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Printed Textiles with Chemical Sensor Properties

Abstract
In this study the authors proposed the introduction of chemical sensors directly on textile surfaces in the form of conductive transmission parts using the screen-printing technique. A liquid vapour-sensitive, printing surface made with the use of multi-walled carbon nanotubes was also evaluated. Carbon nanotubes show effective chemo-sensory properties because the chemical agent leads to changes in electrical conductivity. The research concerned the assessment of sensor efficiency for chemical incentives in the form of selected fluids and their vapours. The best sensory properties were observed for polar vapour at a level of relative resistance over 40%. In the case of vapours of non-polar fluids the sensory reaction of the printed fabrics is much weaker – at a level of relative resistance of about 25%. The printed textile backings subjected to the influence of a fluid show an immediate reaction, while in the case of fluid vapour the reaction occurs after a few seconds. Detection of the presence of dangerous chemical agents such as organic liquids and their vapour is possible by means of a structure composed of sensors.

Key words: *chemical sensor, chemo-resistive sensor, screen printing, carbon nanotubes.*

■ Introduction

Printing is regarded as a decisive and attractive technology with a range of possibilities for creating electroconductive transmission parts which would enable textiles to have intelligent features. Current progress in the miniaturisation of microelectronics with new technological abilities enables the integration of functionality in clothes, allowing for completely new applications. The vision of wearing intelligent clothes involves electronic systems becoming an integral part of our daily clothes [1, 2].

The technology of printing electroconductive transmission parts has broad application in microelectronics, but it is mainly used on lamina, foil, glass and polymers. Most conductive inks contain nanoparticles of silver, gold, copper and blends of these elements as well as silver nitrate. Unfortunately, in most cases, a process high temperature is needed. This high-temperature process should be avoided in the case of textiles [3 - 7].

The authors decided to concentrate on a new area of research dealing with the electroconductive properties of textiles using printing techniques. It should be noted that textile products in the majority do not have smooth surfaces - they are rough and can cause some difficulties in the formation of conductive transmission parts. The printing method used by the authors shows superiority over other printing techniques used so far; the printing method, for example, does not require the interlacing of electroconductive threads in the warp or weft directions for the insertion of tiles or aerials [7 - 11].

Research by B. Karaguzel et al on screen printing was performed on different nonwoven substrates such as Freudenberg's Evolon®, BBA FibreWeb's Resolution Print Media and DuPont's Tyvek® using different conductive silver inks of different viscosity and percentage of silver such as Creative Materials and DuPont. Tyvek® is a flash spun, highly calendared structure which is made from polyethylene fibres. It has a plasma treated surface, which helps the bonding of the conductive ink to the substrate. Tyvek® has very few small capillaries on the surface. The substrate with pores of a larger size experienced a thinner ink layer on the surface, which meant that a large amount of conductive ink penetrated into the substrate. In contrast, the smaller pore size did not allow conductive ink to go through the substrate and showed the lowest resistance on the printed track. The electrical conductivity of printed media is optimised when printing takes place mostly on the surface. Other factors are also involved in printability such as ink viscosity, mesh count, and squeegee hardness. Higher viscosity can prevent ink from spreading over the fabric surface and create a thicker ink layer [12, 13].

Implementation of a new class of electrochemical sensors and biosensors for direct skin-based monitoring of relevant compounds of physiological and safety has been developed in the form of temporary transfer tattoo paper. The new epidermal electrochemical system has broad implications beyond the scope of analytical devices and can facilitate diverse new applications [14].

Y. Yang at al. described the incorporation of amperometric sensors into clothing through direct screen-printing onto the textile substrate. Particular attention was paid to electrochemical sensors printed directly on the elastic waist of underwear, which offers tight direct contact with the skin. The textile-based printed carbon electrodes have suitable voltammetric and chronoamperometric measurements of 0 - 3 mM ferrocyanide, 0 - 25 mM hydrogen peroxide, and 0 - 100 μM NADH [15].

The electroconductive transmission parts can be obtained by conventional printing techniques such as screen-printing as well as by using modern techniques like jet-printing [1, 2, 6, 16].

I. Locher's [1] publication proposes screen-printing using ink as a technology for creating transmission parts with impedance control in textiles. In this method silver-based printing ink is placed on the surface of woven fabrics. The process does not change the structure of the woven fabric, and, thanks to the print obtained, it can achieve new electrical properties due to an electric resistance of about 50 Ω.

