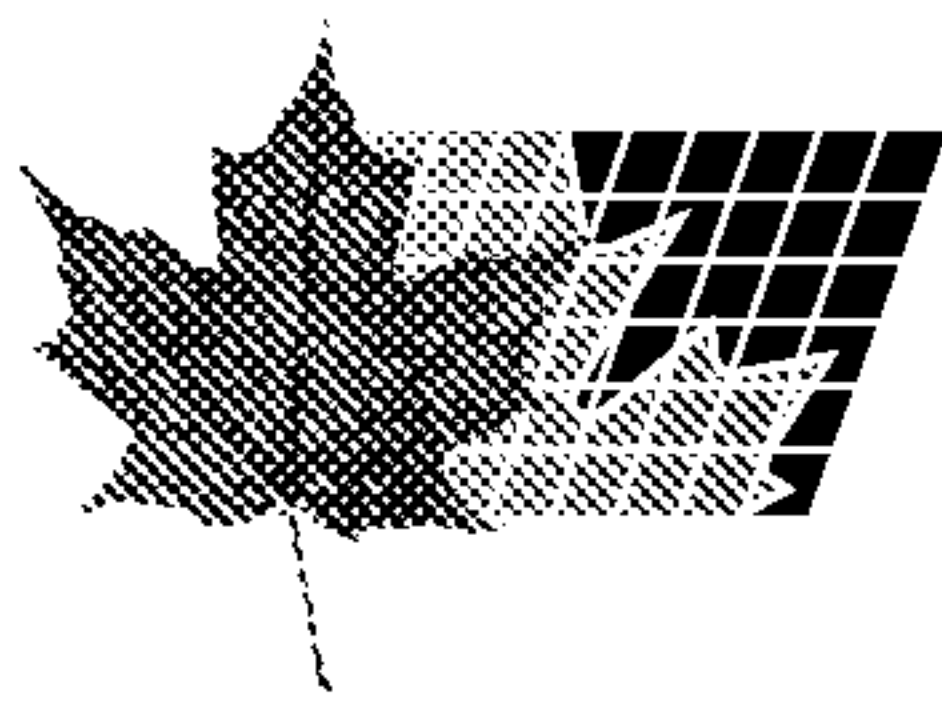




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(51) Int.Cl.⁶ H01B 1/12
(30) 1997/11/07 (9723464.5) GB
(30) 1998/01/21 (9801159.6) GB
(54) **COMPOSITIONS POLYMERES CONDUCTRICES**
(54) **CONDUCTIVE POLYMER COMPOSITIONS**

(57) Un mélange polymère conducteur fluide destiné à être utilisé dans la préparation de revêtements de films et de fibres est principalement constitué d'une polyaniline sous forme de base (de préférence d'émeraldine sous forme de base). Dans cette invention on dope la polyaniline avec un acide sulfonique comprenant en plus d'au moins un groupe acide sulfonique, un deuxième groupe fonctionnel à liaison hydrogène et on disperse cette aniline dopée dans un solvant acide présentant une valeur pK_a inférieure à 4,5 mais sensiblement supérieure (plus positive) à celle de l'acide sulfonique. L'acide sulfonique fonctionnel semble agir en tant qu'agent de solvation ainsi qu'en tant que dopant et permet de former des mélanges à forte teneur en solides dans les solvants acides (jusqu'à environ 15 % en poids si on le compare avec un maximum d'environ 10 % dans des mélanges classiques à base de NMP) desquels on peut extraire le solvant avec un solvant concurrent (par exemple dans un procédé de filage au mouillé); ceci permettant de produire des films et des fibres étirables à froid (et à chaud). L'acide sulfonique préféré est le 2-acrylamido-2-méthyle-1-acide propane sulfonique (AMPSA) ou son oligomère et le solvant acide préféré est l'acide dichloroacétique. Le solvant concurrent peut être l'acétone, le méthyle isobutyle cétone ou l'acétate de butyle.

