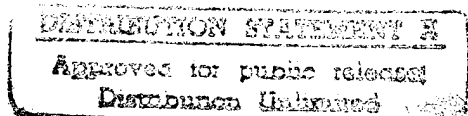


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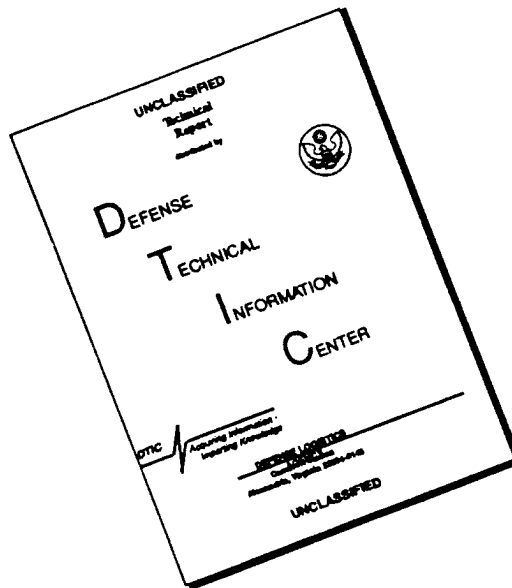
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1 CONDUCTIVE POLYMER COATED FABRICS FOR CHEMICAL SENSING

2
3 **BACKGROUND OF THE INVENTION**

4
5 **Field of the Invention**

6 The presently disclosed invention relates to an apparatus and method for the
7 detection, differentiation, classification, identification and/or quantitation of one or more
8 component chemicals of chemical vapors or various gases using a conductive polymer
9 coated fabric chemical sensor. More particularly, the presently disclosed invention
10 relates to an apparatus and method for detecting and measuring changes in the
11 resistance of a fabric chemical sensor upon exposure of the sensor to chemical vapors
12 and converting that change in resistance into a "fingerprint" pattern of the chemical vapor
13 for classification, identification and/or quantitation of one or more component chemicals
14 of the chemical vapor.

15 **Description of the Related Art**

16 Plasticized poly(pyrrole) sensors for detecting vapors from various chemicals such
17 as solvents (e.g. acetone, chloroform, isopropyl alcohol, methanol, ethanol,
18 tetrahydrofuran, benzene and ethylacetate) are described by Fruend and Lewis. *See*
19 *Fruend, M.S. and Lewis, N.S., A chemically diverse conducting polymer based "electronic*
20 *nose", Vol. 92 Proc. Natl. Acad. Sci. USA pp. 2652-2656 (March 1995), incorporated herein*
21 *by reference in its entirety and for all purposes. Fruend and Lewis describe an air stable*
22 *sensor array of plasticized poly(pyrrole) elements fabricated upon interdigitated metal*
23 *lines of a commercial 22-nF ceramic capacitor. Each of the elements of the sensor*

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1 array consists of poly(pyrrole) and a plasticizer wherein the plasticizer composition is
2 varied to obtain the different sensor elements. While the sensor array of Fruend and
3 Lewis can distinguish between the vapors of various solvents, the use of an interdigitated
4 ceramic capacitor contributes to a sensor array that is not very adaptable to varying
5 environments, a sensor that is cumbersome and difficult to use, a sensor that is expensive
6 to produce and possibly a sensor having little durability. In addition, the ceramic
7 capacitors are inherently difficult to incorporate into useful articles.

8 In U.S. Patent No. 5,145,645, incorporated herein by reference in its entirety and
9 for all purposes, a chemical species detector is disclosed wherein the detector includes a
10 conductive polymer based sensing element. The conductive polymer of U.S. Patent No.
11 5,145,645 (hereinafter the '645 patent) is deposited on an electrically insulating
12 supporting substrate which appear to be a rigid solid (depicted in Figure 3 of the '645
13 patent and described at col. 6, lines 12-16). From Figure 3 of the '645 patent, it appears
14 that a conductive polymer section 14 is deposited on a portion of the underlying
15 electrically insulating section 12, the conductive polymer layer being attached to
16 electrodes 16 and 18, respectively.

17 A similar sensor is depicted in Figure 1 of the article by T. Hanawa, S. Kuwabata,
18 and H. Yoneyama entitled *Gas Sensitivity of Polypyrrole Films to NO₂*, which is published in
19 *J. Chem. Soc., Trans. 1*, 84(5), pp. 1587-1592 (1992), incorporated herein by reference in
20 its entirety and for all purposes. The sensor is built on a rigid electrically insulating glass
21 plate.

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1 No sensors for measuring chemical resistance (or conductivity) are known to date
2 having the flexibility, the strength, the surface area, the ease of production and the
3 mechanical properties of a fabric. There is a need for a sensor for measuring chemical
4 resistance (or conductance) wherein the sensor is formed from sensor elements
5 comprised of fabric materials (e.g. woven fabrics). The incorporation of sensor elements
6 into a fabric will impart the much needed mechanical strength, durability, flexibility, ease
7 of production and incorporability into useful articles of a fabric to the sensor element.

8 **Summary of the Invention**

9 It is therefore an object of the present invention to provide a fabric chemical
10 sensor for detecting one or more chemical components of chemical vapors and/or gases
11 wherein the sensor comprises one or more sensor elements built into a fabric.

12 It is therefore another object of the present invention to provide a fabric chemical
13 sensor for detecting and/or quantitating one or more chemical components of chemical
14 vapors and/or gases wherein the sensor comprises one or more sensor elements built into
15 a fabric.

16 It is therefore still another object of the present invention to provide a fabric
17 chemical sensor for detecting, classifying and/or quantitating one or more chemical
18 components of chemical vapors and/or gases wherein the sensor comprises one or more
19 sensor elements built into a fabric.

20 It is therefore yet another object of the present invention to provide a fabric
21 chemical sensor for detecting, classifying, differentiating, identifying and/or quantitating

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1 one or more chemical components of chemical vapors and/or gases wherein the sensor
2 comprises one or more sensor elements built into a fabric.

3 It is therefore even yet another object of the present invention to provide a sensor
4 element comprising a fabric woven from insulating fibers coated with one or more
5 conductive polymers, optionally doped with one or more dopants, and further optionally
6 coated with one or more polymeric bilayers.

7 It is therefore a further object of the present invention to provide a sensor
8 element comprising a fabric woven from insulating fibers coated with one or more
9 conductive polymers selected from the group consisting of poly(pyrrole), poly(aniline)
10 and mixtures thereof, the fibers being further doped with dopants selected from the
11 group consisting of chloride ion, p-toluene sulfonic acid (PTSA), naphthalene disulfonic
12 acid disodium salt (NDSA), naphthalene-2-sulfonic acid sodium salt (N2SA),
13 anthraquinone-2-sulfonic acid sodium salt (AQSA) and mixtures thereof.

14 It is an even further object of the present invention to provide a sensor element
15 comprising a fabric woven from insulating fibers being selected from the group consisting
16 of polyethylene terephthalate (PET), nylon threads and mixtures thereof, the fibers
17 coated with one or more conductive polymers selected from the group consisting of
18 poly(pyrrole), poly(aniline) and mixtures thereof, the fibers being further doped with
19 dopants selected from the group consisting of chloride, PTSA, NDSA, N2SA, AQSA and
20 mixtures thereof.

21 It is even yet a further object of the present invention to provide a sensor element

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1 comprising a fabric woven from insulating fibers being selected from the group consisting
2 of polyethylene terephthalate (PET), nylon threads and mixtures thereof, the fibers
3 coated with one or more conductive polymers selected from the group consisting of
4 poly(pyrrole), poly(aniline) and mixtures thereof, the fibers being further doped with
5 dopants selected from the group consisting of chloride ion (chloride), PTSA, NDSA,
6 N2SA, AQSA and mixtures thereof, and the doped-conductive polymer coated fibers
7 further coated with a polymeric bilayer selected from the group consisting of
8 polyethyleneimine (PEI), poly(isobutylene) (PIB), fluoroalcoholpolysiloxane (SXFA, or 1-
9 (4-hydroxy, 4-trifluoromethyl, 5,5,5-trifluoro)pentene, methylpolysiloxane), fluoropolyol
10 (FPOL, *infra*) and mixtures thereof.