Since carbon nanotubes were invented in 1991 by Sumio Iijiam from NEC Fundamental Research Laboratories at Tsukuba in Japan, they have had newer and newer applications in electric circuits and sensors as well as in optics [17 - 19].

The electroconductive transmission parts obtained were supposed to be sensitive to chemicals (chemical sensors).

The authors suggest introducing chemical sensors directly on textile surfaces in the form of conductive transmission parts by screen-printing. Screen-printing

enables the overprinting of substrates with different flexibilities, textures and shapes.

The novelty of the work is optimising the durability of the nanomaterial textile substrates connected in order to reduce the possibility of their release into the bloodstream and penetration as much as possible while keeping the sensory properties. To build a correct system to measure the chemical sensor, it is necessary to prepare measuring sensor equipment that processes the signal and a monitoring system that converts the signal collected into readable information, however this is not the subject of this article.

The authors of this paper focused on an innovative approach to screen-printing a conductive carbon nanotube printing paste to measure changes in sensitivity to chemical stimulus via changes in resistance.

■ Experimental details

Carbon nanotubes (Nanocyl®7000 series) were selected as a chemical sensor because of their large surface area, sensitivity to chemicals and other environmental factors, electrical conductivity and durability. Carbon nanotubes have a firm position in the group of nanomaterials used in sensorics. However, it is problematic to apply nanotubes in such a way that they are toxicologicaly safe in use, permanently connected with the substrate and that they guarantee the highest sensitivity to the stimuli examined, with minimum possible content in the sensoric element. A printing paste was prepared on the basis of the water dispersion of nanotubes and the cross-linking composition of the photoinitiator and aliphatic urethane acrylate was selected. Polyester-cotton woven fabrics (70%/30%) were printed using an elaborated paste. Very good dielectric, mechanic and strength properties of fibres from polyester, good resistance to aging and action of light, good thermal resistance, high chemical resistance to the action of diluted acids, alkalis, aliphatic and aromatic hydrocarbons, complete biological resistance, resistance to squishing and stability of dimensions are the parameters thanks to which these fibres are used in different types of textiles and in technical products [20]. Polyester-cotton fabric with a twill weave was purchased from the Dutch company Ten Cate Protect (***Table 1***).

Characteristics of the paste and printing techniques.

An aqueous dispersion of carbon nanotubes, trade name AquaCyl (AQ0101), from Nanocyl, was used for the investigations. This dispersion contained from 0.5 to 1.5% MWCNT of the Nanocyl®7000 series. AquaCyl AQ0101 was characterised by a surface tension of about 57 mN/m, viscosity of 36 cP and pH 7, were determined at 25 °C. Additionally the dispersion contained a dispersing agent at a quantity of 0.1 - 3% [21].

For modification of the commercial dispersions, the following auxiliary substances were used: DBSA ($C_{12}H_{25}C_6H_4SO_3H$) solution 70 wt% in isopropanol (analytically pure from Sigma Aldrich, USA) and SLS ($CH_3(CH_2)_{11}OSO_3Na$ (analytically pure from Sigma Aldrich, USA), Ebecryl 2002 (aliphatic urethane acrylate from Cytec, water compatible, UV curable system) and Esacure DP250 (water dispersion of photoinitiators from Lamberti SPA).

To obtain the printing paste, the dispersion was connected with the selected cross-linking composition of the photoinitiator and aliphatic urethane acrylate. The selection of chemical compounds was based on the assumption that they do not have a destructive influence on the fibre material.

Next, using printing templates, the printing paste was placed on the woven fabric with the inclusion of nanotubes to create an electroconductive surface. The printed surface was made by screen printing (43 mesh/cm²) five sheets of A4.

Next the prints obtained underwent the cross-linking process. The conditions of the cross-linking process were established on the basis of initial works. Optimisation of the cross-linking process was done by total tying cross-linking mixture. The important activity in this process was avoiding destroying the woven fabrics by UV radiation. The prints obtained were fixed in the cross-linking process by UV-C 335 radiation from a 2100-W UV lamp produced by the Philips Company, with a working length of 195 mm. The dose of radiation was 3.5 J/cm².

After the exposure process, twenty-five 1 × 2 cm samples were cut from sheets of A4 (five of each sheet of A4) for investigation of the thickness of the coat applied and for assessment of sensoric properties. Microscopic examinations showed that the thickness of the layer applied on the textiles ranged from 28.5 - 32.0 μm (***Figure 1***) in various places on the five sheets of A4.