(57) A fluid conductive polymer mixture for use in the preparation of coatings, films and fibres is based on a polyaniline in base form (preferably emeraldine-base form). This is doped with a sulfonic acid having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group and is dispersed in an acid solvent having a pK_a less than 4.5 but substantially higher (more positive) than that of the sulfonic acid. The functional sulfonic acid appears to act as a solvating agent, as well as dopant, and allows the formation of high-solids mixtures in the acid solvents (up to around 15 % w/v compared with a maximum of about 10 % in conventional NMP-based mixtures) from which solvent can be extracted with a competing solvent (e.g. in a wet-spinning process); cold- (and hot-) drawable films and fibres can be obtained. Preferred sulfonic acid is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) or its oligomer and preferred acid solvent dichloroacetic acid. The competing solvent may be acetone, methyl isobutyl ketone or butyl acetate.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : H01B 1/12	A1	(11) International Publication Number: WO 99/24991 (43) International Publication Date: 20 May 1999 (20.05.99)
(21) International Application Number: PCT/GB98/03241 (22) International Filing Date: 30 October 1998 (30.10.98) (30) Priority Data: 9723464.5 7 November 1997 (07.11.97) GB 9801159.6 21 January 1998 (21.01.98) GB (71) Applicant (for all designated States except US): BICC PUBLIC LIMITED COMPANY [GB/GB]; Devonshire House, Mayfair Place, London W1X 5FH (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): ADAMS, Phillip, Norman [GB/GB]; 1 Quality Street, High Shincliffe, Durham DH1 2PP (GB). MONKMAN, Andrew, Paul [GB/GB]; Lime Tree House, 50 Front Street, Stanhope, Weardale DL13 2UE (GB). POMFRET, Stephen, John [GB/GB]; 8 Front Street, Frosterley, Bishop Auckland, County Durham DL13 2QJ (GB). (74) Agent: POOLE, Michael, John; BICC Patents & Licensing Dept., Quantum House, Maylands Avenue, Hemel Hempstead, Hertfordshire HP2 7DE (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.
(54) Title: CONDUCTIVE POLYMER COMPOSITIONS (57) Abstract A fluid conductive polymer mixture for use in the preparation of coatings, films and fibres is based on a polyaniline in base form (preferably emeraldine-base form). This is doped with a sulfonic acid having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group and is dispersed in an acid solvent having a pK_a less than 4.5 but substantially higher (more positive) than that of the sulfonic acid. The functional sulfonic acid appears to act as a solvating agent, as well as dopant, and allows the formation of high-solids mixtures in the acid solvents (up to around 15 % w/v compared with a maximum of about 10 % in conventional NMP-based mixtures) from which solvent can be extracted with a competing solvent (e.g. in a wet-spinning process); cold- (and hot-) drawable films and fibres can be obtained. Preferred sulfonic acid is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) or its oligomer and preferred acid solvent dichloroacetic acid. The competing solvent may be acetone, methyl isobutyl ketone or butyl acetate.		

Conductive Polymer Compositions

This invention relates to conductive polymer compositions and more particularly to fluid compositions based on polyaniline from which conductive fibres, films and
5 coatings can be made.

The emeraldine base form of polyaniline, doped with a sulfonic acid, is now well-established as a useful air-stable conductive polymer (and the leuco base form may also be useful), but conventional fluid compositions only form good
10 films if their solids content is rather small, and even then the films do not draw well. The present invention provides compositions which are capable of use in a wet-spinning process for the manufacture of drawn fibres; they are also useful for the manufacture of drawable films and of coatings
15 by processes in which a competitive solvent is used to achieve solidification faster than is possible by solvent evaporation alone.

The polymer composition in accordance with the invention is the reaction product of:

- 20 (a) a polyaniline in base form;
(b) an aliphatic sulfonic acid wholly free of ring structures and having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group; and
(c) an acid solvent having a pK_a in aqueous solution at 25°C
25 less than 5 but substantially higher (more positive) than that of the sulfonic acid.