11 It is still another object of the present invention to provide an apparatus and
12 method for the detection, analysis, differentiation, classification, identification and/or
13 quantitation of one or more component chemicals of chemical vapors and/or gases using
14 a fabric chemical sensor further comprising one or more sensor elements wherein the
15 sensor elements comprise conductive polymer coated fabrics with optional dopants and
16 optional polymeric overcoats (i.e. bilayers).

17 These and other objects are accomplished by the process comprising the steps of:

18 (i) electrically connecting one or more fabric chemical sensors to a
19 power source, said one or more fabric chemical sensors comprising one or more sensor
20 elements, said sensor elements woven into a fabric of insulating fibers, said fibers being
21 coated with one or more conductive polymers, each of said fabric chemical sensors

1 having a baseline resistance;

2 (ii) exposing at time = t_0 over said one or more fabric chemical sensors
3 a chemical vapor, said chemical vapor comprising one or more component chemicals;

4 (iii) detecting and quantifying a change in said baseline resistance of said
5 one or more fabric chemical sensors at a later time = t_1 in response to exposure of said
6 one or more fabric chemical sensors to said chemical vapor; and

7 (iv) resolving and classifying from said change in said baseline resistance
8 the identity of at least one of said one or more component chemicals of said chemical
9 vapor.

10 The above process is accomplished by an apparatus comprising:

11 (i) one or more fabric chemical sensors further comprising one or more
12 sensor elements, said one or more sensor elements being woven from insulating fibers,
13 said fibers being coated with one or more conductive polymers;

14 (ii) a power supply being electrically connected to said one or more
15 fabric chemical sensors, said one or more fabric chemical sensors having a measurable
16 baseline resistance;

17 (iii) a means for exposing a chemical vapor over said one or more fabric
18 chemical sensors sufficient to measure a reproducible change in said baseline resistance,
19 said chemical vapor further comprising one or more component chemicals;

20 (iv) a means for detecting and quantifying said change in said baseline
21 resistance in response to said exposure of said one or more fabric chemical sensors to

1 said chemical vapor; and

2 (v) a means for resolving from said change in said baseline resistance a
3 classification of the identity of at least one of said one or more component chemicals of
4 said chemical vapor.

5 **Brief Description of the Drawings**

6 Figure 1 is a schematic diagram of an exemplary setup of apparatus for
7 simultaneously characterizing the response of four fabric chemical sensors to exposure to
8 gas vapors.

9 Figure 2 is a scanning electron microscope image (SEM) taken of a NDSA-doped
10 poly(pyrrole) conductive polymer on PET woven fibers at a magnification of 500x, the
11 image depicting the nature of the fabric weave and the character of the conductive
12 polymer coating.

13 Figure 3 is a scanning thermo-gravimetric analysis (TGA) plot recorded of PET
14 fibers (dashed lines) and poly(pyrrole)-coated PET fibers (solid lines), respectively. The
15 inset is an isothermal TGA (300 °C in air) plot taken of PET fibers (dashed lines) and
16 poly(pyrrole)-coated PET fibers (solid lines), respectively.

17 Figure 4 is an exemplary plot of $\Delta R/R$ % (wherein ΔR is the change in the
18 resistance from baseline resistance measured prior to exposure of fabric chemical sensor
19 to chemical vapor(s) and R is the baseline resistance). A change in the resistivity is
20 observed from an NDSA-doped poly(pyrrole) conductive polymer coated onto PET fibers
21 (woven into a fabric chemical sensor) to $\text{NH}_3(\text{g})$ (29.4 ppm) exposure and $\text{NO}_2(\text{g})$ (50.1

1 ppm) exposure, in air, respectively.

2 Figure 5A is an exemplary plot of resistance (ohms) versus time (minutes) for an
3 NDSA-doped poly(pyrrole) conductive polymer coated onto PET fibers (woven into a
4 fabric chemical sensor) to increases in relative humidity from 0% to 14% to 29%.

5 Figure 5B is an exemplary plot of resistance (ohms) versus time (minutes) for an
6 NDSA-doped poly(pyrrole) conductive polymer coated onto PET fibers (woven into a
7 fabric chemical sensor) to decreases in relative humidity from 29% to dry air (0%
8 relative humidity).

9 Figure 6 is an exemplary plot of resistance (ohms) versus time (minutes) for an
10 NDSA-doped poly(pyrrole) conductive polymer coated onto PET fibers (woven into a
11 fabric chemical sensor) to exposure to dimethyl methylphosphonate (DMMP) (28 ppm)
12 in dry air.

13 Figure 7 is a scanning electron microscope image (SEM) taken of a NDSA-doped
14 poly(pyrrole) conductive polymer on PET woven fibers further coated with a thin layer of
15 fluoropolyol (FPOL) at a magnification of 1000x, the image depicting the nature of the
16 fabric weave and the character of the conductive polymer coating.

17 Figure 8 is an exemplary table of $\Delta R/R$ % readings for various fabric chemical
18 sensor types upon exposure to various chemical vapors (i.e. various gas vapors) as
19 indicated.

20 Figure 9 is an exemplary table of *change in resistivity* and *initial response slope* of
21 various fabric thicknesses (i.e. various fabric thicknesses can be correlated to various

1 baseline resistivities of exemplary NDSA doped-poly(pyrrole) conductive polymer coated
2 onto PET fibers woven into fabric chemical sensors) upon exposure to DMMP (28 ppm
3 in dry air).

4 Figure 10 is an exemplary table of $\Delta R/R$ % readings for various fabric chemical
5 sensor types coated with various polymer overcoats (as indicated) upon exposure to
6 various chemical vapors (i.e. various gas vapors) as indicated.

7 **Detailed Description of the Preferred Embodiments**

8 Conductive polymers are an effective medium for chemical sensing, based upon
9 electronic changes arising in the polymeric films with the gas phase adsorption of
10 electronically active vapors. The conductivity changes observed in these polymers are
11 attributed to the interaction of electronically active analytes with either the polymer
12 backbone itself, or the dopant molecules incorporated within the film, thereby modulating
13 the mobility and/or number of free charge carriers available.

14 According to the present invention, a format for forming and utilizing fabric
15 chemical sensors for the detection of one or more component chemicals within chemical
16 vapors is disclosed. Broadly, insulating fibers are coated with one or more conductive
17 polymers which conductive polymers may be optionally doped with one or more dopants
18 and further optionally coated with an overcoat polymer layer (i.e. bilayer polymer).
19 These fibers are woven into a fabric and connected to a power source to measure a
20 baseline resistance across the fabric chemical sensor (e.g. the sensor woven from
21 exemplary doped-conductive polymer coated fibers having an optional polymer overcoat).

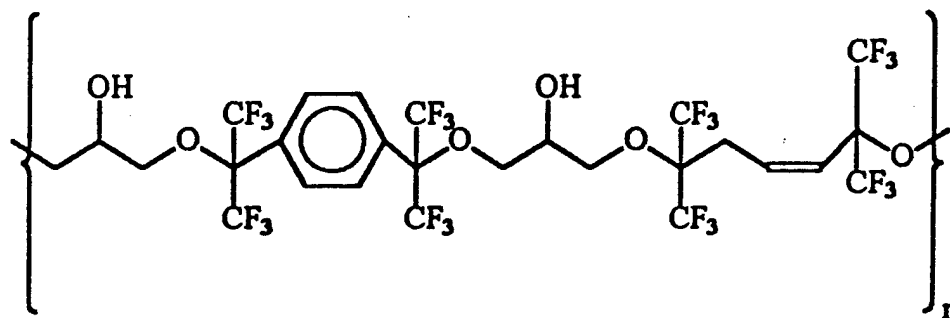
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1 After measuring a baseline resistance, an exemplary array of fabric chemical sensors is
2 exposed to a chemical vapor and a change in the baseline resistance is detected and
3 measured to form a "fingerprint" pattern for the chemical vapor. Typically, the
4 "fingerprint" pattern is obtained by exposing a plurality of fabric chemical sensors (of
5 various dopants, fiber thicknesses, fiber compositions and polymer overcoats,
6 respectively) to the chemical vapor. The "fingerprint" pattern so obtained is analyzed to
7 identify, classify, and/or quantify one or more component chemicals present within the
8 chemical vapor tested.