■ Research methods

Tests of the sensitivity to organic liquid and its vapour were carried out with the use of a laboratory measurement system. Printed textiles are solid polymer bodies in which carbon nanotubes are dispersed appropriately. Under the impact of the organic fluid's vapour, their conformation in the polymeric medium and conductive properties change. The effect of those modifications results in a change in the electrical resistance of the printed textiles.

Sensory properties of the products were assessed from the point of view of different chemicals in their liquid state. The liquids applied were selected based on Standard EN 14605+A1:2009. The sensitivity of the printed fabrics was investigated. For our research work, seven polar and non-polar organic liquids and their vapours were used (standard EN 14605+A1:2009). Under the influence of the organic liquids or vapours, the kinetics of changes in the electrical resistance of the transmission parts of the printed fabrics were recorded. The sensitivity of the printouts obtained to the presence of the fluids' vapours was
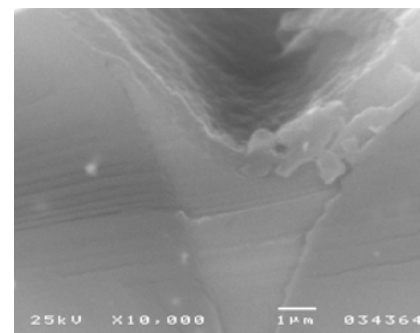

Figure 1. *Microscopic examinations of the thickness of the layer applied on the textiles.*

Table 1. *Physical characterisation of fabrics used.*

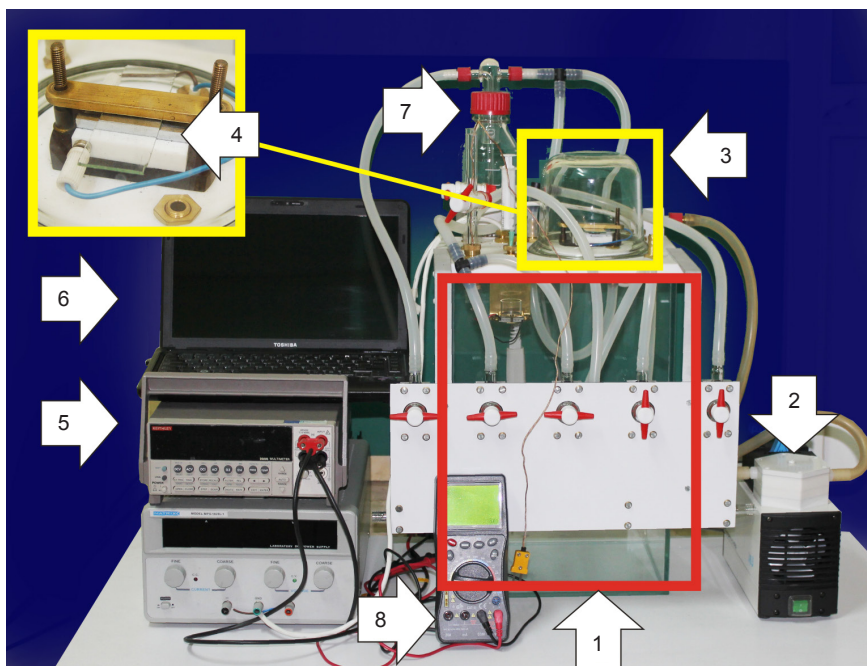| Raw material content	Percentage content, %	Weave	Surface mass, g/m²	Thickness, mm	Apparent density, kg/m³
Polyester/Cotton	70/30	twill	205.5	0.52	387.7

Figure 2. *Measuring system for investigating vapour by textile sensors: 1) Gaseous chamber with a volume of 0.024 m³, 2) pump, 3) Measurement chamber, 4) Measuring electrodes, 5) Keithley multimeter, 6) computer, 7) System ensuring proper humidity of environment, 8) thermometer [20].*

The sensory effect was evaluated on the basis of relative changes in resistance caused by the chemical agent.

The results were recorded on a computer with the use of USB View programs. The measurement results were then sent to an Excel program to be processed.

The sensitivity of the ink-printed woven fabrics to the following liquids and selected liquid vapours was tested: methanol, ethanol, acetone, dioxane and toluene. The selection of the type of substances for the test of liquid vapour sensitivity was based on the norm PN-EN ISO 6529:2005P.

