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<p>(21) International Application Number: PCT/US91/09571 (22) International Filing Date: 18 December 1991 (18.12.91) (30) Priority data: 630,905 20 December 1990 (20.12.90) US (71) Applicant: ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (72) Inventors: HAN, Chien-Chung ; 164 Shunpike Road, Madison, NJ 07940 (US). ELSENBÄUMER, Ronald, L. ; 24 Black Watch Trail, Morristownship, NJ 07960 (US). SHACKLETTE, Lawrence, W. ; 11 Alden Place, Maplewood, NJ 07040 (US).</p>	<p>(74) Agent: ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US). (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: METHOD FOR PROCESSING ELECTRICALLY CONDUCTIVE POLYANILINES IN LEWIS-BASE SOLVENTS</p> <p>(57) Abstract This invention relates to solutions of doped substituted or unsubstituted polyaniline in a Lewis base solvent other than piperidine.</p>		

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**METHOD FOR PROCESSING ELECTRICALLY
CONDUCTIVE POLYANILINES IN LEWIS-BASE SOLVENTS**

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to solutions of
10 electrically conductive substituted or unsubstituted
polyanilines and to methods of forming such solutions.
Another aspect of this invention relates to a method of
using such solutions to form conductive articles, such
as printings, coatings, films and parts.

15

2. Prior Art

There has recently been an increased interest in
the electrochemistry and electrical phenomena of
polymeric systems. Recently, work has intensified with
20 polymers having extended conjugation in at least one
backbone chain.

One conjugated polymer system currently under
study is polyaniline. Kobayashi, Tetsuhiko, et al., J.
Electroanal. Chem., "Electrochemical Reactions
25 Concerned With Electrochromism of Polyaniline
Film-Coated Electrodes", 177 (1984) 281-191, describes
various experiments in which spectro electro-chemical
measurements of a polyaniline film coated electrode
were made. French Patent No. 1,519,729; French Patent
30 of Addition 94,536; U.K. Patent 1,216,549; "Direct
Current Conductivity of Polyaniline Sulfate", M.
Donomedoff, F. Kautier - Cristojini, R. De Surville, M.
Jozefowicz, L-T. Yu, and R. Buvet, J. Chim. Phys.,
Physicochim. Brol, 68, 1055 (1971); "Continuous Current
35 Conductivity of Macromolecular Materials", L-T. Yu, M.
Jozefowicz, and R. Buvet, Chim. Macromol., 1, 469
(1970); "Polyaniline Based Filmogenic Organic

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- Conductive Polymers", D. LaBarre and M. Jozefowicz, C.R. Read. Sci., Ser. C. 269, 964 (1969); "Recently Discovered Properties of Semiconducting Polymers", M. Jozefowicz, L-T. Yu, J. Perichon, and R. Buvet, J. Polym. Sci. Part C, 22, 1187 (1967); "Electrochemical Properties of Polyaniline Sulfates:", F. Cristojini, R. De Surville, and M. Jozefowicz, Cr. Read. Sci., Ser. C. 268, 1346 (1979); "Electrochemical Cells Using Protolytic Organic Semiconductors", R. De Surville, M. Jozefowicz, L-T. Yu, J. Perichon, R. Buvet, Electrochem. Dittn., 13, 1451 (1986); "Oligomers and Polymers Produced by Oxidation of Aromatic Amines:", R. De Surville, M. Jozefowicz, and R. Buvet, Ann. Chem. (Paris), 2 5 (1967); "Experimental Study of the Direct Current Conductivity of Macromolecular Compounds:", L-T. Yu, M. Borredon, N. Jozefowicz, G. Belorgey, and R. Buvet, J. Polym. Sci. Polym. Symp., 16, 2931 (1967); "Conductivity and Chemical Properties of Oligomeric Polyaniline", M. Jozefowicz, L-T. Yu, G. Belorgey and R. Buvet, J. Polym. Sci., Polym. Symp., 16, 2934 (1967); "Products of the Catalytic Oxidation of Aromatic Amines", R. De Surville, M. Jozefowicz, and R. Buvet, Ann. Chem. (Paris), 2, 149 (1967); "Conductivity and Chemical Composition of Macromolecular Semiconductors", Rev. Gen. Electr., 75, 1014 (1966); "Relation Between the Chemical and Electrochemical Properties of Macromolecular Semiconductors", M. Jozefowicz and L-T. Yu, Rec. Gen. Electr., 75, 1008 (1966); "Preparation, Chemical Properties, and Electrical Conductivity of Poly-N-Alkyl Anilines in the Solid State", O. Muller and M. Jozefowicz, Bull. Soc. Chem., Fr. 4087 (1972).

U.S. Patent Nos. 3,963,498 and 4,025,463 describe oligomeric polyanilines and substituted polyanilines having not more than 8 aniline repeat units which are

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described as being soluble in certain organic solvents and which are described as being useful in the formation of semi-conductor compositions having bulk electrical conductivities up to about 7×10^{-3} S/cm and, surface resistivities of 4×10^7 ohm/square.

5 and, surface resistivities of 4×10^7 ohm/square.

European Patent No. 0017717 is an apparent improvement in the compositions of U.S. Patent Nos. 3,963,498 and 4,025,463 and states that the polyaniline can be formed into a latex composite through use of acetone solutions

10 of the oligomers of polyaniline and suitable binder polymers.

U.S. Patent No. 4,855,361 describes a conductive polymer blend which comprises mixing a polyimide with a base-type polymer containing carbon nitrogen linkages,

15 such as polyaniline, having a polyimide-like group covalently linked to the nitrogen atoms of the base-type polymer. The conductive polymer blend is formed by first reacting a base-type non-conductive polymer containing carbon-nitrogen linkages, such as

20 polyaniline, with a carbonyl anhydride, such as 3,4,3',4' benzophenone tetracarboxylic dianhydride to form a conductive polymer containing polyimide-like groups covalently linked to the nitrogen atoms of the base-type polymer mixing such conductive polymer with

25 non-conductive polyimide in a suitable solvent, removing the solvent, and forming a conductive continuous phase blend of the polyimide and the conductive polymer.

U.S. Patent No. 4,798,685 describes the production

30 of base-type conductive polymers, particularly from the family of conductive polyaniline, by reacting a base-group non-conductive polymer containing carbon-nitrogen linkages, e.g. polyaniline, with an R^+ donor compound, where R is an organic group, e.g.

35 methyl iodide, and forming an electrically conductive

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polymer in which the R groups are covalently linked to the nitrogen atoms of the polymer.

U.S. Patent No. 4,806,271 describes the production of base-type conductive polymers, particularly from the family of conductive polyaniline, by reacting a base-type non-conductive polymer containing carbon-nitrogen linkages e.g., polyaniline, with a cation donor compound, such as R_2SO_4 , $R'SO_2Cl$ or R''_3SiCl , where R, R' and R'' are alkyl or aryl, such as dimethyl sulfate or tosyl chloride, and forming an electrically conductive polymer in which the R groups of R_2SO_4 , the $R'SO_2$ groups of $R'SO_2Cl$, or the R''_3Si groups of R''_3SiCl are covalently linked to the nitrogen atoms of the polymer.

U.S. Patent No. 4,822,638 describes a process for fabricating an electronic device on a non-conductive polymer substrate, particularly from the family of polyaniline, which comprises applying a covalent doping agent, such as an R^+ donor compound, where R is an organic group, e.g., methyl iodide, to a preselected portion of a base-type non-conductive polymer substrate containing carbon-nitrogen linkages, and converting such preselected portion of the polymer substrate to an electrically conductive polymer portion, by covalent linkage of the R groups of such donor compound, to the nitrogen atoms of the non-conductive polymer substrate. Electronic devices, such as resistors, capacitors, inductors, printed circuits and the like, can be provided by the invention process, in the form of light-weight polymers containing no metal, and which are stable and wherein the conductive portions are non diffusing.

U.S. Patent No. 4,851,487 describes the production of base-type conductive polymers, particularly from the family of conductive polyaniline, by reacting a

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base-type non-conductive polymer containing carbon-nitrogen linkages, e.g., polyaniline, with an anhydride such as $R-SO_2-O-SO_2-R'$, $R-CO-O-CO-R'$, $R-CO-O-SO_2R$ or mixtures thereof, where R and R' can be
5 the same or different and are alkyl or aryl, e.g., tosylic anhydride or benzophenone tetracarboxylic dianhydride, and forming an electrically conductive polymer in which the SO_2R and COR groups are covalently linked to the nitrogen atoms of the conductive polymer
10 and the anion of the conductive polymers is the RSO_3^- or $R'CO_2^-$ group.

U.S. Patent No. 4,798,685 describes the production of base-type conductive polymers, particularly from the family of conductive polyaniline, by reacting a
15 base-type non-conductive polymer containing carbon-nitrogen linkages, e.g., polyaniline, with an R^+ donor compound, where R is an organic group, e.g., methyl iodide, and forming an electrically conductive polymer in which the R groups are covalently linked to
20 the nitrogen atoms of the polymer.

PCT WO89/01694 describes various forms of electrically conductive polyanilines doped with certain sulfonated dopants. It is disclosed that these materials are thermally stable and can be melt blended
25 with polymers to form blends.

SUMMARY OF THE INVENTION

One aspect of this invention relates to non-electrically conductive solutions and to
30 non-electrically conductive plasticized compositions comprising one or more substituted or unsubstituted polyanilines; one or more Lewis base/dopant complexes, said dopants capable of doping one or more of said polyanilines to form electrically conductive
35 polyaniline on release of said dopants from said

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complexes and said Lewis bases selected from the group consisting of Lewis bases other than piperidine which are in the liquid state under use conditions, which have a pK_a greater than that of said polyanilines, 5 which are capable of complexing with said dopants in the presence of said polyanilines and which are solvents for said complexes and for said undoped polyanilines; and Lewis base in an amount sufficient to dissolve said complexes and said polyanilines, to 10 plasticize said polyanilines or a combination thereof. As used herein a "solution" is a real solution or an ultra-fine dispersion having an average particle size of less than about 100 nanometers; a "plasticized composition" is a polymer or a polymer blend which is 15 softened by incorporation of a liquid or low melting temperature solid generally to a level of more than 1% by weight and less than 20% by weight. As used herein "polyaniline" is a polymer which is synthesized for example by the head-to-tail linkage of substituted or 20 unsubstituted aniline, and which depending on oxidation state consists of phenyl rings and amide linkage (-NH- or -HR- where R is a substituent other than hydrogen) alternating with varying amounts of quinoid rings and imine (-N=) linkages. As used herein "undoped 25 polyaniline" is characterized by an uncharged backbone, and "polyaniline base" is a particular form of undoped polyaniline which contains at least one quinoid diimine linkage in the backbone.

Another aspect of this invention relates to a 30 method of forming a conductive article or forming a conductive polymer coated substrate from a non-electrically conductive solution or plasticized composition of this invention which comprises the steps of:

35 (a) forming a non-electrically conductive

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solution or a non-electrically conductive plasticized composition comprising one or more substituted or unsubstituted polyanilines, one or more Lewis base/dopant complexes, said dopants capable of doping one or more of said polyanilines to form electrically conductive polyanilines on release of said dopants from said complexes and said Lewis bases selected from the group consisting of Lewis bases other than piperidine which are in the liquid state under use conditions, which have a pK_a greater than that of said polyanilines, which are capable of complexing with said dopants in the presence of said polyanilines and which are solvents for said complexes and for said undoped polyanilines; and Lewis base in an amount sufficient to dissolve said complexes and said polyaniline to plasticize said polyanilines or a combination thereof;

(b) placing all or a portion of said solution or composition onto a substrate or in the shape of said article; and

(c) removing all or a portion of said liquid Lewis bases from said solution or plasticized composition to form solidified doped electrically conductive polyanilines having the configuration of said article or a substrate coated with said electrically conductive polyanilines.

Through use of this invention polyaniline can be conveniently processed into useful conductive articles of all shapes.

30

BRIEF DESCRIPTION OF THE INVENTION

The invention will be more fully understood and further advantages will become apparent when reference is made to the following detailed description of the invention and accompanying drawings in which:

35

Figure 1 is a graph showing the Hansen Solubility

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Parameters of solvents for polyaniline base.

Figure 2 is a graph showing the Hansen Solubility Parameters relative to polyaniline base for solvents and non-solvents.

5

DETAILED DESCRIPTION OF THE INVENTION

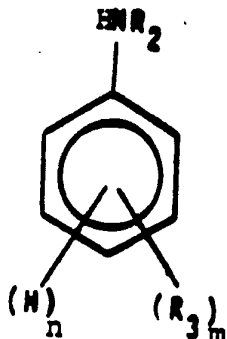
The non-electrically conductive solutions or plasticized composition of this invention comprises three essential ingredients. One essential ingredient
10 is one or more substituted or unsubstituted polyanilines which are capable of being made electrically conductive (conductivity of at least about 10^{-10} Scm⁻¹ by the co-linear four-probe method) with a suitable dopant. Any form of substituted and
15 unsubstituted polyaniline can be conveniently used in the practice of this invention. Illustrative of useful forms are those described in Green, A.G. and Woodhead, A.E., Aniline-black and Allied Compounds, Part I", J. Chem. Soc., 101 pp. 1117 (1912) and Kobayashi, et al.,
20 "Electrochemical Reactions... of Polyaniline Film-Coated Electrodes", J. Electroanal. Chem., 177, pp. 281-91 (1984) and in Shacklette, L.W. et al. "Structure and Properties of polyaniline as modeled by Single-Crystal Oligomers" J. Chem Phys., 88, 3955
25 (1988), which are hereby incorporated by reference. For example, unsubstituted or unsubstituted polyaniline, useful forms, which are characterized by different ratios of phenylene amine and quinone imine backbone segments include leucoemeraldine,
30 protoemeraldine, emeraldine, nigraniline and pernigraniline.