9 Exemplary insulating fibers used according to the present invention include nylon
10 and PET. However, any insulating fiber that can be readily woven into a fabric and
11 accept a coating of a conductive polymer may be used in accordance with the present
12 invention.

13 Exemplary conductive polymers used according to the present invention include
14 poly(pyrrole) and poly(aniline). However, any conductive polymer that can be
15 polymerized onto insulating fibers (the fibers suitable for weaving into fabrics) may be
16 used. Preferably, a suitable conductive polymer will incorporate dopant anions such as
17 NDSA, AQSA and chloride. More preferably, a suitable conductive polymer will also
18 permit deposition of a polymer overcoat such as polyethyleneimine (PEI),
19 fluoroalcoholpolysiloxane (SXFA, or 1-(4-hydroxy, 4-fluoromethyl, 5,5,5-trifluoro)pentene,
20 methylpolysiloxane) and fluoropolyol (FPOL), FPOL having the structure
21



where $n = 5, 6, 7, 8, 9,$ or 10 .

Conductive polymer-coated fabric characteristics

The conductive polymer-coated fabrics used consisted of exemplary weaved fiber filaments coated with conductive polymer overlayers, grown by chemical polymerization or oxidative coupling of the exemplary monomer, pyrrole or aniline. The dopant anion, e.g. naphthalene disulfonic acid (NDSA), anthraquinone-2-sulfonic acid (AQSA) or Cl^- , was simultaneously incorporated into the conductive polymer chain, giving the polymer network its conductivity. The conductive polymers were typically coated onto the fiber filaments by an *in situ* solution polymerization process that is based on oxidative coupling of the monomer species (e.g. pyrrole or aniline) and simultaneous incorporation of the dopant. See Gregory et al., 28 *Synthetic Metals*, C823-C835 (1989), incorporated herein by reference in its entirety and for all purposes. The *in situ* process permits the controlled growth of relatively thin films of conductive polymers on fabric filaments woven into fabrics with conductivities that 1) are uniform over the length of the material, 2) can be varied over a wide range of values, 3) are stable over long time periods, and 4) combine the electrical properties of the conductive polymer coating with the mechanical

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1 properties of the fabric. *See Kuhn et al., Toward Real Applications of Conductive Polymers,*
2 *71 Synthetic Metals 2139-2142 (1995),* incorporated herein by reference in its entirety and
3 for all purposes. *See also Gregory et al., Conductive Textiles, 28 Synthetic Metals C823-*
4 *C835 (1989),* incorporated herein by reference in its entirety and for all purposes.

5 Scanning electron microscope (SEM) images taken of exemplary fabric weaves
6 demonstrate the pristine nature of the chemically grown, polymeric films. Shown in
7 Figure 2 is an SEM image taken of an exemplary NDSA-doped poly(pyrrole) film on
8 polyethylene terephthalate (PET) using an electron voltage of 20 kV and a magnification
9 of 500x. The chemical deposition of the poly(pyrrole) resulted in a smooth, even
10 overlayer on the PET thread, although there do exist regions where the polymer
11 aggregated during polymerization. The fabric weave consists of a series of overlapping,
12 conductive polymer-coated threads, which results in a much more complicated, fabric
13 chemical sensor substrate than that found for films grown on chemiresistor devices,
14 quartz crystal microbalances or field effect transistors, for example. If we presume that
15 the conduction process in poly(pyrrole) and poly(aniline) operates according to a p-type,
16 hole-hopping mechanism, the conduction path for a single hole might be expected to
17 traverse several threads. The swelling of conductive polymers due to gas analyte
18 adsorption will generate considerable changes in the transport pathways of free charge
19 carriers within these films. Exemplary high levels of doping in conductive polymers (e.g.
20 10-30%) make the dopant anion an important consideration in defining the sensor
21 response of each conductive polymer-coated fabric.

1 To assess the relative thermal stability of the exemplary conductive polymer
2 coatings on the exemplary PET thread, thermal gravimetry analysis (TGA) was
3 performed on several exemplary fabric weaves. Thermogravimetry analysis (TGA) was
4 performed in air using a Perkin Elmer TGA-7 analyzer under both isothermal (300°C)
5 and scanning conditions (10°C/sec). A scanning TGA plot of exemplary PET and
6 poly(pyrrole) coated PET fibers in air is shown in Figure 3. The degradation curves for
7 these two materials are essentially identical, maintaining nearly 100% mass retention up
8 to 380°C, before dropping off over the course of 100°C and leveling off at ~20% mass
9 retention above 500°C. Shown in the inset of Figure 3 is an isothermal TGA (300°C in
10 air) plot for a similar set of exemplary PET and poly(pyrrole) coated PET fibers. In this
11 plot, we can differentiate the loss mechanisms apparent in PET from those of the
12 poly(pyrrole) overcoat. The thermal stability of these films suggests the possibility of
13 utilizing temperature as an additional parameter for improving selectivity and recovery
14 time in fabric-based chemical sensors.

15 Analytical characterization of the fabric weaves was undertaken to improve our
16 understanding of the film's interfacial properties. X-ray photoelectron spectroscopy
17 (XPS) measurements were conducted using a Surface Science spectrometer. The XPS
18 spectra were collected using AlK α non-monochromatized radiation and a hemispherical
19 analyzer in the constant analyzer energy mode with a pass energy of 20 eV. A Hitachi
20 Field Emission scanning electron microscope (SEM) operating at an electron voltage of
21 20-25 kV was used to obtain images of the conductive polymer-coated fabrics. Because

1 of the conductive properties associated with these fabric weaves, it was not necessary to
2 generate an electrically conductive overcoat.

3 *Conductive polymer-coated fabrics*

4 Unless mentioned otherwise, all fabrics were used as received from the
5 manufacturer. Exemplary conductive polymer-coated fabrics were acquired from
6 Milliken Research Corp., and included 1) poly(pyrrole) on a 150 denier poly(ethylene)
7 terephthalate (PET) doped with naphthalene disulfonic acid (NDSA)-available
8 resistivities included 211, 775, and 3000 ohms/cm²; 2) poly(pyrrole) on a 150 denier PET
9 doped with anthraquinone-2-sulfonic acid (AQSA)- resistivity 129 ohms/cm²; 3)
10 poly(pyrrole) on a 840 denier nylon doped with NDSA- resistivity 100 ohms/cm²; and, 4)
11 poly(aniline) on a 150 denier PET doped with Cl⁻ resistivity 75 ohms/cm². For all
12 chemical sensing experiments, a 12 cm² square piece of fabric was cut from a sheet of the
13 conductive polymer-coated fabric, and a thin line of silver paint (Alfa Aesar) was applied
14 to opposite ends of the fabric and allowed to dry. An additional, small amount of silver
15 paint was then utilized for making an electrical connection between a teflon-coated wire
16 and the opposing sides of the fabric. After drying overnight, the fabric swatches were
17 placed within the testing apparatus and allowed to equilibrate in a stream of dry air.