■ Results and discussion

In **Table 2** and **Figures 3 & 4** (see page 71) results of the influence of the organic fluids and their vapours (at a concentration of 100 ppm in the chamber) on textiles are displayed.

Based on the data collected, diagrams of the changes in vapours and resistance as functions of time were generated. The sensitivity of the samples to the vapours and liquid was determined from relative changes in resistance, which were calculated separately for each cycle according to **Equation 1**.

$$R_{rel} = \frac{R - R_o}{R_o} \qquad (1)$$

where: R_{rel} - relative resistance, R_o - initial resistance, R - final resistance.

Data from **Table 2** are illustrated in **Figures 3** and **4**.

On the diagrams the arrow presents the moment of immersing of the samples in the liquids selected. The diagrams present the sensory reaction due to the given external stimulus.

The strongest sensory reaction of the printed backing in the case of fluids was observed for polar fluids, e.g. acetone, at a level of the R_{rel} factor of over 80%. In the case of non-polar fluids the sensory reaction of the printed fabrics is much weaker – at a level of the R_{rel} factor of about 50%.

Analysing the results of the research presented in **Table 2** and **Figures 3 - 4** for the fluids' vapours, one can notice that the printouts obtained react strongest to the vapours of polar fluids. The best sensory properties were observed for vapours of ethanol at a level of the R_{rel} factor of over
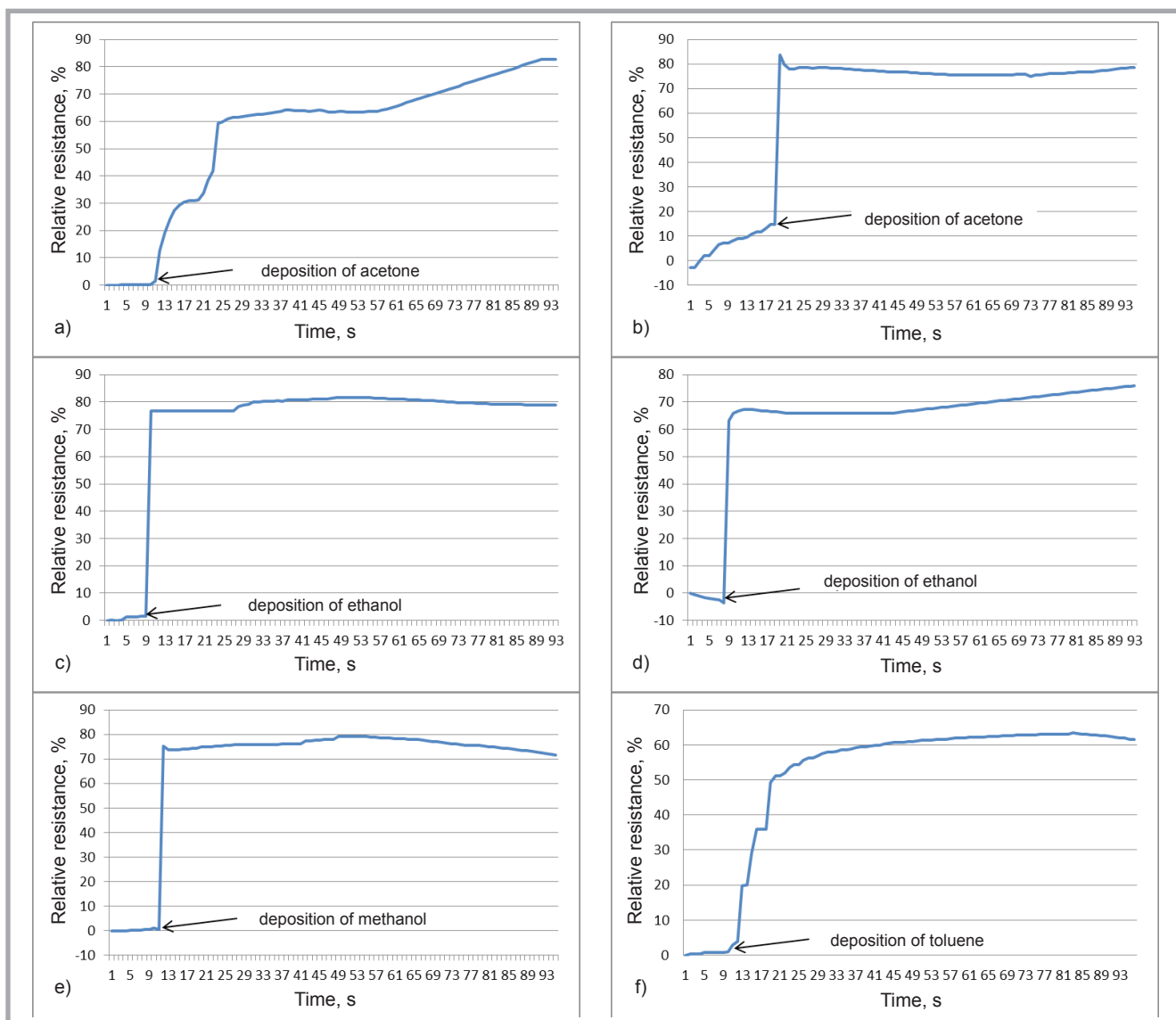
examined with the use of a specially constructed station (**Figure 2**). This consists of two parts: The first is used for evaporating the fluid. The amount of fluid to obtain concentrations of vapour at a level of 100 ppm inside the measuring chamber is calculated. The second consists of the measuring chamber and devices responsible for keeping the temperature and humidity inside the chamber at the level of 23 °C and 25% (humidity). Inside the chamber there are measuring electrodes connected to a Keithley multimeter. Sensory sensitivity measurements of the samples were performed by dosing vapours of different solvents and measuring the changes in their electric resistance. The vapours of selected fluids were prepared by evaporating the amount of fluid per unit of the system's surface cal-