In the preferred embodiments of the invention, polyanilines for use in the invention are homopolymers and copolymers of the type derived from the
35 polymerization of unsubstituted and substituted

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anilines of the Formula I:

5



10 wherein:

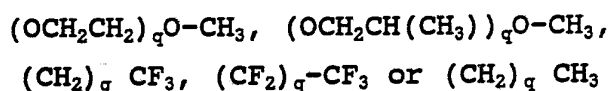
n is an integer from 0 to 5;

m is an integer from 0 to 5 with the proviso that the sum of n and m is equal to 5;

15 R_2 is the same or different at each occurrence and is R_3 substituents or hydrogen; and

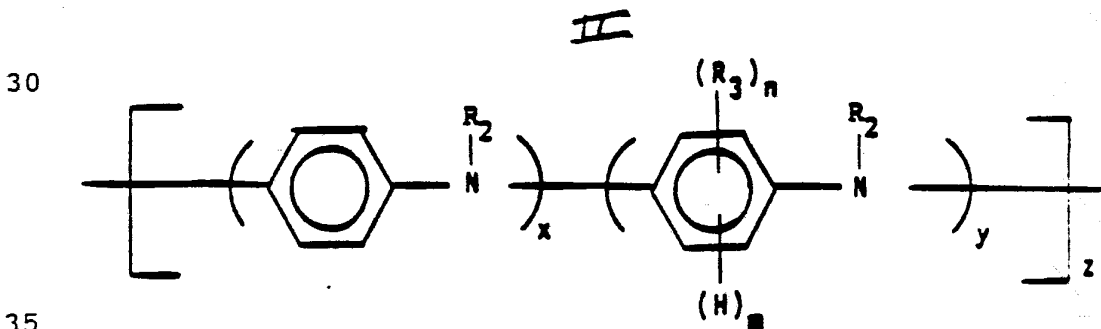
20 R_3 is the same or different at each occurrence and is selected from the group consisting of phosphonic acid, cyano, nitro, boric acid, phosphoric acid, halo, sulfinate, carboxylic acid, phosphonic acid, halogen, hydroxy, cyano, sulfinic acid, phosphinic acid, carboxylate, borate, phosphate, amido, sulfonate, phosphinate, phosphonate, hydroxyamine, sulfonic acid, nitro, deuterium, amino, or substituted or unsubstituted alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkythio, alkyl, aryloxy, alkylthioalkyl, arylalkylamino, alkylaryl, arylalkyl, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxyalkyl, alkylsulfinylalkyl, alkoxyalkyl, alkylsulfonyl, arylthio, 30 alkylsulfonylalkyl, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, alkylsilane or alkyl wherein permissible substituents are one or more phosphonic acid, sulfonic acid, phosphoric acid, boric acid, sulfate, sulfinic acid, carboxylate, borate, sulfonate, phosphinate, 35 sulfinate, quaternary ammonium, phosphonate,

hydroxylamine, amido, phosphate, phosphinic acid, carboxylic acid, halo, hydroxyamine, nitro, cyano or epoxy substituents; or any two R₃ groups together or one or more R₃ group together with an R₂ group may form
 5 a substituted or unsubstituted alkylene, alkenylene, or alkynylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroalicyclic, heteroaromatic or alicyclic ring, which ring may optionally include one or more divalent nitrogen, sulfur, sulfinyl, ester,
 10 carbonyl, sulfonyl, or oxygen atoms wherein permissible substituents are one or more phosphonic acid, sulfonic acid, phosphoric acid, boric acid, sulfate, carboxylate, borate, sulfonate, sulfinic acid, phosphinate, quaternary ammonium, phosphonate,
 15 sulfinate, amido, hydroxylamine, phosphate, phosphinic acid, carboxylic acid, hydroxyamino, halo, nitro, cyano or epoxy moieties; or R₃ is a divalent organic moiety bonded to the same or a different substituted or unsubstituted aniline moiety or R₃ is an aliphatic
 20 moiety having repeat units of the formula: .

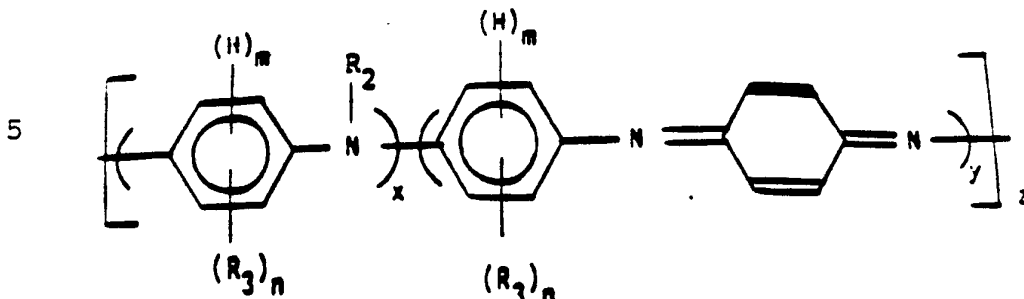


25 wherein q is a positive whole number.

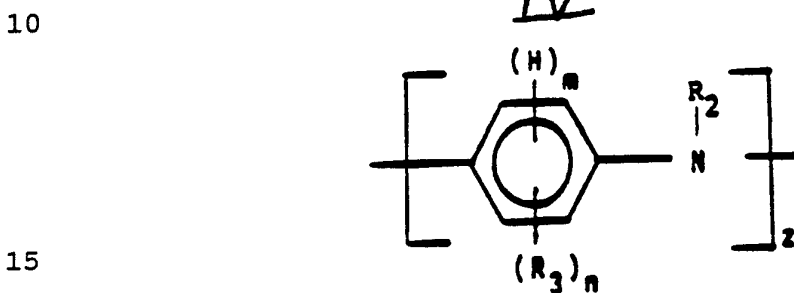
Illustrative of the polyanilines useful in the practice of this invention are those of the Formulas II to V:



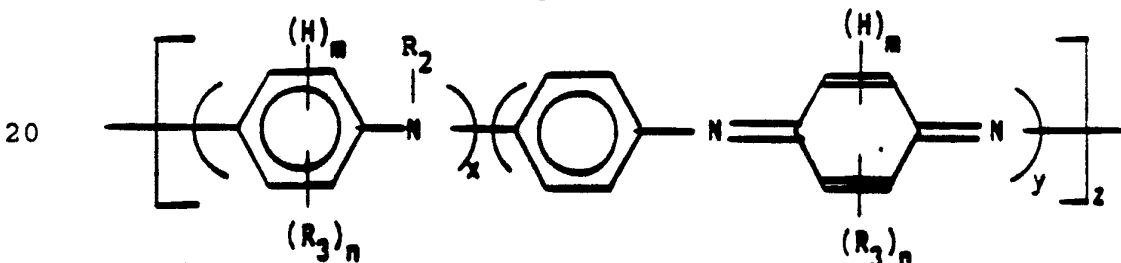
III



IV



V



wherein:

n is an integer from 0 to 4;

25 m is an integer from 0 to 4; with the proviso that the sum of n and m is 4;

R₂ and R₃ are as described above;

x and y are the same or different at each occurrence and are integers equal to or greater than 0, with the proviso that the sum of x and y is greater than 0; preferably were x is an integer equal to or greater than about 1, and/or the ratio of x to y is greater than or equal to about 0.5; and

30

z is an integer equal to or greater than 1.

35 The following listing of substituted and

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unsubstituted anilines are illustrative of those which can be used to prepare polymers and copolymers useful in the practice of this invention.

- 2-Cyclohexylaniline 2-Acetylaniline
5 Aniline 2,5-Dimethylaniline
o-Toluidine 2,3-Dimethylaniline
4-Propanoylaniline N-Pentylaniline
2-(Methylamino)aniline 4-Benzylaniline
2-(Dimethylamino)aniline 4-Aminoaniline
10 2-Methyl-5-methoxy- 2-Methylthiomethylaniline
carbonylaniline 4-(2,4-Dimethylphenyl)
N-Ethylaniline aniline
4-Carboxyaniline 2-Ethylthioaniline
N-Methyl aniline N-Methyl m-Toluidine
15 2,4-Dimethylaniline N-Butyl o-Toluidine
N-Propyl aniline N-Propyl m-Toluidine
N-Hexyl aniline N-Methyl-o-Cyanoaniline
m-Toluidine 2,5-Dibutylaniline
o-Ethylaniline 2,5-Dimethoxyaniline
20 m-Ethylaniline Tetrahydronaphthylamine
o-Ethoxyaniline o-Cyanoaniline
m-Butylaniline 2-Methylthioaniline
m-Hexylaniline 2,5-Dichloroaniline
m-Octylaniline 3-(n-Butanesulfonic acid)
25 4-Bromoaniline aniline
2-Bromoaniline 3-Propoxymethylaniline
3-Bromoaniline 2,4-Dimethoxyaniline
3-Acetamidoaniline 4-Mercaptoaniline
4-Acetamidoaniline 4-Ethylthioaniline
30 5-Chloro-2-methoxy-aniline 3-Phenoxyaniline
5-Chloro-2-ethoxy-aniline 4-Phenoxyaniline
N-Hexyl-m-Toluidine N-Octyl m-Toluidine
4-Phenylthioaniline 4-Trimethylsilylaniline
3-Amino-9-methylcarbazole 3-Amino carbazole
35 4-Amino carbazole 2-Amino carbazole

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3-Butoxyaniline N-(p-Aminophenyl)aniline
2,5-Dibutoxyaniline 2-Butoxyaniline

Exemplary of useful R₂ groups are hydrogen,
methyl, ethyl, isopropyl, butyl, isobutyl, hexyl, octyl
5 and the like.

Illustrative of useful R₃ groups are hydrogen,
hydroxyl, alkyl such as methyl, ethyl, octyl, benzyl
nonyl, tert-butyl, neopentyl, isopropyl, sec-butyl,
dodecyl and the like, alkenyl such as 1-propenyl,
10 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl
and the like; alkoxy such as propoxy, butoxy, methoxy,
isopropoxy, pentoxy, nonoxy, ethoxy, octoxy, and the
like; cycloalkenyl such as cyclohexenyl, cyclopentenyl
and the like; alkanoyl such as butanoyl, pentanoyl,
15 octanoyl, ethanoyl, propanoyl and the like;
alkylsulfinyl, alkylsulfonyl, alkylthio, arylsulfonyl,
arylsulfonyl, and the like, such as butylthio,
neopentylthio, methylsulfinyl, benzylsulfinyl,
phenylsulfinyl, propylthio, octylthio, nonylsulfonyl,
20 octylsulfonyl, methylthio, isopropylthio,
phenylsulfonyl, methylsulfonyl, nonylthio, phenylthio,
ethylthio, benzylthio, phenethylthio, sec-butylthio,
naphthylthio and the like; alkoxy-carbonyl such as
methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl and the
25 like; cycloalkyl such as cyclohexyl, cyclopentyl,
cyclo-octyl, cycloheptyl and the like; alkoxyalkyl
such as methoxymethyl, ethoxymethyl, butoxymethyl,
propoxyethyl, pentoxybutyl and the like; aryloxyalkyl
and aryloxyaryl such as phenoxyphenyl, phenoxy-methyl
30 and the like; amino, arylamino, alkylamino,
diarylamino, dialkylamino and alkylarylamino such as
amino, methylamino, dimethylamino, phenylamino,
methylethylamino, diphenylamino, methylphenylamino and
the like; various substituted alkyl and aryl groups
35 such as 1-hydroxybutyl, 1-aminobutyl, 1-

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hydroxylpropyl, 1-hydroxypentyl, 1-hydroxyoctyl, 1-hydroxyethyl, 2-nitro-ethyl, trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 3-chloropropyl, 4-nitrophenyl, 3-cyanophenyl, and the like; acid groups and salts thereof such as sulfonic acid, carboxylate, 5 carboxylic acid, carboxylate, phosphoric acid and the like; and organic radicals such as alkoxy, alkoxyalkyl, arylamino, alkyl or aryl groups substituted with one or more acid groups and/or salts thereof such as 10 phosphonic acid, phosphinic acid, sulfinic acid, sulfonic acid, sulfinic acid, borate, phosphoric acid, carboxylate, boric acid, or carboxylic acid groups such as ethylsulfonic acid, propylsulfonic acid, butylsulfonic acid, phenylsulfonic acid, and the like.

15 Also illustrative of useful R_3 groups are divalent moieties derived from any two R_3 groups or a R_3 group with an R_2 group such as moieties of the formula:



wherein a is an integer from about 3 to about 7, and b is an integer from 1 to 2 and R_5 is the same or different at each occurrence and is hydrogen or alkyl, 25 as for example $-(CH_2)_4-$, $(CH_2)_3-$, $-(CH=CH-CH=CH)-$, $-CH_2-CH(CH_3)-CH_2-$ and $-(CH_2)_5$, such moieties which optionally include heteroatoms of oxygen, nitrogen, ester, sulfonyl, carbonyl, sulfinyl, and/or sulfur such as $-CH_2SCH_2-$, $-CH_2NHCH_2-$, $-SCH_2NHCH_2-$, $O-CH_2O-$, 30 $-O-CH_2-S-CH_2-$, $-CH_2S(O_2)CH_2-$, $-CH_2S(O)CH_2-$, $-OC(O)CH_2CH_2-$, $-CH_2C(O)CH_2$ and $-CH_2-O-CH_2-$ to form heterocyclic amino compounds such as tetrahydronaphthylamine, dihydrobenzopyrroleamine, benzofuranamine, dihydrobenzopyranamine, dihydrobenzofuranamine, 35 dihydrobenzoparaxazineamine,

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dihydrobenzoparadiazineamine,
dihydrobenzotriazoleamine,
dihydrobenzothiazineamine, benzothiopyranamine,
dihydrobenzoxazoleamine and the like. Exemplary of
5 useful R_3 groups are divalent alkenylene chains
containing 1 to about 3 unsaturated bonds such as
divalent 1,3-butadiene and like moieties which may also
include one or more divalent oxygen, nitrogen,
sulfinyl, sulfonyl, carbonyl, ester, and/or sulfur
10 groups which form such compounds as benzodiazineamine,
benzodiazoleamine, benzotriazepine amine,
benzimidazolylamine, benzisoxazoleamine,
benzoxazolylamine, benzotriazineamine,
benzoxazineamine, naphthaleneamine, benzopyranamine,
15 benzothiazineamine, anthraceneamine,
aminobenzothio-pyran, aminobenzodiazine,
benzthiopyroneamine, aminocoumarin,
benzothiopheneamine, benzothiadiaazoleamine, and the
like.