18 *Apparatus and instrumentation*

19 Shown in Figure 1 is a diagram of an exemplary experimental configuration
20 employed for examining the chemical sensing characteristics of the coated fabric
21 materials (i.e. fabric chemical sensors). Four fabric swatches were examined

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1 simultaneously by positioning them within a teflon (PTFE, Dupont) support containing
2 four exposure holes (2 cm diameter). The teflon support was contained within a 0.5 liter
3 glass chamber which held a set of baffled, teflon discs at the front and back of the
4 chamber in order to promote laminar flow across the fabric surface. Air flow within the
5 testing chamber was maintained using Matheson Model 8200 series mass flow controllers
6 at a constant flow rate of either 1 l/min or 10 l/min. Given a cross-sectional area of 23.8
7 cm², the face velocities were calculated to be between 42 and 420 cm/min (1.4-14 ft/min),
8 velocities that closely approximate exchange rates in typical indoor environments. Gas
9 standards containing 450 ppm NH₃ in N₂ and 1053 ppm NO₂ in N₂ were obtained from
10 Matheson, Inc. and Potomac Airgas, Inc., respectively. Dimethyl methylphosphonate
11 (DMMP) was acquired from Aldrich, Inc., and placed within a bubbler held at a constant
12 temperature of 15°C using a temperature controlled water bath manufactured by GCA,
13 Inc.. Previous studies have calibrated the DMMP bubbler to generate ~2960 mg of
14 DMMP per m³ while being maintained at this temperature. See Grate et al., 65 *Anal.*
15 *Chem.*, 1868 (1993), incorporated herein by reference in its entirety and for all purposes.
16 Humidity was controlled via the use of bubblers and line mixers, and quantitated using a
17 HygroDynamics hygrometer. All resistivity measurements were made using a Keithley
18 617 programmable electrometer (at an applied potential of 0.0946 V) and a Keithley 705
19 scanner which enabled the sequential sampling of the resistivity for each of the
20 conductive polymer-coated fabrics held within the testing chamber. National Instruments'
21 LabView for Windows controlled the data acquisition across an AT-GPIB interface

1 board.

2 *Fabric response to $\text{NH}_3(\text{g})$ and $\text{NO}_2(\text{g})$*

3 The conductive polymer-coated fabric weaves were initially exposed to ppm levels
4 of $\text{NH}_3(\text{g})$ and $\text{NO}_2(\text{g})$, in order to assess the responsivity of these materials to toxic gases
5 known to interact electronically with conductive polymer, thin films. Shown in Figure 4 is
6 a plot of the change in resistivity for a NDSA doped poly(pyrrole) film on PET upon the
7 introduction and cessation of 29.4 ppm $\text{NH}_3(\text{g})$ and 50.1 ppm $\text{NO}_2(\text{g})$ in a stream of dry
8 air. For NDSA doped poly(pyrrole) films on fabric, 1) ammonia resulted in an increase
9 in the resistivity which was nearly linear with time and essentially irreversible; while 2)
10 nitrogen dioxide caused a monotonic decrease in the resistivity which was reversible in its
11 response. The fabric shown in Figure 4 was found to be nearly 14 times more sensitive
12 to the detection of ammonia, when compared to nitrogen dioxide, although both have
13 demonstrated responses in the low ppm regime.

14 Because conductive polymers are generally acknowledged to exhibit behavior
15 which is in accordance with p-type conductive materials, it is reasonable to expect that 1)
16 $\text{NH}_3(\text{g})$, a strong reductant, will result in a decrease in the conductivity due to the
17 elimination of free hole charge carriers, while 2) $\text{NO}_2(\text{g})$, a strong oxidant, will cause an
18 increase in the conductivity due to the formation of additional, free hole charge carriers
19 within the film.

20 Figure 8 summarizes the $\Delta R/R$ percent changes measured for four different,
21 conductive polymer-coated fabrics upon exposure to the various gases examined as

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1 indicated. The first two fabric weaves consisted of the same dopant and conductive
2 polymer type (PP/NDSA), differing only in the thread substrate (PET or nylon). The
3 third fabric also consists of poly(pyrrole) on PET, but in this case the dopant was AQSA.
4 The final material was weaved from PET fibers coated with Cl^- doped poly(aniline).
5 Focussing on the results obtained for $\text{NH}_3(\text{g})$ and $\text{NO}_2(\text{g})$, we note that the direction of
6 the resistivity changes matched the expected responses, with the exception of the Cl^-
7 doped poly(aniline) on PET fabric's response to $\text{NO}_2(\text{g})$. Of the two dopants utilized for
8 the poly(pyrrole) films, NDSA and AQSA, NDSA reported the largest signal with respect
9 to the detection of $\text{NH}_3(\text{g})$ and $\text{NO}_2(\text{g})$.

10 The role $\text{O}_2(\text{g})$ must also be considered on defining the conductivity of these
11 materials. For each of the fabric weaves investigated, the introduction of pure $\text{O}_2(\text{g})$ (1
12 l/min) to a film equilibrated in an inert atmosphere of nitrogen, resulted in a small but
13 steady increase in the resistivity that leveled off after several hours of exposure ($\sim 2\%$).
14 Under normal atmospheric conditions (20% oxygen levels), it is expected that the surface
15 of these exemplary fabric swatches (i.e. fabric chemical sensors) will be electronically
16 perturbed by the chemisorption of oxygen onto the surface of the conductive polymer.
17 Because of this interaction, an additional factor to consider in assessing the resistivity
18 changes observed in these materials, is the displacement of weakly chemisorbed $\text{O}_2(\text{g})$
19 molecules by competing analytes within the air stream- a displacement of the $\text{O}_2(\text{g})$
20 molecules will cause a resultant decrease in the resistivity of the film. In addition to the
21 reversible response of oxygen with the surface of these fabric weaves, there is a slow,

1 irreversible decay in the conductivity (i.e. increase in resistivity) linked to the degradation
2 of the conductive polymer via a reaction between oxygen and the polymer backbone that
3 gives rise to the formation of non-conjugated moieties. See J. Janata, 63 *Anal. Chem.*
4 2546 (1991), incorporated herein by reference in its entirety and for all purposes.

5 *Response to Chemical Warfare Agent Simulant (DMMP)*

6 In order to investigate the feasibility of using the electroactive polymer coated
7 fabric materials for the detection of chemical warfare agents, a series of experiments
8 were designed to examine the responsivity of the fabrics to an organophosphonate,
9 chemical warfare agent simulant, dimethyl methylphosphonate (DMMP). A typical
10 response curve obtained for the introduction of 28 ppm DMMP in dry air to a NDSA
11 doped poly(pyrrole) on PET fabric is shown in Figure 6. DMMP interacts electronically
12 with the polymer, generating a resistivity drop that is responsive in the low ppm regime.
13 Apparently, DMMP interacts with the conductive polymer to increase the quantity of free
14 and mobile hole charge carriers. The response observed for the fabric materials is
15 reversible and somewhat dependent upon the dopant and conductive polymer type, as
16 well as the substrate material (see Figure 8). The chloride ion doped poly(aniline) was
17 not nearly as sensitive to DMMP, despite having responded so well to the other vapors
18 studied here.

19 The NDSA doped poly(pyrrole) fabric was further examined for the detection of
20 DMMP wherein attention was focussed on the properties of the conductive polymer for
21 improving DMMP detection. More specifically, the effect of film thickness on response

1 time and responsivity to DMMP were examined in a set of three different NDSA doped
2 poly(pyrrole) on PET fabrics (see Figure 9). The three materials differed according to
3 their inherent surface resistance, a factor which was not a feature of the extent of doping,
4 but rather a measure of the film thickness. Qualitatively, the thickness of the conductive
5 polymer films decreased in the order $3000 > 775 > 211$ ohms/cm². Examining first the
6 magnitude of response to the introduction of 28 ppm DMMP in dry air, the best signal-
7 to-noise ratio was attained for the 775 ohm/cm² film, although the 3000 ohms/cm² was
8 nearly as sensitive. The speed of response, however, was most rapid in the 3000
9 ohms/cm² film, as evidenced by the initial response slope recorded upon the introduction
10 of DMMP. In addition, the mobile charge carriers generated by the adsorption of a
11 single molecule of DMMP are more easily detected in films possessing lower
12 conductivities. The 775 ohms/cm² poly(pyrrole) coated material was selected for all
13 further investigations.

