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# Sensitivity of Organic Humidity Sensor Element on Organic Vapours

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**Abstract**

The paper deals with an impact of various organic vapours on electrical parameters of organic humidity sensor element. This impact was researched in order to find out a potentially negative impact of organic vapours on sensitive organic layer. The sensitive layer of sensor element was deposited from the liquid phase of phthalocyanine on a ceramic substrate with interdigital electrode system. The sensor element was exposed to the effect of different analytes. Subsequently, the impedance characteristic of the thin film sensitive layer was measured. The comparison of responses to various gases and vapours is discussed in more detail as well.



*Keywords:* *Phthalocyanine; humidity sensor element; interdigital electrodes; organic vapours*

## 1. Introduction

In the last decade, there has been enormous interest in the development of a wide range of low-cost electronic (RFID [1], sensors [2] [4], displays [8] and batteries [5]). The one of the possible way how to produce a low-cost electronic is used organic conductive and semiconductive materials. The organic electronics is also called plastic or printed electronics. The prognosis of electronic market development in the area of organic electronic is shown in the following picture (Fig. 1.). The OE-A is the leading international industry association for organic and printed electronics. The prognosis of OE-A shows the increasing market share of organic and printed electronic. Conductive and semiconductive organic materials could not substitute classical inorganic materials in all applications, but they

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could be very useful in many applications because of their special properties. They can be preferably used in the fabrication of flexible and lightweight devices.

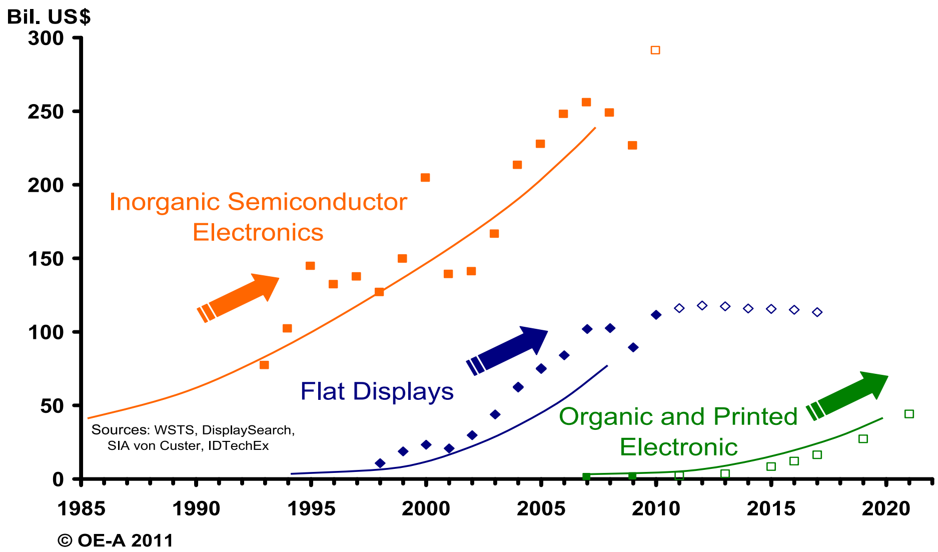


Fig . 1. Electronics market, Prognosis 2020.

The difficult preparation of inorganic and high cost of pure base material is the generally problem of inorganic materials. The vacuum techniques, which are usually used for the application of inorganic materials, are expensive but also time and power consuming. The price of pure organic sensitive material, produced in great volumes, can be also lower than inorganic ones. The application of organic materials is easier. Organic conductive and semiconductive materials can be applied by screen printing, inkjet printing or other suitable printing techniques [16].

## 2. Phthalocyanines

The typical example of semiconductive organic materials are phthalocyanines. Phthalocyanines (PCs) are organic materials with an intrinsic conductivity. They are quite well known as organic pigments used in paint industries [7], photosensitizers in photodynamic therapy [11] and as industrial catalysts [3].

There are a lot of possibilities how to use these materials in the other branches [6] [7]. Nowadays, the research activities are focused on the use of phthalocyanines in the electrical engineering industry. PCs are usable in optical data storage [9], organic solar cells [10], optoelectronic devices [12] [17] and components [13].

Molecules of phthalocyanine can exist as multiple stacks based only on a weak mutual bonds or in single compact molecular units holding a specific spatial conformation. The central metal atom of molecule is strongly bonded to the organic ligand (Fig. 2.) [14].

Phthalocyanines could be substituted by different substances. A substitution of a hydrogen atom or hydrogen atoms, bonded to benzene rings in phthalocyanine molecule, enables its solubility in dissolving agents. Unsubstituted phthalocyanines are insoluble in polar and non-polar dissolving agents. This form of phthalocyanines is very difficult to process. Different types of substituents significantly affect the electrical and mechanical properties of phthalocyanines as well as their solubility [15].