20 Preferred for use in the practice of this
invention are polyanilines of the above Formulas II to
V in which:

n is an integer from 0 to about 2;

m is an integer from 2 to 4, with the proviso that
25 the sum of n and m is equal to 5;

R_2 is the same or different at each occurrence and
is R_3 or hydrogen; or

R_3 is alkyl or alkoxy having from 1 to about 30
carbon atoms, sulfonic acid, hydroxylamine, carboxylic
30 acid, phosphoric acid, amino, alkylamino, dialkylamino,
arylamino, diarylamino, boric acid, borate, phosphate,
phosphonic acid, phosphonate, phosphinic acid,
phosphinate, sulfinic acid, sulfinate, sulfonate,
carboxylate, alkylarylamino, cyano, halo, or alkyl,
35 aryl or alkoxy substituted with phosphonic acid,

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phosphate, phosphoric acid, halo, alkoxy, alkyl,
borate, sulfonate, carboxylate, phosphonate, boric
acid, phosphinic acid, amino, alkylamino, sulfinic
acid, sulfinic acid, dialkylamino, arylamino, diarylamino,
5 alkylarylamino, phosphinate, carboxylic acid or
sulfonic acid substituents;

x is an integer equal to or greater than 1;

y is equal to or greater than 0,

with the proviso that the ratio of x to y is greater
10 than about 1; and

z is an integer equal to or greater than about 5;

Particularly preferred for use in the practice of
this invention are polyanilines of the above Formulas
II to V in which:

15 n is an integer from 0 to 1;

m is an integer from 3 to 4, with the proviso that
the sum of n and m is equal to 4;

R₂ is the same or different at each occurrence and
are hydrogen or methyl;

20 R₃ is alkyl or alkoxy having from 1 to about 20
carbon atoms, alkylamino, amino, dialkylamino, boric
acid, borate, arylamino, diarylamino, alkylarylamino,
sulfonic acid, carboxylic acid, halo, phosphoric acid,
sulfonate, carboxylate, or phosphate, or alkyl or aryl
25 substituted with carboxylic acid, phosphonic acid,
phosphate, boric acid, phosphoric acid, borate,
sulfonate, halo, carboxylate, alkylamino, amino,
dialkylamino, arylamino, diarylamino, alkylarylamino,
phosphonate, or sulfonic acid substituents;

30 x is an integer equal to or greater than 2;

y is equal to or greater than 0, with the proviso
that the ratio of x to y is greater than about 2; and

z is an integer equal to or greater than about 5.

Amongst the particularly preferred embodiments,
35 most preferred for use in the practice of this

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invention are polyanilines of the above Formulas in which:

n is an integer from 0 to 1;

m is an integer from 3 to 4, with the proviso that
5 the sum of n and m is equal to 4;

R₂ is hydrogen;

R₃ is alkyl or alkoxy from 1 to about 15 carbon
atoms carboxylic acid, carboxylate, halo, sulfonic
acid, sulfonate, or alkyl substituted with one or more
10 halo, sulfonic acid, sulfonate, carboxylic acid or
carboxylate groups;

x is an integer equal to or greater than 2;

y is equal to or greater than 1, with the proviso
that the ratio of x to y is greater than about 2; and

15 z is an integer equal to or greater than about 5.

In the most preferred embodiments of this
invention, the polyaniline is derived from
unsubstituted aniline, or alkyl, alkoxy, sulfonic acid
or sulfonate substituted aniline.

20 The number of repeat units in the polyaniline may
vary widely. In general, the greater the number of
aniline repeat units the greater the viscosity and
molecular weight of the polyaniline. In those
embodiments where a polyaniline of lower molecular
25 weight and viscosity is required, such material may be
used; and in those applications where a polyaniline of
higher molecular weight and viscosity is required, then
such material can be used. The number of aniline
repeat units may be as low as 2 or 3 but is preferably
30 at least about 10. The upper limit can vary depending
on the required viscosity and molecular weight. In the
more preferred embodiments of the invention, the number
of aniline repeat units is at least about 20, and in
the particularly preferred embodiments, the number of
35 repeat units is at least about 30. Amongst the

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particularly preferred embodiments, most preferred are those embodiments in which the number of repeat units is at least about 40.

Useful polyanilines can be prepared through use of
5 chemical and electrochemical synthetic procedures. For example, one form of polyaniline can be prepared by treating aniline with ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in excess 1M HCl. This powdered form of polyaniline is blue green in color. After methanol washing and air
10 drying this material exhibits a conductivity of about 10 S/cm. This conductive form of polyaniline can be treated with ammonium hydroxide in ethanol to form a non-conductive form of polyaniline which is dark blue in color and which has a conductivity equal to or
15 greater than about 10^{-10} S/cm. Other chemical procedures for preparation of various chemical forms of polyaniline are described in detail in Green et al. described above.

Useful forms of polyaniline can also be prepared
20 electrochemically. For example, useful forms of polyaniline can be prepared by the electrochemical oxidation of aniline in aqueous fluoroboric acid electrolyte on a platinum foil anode.

Other chemical and electrochemical syntheses and
25 transformations of the conductive form of polyaniline may be discovered and are presently contemplated as being useful. Moreover, additional forms or types of polyaniline may be elucidated in the future. Accordingly, no limitation to the syntheses,
30 transformation, or structures herein described or postulated is intended beyond the limitations of the appended claims.

The second essential ingredient of the solution or
plasticized composition of this invention is one or
35 more Lewis base/dopant complexes. The purpose of the

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dopant component of the complex is to dope the polyaniline and render it electrically conductive on release of the dopant from the complex and/or removal of the solvent and/or Lewis base from the solution or composition. While we do not wish to be bound by any theory, it is believed that such dopant solute is derived from a compound, which upon addition to the polyaniline, ionizes the polymer via oxidative electron transfer or protonation with co-committent formation of a dopant solute species to form a charge transfer complex with polyaniline, which complex has a conductivity equal to or greater than about 10^{-10} ohm⁻¹cm⁻¹, preferably equal to or greater than about 10^{-4} ohm⁻¹cm⁻¹, more preferably equal to or greater than about 10^{-2} ohm⁻¹cm⁻¹ and most preferably equal to or greater than about 10^{-1} ohm⁻¹cm⁻¹.

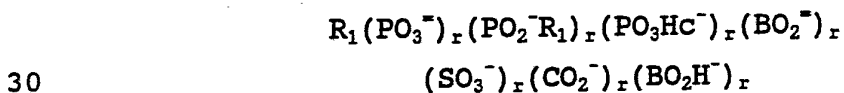
Dopants for use in the practice of this invention can vary widely and can be such materials which are known in the art for use in doping conjugated backbone polymers to form conductive or semiconductive polymers, as for example, those described in detail in U.S. Patent Nos. 4,442,187 and 4,321,114 which are hereby incorporated by reference. Illustrative of useful dopant species are oxidizing dopants. Oxidizing dopants are well known in the conductive polymer art, and any of such known oxidizing dopants can be used. Illustrative of useful oxidizing dopants are AsF₅, MoOCl₄, MoCl₅, PCl₅, POCl₃, PCl₃, AlCl₃, NO⁺ and NO₂⁺ salts (such as NOBF₄, NOPF₆, NOSbF₆, NOAsF₆, NOCH₃CO₂, NO₂BF₄, NO₂PF₆, NO₂AsF₆, NO₂SbF₆, and NO₂CF₃SO₂), HClO₄, HNO₃, H₂SO₄, benzoylperoxide, SO₃, Br₂, (FSO₃)₂, FSO₃H, and Fe(III) salts (such as Fe(BF₄)₃, FeBr₃, Fe(CH₃SO₃)₃, Fe(ClO₄)₃, FeCl₃, Fe(OTs)₃, and Fe(CF₃SO₃)₃ which give rise to doped polymers containing dopant solutes such as NO₃⁻, CH₃SO₃⁻, AlCl₄⁻, BF₄⁻, PCl₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻,

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CF_3SO_3^- , ClO_4^- , OTs^- , SO_3^- , $\text{C}_6\text{H}_5\text{CO}_2^-$, CH_3SO_3^- , FSO_3^- , and FeCl_4^- . Other useful oxidizing dopants include electrolyte salts such as LiClO_4 , LiBF_4 , LiAsF_6 , NaPF_6 , Bu_4NClO_4 , Bu_4NOTs , $\text{Bu}_4\text{NCF}_3\text{SO}_3$, LiCF_3SO_3 , AgOTs , and the like. Preferred oxidizing dopants for use in the practice of this invention are oxidizing dopants selected from the group consisting of MoOCl_4 , MoCl_5 , PCl_5 and Fe (III) salts such as $\text{Fe}(\text{ClO}_4)_3$, FeCl_3 , FeBr_3 , and $\text{Fe}(\text{CF}_3\text{SO}_3)_3$, and particularly preferred oxidizing dopants for use in the practice of this invention are dopants selected from the group consisting of MoOCl_4 , MoCl_5 , and Fe (III) salts such as $\text{Fe}(\text{ClO}_4)_3$, FeCl_3 , FeBr_3 , and $\text{Fe}(\text{CF}_3\text{SO}_3)_3$, and particularly preferred oxidizing dopants for use in the practice of this invention are dopants selected from the group consisting of MoOCl_4 , MoCl_5 , and FeCl_3 . Amongst these particularly preferred embodiments, most preferred oxidizing dopants are those embodiments in which the oxidizing dopant is FeCl_3 .

Illustrative of still other dopants are protonic acid dopants. Such dopants include inorganic acids such as hydrofluoric acid, hydriodic acid, hydrochloric acid, phosphoric acid, nitric acid, boric acid, fluoroboric acid, sulfuric acid, and the like.

Illustrative of still other useful dopants are protonic acids or acid derivatives thereof such as those containing anionic moieties of the formula:



and having one or more cationic moieties selected from the group consisting of:



wherein:

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R_1 is the same or different at each occurrence and is an organic radical or amino group;

M is a species having a positive charge equal to s ;

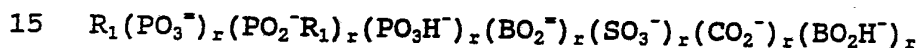
5 s is a positive integer equal to or greater than 1, preferably from 1 to about 8; and

r is the same or different at each occurrence and is 0 or a positive integer equal to or greater than 1, with the proviso that at least one of r is other than
10 0.

The R_1 group may vary widely and can be amine or a substituted or unsubstituted aliphatic radical such as alkyl, nitroalkyl, alkylamine, dialkylamine, perfluoroalkyl, alkoxyalkyl, alkoxy, haloalkyl and the
15 like, or a substituted or unsubstituted aromatic radical such as phenyl, indanyl, benzyl, biphenyl, benzhydryl, halophenyl, nitrophenyl, anthracyl, naphthyl, phenylamine, diphenylamine, phenanthryl and the like, or a substituted or unsubstituted
20 heteroaromatic or heteroaliphatic radical such as pyrrolidyl, piperidyl, benzofuryl, benzopyranyl, carbazoyl, triazyl, imidazolyl, isoxazolyl as the like. R_1 may also be a polymeric or oligomeric radical such as a polymer having recurring pendant phenyl groups in
25 the polymeric backbone substituted with sulfonic acid and derivatives thereof such as salts, phosphoric acid and derivatives thereof such as salts, phosphonic acid and derivatives thereof such as salts, sulfinic acid and derivatives thereof such as salts, carboxylic acid
30 and derivatives thereof such as salts, boric acid and derivatives thereof such as salts, or phosphonic acid and derivatives thereof such as salts; moieties such as sulfonated or phosphonated polystyrene,
poly(2-methylstyrene), poly(4-phenylstyrene),
35 poly(2-vinyl naphthalene), poly(vinyl benzoate),

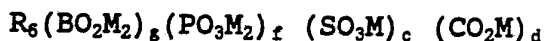
poly(benzyl methacrylate) and the like. In the particularly preferred embodiments of the invention, R_1 is an aromatic radical and in the most preferred embodiments R_1 is substituted or unsubstituted phenyl or naphthyl. The nature of the M^{+n} group may vary widely. For example, M^{+n} may be a non-metal cation such as Bu_4N^+ , H^+ , NO^+ , NO_2^+ , NH_4^+ and the like, or may be a metal cation such as Na^+ , Li^+ , Ag^+ , Ba^{+2} , Co^{+3} , Al^{+3} , Fe^{+3} and the like.

Preferred for use in the practice of this invention are organic acid dopants, more preferably totally or partially protonized forms of those having anionic portions of the formulas:

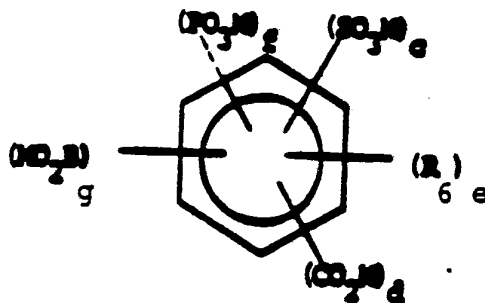


where R_1 and r are as described above.