14 The response of the conductive polymer-coated fabrics to DMMP within a carrier
15 stream of dry air demonstrated the possibility for utilizing these materials for the
16 detection of ppm levels of chemical warfare agents. Unfortunately, the same sensitivity
17 was not observed for fabrics supported within a carrier stream of humid air. Following
18 equilibration of the material's conductivity within any given humidity, the addition of
19 DMMP failed to generate a measurable change in the resistivity. This was in contrast to
20 the addition of NH₃(g) in humid air, which caused an identical resistivity change in the
21 film to that seen in dry air. Apparently the chemisorption of DMMP to the conductive

1 polymer surface is relatively weak, and, as a result, the DMMP is unable to displace
2 water molecules from surface sites which were previously accessible under dry conditions.

3 *Influence of humidity on conductivity*

4 Humidity strongly influenced the conductivity level apparent in the conductive
5 polymer-coated fabric weaves. With the exception of the Cl^- doped poly(aniline) on PET
6 fabric, which reported only a decrease in the resistivity, each of the exemplary fabric
7 chemical sensors studied reported a dual response in the resistivity to increasing levels of
8 humidity. Figure 5a illustrates the change in resistivity seen for a NDSA doped
9 poly(pyrrole) film on PET upon the introduction and equilibration of two increasing
10 levels of humidity, 14% and 29%. When the fabric's environment was changed from a
11 stream of dry air to a stream of humid air, the resistivity underwent a rapid decrease in
12 the resistivity, which maintained a slow but steady decline for hours. Following
13 equilibration, the resistivity increased slightly for all subsequent increases in the humidity.
14 This dual response to humidity is mirrored in the resistivity changes seen for the
15 conductive polymer-coated fabrics following a switch from a humid carrier stream to dry
16 air (see Figure 5b). As expected, the immediate response is a dramatic decrease in the
17 resistivity, which is followed shortly by a gradual increase in resistivity.

18 Shown in Figure 8 are the magnitudes of the negative, resistivity changes recorded
19 upon the introduction and equilibration of 60% humidity for several different fabric
20 materials. The Cl^- doped poly(aniline) on PET responded to increasing humidity levels
21 with monotonic decreases in the resistivity. In addition to lacking the dual response

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1 reported by the poly(pyrrole) based fabrics, the poly(aniline) coated fabric was more than
2 10 times as sensitive to humidity.

3 *Polymer bilayers*

4 Bilayer films, or polymer coatings deposited onto the surface of the conductive
5 polymer-coated fabrics, were investigated for two reasons: 1) to investigate the feasibility
6 of improving sensitivity and selectivity to a given analyte by coating the conductive
7 polymer with a sorbent coating bearing particular functionality groups and properties
8 which favor the adsorption of certain molecules over others; and 2) to coat the
9 conductive polymer film with a hydrophobic coating which would maintain its responsivity
10 to the analyte of interest while avoiding problems associated with the chemisorption of
11 water vapor onto the conductive polymer surface. FPOL, SXFA, PEI and PIB sorbent
12 polymers (i.e. bilayers) were used as coatings on exemplary fabric chemical sensors.

13 *Polymer bilayer deposition*

14 Optional polymeric overcoats (i.e. bilayer films) were deposited on the conductive
15 polymer-coated fabrics by either spraying or dip-coating. Polyethyleneimine (PEI) was
16 obtained from Phase Separations, Inc. and poly(isobutylene) (PIB) from Aldrich, Inc..
17 Fluoroalcoholpolysiloxane (SXFA, or 1-(4-hydroxy, 4-trifluoromethyl, 5,5,5-
18 trifluoro)pentene, methylpolysiloxane) was prepared and donated by Dr. Andrew McGill
19 of Geo-Centers. See Kunugi et al., *J. Chem. Soc. Chem. Commun.*, pp. 873 (1994),
20 incorporated herein by reference in its entirety and for all purposes. Fluoropolyol (FPOL,
21 *supra*), an oligomer, was synthesized in-house by Dr. Jim Griffith of the Naval Research

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1 Laboratory. See Josowicz et al., 58 *Anal. Chem.* 514 (1986), incorporated herein by
2 reference in its entirety and for all purposes. See also McGill et al., 24 *CHEMTECH* 27
3 (1994), incorporated herein by reference in its entirety and for all purposes. For those
4 films prepared by spray-coating, a Badger Model 200-3 Air Brush was used to
5 exhaustively spray 15 ml of a 0.7% solution of the polymer dissolved in chloroform onto
6 the fabric swatch. For those films prepared by dip-coating, 33% (FPOL) and 11%
7 (SXFA) solutions were prepared in butyl acetate, with the polymer uptake by the fabric
8 being monitored gravimetrically. In order to drive off any excess solvent, the dip-coated
9 fabrics were pumped under dynamic vacuum (1mm) at 50°C for 24 hours.

10 Two methods were utilized for coating the fabric weaves with a thin coating of
11 polymer: spraying and dip-coating. In order to ensure the quality of the film deposited,
12 the films were characterized by XPS and SEM. Shown in Figure 7 is a SEM taken of a
13 NDSA doped poly(pyrrole) film on a PET fabric weave which was dip-coated with 0.33
14 g/cm³ of FPOL. The deposition resulted in a smooth film, which coagulates in certain
15 areas, literally connecting two fibers together, as can be seen in Figure 7. XPS analysis
16 verified the presence of the FPOL coating on the surface of the conductive polymer
17 coated weave via the loss of the nitrogen 1s electron peak associated with the
18 poly(pyrrole). The XPS data combined with the SEM analysis indicated the deposition
19 of a smooth overlayer of FPOL which completely coated the poly(pyrrole) underlayer.

20 Figure 10 summarizes the relative resistivity changes recorded for the blank and
21 each of the bilayer films to the different gases within a carrier stream of dry air as

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1 indicated. With regards to the introduction of water vapor (10% humidity), the film
2 exhibiting the largest decrease in resistivity was the PEI coated film. For the detection of
3 $\text{NH}_3(\text{g})$, the PEI film which exhibited the smallest change in its resistivity. In contrast,
4 the SXFA coated fabric displayed the largest increase in resistivity due to the strong
5 chemical sorption of $\text{NH}_3(\text{g})$.

6 With respect to detection of DMMP, the worst signal response was observed for
7 the SXFA coated fabric. It is further noted that the FPOL and PEI films caused little to
8 no effect on their response to DMMP, while the PIB film caused a decrease in the
9 resistivity change. Despite the presence of these sorbent polymer coatings, humidity still
10 resulted in a complete swamping out of the signal generated by DMMP.

11 For the detection of $\text{NO}_2(\text{g})$, the PEI coated film was more sensitive to $\text{NO}_2(\text{g})$
12 than either the FPOL-coated fabric or the blank
13
14
15

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ABSTRACT

A fabric chemical sensor, a process and an apparatus is disclosed. The sensor, process and apparatus are for the detection, classification, identification and/or quantitation of one or more component chemicals of a chemical vapor via a resistance measurment made across sensor in response to exposure of the sensor to the chemical vapor.