culated. The vapours are collected in a glass container and next, with the use of a pump, supplied to the measuring chamber, where the printed samples were previously placed. The measurements were performed before and after supplying the fluids' vapours.

Samples for measurements of the sensitivity of the presence of fluids were cut in the shape of the letter U. The ends of the samples were clamped in electrodes connected to the multimeter, and their bottom part was dipped up to ¾ of their height in the fluids researched (aimed at avoiding the dipping of electrodes in the fluid). Next the samples remained in a state of relaxation. The samples were subjected to a constant measuring of resistance, during which a voltage of 3 - 4V was applied to the sample.

Table 2. *Sensory factor R_{rel} of textile substrates printed with MWCNT.*

Kind of chemical substance		Sensory factor (R_rel), %		Standard deviation δ	
		Before washing	After washing (25 cycles)	Before washing	After washing (25 cycles)
Organic liquids	Methanol	74	72	2.96	2.35
	Ethanol	76	72	3.11	2.99
	Acetone	84	83	2.99	3.00
	Dioxan	22	21	1.86	1.79
	Toluene	54	53	2.15	2.00
Liquid vapours	Methanol	38	35	1.68	1.61
	Ethanol	42	41	1.66	1.68
	Acetone	37	32	1.75	1.56
	Dioxan	19	15	1.95	1.99
	Toluene	27	24	1.77	1.78

Figure 3. *Diagrams characterising the sensitivity of the printing compounds to selected liquids before washing: a) acetone, c) ethanol, e) methanol, f) toluene; and after washing: b) acetone, d) ethanol.*

40%. In the case of vapours of non-polar fluids the sensory reaction of the printed fabrics with a share of polyester fibres is much weaker – at a level of the R_{rel} factor of about 25%.

The printed textile backings with a share of polyester fibres subjected to the influence of a fluid show an immediate reaction, while in the case of the fluids' vapours the reaction occurs after a few seconds.

Based on the diagrams presented, the moment of implementing the vapours of the solvents selected into the measurement chamber of the measuring system in which the sample investigated is placed, is marked with an arrow. The diagrams show the sensory reaction to the given stimulus.

It is a significant fact that the results are repeatable, which can be certified by the low coefficient of their changes in the Table presented.

The samples examined were rinsed with nitrogen every time after subjecting them to vapours of the fluids selected, in order to return them to the previous level of electric resistivity. The research were done cyclically for each of the samples. It should be noted that the samples subjected to the action of polar fluids, after rinsing with nitrogen, return to the original state, which testifies their real possibility of multiple uses. In the case of non-polar fluids the reaction is weakened. The time of regeneration of the sensors is equal to 100 seconds in nitrogen, while in air the time of regeneration increases twice.