More preferred for use as dopants in the practice of this invention are acids or acid derivatives of the formula:



or



wherein:

M is a metal or hydrogen or other non-metal cation;

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c is 0, 1, 2, 3 or 4;

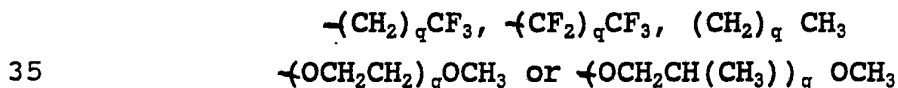
d is 0, 1 or 2;

e is 0, 1 or 2

f is 0, 1 or 2;

5 g is 0, 1 or 2, with the proviso that at least one of c, d, f and g is other than 0; and

R₆ is nitro, cyano, hydroxy, halo, amido, sulfinic acid, amino, alkylamino, dialkylamino, arylamino, diarylamino, sulfinate, phosphonic acid, phosphonate,
 10 phosphinic acid, phosphinate, alkylarylamino, substituted or unsubstituted alkoxy, alkoxyalkyl, aryl or alkyl having from 1 to about 30 carbon atoms wherein permissible substituents include perhaloalkyl, phenyl, alkoxy, halo, cyano, sulfate, haloalkyl, hydroxy,
 15 sulfonate, sulfonic acid, phosphate, phosphoric acid, boric acid, sulfinate, borate, phosphonic acid, phosphonate, phosphinic acid, phosphinate, sulfinic acid, quaternary ammonium, carboxylic acid, nitro, carboxylate and the like, or any R₆ may form an
 20 alkylene, alkynylene or alkenylene chain completing aromatic, heteroaromatic, alicyclic or heteralicyclic ring a fused-ring system which chain may include one or more oxygen, nitrogen, ester, sulfur, carbonyl or a combination thereof and/or which chain may be
 25 unsubstituted or substituted with one or more halo, phosphoric acid, hydroxy, boric acid, amino, alkylamino, dialkylamino, arylamino, alkyl diarylamino, alkylarylamino, nitro, cyano, sulfinate, phosphoric acid, sulfinic acid, phosphate, amido, alkoxy,
 30 carboxylate, phosphonic acid, phosphonate, sulfonate, borate, sulfonic acid or carboxylic acid groups, or R₆ is a moiety of the formula:

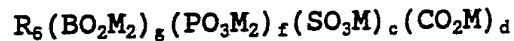


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wherein:

g is a positive whole number from 1 to about 10;
and

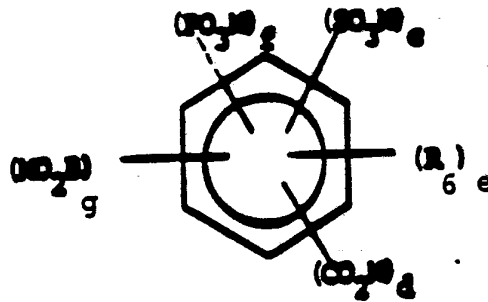
In the particularly preferred embodiment of this
5 invention, useful dopants are acids of the above
formula:



10

or

15



wherein:

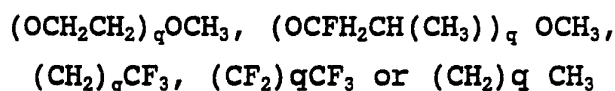
20 c is 0, 1, 2 or 3;
d is 0 or 1;
e is 0 or 1;
f is 0 or 1;
g is 0 or 1, with the proviso that at least one of
25 c, d, f and g is other than 0;

R₆ is amino, alkylamino, dialkylamino, arylamino,
diarylamino, arylalkylamino, alkyl, halo, hydroxy,
aryl, phenyl, haloalkyl, perhaloalkyl, cyano, nitro,
alkoxy, boric acid, borate, phosphonate, phosphonic
30 acid, carboxylate, sulfonate, phosphate, sulfonic acid,
carboxylic acid, phosphoric acid, sulfinic acid,
sulfinate or substituted or unsubstituted aryl alkyl
wherein permissible substituents are selected from the
group consisting of amino, alkylamino, dialkylamino,
35 arylamino, diarylamino, arylalkylamino, alkyl, halogen,

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hydroxy, phenyl, haloalkyl, amido, perhaloalkyl, cyano,
 nitro, alkoxy, boric acid, borate, phosphonate,
 phosphonic acid, carboxylate, phosphinic acid,
 sulfonate, phosphate, sulfonic acid, carboxylic acid,
 5 phosphinate, phosphoric acid, sulfinic acid or
 sulfinate or any R_6 may form an unsubstituted or
 substituted alkenylene chain completing a naphthalene,
 anthracene or phenanthracene fused ring system or R_6 is
 a moiety of the formula:

10



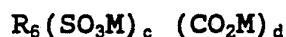
wherein:

q is a positive whole number from 1 to about 10;

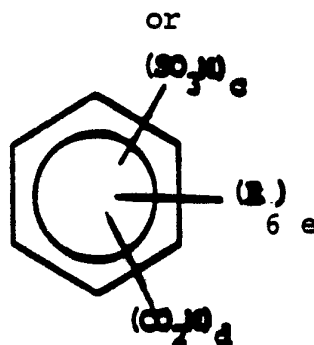
15

M is a cation such as NO^+ , NO_2^+ , $Fe(III)$, H^+ ,
 $Pb(IV)$, $Ce(IV)$, $Al(III)$, $Sr(IV)$, $Cr(VI)$, $Mn(VII)$,
 $Co(III)$, $Au(III)$, $Os(VIII)$, $Na(I)$, $Li(I)$, $K(I)$ or
 $Bu_4N(I)$.

In the most preferred embodiments of this
 20 invention, useful dopants are acids of the formula:



25



30

wherein:

c is 1, 2 or 3;

d and e are the same or different and are 0 or 1;

35

R_6 is fluoro, alkoxy, amino, biphenyl, alkylamino,

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arylamino, dialkylamino, diarylamino, alkylarylamino,
hydroxy, nitro, cyano, alkyl, phenyl, alkyl or phenyl
substituted with one or more alkyl, alkoxy, fluoro,
fluoroalkyl, sulfonic acid, sulfonate, perfluoroalkyl,
5 carboxylate, hydroxy, nitro, cyano, or carboxylic
groups or any R_6 may form an unsubstituted or
substituted alkenylene chain completing a naphthalene,
anthracene or phenanthracene fused system which may be
substituted with one or more alkyl, alkoxy, fluoro,
10 perfluoroalkyl, fluoroalkyl, sulfonic acid, sulfonate,
carboxylic acid, carboxylate, hydroxy, nitro or cyano
groups; and

M is a cation.

The following is a listing of dopants which are
15 useful in the practice of the most preferred
embodiments of this invention for formation of the
dopant solute.

1-anthracene sulfonic acid,
9-anthracene sulfonic acid,
20 2-phenanthracene sulfonic acid,
3-phenanthracene sulfonic acid,
9-phenanthracene sulfonic acid,
 $\text{NO}_2\text{CF}_3\text{SO}_3^-$,
 $\text{CF}_3\text{SO}_3\text{H}$,
25 perfluoro octyl sulfonic acid
perfluoro octyl carboxylic acid
octylsulfonic acid,
dodecylsulfonic acid,
cetyl sulfonic acid,
30 toluenesulfonic Acid (TsOH),
 $\text{Fe}(\text{OTs})_3$,
 $\text{Fe}(\text{CH}_3\text{SO}_3)_3$,
 $(\text{FSO}_3)_2$,
AgOTs,
35 Me_3SiOTs ,

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dodecylbenzene sulfonic acid,
naphthalene sulfonic acid,
benzene disulfonic acid,
benzene sulfonic acid,
5 1,3-benzene disulfonic acid,
2,5-dihydroxy-1,4-benzene disulfonic acid,
camphor sulfinic acid
naphthalene trisulfonic acid
dodecylbenzene sulfonic acid,
10 isoethionic acid,
1,5-naphthalene disulfonic acid,
nickel phthalocyanine tetrasulfonic acid,
phenyl phosphonic acid,
poly(vinyl sulfonic acid),
15 3-sulfopropyl acrylate,
3-sulfopropyl methacrylate,
sulfamic acid,
5-sulfosalicyclic acid,
(4,5-dihydroxy-1,3-benzene disulfonic acid),
20 vinyl sulfonic acid,
sulfanilic acid,
4-sulfophthalic acid,
sulfoacetic acid,
methyl orange,
25 sulfonated polystyrene,
sulfonated poly(α -vinyl naphthalene),
naphthol yellow,
naphthol blue black,
1,2-naphthoquinone-4-sulfonic acid,
30 naphthylazoxine S,
1-octane sulfonic acid,
t-butyl phosphonic acid,
ethyl phosphonic acid,
butyl phosphonic acid,
35 1,2-benzene disulfonic acid,

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4-octylbenzene sulfonic acid,
2-mesitylene sulfonic acid,
2,6-naphthalene disulfonic acid,
2-naphthalene sulfonic acid,
5 1,3,6-naphthalene trisulfonic acid,
1,3,7-naphthalene trisulfonic acid,
sulfonazo III acid,
biphenyl disulfonic acid,
biphenyl sulfonic acid,
10 1,8-dihydroxynaphthalene-3,6-disulfonic acid,
3,6-dihydroxynaphthalene-2,7-disulfonic acid,
4,5-dihydroxynaphthalene-2,7-disulfonic acid,
6,7-dihydroxy-2-naphthalene sulfonic acid,
1-naphthalene phosphoric acid,
15 1-naphthalene sulfonic acid,
1-naphthalene-5,7-dinitro-8-hydroxy sulfonic acid,
1-naphthalene-4-hydroxy sulfonic acid,
4-bromo benzene sulfonic acid,
4-hydroxy-5-isopropyl-2-methyl
20 benzene sulfonic acid
3,4-diamino benzene sulfonic acid
benzenephosphoric acid,
1,3,5-benzene trisulfonic acid,
2-methyl-5-isopropyl benzene sulfonic acid,
25 3,4-dinitro benzene sulfonic acid,
2-methoxy benzene sulfonic acid,
1-naphthalene-5-hydroxy sulfonic acid,
1-naphthalene-7-hydroxy sulfonic acid,
1-naphthalene-3-hydroxy sulfonic acid,
30 2-naphthalene-1-hydroxy sulfonic acid,
4-phenylamino benzene sulfonic acid,
1,6-naphthalene disulfonic acid,
1,5-naphthalene disulfonic acid,
1,3-naphthalene-7-hydroxy disulfonic acid, and
35 $\text{Me}_3\text{SiOSO}_2\text{CF}_3$.

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The amount of dopant included in the complex is not critical and may vary widely. In general, sufficient dopant is included in the complex such that an amount of dopant is released from the complex on
5 removal of the Lewis based and/or solvent from the complex and/or from the solution and/or composition such that the polyaniline is doped the desired extent, usually an amount such that the polyaniline is doped to a conductivity of at least about 10^{-10} ohm⁻¹cm⁻¹. The
10 upper level of conductivity is not critical and will usually depend on the type of aniline polymer employed. In general, the highest level of conductivity obtained is provided without unduly adversely affecting the environmental stability of the polymer. In the
15 preferred embodiments of the invention the amount of dopant employed is sufficient to provide a conductivity of at least about 10^{-6} ohm⁻¹cm⁻¹ and in the particularly preferred embodiments is sufficient to provide a conductivity of from about 10^{-4} ohm⁻¹cm⁻¹ to about
20 10^{+2} ohm⁻¹cm⁻¹. Amongst these particularly preferred embodiments, most preferred are those embodiments in which sufficient dopant is employed to provide a conductivity of at least about 10^{-1} ohm⁻¹cm⁻¹ to about 10^{+2} ohm⁻¹cm⁻¹, with amounts sufficient to provide a
25 conductivity from about 10^0 ohm⁻¹cm⁻¹ to about 10^{+2} ohm⁻¹cm⁻¹ usually being the amounts of choice.

The second component of the Lewis base/dopant complex is a Lewis base other than piperidine, an excess of which forms the third essential component of
30 the solutions of this invention and functions as a solvent or plasticizer. The Lewis base has several essential characteristics. The base has a pK_a greater than that of the polyaniline in the solution or the composition; the base must be capable of complexing
35 with the dopant in the electrically conductive

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polyaniline in the presence of the polyaniline to form a dopant/Lewis base complex; and the base must be a liquid under use conditions and be a solvent for the neutral undoped polyaniline and for the dopant/Lewis base complex.

The pK_a for the conjugate acid of the neutral (undoped) form of polyaniline is estimated to be in the range of 5.4 ± 0.4 . The pK_a for the conjugate acid of the neutral form of the polyaniline ($n = 4$, $m = 0$, $x = 2$, $y = 1$ and $Z > 1$ of the Formula III) is estimated to be in the range of 5.4 ± 0.4 . The pK_a of the conjugate acid of the Lewis base component of the complex is then preferably greater than 5.4., more preferably greater than 6 and most preferably greater than 9.

The Lewis base is such that it can be removed from the complex releasing the dopant to dope the polyaniline and preferably is removable from the solution or the composition. Lewis bases can be removed from the complex by any suitable means as for example chemical reaction, extraction, volatilization and the like.