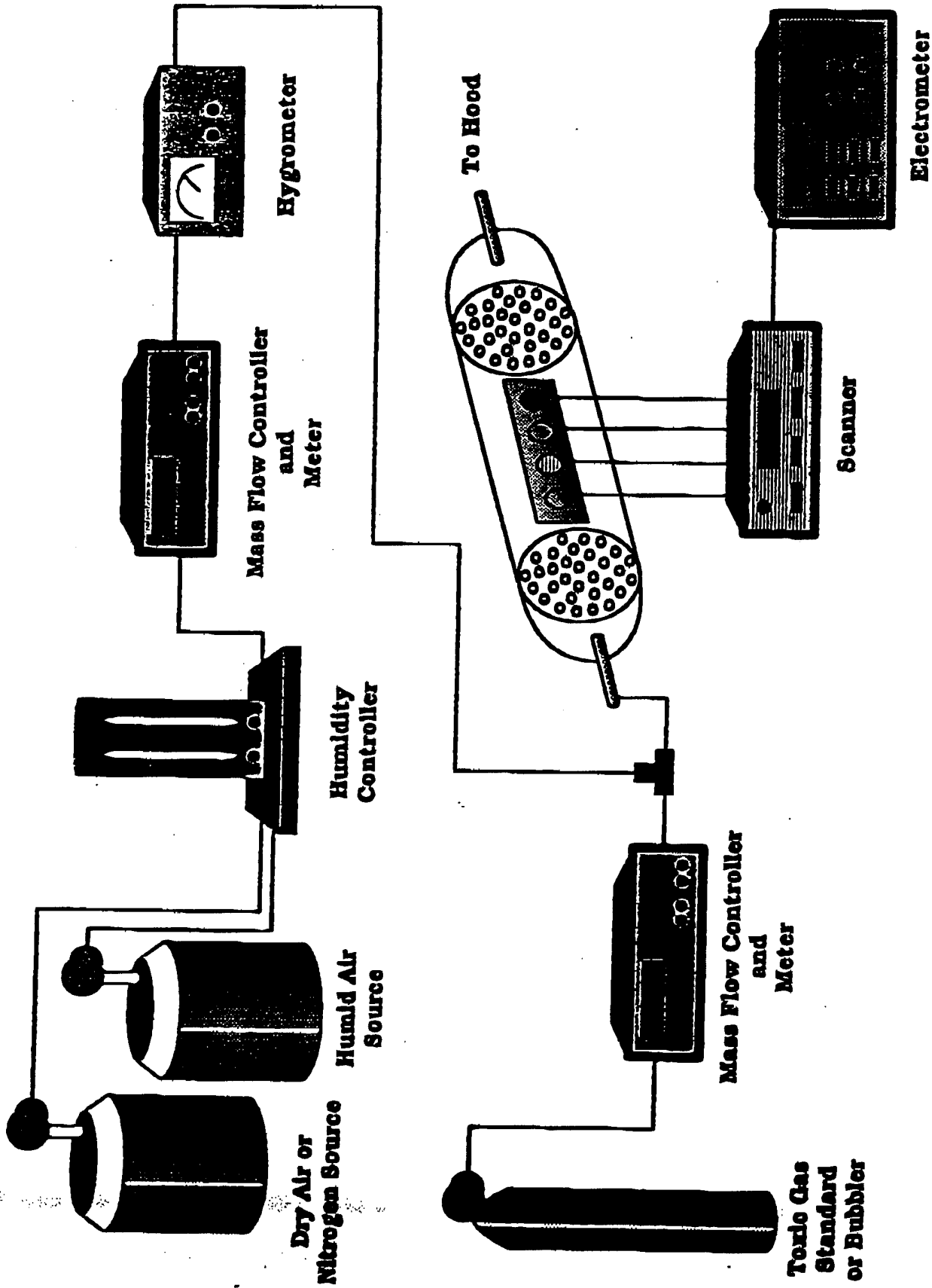


Figure 1

FIG. 1



033011 20KV X500 60 μ m

FIG. 2

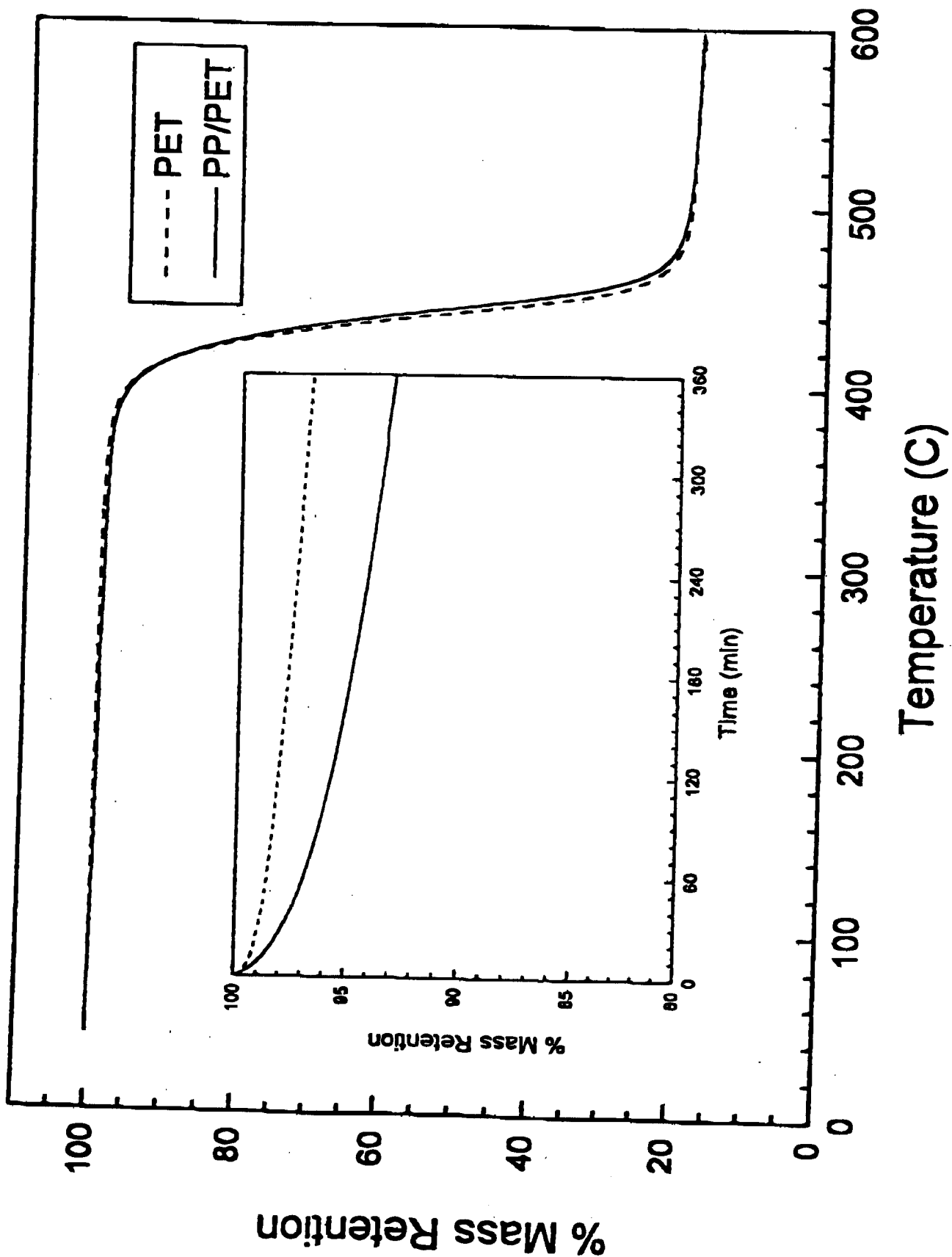