While the invention does not depend on any theory and the applicants do not intend to be bound by theory, it is thought that the sulfonic acid not only acts as a dopant to
30 make the polyaniline conductive but also as a solvating agent to increase the "solubility" of the polymer (the word has been put in inverted commas because the mixtures are sometimes considered to be, at least partly, stable dispersions rather than true (fully solvated) solutions: a
35 homogenising step will usually be required in forming them). It is also thought that aliphatic sulfonic acids are less

liable than the bulky sulfonic acids currently in general use (dodecyl benzene sulfonic acid and camphor-10-sulfonic acid) to inhibit the alignment of polyaniline molecules that is presumably desirable for both drawability and conductivity.

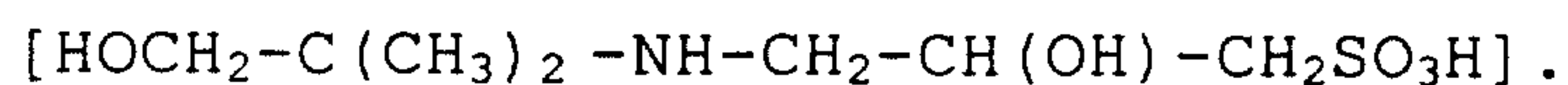
5 The polyaniline is preferably as free of branching and other defects as possible, and polyanilines of the kind showing only two substantial peaks in their ^{13}C NMR spectra in the *leuco* base form, in accordance with WO95/23822, are preferred. For making fibres and drawn film, high molecular
10 weight is normally also desirable, but this may not always be so if the mixture is for use in making coatings.

Preferably the polyaniline is in its emeraldine base form; alternatively it is possible to use the *leuco* base form, though for most applications this will eventually need
15 to be oxidised to the emeraldine form.

The aliphatic sulfonic acid is preferably free of bulky substituents. Polymerised or polymerisable aliphatic sulfonic acids have the advantage that they are less likely to migrate away from the polyaniline, and may therefore be preferred.
20 High molecular weights are undesirable. Preferred functional groups are carbonyl, amido, amino and hydroxy, especially amido and carbonyl.

Specific aliphatic sulfonic acids that appear to be commercially available and are considered suitable are:
25 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA)
 $[\text{H}_2\text{C}=\text{CH}-\text{CO}-\text{NH}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{SO}_3\text{H}]$ (the hydrogenated derivative of this acid can also be used);
N-(2-acetamido)-2-aminoethanesulfonic acid (ACES)
 $[\text{H}_2\text{N}-\text{CO}-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{H}]$;
30 *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES)
 $[(\text{HO}-\text{CH}_2-\text{CH}_2-)_2\text{N}-\text{CH}_2-\text{CH}_2-\text{SO}_3\text{H}]$;
3-(amidinothio)-1-propanesulfonic acid
 $[\text{H}_2\text{N}-(\text{C}=\text{NH})-\text{S}-(\text{CH}_2)_3-\text{SO}_3\text{H}]$
3-[*bis*(2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid
35 $[(\text{HOCH}_2-\text{CH}_2-)_2\text{N}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2\text{SO}_3\text{H}]$ and

3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxy-
1-propanesulfonic acid



Of these, ACES and most especially AMPSA (and its oligomers)
5 are preferred.

The pK_a values of aliphatic sulfonic acids are difficult to measure and not readily accessible, but it may be assumed that they all have pK_a values lower than 1, and in many cases below 0.

10 The proportion of sulfonic acid in the mixture may vary in the usual ranges; mostly a proportion in the range from 0.3 to 1.0 calculated by reference to the number of nitrogen atoms in the polyaniline will be suitable.