The Lewis base is preferably a relatively volatile liquid which enhances the quality of conductive polyaniline articles formed from the solution or plasticized composition. As used herein, "volatile" means that the Lewis base is a liquid and has a boiling point of less than about 300 °C under use conditions preferably at atmospheric or autogenous pressure. The lower boiling point is not critical and usually those bases with the lowest boiling point are employed, provided that the base is in the liquid state under use conditions. The boiling point of the Lewis base may vary and is preferably less than about 250°C, more preferably from about 30 to about 150°C most preferably from about 35 to about 100°C

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Illustrative of suitable Lewis bases are secondary, primary and tertiary aromatic and aliphatic amine and phosphine compounds and polymers such as morpholine, 4-aminomorpholine, 2-picoline, methyl amine, pyridine, pyrrolidine, 4-picoline, piperazine, allylmethylamine, aniline, dibutylamine, diethylamine, diisopropyl amine, dipropylamine, benzylamine, cyclohexylamine, 1-aminopiperidine, 2,3-cylohexenopyridine, 1-(3-amino-propyl)-2-pipicoline, 1,1-dimethylhydrazine, amylamine propylamine, butylamine, ethylenediamine, N,N-dimethylethylene diamine, N,N'-dimethyl-ethylenediamine, 2-(ethylamino)ethanol, tetrahydrofurfurylamine, 2-(methylamino)pyridine, 1,2,3,4-tetrahydroisoquinoline, 2-imidazolidine, imidazole, ammonia, ethylene diamine, cyclohexylamine, hexamethylenediamine, and the like. Other suitable Lewis bases are amide and phosphoramidate compounds with pK_a greater than about 5.4 including 2-pyrrolidone, 2-oxazolidone, hexamethyl phosphoramidate and the like.

In the preferred embodiments of the invention, the Lewis base of choice is selected from the group consisting of amines and amides. In the most preferred embodiments of the invention, the Lewis base of choice is selected from the group consisting of amines and diamines. Such amines and diamines are most preferred because they are liquid at room temperature, complex with the preferred protonic acid dopants, are good solvents for the neutral polyaniline and for amine acid salts, and are relatively volatile so that on casting of the solution in the desired form they evaporate to form the desired article. Most preferred Lewis bases are amines and diamines such as pyrrolidine, 2-picoline, 2,3-cyclohexenopyridine, 2-(methylamino)pyridine, tetrahydroquinoline,

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2-(ethylamino)ethanol, N,N-dimethylethylene diamine, N,N'-dimethylethylene diamine, ethylene diamine, benzylamine, morpholine, tetrahydrofurfurylamine and the like.

5 The amount of Lewis base may vary widely but is usually at least an amount which is sufficient to complex with sufficient dopant to form the desired amount of the electrically conductive polyaniline on
10 release of the dopant from the complex, and which is sufficient to dissolve some amount of the dopant/Lewis base complex and the neutral polyaniline. In general, the greater the amount of dopant and polyaniline, and the lower the solubility of the dopant/Lewis base
15 complex and neutral polyaniline in the Lewis base liquid, the greater the amount of Lewis base required to form the dopant/Lewis base complex and to dissolve the complex and neutral polyaniline to the desired
20 extent; conversely, the smaller the amount of dopant and polyaniline and the greater the solubility of the dopant/Lewis base complex and non-conductive
 polyaniline in the liquid Lewis base, the smaller the amount of Lewis base required to complex the dopant and to solvate the desired amount of complex and
25 non-conductive polyaniline. Preferably, the amount of Lewis base is at least about 50 mole percent and more preferably at least about 100 mole percent based on
 total moles of polyaniline repeat units in the polyaniline.

 Preferred Lewis bases have a relatively strong
30 hydrogen bonding capability. The degree of hydrogen bonding capability can be assessed by a variety of techniques. One method which we find to be most predictive of suitable Lewis base liquids for the present invention is that Craver, J. Appl. Polym Sci.
35 14, p. 1755 (1970). This method is based upon the

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relative sound velocity (g_w) in paper wetted by the solvent, where water is arbitrarily assigned a value of 100. By this measure, suitable Lewis base liquids are those which have a hydrogen bonding capability greater than about 50, and more preferably greater than about 60.

Another useful measure of suitable Lewis base liquids is the solubility parameter of the liquid, also referred to as the Hildebrand Parameter (d). Preferred Lewis base liquids have a Hildebrand Parameter which lies in the range of from about 17 to about 29, more preferably in the range of from about 18 to about 26, and most preferably in the range of from about 19 to about 25.

An even more useful measure of suitable Lewis base liquids is based on dividing the Hildebrand Parameter of the liquid into separate contributions from dispersion (d_d), from polar interactions (d_p), and from hydrogen bonding interactions (d_h). In this scheme (which is disclosed in "Handbook of Solubility Parameters and Other Cohesion Parameters", by Allan F.M. Barton (CRC Press, 1983) pp 141-162, 94-110), the Hildebrand Parameter is related to the contributions from dispersion (d_d), polar interactions (d_p) and hydrogen bonding (d_h) ("Hansen Parameters") by the relation

$$d^2 = d_d^2 + d_p^2 + d_h^2$$

For example, in order to judge the suitability of a Lewis base liquid for polyaniline, we have empirically determined solubility parameters for the neutral (or base) form of the polyaniline which contains approximately a 50/50 ratio of amine to imine nitrogen linkages (Formula III where the ratio of x and y equals

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about 2 and $z > 1$) as follows:

$$\begin{aligned}d_d &= 17.4 \text{ MPa} \\d_p &= 8.5 \text{ MPa} \\5 \quad d_h &= 10.4 \text{ MPa} \\d &= 22.0 \text{ MPa}\end{aligned}$$

If we define a quantity (r) as:

$$10 \quad r = [4(17.4-d_d)^2 + (8.5-d_p)^2 + (10.4 -d_h)^2]$$

where d_d , d_p and d_h are the Hansen Parameters for a perspective Lewis base solvent for polyaniline base, then suitable solvents are those for which r is less than about 7, more preferably less than about 6, and most preferably less than about 5.

When employing mixtures of Lewis base solvents, an average set of Hansen Parameters can be calculated using the techniques of matrix algebra. Suitable solvent mixtures are then those whose average values of d_d , d_h , and d_p lead to a value of r which is less than about 7.

In addition to the essential polyaniline, Lewis base/dopant complex and liquid Lewis base, the solutions and compositions of this invention can include other optional ingredients which either dissolve or do not dissolve in the solution. The nature of such optional ingredients can vary widely, and include those materials which are known to those of skill in the art for inclusion in polymer articles. In the case of dissolvable components, materials may be present which alter the physical or mechanical properties of either the solution or the articles eventually cast from the solution. Examples of such materials include salts such as LiCl, LiBr, LiCF₃SO₃,

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LiCH₃(C₆H₄)SO₃, KCF₃(CF₂)₂SO₃, and the like which may promote solubility or provide dopant anions to the polyanilines. Other examples of such materials include other conventional polymers such as polycarbonate,
5 polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl alcohol, poly(metaphenylene isophthalamide), polyethylene oxide, polystyrene, nylon 6, cellulose, nylon 66, nylon 12, poly(1,4-cyclohexylidene dimethylene terephthalate),
10 nylon 6,10, nylon 4, poly(phenylene sulfide), poly(ethylene terephthalate), poly(2,6-dimethyl-1,4-phenylene oxide), poly(2,6-diphenyl-1,4-phenylene oxide), sulfonated polystyrene, poly(acetate butyrate),
15 poly(4-aminobutyric acid), poly(hexamethylene adipamide), poly(p-phenylene terephthalamide), poly(tetrafluoroethylene), poly[methane bis(4-phenyl)carbonate], poly(p-phenylene terephthalamide), polypropylene, polyethylene,
20 cellulose acetate, poly(ethylene oxybenzoate), poly(p-hydroxy benzoate), polyphenylene oxide, polyvinyl alcohol, and the like. These fourth components include other conductive polymers, such as conjugated backbone polymers as for example
25 polyacetylene, poly(dialkoxy phenylene vinylene), poly(thiophene) poly(thienylene vinylene), poly(pyrrole), poly(furan), poly(phenylene), poly(phenylene vinylene) and the like which may become conductive upon doping, graphite, metal conductors,
30 reinforcing fibers and inert fillers (such as clays and glass). In the case of nonsoluble fourth components, materials may be present which either fill or form a substrate for the conductive polymer cast from the solution.

35 The proportion of polymer, complex and solvent in

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the solution or plasticized composition of this invention containing the substituted or unsubstituted polyaniline homopolymer or copolymer, the Lewis base/dopant complex and the Lewis base solvent are not
5 critical and can vary widely, such that the composition varies from a solution to a plasticized composition. However, the following guidelines are believed important for achieving solutions and plasticized compositions particularly useful in the present
10 invention. In general, the amount of solvent as a proportion of the amount of solution is not believed to be critical, since any amount as a liquid will form at least a viscous gel or a plasticized composition with the polymer. These viscous gel embodiments of the
15 invention are particularly useful for silk screening conductive circuitry and for applying thick film coatings on substrates. For other applications, it may be preferred, however, to use sufficient liquid to lower the viscosity of the gel composition or solution
20 to a point where it flows at least sufficiently to conform to a container shape or mold in a reasonably short period of time, e.g., in 30 minutes or less. Preferably, the solvent is present in sufficient amounts to lower the viscosity of the solution to less
25 than about 10,000 centipoise or preferably from about 1 to about 1000 centipoise.

The method of forming the solutions or plasticized compositions of this invention is not critical and can vary widely. For example, one preferred method of
30 forming the present solution and plasticized composition containing the substituted or unsubstituted polyaniline or copolymer is to add the polyaniline doped with a suitable dopant such as toluenesulfonic acid to a suitable Lewis base or combination of Lewis
35 bases such as pyrrolidine in a mixing vessel. While we

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do not wish to be bound by any theory, it is believed that a portion of the Lewis base complexes with the dopant for the polyaniline forming the Lewis base/acid complex and neutral polyaniline. Another portion of the Lewis base then dissolves the complex and the neutral polyaniline or plasticizes the polyaniline. In use, the solution can be placed in any desired configuration, as for example on the surface of a substrate, in the shape of an article and the like. As the Lewis base is removed such as by volatilization, the complex decomposes releasing the dopant which then dopes the polyaniline forming the doped electrically conductive polyaniline in the desired configuration. As used herein, "to complex" means to form an association between the dopant and Lewis base such as a conjugate acid base pair of the Lewis base and the acid dopant of the electrically conductive polyaniline.

Another preferred method is to dissolve and react, simultaneously, the undoped polymer, the dopant and the Lewis base as a liquid. Thus, for example, by introducing an undoped powdered polyaniline such as a polyaniline of the Formula III, $y > 1$, $x > 1$ and $z > 1$, or a mixture of a polyaniline of the Formula III ($x = 0$ and y and $z > 1$) (pernigraniline form) and a polyaniline of the Formula IV (leuco form), a suitable Lewis base solvent, such as propylamine, morpholine or pyrrolidine as a liquid Lewis base and a dopant such as toluene sulfonic acid, dodecylbenzene sulfonic acid, and naphthalene disulfonic acid as a solid into a mixing vessel, a solution of the polymer and dopant/Lewis base complex is quickly formed, from which conductive polymer can be cast. Similarly, undoped polyaniline in the leuco form of the Formula IV can be added to a mixing vessel with a suitable Lewis base such as pyrrolidine or morpholine and a suitable oxidizing dopant such as NOSbF_6 , FeCl_3

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or a mixture of an acid and an oxidizing agent such as a mixture of toluenesulfonic acid and oxygen to form the claimed solution or composition from which the conductive polyaniline can be cast. The conditions of such mixing are not critical, provided that sufficient toluenesulfonic acid is used to dope the desired quantity of polyaniline and sufficient morpholine or pyrrolidine is employed to reduce the viscosity of the solution to manageable levels. An alternate technique of preparing the solution or plasticized composition of this invention containing the doped polymer is to mix first the polyaniline and the Lewis base solvent, and thereafter add the dopant to the solution. Thus, for example, if undoped polyaniline (base) powder is admixed with a Lewis base solvent such as pyrrolidine, morpholine or the like, the addition of a suitable dopant to this suspension, such as toluenesulfonic acid, dodecylbenzenesulfonic acid, and naphthalenedisulfonic acid causes the Lewis base solvent and dopant to complex and if the dopant itself is insoluble, almost instantaneously thereafter, causes the complexed dopant and base to go into solution or from the composition.

Various methods are contemplated for using the solution or plasticized composition of the present invention. The Lewis base solvent can be removed from the solution or plasticized composition through use of any conventional solvent removal method but is removed preferably by evaporation to form a conductive polyaniline. Alternatively, the Lewis base solvent can be removed by extraction with an extractant which the Lewis base solvent is substantially more soluble than the doped polymer.

As will be appreciated by those skilled in polymer processing, the ability to form polymer articles by

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removing a solvent from a solution or plasticized composition enables one to prepare articles of a wide variety of shapes and sizes. Thus, for example, by removing volatiles from the present solution or plasticized composition spread on a surface, films and coatings of any desired thickness can be prepared. Extremely thin films and coatings can be prepared which are substantially transparent. By extruding the solution or plasticized composition through a die, fibers or films can be made. Similarly, by removing volatiles from the solution or plasticized composition in a mold of various shapes, shaped articles conforming in shape to the mold can be prepared. It will be appreciated that some shrinkage might occur between the solution or plasticized composition in it's last flowable state to the final article, but such shrinkage is conventionally accounted for in molding polymers from solution or plasticized composition. It is also contemplated that, once a solution or plasticized composition is formed, a partial or substantial removal of solvent will occur prior to placing the solution or plasticized composition on a surface or in a mold, with the final removal of solvent occurring on the surface or in the mold. It is contemplated that, if additional soluble components are introduced into the solution, they will, unless also volatile, be present in the shaped article formed. If the additional component is a non-volatile liquid, then the removal of very volatile components may leave a new liquid or plasticized form of doped conducting polymer or undoped neutral polymer. If the additional components are volatile, then foamed or expanded cellular forms of the polymer may be formed.