FIG 3

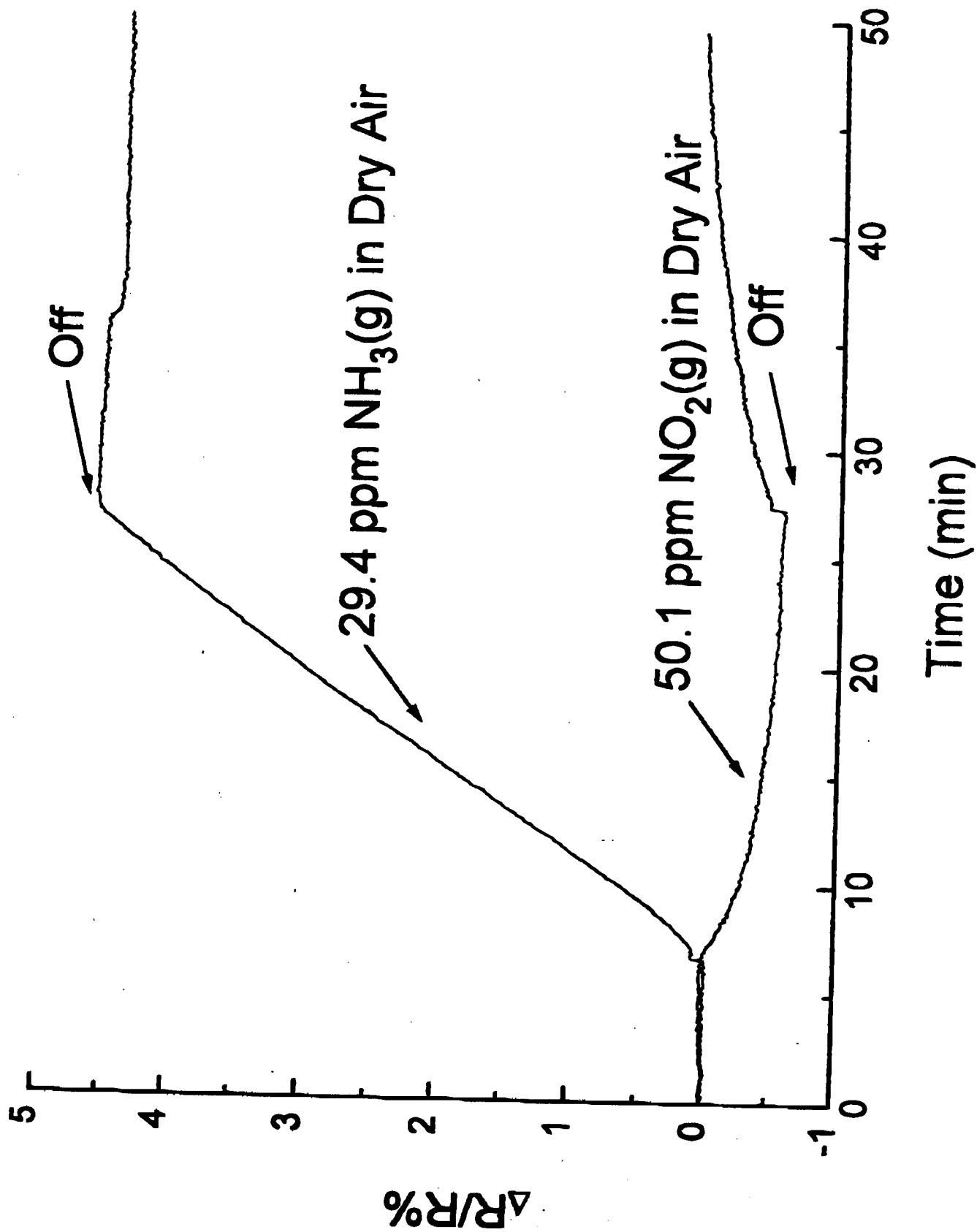
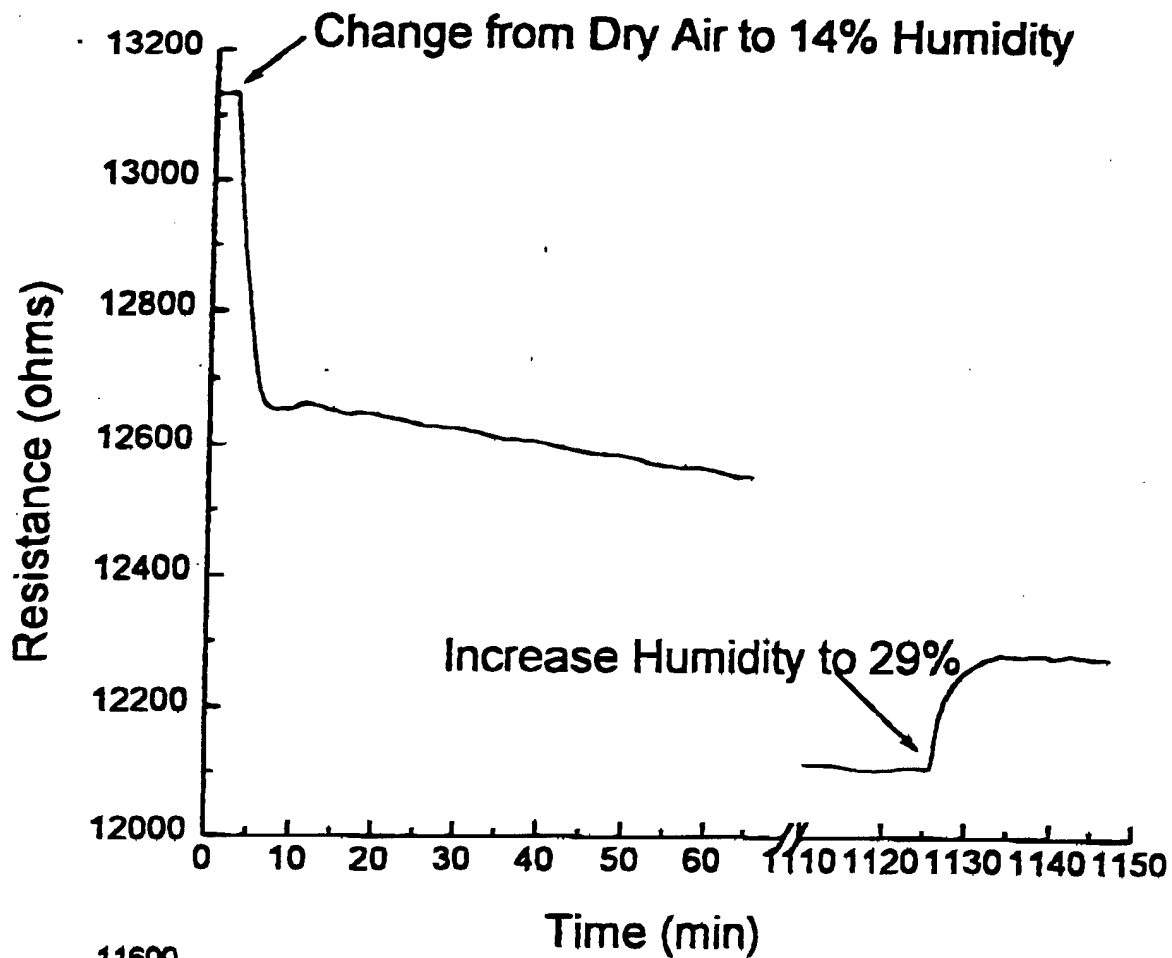


Fig. 4

A)



B)