Preferably the acid solvent has a pK_a not greater than 4
15 and more especially not greater than 3 or better still 2 or even 1.5; preferably it is at least 0.5 units larger (more positive) than that of the sulfonic acid. We prefer to use carboxylic acids that meet these criteria and especially those with halogeno- substituents (meaning -Cl, -F or -CN).
20 Acid solvents that are liquid at ambient temperature, or not far above, are preferred. Most preferred is dichloroacetic acid ($pK_a = 1.48$, melting point 11°C). Other representative acid solvents and their pK_a 's (and melting points) are:

acid solvent	pK_a	m. pt ($^\circ\text{C}$)
bromoacetic acid	2.69	51
chloroacetic acid	2.85	64
cyanoacetic acid	2.45	68
pyruvic acid	2.39	12
2-chloropropionic acid	2.83	#
2-ketobutyric acid	2.5	34
2-chlorobutyric acid	2.86	#
2-oxo-3-methylpentanoic acid	2.3	14
phosphorous acid	1.3	#
formic acid	3.75	8

acrylic acid	4.2	13
acetic acid	4.7	17

melting points not readily available

The mixtures in accordance with the invention may include more than one such acid solvent; they may also include additional solvents (diluent) and/or host polymers that may become incorporated into the fibres, films or coatings; we prefer that they do not contain lithium chloride (or any inorganic electrolytes). The fluid mixtures in accordance with the invention are green, indicating protonation of the polyaniline.

The invention includes processes for making fibres, films and coatings characterised by the step of removing the acid solvent from the mixtures described by exposing the mixture to the action of a competitive solvent, by which is meant a liquid in which the acid solvent in the mixture is readily soluble but polyaniline is substantially insoluble.

We have found that selected esters and ketones, including in particular acetone, methylisobutyl ketone and butyl acetate are effective and suitable competitive solvents. Water may be too effective for some processes, as it is usually desirable for some of the acid solvent to remain as an aid to subsequent drawing (a plasticiser) and over-rapid solidification may not be conducive to optimum structure; but aqueous solutions of alcohols, ketones and esters may prove usable.

Thus the invention includes

- 1.a process for the manufacture of polyaniline fibre which is a wet-spinning process in which the mixture described is caused to pass through the opening(s) of a spinneret into a bath of competitive solvent and the resulting filament optionally drawn simultaneously or subsequently;
- 2.a process for the manufacture of a polyaniline-coated substrate in which the mixture described is applied in at least one layer on the surface of the substrate, the layer,

or each layer in turn, is exposed to competitive solvent, and the coating is subsequently dried; and

3. processes for manufacture of polyaniline film in which a coating made as just outlined is freed from the substrate (before or after drying) and optionally uniaxially or biaxially drawn.

Both fibres and films can be cold-drawn (at room temperature) or drawn at elevated temperatures, up to about 150°C. At present we prefer to draw at temperatures in the range from 80 to 120, and more especially 90-100°C for fibres and 100-110°C for films and most especially at the higher end of each of these last two ranges.

EXAMPLES

The polyaniline starting material for these examples is an emeraldine base prepared according to the teaching of WO95/23822 and having a molecular weight (M_p) measured as described in that application of about 150,000 Daltons.

Example 1

Polyaniline (3.467g) was ground by a pestle and mortar with AMPSA (4.533g, 57 molecules per hundred nitrogen atoms in the polyaniline) using a glove box with dry nitrogen atmosphere to avoid gelation. The ground mixture was added to dichloroacetic acid (92.0g) to give a mixture with a solids content of 8% by weight (or about 12%w/v, as the acid has a specific gravity of about 1.5). The mixture was homogenised for 10 minutes in a Ultraturrax homogeniser running at 20,000 rpm. The homogenisation/protonation is appreciably exothermic. A portion of the resulting dark green mixture was cast onto a 125 mm diameter polished silicon wafer and dried in an oven at 80°C for about 24 hours. The dried film was peeled from the substrate and found to be 0.202 ± 0.004 mm thick; its electrical conductivity was measured using a 4-wire probe and found to be 177 ± 6 S/cm. A dumbbell with a bar section 25 mm long and 4.0 mm wide was die-cut from this film and clamped in a stretching rig; it was heated to 110°C and

then stretched slowly until the applied force reached 6.0 N. The bar portion of the sample was then 58 mm long (elongation 130%), 0.114 ± 0.004 mm thick and 2.7 mm wide; its longitudinal conductivity was 540 S/cm.