In the event that additional non-soluble components are present (or suspended) in the solution,

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the doped polymer will form around, or be filled with, the insoluble material. If, for example, the additional components are glass fibers, the relative amounts of fibers and doped polymer remaining will
5 cause either the polymer to be fiber-filled, the fibers to be polymer coated or impregnated, or some intermediate composite of fibers and doped polymer to be formed. In the case of systems wherein the amount of non-soluble component greatly exceeds the doped
10 polymer remaining, individual particles or shapes of non-soluble components coated or impregnated with doped polymer will be formed.

Examples of articles formed from non-soluble components and the present polymer solutions include
15 conductive polymer coated-housings for sensitive electronic equipment (microprocessors), infrared and microwave absorbing shields, flexible electrical conducting connectors, conductive bearings, brushes, semiconducting junctions, photocells, antistatic
20 materials for packaging electronic components, carpet fibers, waxes and tiles for floors in computer rooms and an antistatic spray finisher for plastics, and thin, optically transparent antistatic finishes for CRT screens, aircraft or automobile display panels, and the
25 like.

A third application for the present polymer solutions is in the doping of other materials, and especially other conjugated backbone polymers which could also be doped by the electron-acceptor dopant
30 alone. Such doping may occur as a part of the process of casting the polymer solution onto the second polymer article, but may also be accomplished without, necessarily, casting the conductive polymer from the solution.

35 The following specific examples are present to

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illustrate the invention and are not to be construed as limitations thereon.

EXAMPLE 1

5 Into a solution containing 1770ml of H₂O, 50g of aniline (0.54 mole) and 172g of p-toluenesulfonic acid (0.90 mole), was added dropwise at 15°C a solution of ammonium persulfate (153.4g in 336.5 ml H₂O) over a period of 40 minutes. The reaction was then allowed to
10 continue at 15°C for 0.5 hours.

The resulting solid precipitate was collected and washed with 6L of an aqueous toluene sulfonic acid solution (10 wt%) and then by 3L of methanol. The resultant blue-black solid was dried in air for 25hrs
15 and dried at 130°C for 3hrs under dynamic vacuum to give poly(anilinium tosylate) as a green powder.

The yield was 78g. The intrinsic viscosity (in H₂SO₄, at 25°C) was 0.66dl/g. Elemental analysis of the dried green powder gave:

20 C:64.37%(wt%) H:4.86% N:8.59%
 S:8.40% O:13.51%
 moisture: less than 0.8 wt%.

The conductivity of the dried and pressed pellet was 5/Scm⁻¹ by the co-linear four probe method. The
25 conductivity of the moisture-saturated pellet was 20/Scm⁻¹.

EXAMPLE 2

Various amines were evaluated for their ability to
30 dissolve the poly(anilinium tosylate) prepared in Example 1. The experiments were conducted by mixing 2 mg of poly(anilinium tosylate) with 1 ml of amine. The results are set forth in the following Table 1.

In Table 1, the abbreviations are defined as
35 follows:

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- (a) "VS" is very soluble.
 (b) "S" is soluble.
 (c) "SS" is slightly soluble.
 (d) "I" is insoluble.

5

TABLE 1

	<u>Amine Liquid</u>	<u>Solubility</u>
	triethylamine	I
	tripropylamine	I
10	tributylamine	I
	triisobutylamine	I
	pyridine	I
	2-picoline	S
	3-picoline	I
15	4-picoline	SS
	2,6-lutidine	I
	2,3-cyclopentenopyridine	I
	2,3-cyclohexenopyridine	S
	2,4,6-collidine	I
20	2-bromopyridine	I
	2-(methylamino)pyridine	SS
	1-(3-aminopropyl)-2-pipecoline	S
	quinoline	I
	isoquinoline	I
25	tetrahydroisoquinoline	SS
	tetrahydroquinoline	I
	imidazole	S
	aniline	I
	2-ethylaniline	I
30	N-methylaniline	I
	diethylamine	I
	dipropylamine	I
	diisopropylamine	I
	dibutylamine	I
35	diisobutylamine	I

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TABLE 1 CON'TD

	<u>Amine Liquid</u>	<u>Solubility</u>
	dipentylamine	I
5	N,N-dimethylethylenediamine	S
	N,N'-dimethylethylenediamine	S
	ethylenediamine	S
	1,1-dimethylhydrazine	SS
	pyrrolidine	VS
10	morpholine	S
	2-pyrrolidone	S
	N-methyl-2-pyrrolidone	I
	hexamethylphosphoramide	S
	1,1,3,3-tetramethyl urea	I
15	N-methylpiperidine	I
	1-aminopiperidine	SS
	tetrahydrofurfurylamine	S
	butylamine	SS
	propylamine	SS
20	benzylamine	S
	piperidine	S
	2-(ethylamino)ethanol	S

EXAMPLE 3

25 A piece of colorless poly co(trichlorofluoro ethylene/tetrafluoroethylene) film (7.6 x 7.6 cm) was dip coated with a 0.8 wt% solution of poly(anilinium tosylate) in pyrrolidine to provide a polyaniline-coated blue film. The coated film was then

30 let stand in air at ambient temperature. The color of the film changed with time from blue through blue-green, to green. These results showed that the polyaniline coating returned to its conductive state (green) from its originally non-conductive state (blue)

35 as the amine solvent gradually evaporated. The surface

resistance of the film was evaluated as a function of time using the co-linear four-probe method. The surface resistance of the film indeed changed as the color changed and the greener the coating, the lower the surface resistance of film. The results are summarized in the following Table 2.

TABLE 2

	<u>TIME AFTER COATING</u>	<u>COLOR</u>	<u>SURFACE RESISTANCE (ohm/sq)</u>
10	10 min	blue	$>10^{12}$
	5 h	blue-green	2×10^{10}
	1 day	light-green	6×10^9
	4 days	green	1×10^8
	10 days	deeper green	5×10^6

EXAMPLE 4

Using the dip coating technique of Example 3 other plastic films, such as poly(ethylene terephthalate) (PET), (poly(co-tetrafluoro ethylene/chlorotrifluoroethylene) (PTFE/CTF), Nylon 6 and polycarbonate (PC) were dip coated with poly(anilinium tosylate) and the surface resistance of the coated film evaluated.

The experiments were conducted by dip coating the plastic films (5 x 5 cm) with a 0.8 wt% solution of poly(anilinium tosylate) in pyrrolidine. The surface resistances were measured 10 days after coating. The results are summarized in the following Table 3.

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TABLE 3

	<u>BASE FILM</u>	<u>SURFACE RESISTANCE</u> <u>(ohm/sq)</u>
	PTFE/CTF	4.8×10^6
5	Nylon-6	2×10^7
	PET	4.6×10^5
	PC	1×10^5

EXAMPLE 5

10 A piece of poly (co-tetrafluoroethylene
chlorotrifluoroethylene) film (10 x 10 cm) was coated
with 1.6wt% solution of poly(anilinium tosylate) in
pyrrolidine by a transfer coating technique. In this
technique, polyaniline solution was homogeneously laid
15 down on the plastic film by a metal screen roller which
contains hundreds of regularly engraved cells per
square inch. The coated blue film was then heat-dried
to give a green film. SIMS (secondary Ion Mass
Spectroscopy) studies measured the thickness of the
20 polyanilinium tosylate) coating which was 0.48 microns.
XPS (X-ray photoelectron spectroscopy) studies
conducted 10 days after coating, measured the ratio of
nitrogen to sulfur in the green coating to be about 2
to 1, a ratio which was approximately equal to the N/S
25 mole ratio of the original doped polyaniline powder of
Example 1.

EXAMPLE 6

30 A piece of polyethylene terephthalate film (7.5 x
10 cm) was coated with the same solution as in Example
5 by a transfer coating technique. The film was blue.
Using the procedure of Example 3, the surface
resistance was measured right after coating and was
greater than 10^{12} ohm/sq. The evaporation of the amine
35 solvent residue was accelerated by a heat treatment.

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The surface resistance measured after heat treatment was 5×10^7 ohm/sq. The elimination of the amine solvent residue was forced to completion by soaking the coated film in a 10wt% aqueous solution of p-toluene sulfonic acid for 15 minutes. The surface resistance measured after the soaking treatment was 2×10^5 ohm/sq.

EXAMPLE 7

Calculations were carried out to suggest suitable solvents for use with unsubstituted undoped polyaniline using group additive contributions for determining individual components of the Hildebrand parameter (d). In the representations of Hansen, the following nomenclature is used

15

A) Nomenclature

(1) d is the Hildebrand Parameter (units: MPa) and is related to the Hansen Parameters (d_d , d_p , d_h) as follows:

20

$$d^2 = d_t^2 = d_d^2 + d_p^2 + d_s^2$$

(2) d_d is the contribution from dispersion interactions.

25

(3) d_p is the contribution from polar interactions.

(4) d_h is the contribution from hydrogen bonding interactions.

30

These components of d can be estimated from tabulated group molar attraction contributions from dispersion interactions (F_d), and polar interactions (F_p) and from the cohesive hydrogen bonding energy

35

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(U_h). This analysis led to the estimate for the solubility parameter of the undoped (base) form of polyaniline given below:

$$\begin{aligned} 5 \quad d_d &= 18.5 \text{ MPa} \\ d_p &= 4.1 \text{ MPa} \\ d_h &= 7.4 \text{ MPa} \end{aligned}$$

$$d = (d_d^2 + d_p^2 + d_h^2) = 20.3 \text{ MPa}$$

10

An estimate of the Hildebrand Parameter based on group contributions to the heat of vaporization gave $d = 23.8$ MPa. Solvents which dissolve or swell undoped polyaniline will be those whose own solubility parameters are close to those characteristic of the polymer. Polar solvents with relatively strong hydrogen bonding were suggested.

EXAMPLE 8

20 A series of potential solvents with significant polar and hydrogen bonding contributions were tested with polyaniline which had been synthesized as in Example 1 and then undoped (neutralized) by treatment with an aqueous solution of sodium carbonate. Solvents
25 which were demonstrated to dissolve undoped polyaniline are shown in Table 4 below and in Figure 1.

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TABLE 4
Observed Solvents For Unsubstituted
Undoped Polyaniline

5	<u>Liquid</u>	<u>BP(°C)</u>	<u>g_w</u>	<u>e</u>	<u>m</u>	<u>d</u>
	Morpholine	129	200.0	7.3	5.0	22.1
	Pyridine	115	80.0	12.3	7.3	21.7
	Pyrrolidine	88	-	-	5.3	-
	N-methylpyrrolidone	204	-	32.0	-	23.7
10	Dimethylformamide	158	68.0	37.0	11.2	24.1
	Dimethylhydrazine	64	-	-	-	19.8
	Propylamine	48.5	-	5.3	4.7	19.7
	Butylamine	78	-	5.3	4.7	18.6
	Picoline	129	-	9.8	6.3	20.9
15	Aniline	182	94.0	6.9	5.0	22.6
	Quinoline	114	-	9.0	7.6	22.0
	2-Pyrrolidone	245	-	-	7.7	28.4
	Dimethylacetamide	165	87.0	38.0	12.7	22.7
	Tetramethylurea	177	-	23.1	13.0	21.7
20	Ethylenediamine	117	-	12.9	6.6	25.3
	Hexamethyl Phosphoramidate	235	-	30.0	17.6	23.2

25

"--" means that the data is not available.

The parameters listed in Table 4 are as follows:
 "B.P." is the boiling point in °C, "g_w" is the relative
 30 sound velocity in the paper method by the solvent
 (water = 100) which is a measure of hydrogen bonding
 capability), "e" is the dielectric constant relative to
 the permittivity of free space ($\epsilon_0 = 8.854 \times 10^{-12}$
 F/m), "m" is the dipole moment in 10^{-30} Cm, and "d" is
 35 the Hildebrand (solubility) parameter in MPa . The

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data were used to establish an empirical measure of the solubility parameters which characterize the interactions of undoped polyaniline according to a method developed by Hansen. Values of the Hansen parameters for the solvents used were taken from "Handbook of Solubility Parameters and other Cohesive Parameters" by A.F.M. Barton (CRC Press, 1983). When multiple literature source were found with widely differing values, those sets of values were taken which were the closest to those theoretically predicted for the given solvent.

B) Hansen's Method for Solubility Parameter:

(1) In this method, the polymer is characterized as having a "solubility sphere" in a three dimensional space defined by the coordinates d_d , d_p , d_h . The center point of the solubility sphere is $(2d'_d, d'_p, d'_h)$ and the radius of the sphere is R.

20

(2) An interaction distance for a given solvent is defined as:

$$r = [4(d_d - d'_d)^2 + (d_p - d'_p)^2 + (d_h - d'_h)^2]$$

25

(3) The polymer should be soluble in a given solvent when $r < R$.

C) Hansen Method with Polyaniline and Various Solvents

(1) The following values of the Hansen Parameters (all in units of MP_a) were determined for polyaniline by sampling Hansen Space (i.e., the range of possible values for d_d , d_p and d_h) with the series of solvents in Table 5.

35

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(i) $d'_d=17.4$ (ii) $d'_p=8.5$ (iii) $d'_h=10.4$ (iv) $R=6$

5

(v) $d=22.0$

The following Table 5 sets forth the Hansen Parameters of various liquids which have been shown to be solvents for unsubstituted and undoped polyaniline base.