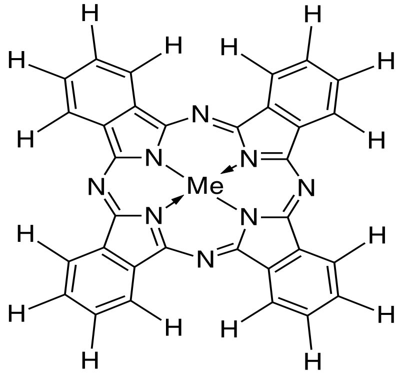

Fig. 2. Chemical structure of unsubstitued phthalocyanine.

## 3. Humidity sensor element

### *3.1. Substrate and electrode system*

The humidity sensor element consists of the electrode system and the base substrate. The thin sensitive layer of appropriate phthalocyanine is applied on electrode system. The substrate consists of 99.5 % $Al_2O_3$.

The electrode system is prepared by the sequential deposition of NiCr, Ni, and Au layers using a lift of method. Thickness of this electrode system is 400 nm. The electrode fingers are 25 μm wide and the wide of insulation gap is the same. Figure 3. (a) shows the model of a base substrate with the deposited phthalocyanines layer.

### *3.2. Organic sensitive layer*

The electrical properties of phthalocyanine are given by the electron and ion conductivity. The electron conductivity of phthalocyanine molecule is ensured by alternating single and double bonds which lead to the broad π electron conjugation. A conjugated bond means the alternation of single and multiple bonds. The presence of electric charge carrier is the next demand to achieve proper electrical conductivity. It is usually assured by the phthalocyanine oxidation.

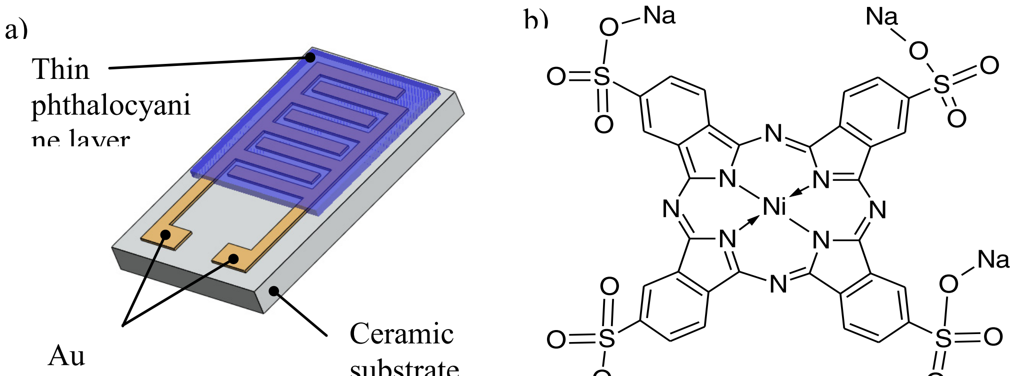


Fig. 3. (a) Humidity sensor element model; (b) Chemical structure of sulphonated nickel phthalocyanine molecule.

The ion conductivity could be increased by adding suitable substituents. Substituted phthalocyanines ion conductivity can be affected by the environmental conditions. Based on the previous experiments the sensing properties of phthalocyanines were observed. The sensitivity of phthalocyanine layer on the level of humidity was increased by substitution hydrogen atoms for sulphonated groups. In the case of humidity absorption, the water molecules dissociate sulphonated groups $SO_3Na$ to $SO_3$- and Na+. This dissociation causes increasing of the ion conductivity and the level of humidity sensor impedance will be lower.

Nickel tetrasulfonated phthalocyanine ($NiPc(SO_3Na)_4$) was selected as a material for sensitive layer of the humidity sensor element (Fig.3. (b)). The solid phase of the phthalocyanine was dissolved in 0.03 g/ml of water. This liquid phase of PC was deposited by spin coating method. In this case, we have used 3000 RPM.

## 4. Testing methodology

High sensitivity of $NiPc(SO_3Na)_4$ phthalocyanine to the humidity exposure is known from previous experiments (Fig. 4. (a)). The next step is the evaluation of an impact of organic vapours on the sensor layer electrical parameters.

Sensor element was exposed to various organic vapours and the level of its impedance was measured. The precision LCR meter (1 kHz, 1 V) in four wire connection was used for the measurement.

The experiment was done in a special apparatus where the presence of analyte could be regulated. It is done by two - state valves. The sample could be exposed to a defined relatively dry air (t = 23 °C, RH = 10 %) or to an analyte. Vapours of analyte are produced by the bubbling of dried air in a liquid phase of analyte. The measuring cycle consist of rapid changes of dry air and defined analyte (Tab.1).

## 5. Experiment results

Results of experiments are summarized in Tab.1. The impact of water vapour to the level of impedance of organic sensor element is also included in table for the comparison.

Tab. 1. The impact of different chemicals on humidity sensor element.

| | Level of impedance | | |
|---|---|---|---|
| **Analyte vapours** | **Dry air** ***(23 °C, 10% RH)*** **$Z_{DA}$ *(kΩ)*** | **Analyte $Z_A$ *(kΩ)*** | **Relative impedance change $Z_X$ *(-)*** |
| Water | 2450 | 0,82 | -2986,80 |
| Ethanol | 1100 | 2068 | 0,47 |
| Acetone | 2600 | 3500 | 0,26 |
| Toluene | 1250 | 1550 | 0,19 |
| Chloroform | 1560 | 1843 | 0,15 |

The impact of various organic vapours on the level of sensor element impedance may be represented by the formula:

$$Z_x = \frac{\Delta Z}{Z_A} = \frac{Z_A - Z_{DA}}{Z_A} \; (-) \tag{1}$$

$Z_X$ is the relative impedance change; ΔZ is the difference between the level of impedance of sensor element exposed to analyte ($Z_A$) and the level of impedance of sensor element exposed to dry air ($Z_{DA}$).