5 Example 2

Polyaniline (0.632 g) was ground with AMPSA (0.868 g, 60 molecules per hundred nitrogen atoms) and added to dichloroacetic acid (28.5 g) and homogenised, using the same procedure as before but under ambient atmosphere as the
10 solids content was only 5%, at which level gelation is not experienced. The solution was cast onto a silicon wafer as before but then immersed in acetone at room temperature for ten minutes to "coagulate" the coating by dissolving part of the dichloroacetic acid. It was dried overnight in the 80°C
15 oven before peeling from the substrate and cutting dumbbells as before. The as-cast film had a conductivity of 168 ± 13 S/cm. A sample with an initial cross-section 4 mm by 0.16 mm was stretched at room temperature at a rate of about 1 mm/min without the load exceeding 5.5 N; in a few minutes,
20 an elongation of 115%, retracting reversibly to 100% on removal of the tension, was obtained. The cross-section after stretching was 3 mm by 0.11 mm and longitudinal conductivity 344 ± 35 S/cm. The sample was returned to the stretch rig and held under a tension of 5.5 N at 110°C; after 10 minutes, the
25 conductivity was found to be 408 ± 40 S/cm, after an hour 459 ± 40 S/cm and after 3 hours 450 ± 40 S/cm. The cross-section at 115% extension was now 2.7 mm by 0.10 mm. It is assumed that residual solvent was lost during this annealing process; there was an appreciable loss of elasticity.

30 Unstretched samples were also annealed at 110° (for an hour); this was found to produce a steady decline in conductivity.

Example 3

Polyaniline (1.517 g) was ground with AMPSA (2.083 g,
35 60 molecules per hundred nitrogen atoms) and then added under

nitrogen to dichloroacetic acid (36.4 g) over a 5-minute period while homogenising at 20,000 rpm, generally as in the preceding examples. Homogenising was continued for a further 10 minutes to obtain a 9%-solids mixture (by weight - about 5 15% w/v). The mixture was transferred immediately, without cooling, to a cylindrical dope-pot 25 mm in diameter having at its bottom end a 140-micrometre filter and a spinneret consisting of a single hole with a diameter of 150 μ m. The pot was removed from the glove box and promptly connected at its 10 top end to a nitrogen gas supply. An electric heating tape was wrapped round the pot to enable it to be brought to and held at a temperature of $50 \pm 5^{\circ}\text{C}$, and its bottom end was dipped into two litres of cold butyl acetate in a measuring cylinder. The nitrogen pressure in the pot was raised to 15 0.7 MPa (100 psi) to spin a continuous filament, which was left in the butyl acetate for up to 10 minutes and then dried in air.

The filament was measured with a micrometer and found to have a diameter of 0.30 ± 0.01 mm, and examination with a 20 scanning electron microscope (including examination of a surface formed by fracture at liquid nitrogen temperature) showed it to be smoothly cylindrical and without apparent voids or granules. Longitudinal conductivity of the filament was 70 ± 9 S/cm.

25 A ten-millimetre length of the filament was stretched at room temperature at a rate of about 10mm/sec, and was thus elongated into a fibre 50 mm long and with a uniform cross-section of 0.10 ± 0.01 mm. Its conductivity was 810 ± 200 S/cm and tensile strength at break about 45 MPa 30 (breaking load 0.4 N).

Example 4

This was substantially the same as Example 3 except that the butyl acetate was replaced by acetone.