Table 5

10 Hansen Parameters of Solvents For Unsubstituted
Undoped Polyaniline Base

Liquid	d_d	d_p	d_h	r
Morpholine	16.0	11.4	10.1	4.0
15 Pyridine	17.6	10.1	7.7	3.2
N-methylpyrrolidone	16.5	10.4	13.5	4.4
Dimethylformamide	17.4	13.7	11.3	5.3
Dimethylhydrazine	15.3	5.9	11.0	5.0
Propylamine	13.9	9.3	7.2	4.1
20 Butylamine	13.6	8.1	8.0	4.9
Picoline	18.2	7.8	6.8	4.0
Aniline	19.4	5.1	10.0	5.3
Quinoline	19.4	7.0	7.6	5.1
2-Pyrrolidone	19.4	17.4	11.3	99.8
25 Dimethylacetamide	16.8	11.5	10.2	3.2
Tetramethylurea	16.8	8.2	11.1	1.4
Ethylene Diamine	16.6	8.8	17.0	6.8
Hexamethyl phosphoramide	18.3	8.6	11.3	2.0

30

The average values of the Parameters, d_d , d_p and d_h , in Table 5 determine the approximate center of the solubility sphere ($2d'_d$, d'_p , d'_h) and the span of r values determine the approximate radius, R .

35

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(2) Examples:

(i) N-methyl Pyrrolidone (NMP):

$$d_d=16.5, d_p=10.4, d_h=13.5$$

5

$$r=[4(16.5-17.4)^2 + (10.4-8.5)^2 + (13.5-10.4)^2] = 4.1$$

Since $r < R$, N-methylpyrrolidone is predicted and found to be a solvent.

10

EXAMPLE 9

A number of prospective solvents were examined and found to be non-solvents for undoped polyaniline and for poly(anilinium tosylate). These non-solvents are summarized in the following Table 6 along with the predicted interaction distance (r) of the Hansen Method.

15

20

TABLE 6
Non-Solvents of Polyaniline Tosylate
and Polyaniline Base Non-Solvent

	Non-Solvent	α_x	m_p	d	d_d
25	Dipropylamine	-	-	16.3	14.0
	Triethylamine	-	2.2	15.3	14.6
	Tributylamine	-	2.3	15.9	15.1
	Diisopropylamine	-	-	15.2	13.8
	N-Ethylaniline	-	-	21.5	17.1
30	4-Butylaniline	-	-	20.4	16.9
	Dipropylamine	6.2	5.8	8.5	
	Triethylamine	3.7	1.9	11.3	
	Tributylamine	2.8	4.0	9.7	
	Diisopropylamine	6.2	2.0	11.3	
35	N-Ethylaniline	10.5	7.7	3.4	
	4-Butylaniline	9.1	6.6	4.0	

"-" denotes tht the data is not available.

40

The Hansen Parameters of these Lewis base non-solvents are graphically compared to those for the Lewis base solvents of Example 8 in Figure 2. The

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majority of non-solvents in Table 6 have, as expected $r < R$ ($R = 6$ from Example 8); however, there are also a few exceptions. Such exceptions are frequently seen and can stem from inaccurately known Hansen Parameters.

- 5 Reference to Table 4 reveals that Lewis base solvents of polyaniline possess a hydrogen bonding parameter, g_w , in cases where it is known, that is greater than 68.

10

EXAMPLE 10

- Doped polyaniline powder was prepared as in Example 1 and dissolved as in Example 2. The following Table 7 indicates the correlations found for solvents of polyaniline tosylate between the physical
 15 parameters: Boiling Point (B.P.), Hydrogen Bonding (g_w), Dielectric Constant (ϵ), Dipole Moment (m_p) Hildebrand Parameter (d) and pK_a .

TABLE 7

20

Single Solvents for Polyaniline Tosylate

Solvent	B.P.	g_w	ϵ	m_p	d	pK_a
Morpholine	129	200.0	7.3	5.0	22.1	8.3
Pyrrolidine	88	-	-	5.3	-	11.3
Piperidine	106	89.0	5.8	4.0	19.3	11.1
25 Propylamine	48.5	-	5.3	4.7	18.2	10.8
Butylamine	78	-	5.3	4.7	17.7	10.8
2-Pyrrolidone	245	-	-	7.7	28.4	-
Ethylenediamine	117	-	12.9	6.6	25.3	10.1
Hexamethylphosphoramide	235	-	30.0	17.6	23.2	-
30 Benzylamine	185	-	-	-	-	9.3
2-(methylamino)pyridine	201	-	-	-	-	-
2-Picoline	129	-	9.8	6.3	20.9	-
4-Picoline	145	-	-	8.6	-	6.0
Imidazole	256	-	-	-	-	7.1
35 1,1-Dimethylhydrazine	64	-	-	-	19.8	-

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Tetrahydrofurfurylamine	154	-	-	-	-	-
Tetrahydroisoquiniline	233	-	-	-	-	-
1-Aminopiperidine	150	-	-	-	-	-
2-(Ethylamino)ethanol	170	-	-	-	-	-

5

"-" indicates that the data is not available.

These solvents were moderately polar with dipole
moment, μ , equal to or greater than 4.0×10^{-30} Cm and
10 were all characterized by relatively high basicity (pK_a
> 6).

WHAT IS CLAIMED IS:

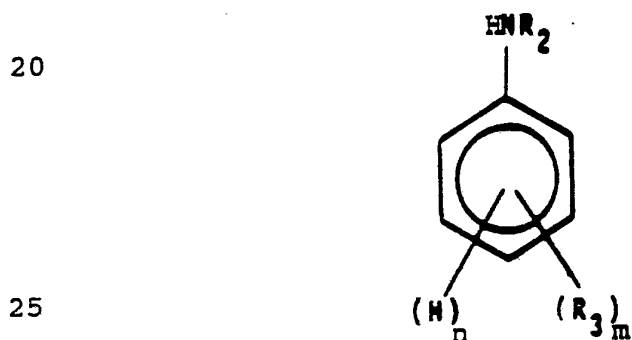
1. A non-electrically conductive solution or plasticized composition comprising:

(a) one or more substituted or unsubstituted
5 polyanilines;

(b) one or more Lewis base/dopant complexes comprising a liquid Lewis base other than piperidine which has a pK_a greater than that of said polyanilines; and which is a solvent for said complexes and said
10 polyaniline, and said dopant capable of doping said polyaniline to form electrically conductive polyaniline on release of said dopant from said complex; and

(c) said liquid Lewis base.

2. A solution according to claim 1 wherein
15 polyaniline is a homopolymer or copolymer doped with one or more dopant solvents comprising a substituted or unsubstituted polyaniline of the type derived from polymerizing an aniline of the formula:



n is an integer from 0 to 5;

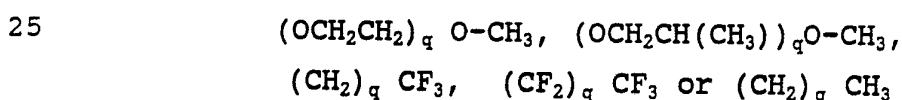
m is an integer from 0 to 5, with the proviso that the sum of n and m is 5;

30 R_2 is the same or different at each occurrence and is R_3 substituents or hydrogen; and

R_3 is deuterium, nitro, phosphinic acid, cyano, amino, phosphonic acid, sulfonic acid, boric acid, phosphoric acid, sulfonate, borate, phosphonate,
35 phosphinate, phosphate, sulfinic acid, sulfinate, hydroxyamino, carboxylic acid, halogen, carboxylate, cyano, or substituted or unsubstituted alkyl, alkenyl,

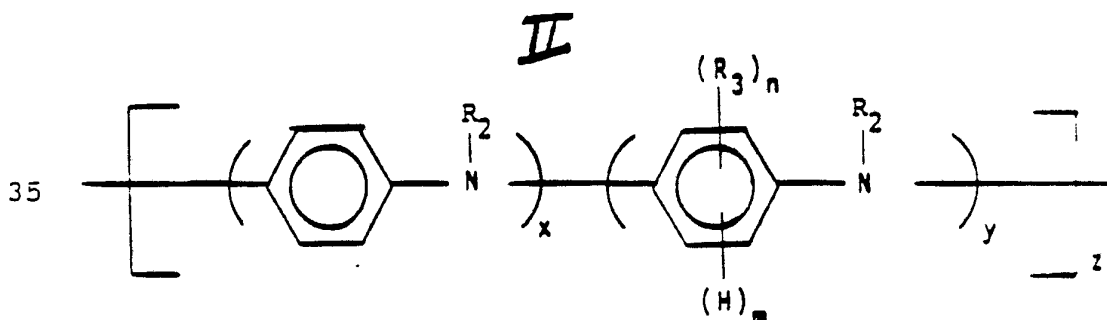
- 55 -

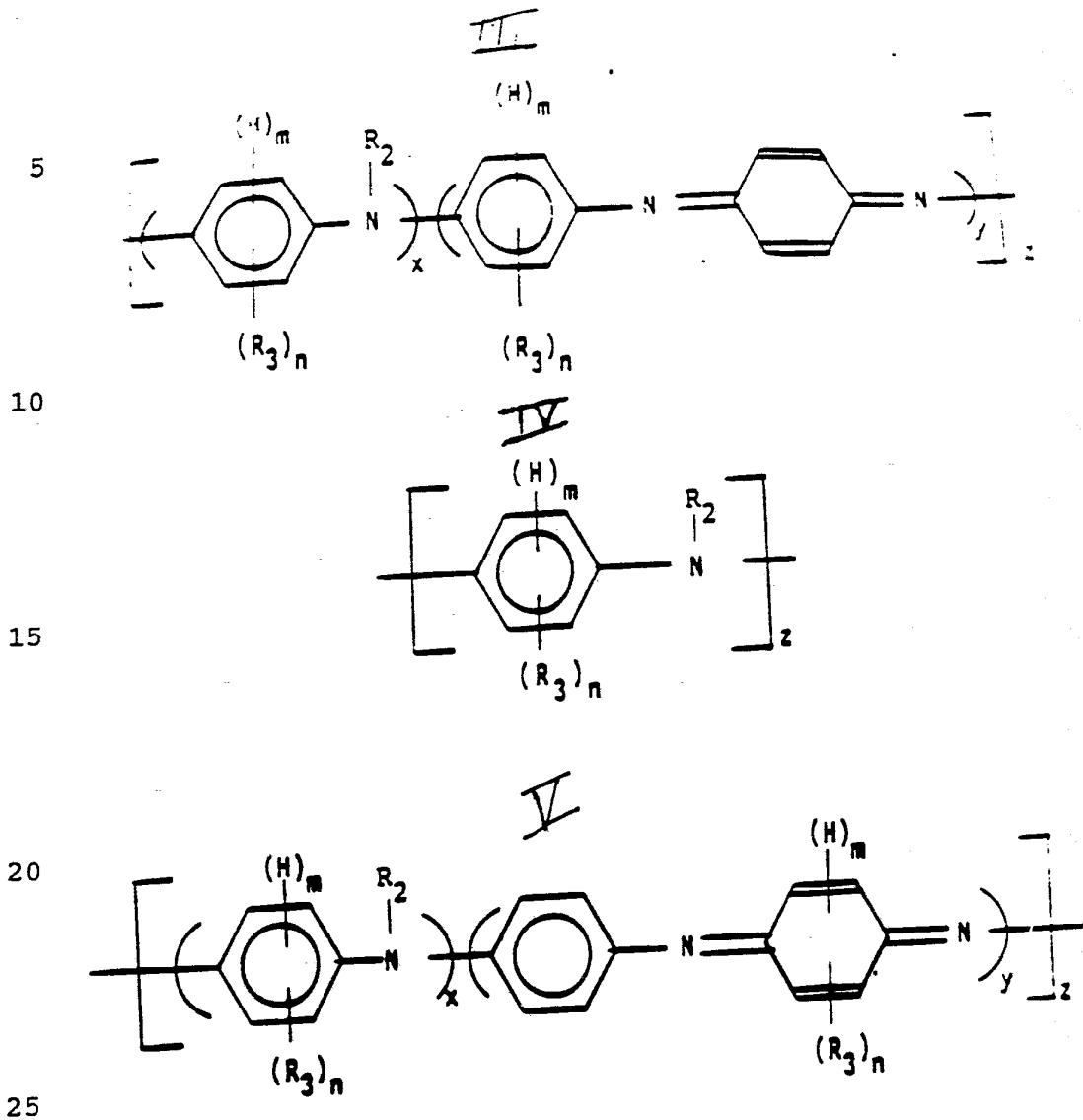
alkoxy, cycloalkyl, hydroxy, cycloalkenyl, alkanoyl, alkylthio, aryloxy, alkylsilane, alkylamino, dialkylamino, arylamino, diarylamino, alkylarylamino, alkylthioalkyl, alkylaryl, arylalkyl, aryloxy, 5 alkylthioalkyl, alkylaryl, arylalkyl, alkylsufinyl, alkylsufinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, arylsufinyl, or alkoxycarbonyl, or any two R_3 substituents or any one R_3 substituent and any one R_2 substituent taken together may form a substituted or 10 unsubstituted alkylene, alkenylene or alkynylene chain completing a 3, 4, 5, 6, 7, 8, 9 or 10 membered aromatic, heteroalicyclic, heteroaromatic or alicyclic carbon ring, which ring may optionally include one or more divalent ester, carbonyl, nitrogen, sulfur, 15 sulfinyl, sulfonyl or oxygen, wherein permissible substituents are one or more phosphonic acid, sulfonic acid, boric acid, sulfinic acid, sulfinate, phosphoric acid, quaternary ammonium, sulfonate, borate, carboxylate, phosphonate, amino, alkylamino, alkoxy, 20 dialkylamino, arylamino, diarylamino, alkylarylamino, phosphate, amido, carboxylic acid, halogen, nitro, hydroxy, cyano or epoxy moieties or R_3 is an aliphatic moiety having repeat units of the formulas:



wherein q is a positive whole number.