A very important aspect of the research conducted is that the sensors can be used multiple times because they do not damage under chemical agent treatment. The investigation was repeated 25 times for each of the chemicals used. In **Table 2** the mean value of the results is presented. On the basis of our examinations, it can be stated that the prints obtained can successfully operate as electroconductive transmission parts.

■ **Summary**

The printing paste composition used, which is based on carbon nanotubes, shows high rates of exposure during sensory testing of chemical agents at work. This printing technique allows for the use of carbon nanotubes for durable connection to a textile base.

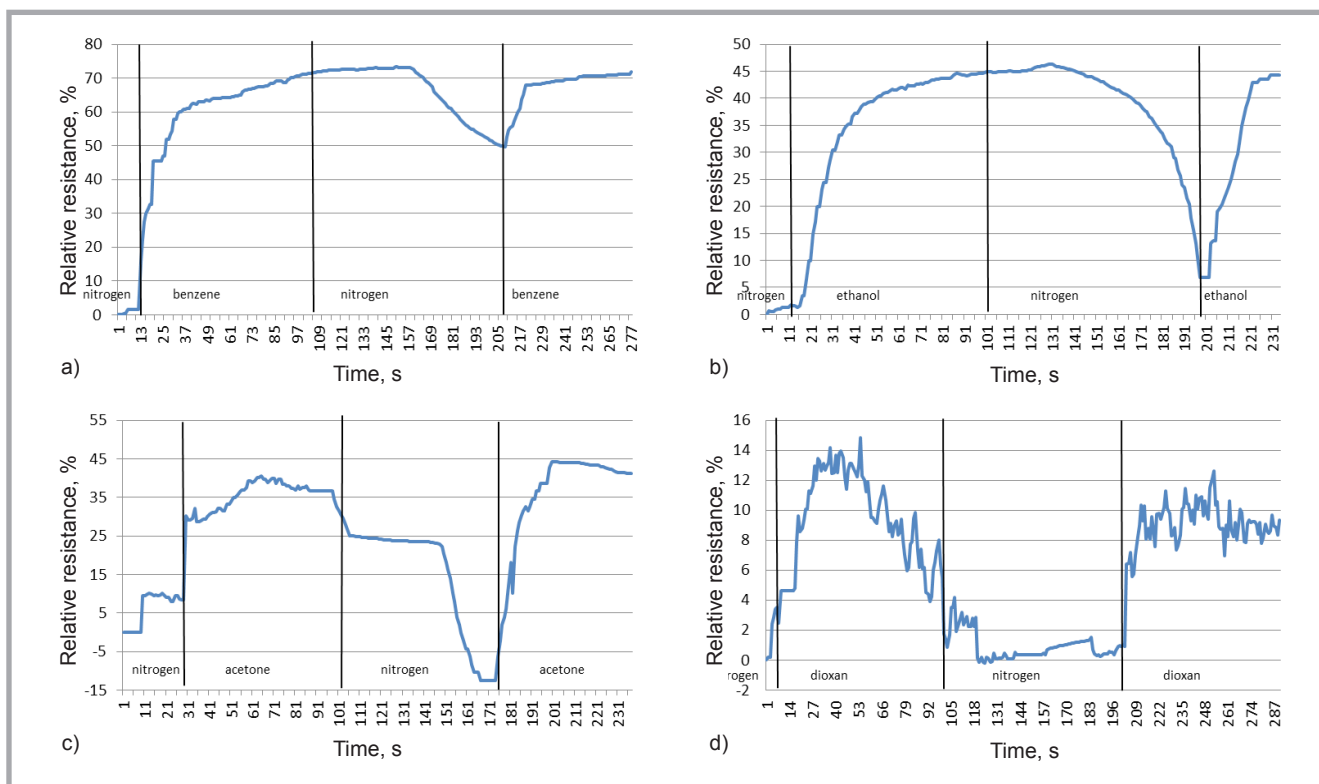The ink compositions obtained can be employed for making chemical sensors

Figure 4. *Diagrams characterising the sensitivity of the printing compounds to selected vapours before washing: a) benzene, b) ethanol and c) acetone, d) after washing with dioxan.*

in explosion endangered areas. They can be placed in the outer layer of work clothing, for e.g. with velcro, as well as situated, for example, in production facilities. The sensors can also be placed in an area of containers with flammable fluids. For their employment in industrial production it is necessary to carry out an integration of the fabricated sensor with a digitalising computer system. It is also necessary to perform an analysis of the influence of maintenance processes of those sensors in further works.

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