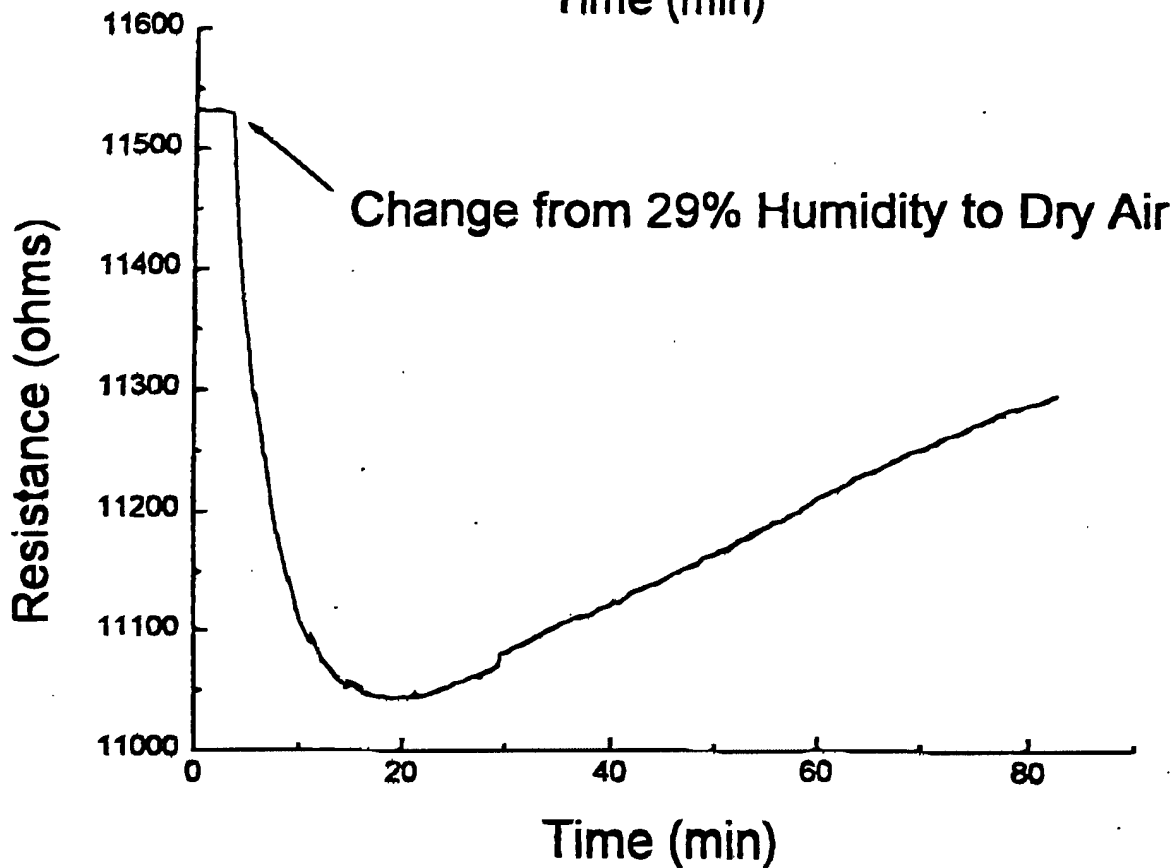


FIG. 5

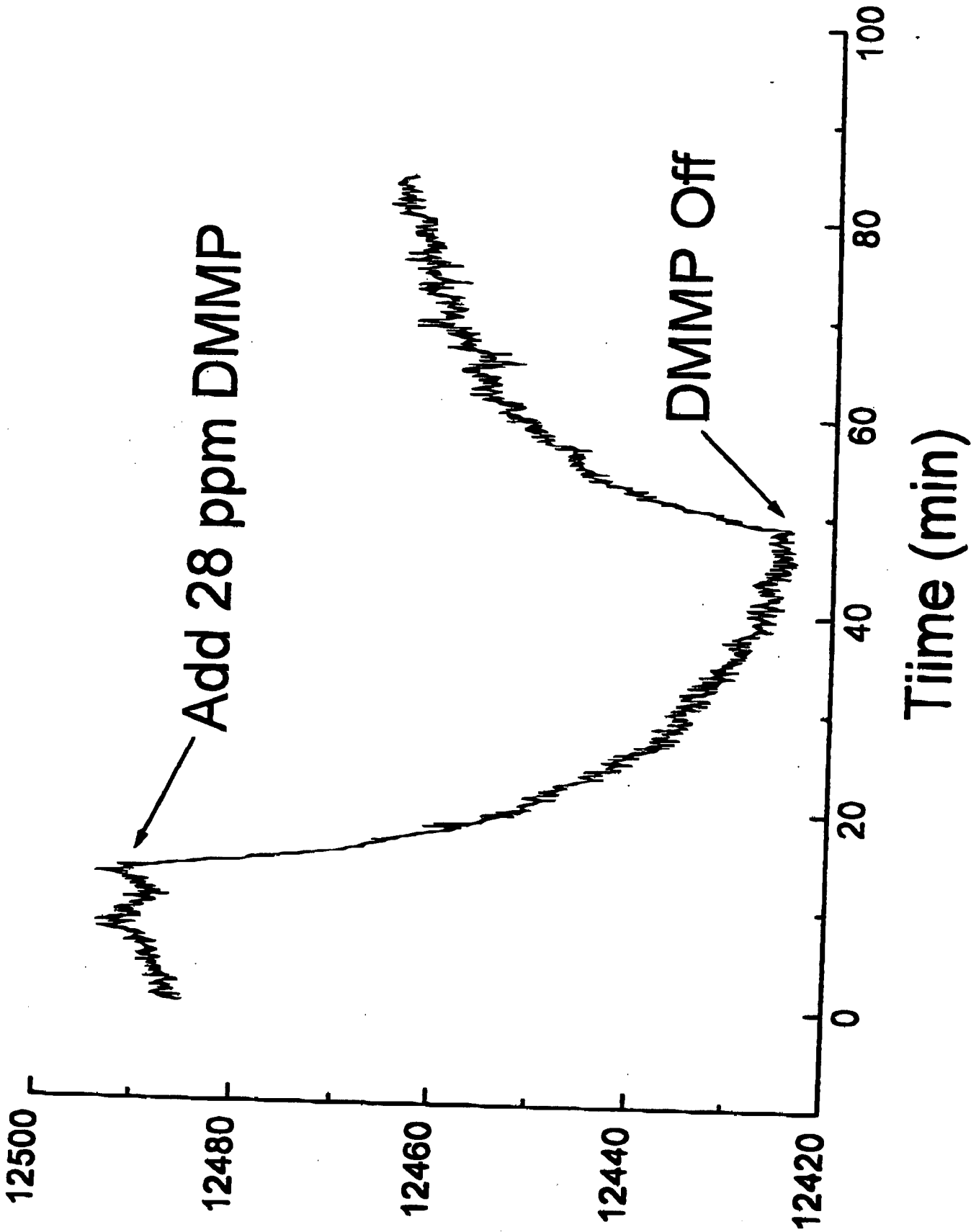


FIG. 6



FPOL

F16.7

$\Delta R/R \%$					
Fabric Type	Dry Air	29 ppm NH_3	69 ppm NO_2	28 ppm DMMP	H_2O 60% Rel. Humidity
PP/NDSA/Nylon	0.23	1.76	-0.50	-0.40	-6.36
PP/NDSA/PET	0.55	3.82	-0.45	-0.31	-8.92
PP/AQSA/PET	0.42	1.13	-0.27	-0.35	-4.26
PAN/Cr	0.17	7.41	13.7	-0.09	-107.6

FIG. 8

Exposure to 28 ppm DMMP in Dry Air		
Fabric Resistivity for PP/NDSA on PET	Resistivity Change (Signal/Noise)	Initial Response Slope ($-\Delta R/\Delta t$ /Noise, 1/min)
211 ohms/cm ²	8.7	0.65
775 ohms/cm ²	59.4	3.53
3000 ohms/cm ²	50	8.42

FIG. 9

$\Delta R/R$ %				
Polymer Overcoat	21 ppm NH_3	50 ppm NO_2	28 ppm DMMP	H_2O 10% Rel. Humidity
PP/NDSA Blank	4.33	-0.57	-2.05	-13.3
FPOL Coated	3.86	-0.76	-1.96	-12.1
PEI Coated	0.12	-0.88	-2.01	-29.4
PIB Coated	4.74	-1.90	-0.77	-9.4
SXFA Coated	5.03	—	-0.12	-7.7

FIG. 10