The filament diameter (as formed) was 0.26 ± 0.01 mm and 35 its longitudinal conductivity 90 ± 8 S/cm.

A ten-millimetre length of the filament was stretched as before and thus elongated into a fibre 80 mm long and with a uniform cross-section of 0.09 ± 0.01 mm. Its conductivity was then 1014 ± 200 S/cm and tensile strength at break about
5 60 MPa (breaking load 0.41 N).

Example 5

A filament was made by the same procedure as in Example 4 but in this case the diameter of the filament as formed (which is very sensitive to precise conditions) was
10 found to be 0.15 mm; its conductivity was still about 90 S/cm.

A 29-mm length of this filament was heated to 90°C and drawn at a uniform rate to achieve a length of 185 mm over a ten-minute period. This resulted in a fibre 0.059 ± 0.02 mm
15 in diameter with a conductivity in a longitudinal direction of 1950 ± 180 S/cm.

Example 6

A solution was made using the same procedure as before with the same polyaniline emeraldine base, AMPSA and
20 dichloroacetic acid, but in proportions to give 50 molecules of AMPSA per hundred nitrogen atoms in the polyaniline and a solids content of only 1.5% by weight and using a 5-minute homogenisation step followed by centrifuging for 30 minutes in a typical laboratory centrifuge at 4,500 rpm. Flat glass
25 substrates were coated with enough of this solution to cover the surface and spun, using a commercial spin coater, at 1700 rpm about an axis normal to the coated surface and through its centre and while spinning heated to 120°C using an infra-red heat lamp until dry (around 3 minutes) to obtain a coating
30 $0.07\mu\text{m}$ thick, as measured with an "-step" profilometer. The film had a conductivity of 60 S/cm, a sheet resistance of 800 ohms per square and an optical transmission of 95% at 550 nm.

CLAIMS

- 1 A fluid conductive polymer mixture for use in the preparation of coatings, films and fibres which is the reaction product of:
- 5 (a) a polyaniline in base form;
- (b) an aliphatic sulfonic acid wholly free of ring structures and having in addition to at least one sulfonic acid group a second hydrogen-bonding functional group; in combination with
- 10 (c) an acid solvent having a pK_a less than 5 but substantially higher (more positive) than that of the sulfonic acid.
- 2 A fluid mixture as claimed in claim 1 in which the polyaniline is of the kind showing only two substantial peaks
- 15 in the ^{13}C NMR spectrum of its *leuco* base form.
- 3 A fluid mixture as claimed in claim 1 or claim 2 in which the polyaniline is in its emeraldine base form.
- 4 A fluid mixture as claimed in any one of claims 1-3 in which the aliphatic sulfonic acid is polymerisable.
- 20 5 A fluid mixture as claimed in any one of claims 1-4 in which the said functional groups in the sulfonic acid are selected from the group consisting of carbonyl, amido, amino and hydroxy.
- 6 A fluid mixture as claimed in any one of claims 1-4 in
- 25 which the said functional groups in the sulfonic acid are selected amido or carbonyl.
- 7 A fluid mixture as claimed in claim 1 or claim 2 in which the aliphatic sulfonic acid is 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA).
- 30 8 A fluid mixture as claimed in claim 1 or claim 2 in which the aliphatic sulfonic acid is selected from:
- N*-(2-acetamido)-2-aminoethanesulfonic acid (ACES);
- N,N*-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (BES);
- 3- (amidinothio)-1-propanesulfonic acid; 3-[bis(2-
- 35 hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic

acid; 3-[(1,1-dimethyl-2-hydroxyethyl)amino]-2-hydroxy-1-propanesulfonic acid; and the hydrogenated derivative of AMPSA.

9 A fluid mixture as claimed in any one of claims 1-8 in
5 which the proportion of sulfonic acid in the mixture is in the range from 0.3 to 1.0 calculated by reference to the number of nitrogen atoms in the polyaniline.

