{ 100° C. 1000 hr.}=\frac{\varphi_1}{\varphi_0}$$

wherein φ_0 is a volume resistivity value at 100° C. before aging; and φ_1 is a volume resistivity value after aging at 100° C. for 1000 hours. Accordingly, $\Delta\varphi=1$ shows the case where no variation in volume resistivity value has been observed at all. In practice, $\Delta\varphi$ is desirably 2 or less.

Comparison in processability and moldability was made by measuring flow properties by use of "Koka Flow Tester" manufactured by Shimadzu Co., Kyoto, Japan. The results are shown in FIGS. 1 to 3.

(2) Features of plastic thermistors

(1) Electronic conduction: The plastic thermistors of the present invention display their effects according to conduction mechanisms ascribable to anion radicals or charge transfer electrons formed from the chanrge transfer complexes employed, and therefore current carriers are electrons or halls. Accordingly, the plastic thermistors of the present invention do not cause any polarization even when direct current is applied thereto. In the complexes of the present invention, there is observed no such absorption current as seen in the case where direct current is applied to ionic conduction materials. Furthermore, even when the polarity of electrodes is reversed, no maximum current is observed. Thus, the present complexes are same in conduction behavior as inorganic semiconductors. For the above reason, the plastic thermistors of the present invention are usable in electronic circuits. When the present plastic thermistor is inserted between two wires of an electric blanket, one wire can act as heater. The temperature is detected by the variation of resistivity between two wires by applying direct current and one wire is heated by applying alternative current. By virtue of the present plastic thermistors which do not polarize even when direct current is applied thereto, it has first become possible to produce heat-sensitive heaters.

(2) Volume resistivity and temperature characteristics: In accordance with the present invention, it is possible to produce thermistors having such characteristics as volume resistivity values at room temperature of 5.8×10^3 to 3.1×10^{12} (Ω cm.) and thermistor temperature coefficients at 30°–60° C. of 1,500 to 14,800 (° K.). Particularly, when the content of electron donor group in the same copolymer composition is varied, it is possible to freely produce thermistors having volume resistivity values of 10^3–10^{11} Ω cm. and thermistor temperature coefficients of 1,500–9,000 (° K.), as shown in Example 3. In the case of organic semiconductors, in general, the thermistor temperature coefficients become greater with increasing volume resistivity. According to the present invention, thermistors having desired volume resistivity values and temperature coefficients can be freely obtained. In case a thermistor is desired to be applied to, for example, an electric blanket, the detecting wire becomes necessarily longer (10 m. or more), and therefore it is desirable, from the standpoint of prevention of self-heat generation also, to use a thermistor having a volume resistivity at room temperature of about 10^9 Ω cm. and a temperature coefficient of about 8,000° K. The plastic thermistors of the present invention which have the abovementioned characteristics are high in temperature coefficient, and the detection sensitivity thereof reaches as high as 5–6 times the sensitivity of metal oxide thermistors.

(3) Heat resistance stability in volume resistivity: The heat resistance of the present plastic thermistors was evaluated by continuously applying direct current at 100° C. for 1000 hours to obtain volume resistivity values of 1.0–1.6. However, when direct current is applied to conventional thermistors, volume resistivity values vary from 3.0–3.5, in the case of those which are superior in quality, to 12.0–15.0, in the case of those which are obviously ionic conductive. The stableness in volume resistivity values of the present plastic thermistors is ascribable to the points (1) the conduction mechanisms are electronic and (2) the plastic thermistors themselves are conductive polymers (Examples 1–11) or have been molecularly dispersed in matrix polymers. It is considered that, in the case of particle dispersion, like in conventional Examples 2 and 4, the molecular movement of matrix polymers necessarily becomes vigorous at elevated temperatures and therefore uniform inter-particle contact cannot be attained to bring about unstableness in electric resistance. It is a third characteristic of the present invention that the above drawback has been overcome by use of groups capable of being molecularly dispersible with ease or by adoption of polymerization.

(4) Moldability and flexibility: All the plastic thermistors shown in Examples 1 to 21 have moldability and flexibility. Since the flow properties of polyvinyl chloride compounds of general use are as shown in conventional Example 3 (FIG. 3), the plastic thermistors of the present invention have properties equal to or more easily processable than plasticized polyvinyl chloride compounds. Accordingly, they can be shaped into any forms of lines, sheets and ribbons according to the objects of temperature detection appliances employed.

As detailed above, the plastic thermistors of the present invention are heat-sensitive materials which are higher in detection sensitivity than the conventional thermistors, can be produced at low costs, are moldable into any forms, and have flexibility. Particularly, the point that direct current is applicable is the greatest industrial effect of the present plastic thermistors over the conventional heat-sensitive high molecular weight resistors.

We claim:

1. A heat-sensitive high molecular weight resistor comprising a high molecular charge transfer complex alone or dispersed in a high molecular matrix,

said high molecular charge transfer complex formed from

an electron acceptor selected from the group consisting of homopolymers and copolymers of maleic anhydride, tetracyanobutadiene and trinitrostyrene and

an electron donor selected from the group consisting of p-phenylenediamine and copolymers containing a member selected from 2-vinyl pyridine and N-vinylcarbazole.

2. A heat-sensitive high molecular weight resistor, according to claim 1, wherein said high molecular matrix is selected from the group consisting of a styrene/butadiene copolymer and polyvinyl chloride.

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DOUGLAS J. DRUMMOND, Primary Examiner

U.S. Cl. X.R.

260—78.4 R, 80 P, 88.7 A, 874, 887, 892, 894, 895, 899

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,632,526 Dated January 4, 1972

Inventor(s) Kazumasa YAMAMOTO et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

One of the four Japanese applications in the Claim for Convention Priority is omitted and should be inserted as follows:

--Japan, Appln. N° 43/44406 filed June 24, 1968--.

Signed and sealed this 27th day of June 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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