3. A solution according to claim 2 wherein said 30 homopolymer or copolymer is of the formulas II to V:





wherein:

x is an integer equal to or greater than 1;

30 y is equal to or greater than 1, with the proviso that the ratio of x to y is greater than about 0.5;

z is equal to or greater than about 1;

n is an integer from 0 to 4;

35 m is an integer from 0 to 4 with the proviso that the sum of n and m is 4;

R₂ is the same or different at each occurrence and is R₃ substituents or hydrogen;

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R_3 is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, amino alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, 5 alkylsulfonyl, aryl, arylthio, arylsulfinyl, alkoxy carbonyl, phosphinic acid, phosphonic acid, alkylsilyl, boric acid, arylsulfonyl, carboxylic acid, halogen, hydroxy, phosphate, sulfonate, phosphonate, borate, phosphinate, carboxylate, nitro, cyano, 10 sulfonic acid, phosphoric acid or alkyl or alkoxy substituted with one or more sulfonic acid, carboxylic acid, sulfinic acid, phosphoric acid, boric acid, sulfonic acid, halogen, sulfate, nitro, cyano, epoxy, amino, hydroxy, quaternary ammonium, sulfonate, phosphate, 15 phosphonate, phosphinic acid, phosphinate, carboxylate, phosphonic acid or borate moieties; or any two R_3 groups or any one R_3 group and any R_2 or R_4 group together may form a substituted or unsubstituted alkylene or alkenylene chain completing a 3, 4, 5, 6, 20 7, 8, 9 or 10 membered aromatic heteroalicyclic, heteroaromatic or alicyclic carbon ring, which chain may optionally include one or more divalent nitrogen, ester, carbonyl, sulfur, sulfinyl, sulfonyl or oxygen, wherein permissible substituents are one or more 25 sulfonic acid, carboxylic acid, sulfinic acid, phosphoric acid, boric acid, sulfonic acid, halogen, sulfate, nitro, cyano, epoxy, amino, hydroxy, quaternary ammonium, sulfonate, phosphate, phosphonate, phosphinic acid, phosphinate, carboxylate, phosphonic acid or 30 borate moieties.

4. A solution according to claim 2 wherein:

R_2 is hydrogen;

R_3 is alkyl or alkoxy;

m is 3 or 4; and

35 n is 0 or 1.

5. A solution according to claim 4 wherein n is 0 and m is 4.

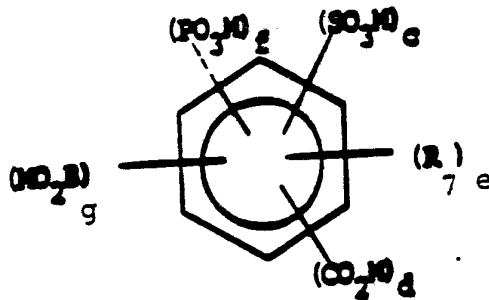
6. A solution according to claim 5 wherein said Lewis base has a pK_a of equal to or greater than about 5.4 and is a liquid having a boiling point equal to or less than about 150°C at 760mm of Hg.

5 7. A solution according to claim 6 wherein said Lewis base is selected from the group consisting of primary, secondary, and tertiary aromatic or aliphatic amines, phosphines or amides.

8. A solution according to claim 7 wherein said Lewis base is 2-pyrrolidone, 2-oxazolidone, and 2-imidazolidone.

9. A solution according to claim 7 wherein said dopant is a compound of the formula:

15



20

wherein:

25 M is a metal cation or non-metal cation with the proviso that at least one of M is a proton;

c is 1, 2, 3 or 4;

e is 0, 1 or 2;

f is 0, 1 or 2;

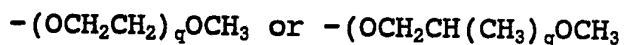
g is 0, 1 or 2;

30 d is 0, 1 or 2; and

R_7 is hydroxy, alkyl, halogen, cyano, phosphonic acid, phosphonate, phosphinic acid, phosphinate, alkoxy, hydroxy, sulfinic acid, sulfinate, or substituted or unsubstituted aryl or alkyl having from 35 1 to about 30 carbon atoms wherein permissible substituents are perhaloalkyl, halogen, cyano, phosphonate, borate, phosphonic acid, sulfonate,

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carboxylate, phosphate, haloalkyl, sulfonic acid,
sulfinic acid, sulfinate, phosphoric acid boric acid,
carboxylic acid, or any two R₇ substituents together
5 may form an alkenylene chain completing a fused
aromatic ring system, which chain may be unsubstituted
or substituted with one or more halogen, hydroxy,
phosphonate, borate, phosphonic acid, sulfonate,
phosphate nitro, boric acid, phosphoric acid,
10 carboxylate, cyano, sulfonic acid or carboxylic acid
groups, or R₇ is a moiety of the formula:



wherein q is 1 to about 10.

15 10. A solution according to claim 9 wherein:
M is a cation, with the proviso that at least
one of M is a proton.

c is 1, 2 or 3;

d, g and f are 0;

20 e is 0, 1 or 2; and

R₇ is alkyl, fluoro or alkyl substituted with one
or more fluoro substituents or any two R₇ group
together may form a substituted or unsubstituted
divalent alkenylene chain completing a naphthalene,
25 anthracene or phenanthracene ring structure, wherein
permissible substituents are one or more sulfonic
acid, fluoro or alkyl substituted with one or more
sulfonic acid or fluoro groups.

FIG. 1

1/2

Hansen Solubility Parameters
of Solvents for Polyaniline Base

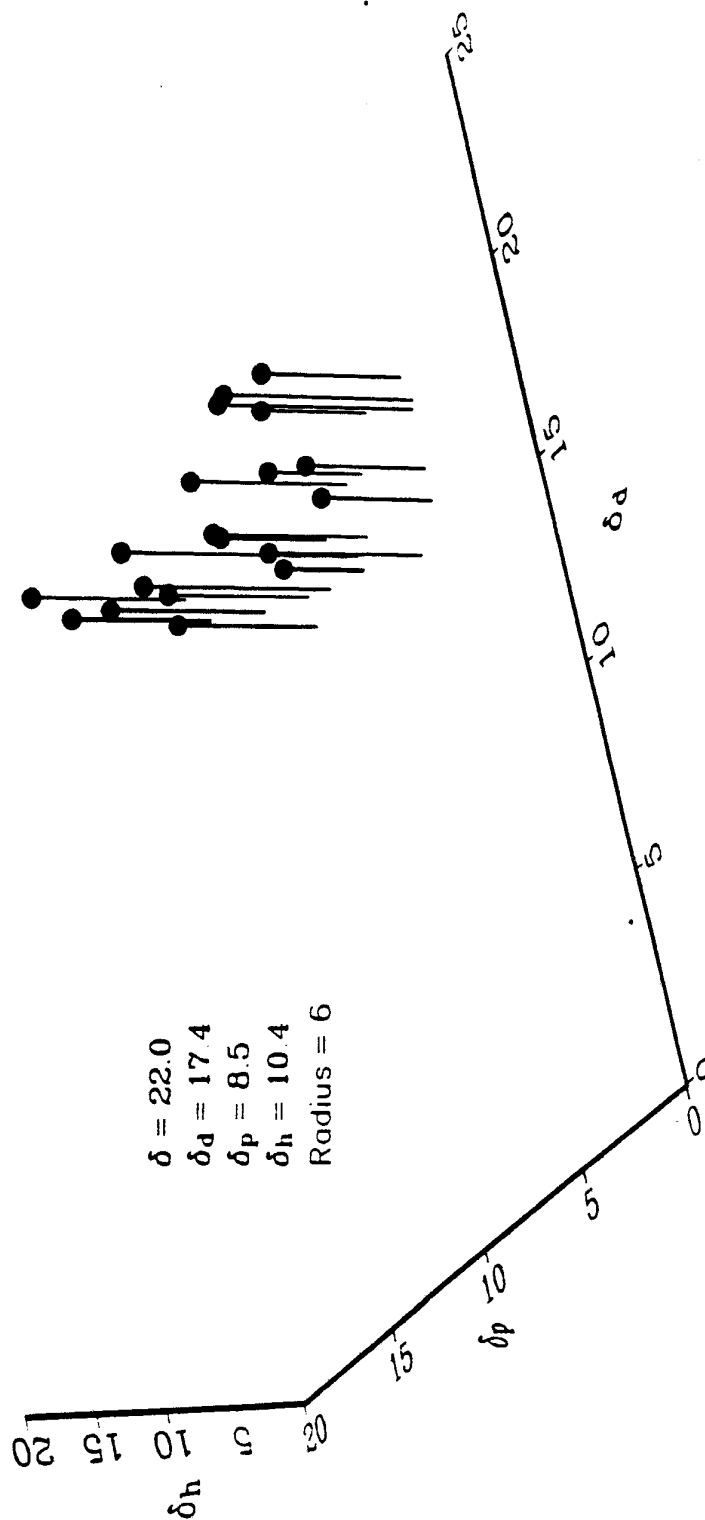
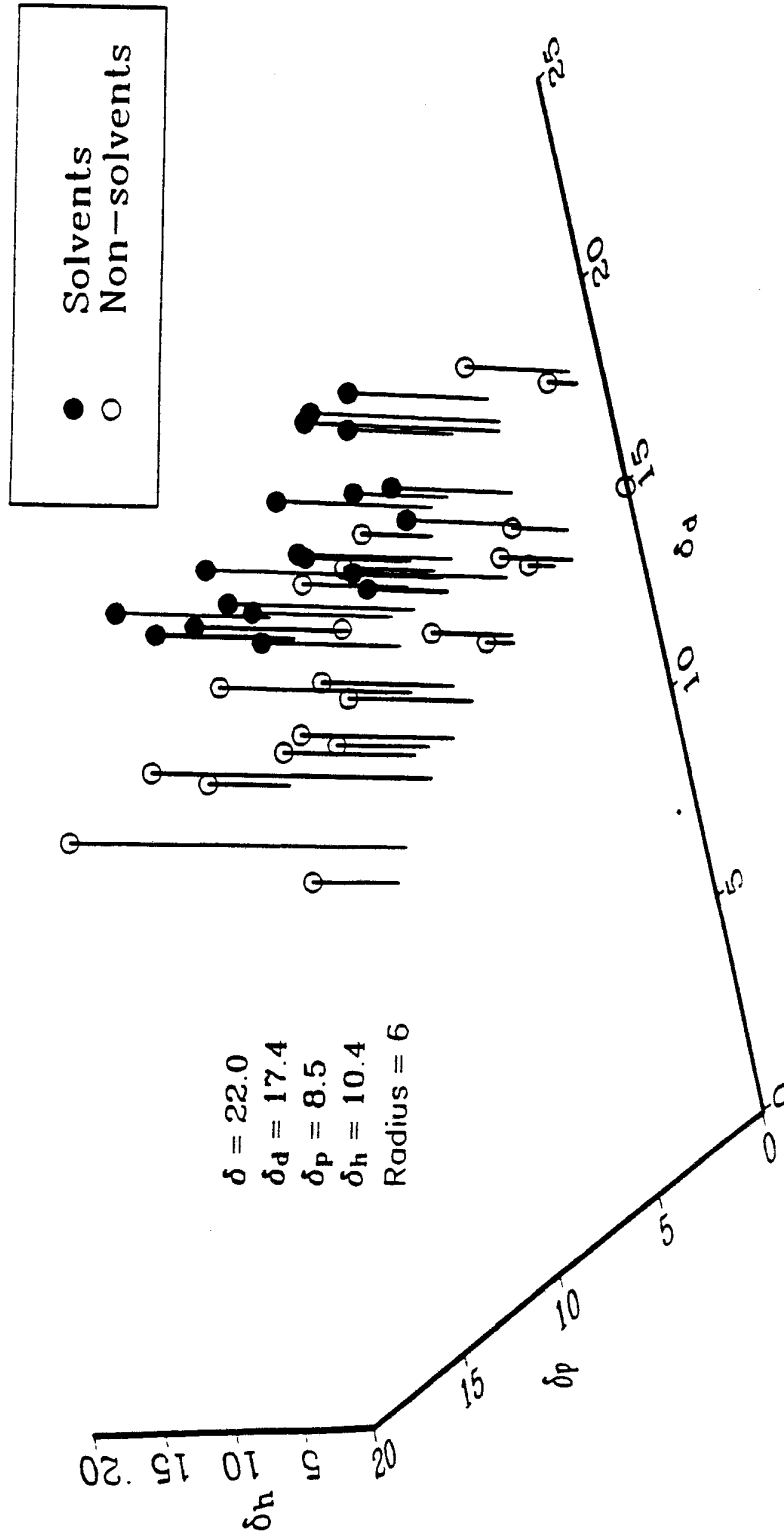


FIG. 2

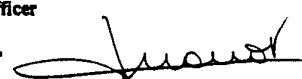
Hansen Solubility Parameters
of Solvents and Non-solvents for Polyaniline Base



INTERNATIONAL SEARCH REPORT

PCT/US 91/09571

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.C1. 5 H01B1/12; C08G73/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.C1. 5	H01B ; C08G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ^o	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
P,X	US,A,5 006 278 (R.L.ELSENBAUMER) 9 April 1991 see the whole document ---	1-5,7,8
P,X	US,A,4 983 322 (R.L.ELSENBAUMER) 8 January 1991 see the whole document ---	1-5,7,8
X	US,A,4 940 517 (Y.WEI) 10 July 1990 see the whole document ---	1-5,7
A	WO,A,9 010 297 (ALLIED-SIGNAL) 7 September 1990 see the whole document ---	1-5,9,10
<p>^o Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
21 APRIL 1992	28. 04. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	DROUOT M.C. 	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9109571
SA 55897**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US-A-4983322	08-01-91	US-A- 5006278	09-04-91
US-A-4940517	10-07-90	None	
WO-A-9010297	07-09-90	CA-A- 2011189	01-09-90
		EP-A- 0461182	18-12-91
		JP-T- 3505892	19-12-91