10 A fluid mixture as claimed in any one of claims 1-9 in which the acid solvent has a pK_a not greater than 4.

10 11 A fluid mixture as claimed in any one of claims 1-9 in which the acid solvent has a pK_a not greater than 3.

12 A fluid mixture as claimed in any one of claims 1-9 in which the acid solvent has a pK_a not greater than 2.

13 A fluid mixture as claimed in any one of claims 1-9 in
15 which the acid solvent has a pK_a not greater than 1.5.

14 A fluid mixture as claimed in any one of claims 1-13 in which the acid solvent has a pK_a at least 0.5 units larger (more positive) than that of the sulfonic acid.

15 A fluid mixture as claimed in any one of claims 1-14 in
20 which the acid solvent is a carboxylic acid.

16 A fluid mixture as claimed in any one of claims 1-14 in which the acid solvent is a carboxylic acid with halogeno-substituents (-Cl, -F or -CN).

17 A fluid mixture as claimed in any one of claims 1-14 in
25 which the acid solvent is dichloroacetic acid.

18 A fluid mixture as claimed in any one of claims 1-14 in which the acid solvent is selected from trichloroacetic acid, bromoacetic acid, chloroacetic acid, cyanoacetic acid, pyruvic acid, 2-chloropropionic acid, 2-ketobutyric acid,
30 2-chlorobutyric acid, 2-oxo-3-methylpentanoic acid, phosphorous acid, formic acid, acrylic acid and acetic acid.

19 A process for making conductive polymer fibre, film or coating including preparing a fluid mixture as claimed an any one of claims 1-18 and removing acid solvent by exposing the
35 mixture to the action of a liquid in which the said acid is

readily soluble but polyaniline is substantially insoluble.

20 A process for the manufacture of polyaniline fibre which is a wet-spinning process comprising preparing a fluid mixture as claimed in any one of claims 1-18, and causing it
5 to pass through the opening(s) of a spinneret into a bath of a liquid in which the said acid is readily soluble but polyaniline is substantially insoluble.

21 A process as claimed in claim 20 comprising simultaneously or subsequently drawing the resulting
10 filament.

22 A process as claimed in claim 21 in which the filament is drawn at room temperature.

23 A process as claimed in claim 21 in which the filament is drawn at a temperature in the range 90-100°C.

15 24 A process as claimed in any one of claims 19-23 in which the said liquid is acetone, methylisobutyl ketone or butyl acetate.

25 A process for the manufacture of a polyaniline-coated substrate comprising preparing a fluid mixture as claimed in
20 any one of claims 1-18, applying it in at least one layer on the surface of the substrate, exposing the layer, or each layer in turn, to a liquid in which the said acid is readily soluble but polyaniline is substantially insoluble, and subsequently drying the coating.

25 26 A process for the manufacture of a polyaniline film comprising preparing a mixture as claimed in any one of claims 1-18, applying it in at least one layer on the surface of the substrate, exposing the layer, or each layer in turn, to a liquid in which the said acid is readily soluble but
30 polyaniline is substantially insoluble, freeing the coating from the substrate and then drying it.

27 A process for the manufacture of a polyaniline film comprising preparing a mixture as claimed in any one of claims 1-18, applying it in at least one layer on the surface
35 of the substrate, exposing the layer, or each layer in turn,

to a liquid in which the said acid is readily soluble but polyaniline is substantially insoluble, subsequently drying the coating, and freeing it from the substrate.

28 A process as claimed in claim 26 or claim 27 in which
5 the said liquid is acetone, methylisobutyl ketone or butyl acetate.

29 A process as claimed in any one of claims 26-28 in which the film is uniaxially or biaxially drawn.

30 A process as claimed in claim 29 in which the film is
10 drawn at room temperature.

31 A process as claimed in claim 30 in which the film is drawn at a temperature in the range 100-110°C.