The level and orientation of relative impedance change shows the impact of analytes on the electrical parameters of humidity sensor element.

Tab 1. shows that water vapour has the biggest impact on electrical parameters of thin layer of tetrasulfonated phthalocyanine. The response is negative so the level of impedance decreased.

The impact of ethanol vapour on the level of impedance of organic sensor element is different from other analytes. There is gradual increasing of the impedance of sensor element. This fact could be clarified by the theory of interaction of ethanol molecules with molecules of phthalocyanine. We expected that this interaction blocks charge transfer trough the phthalocyanine molecule.

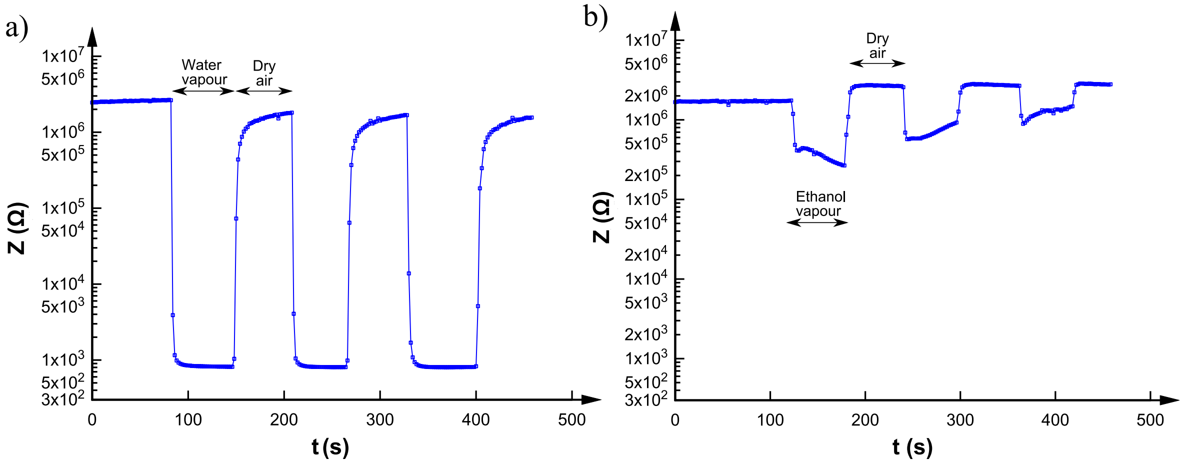


Fig. 4. (a) Water vapour impact on the level of impedance of humidity sensor element, (b) Ethanol vapour impact on the level of impedance of humidity sensor element.

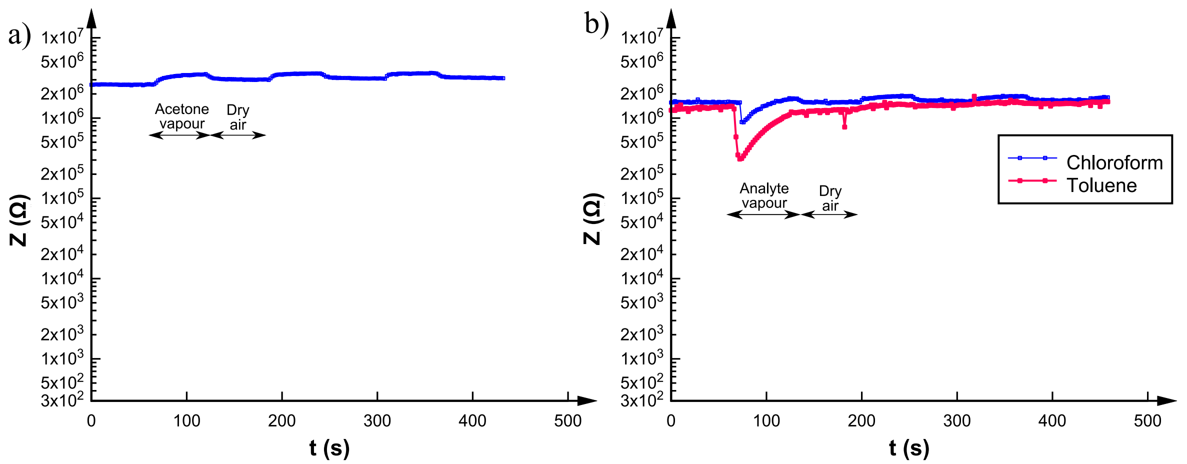


Fig. 5. (a) Acetone vapour impact on the level of impedance of humidity sensor element; (b) Toluene and chloroform vapour impact on the level of impedance of humidity sensor element.

Fig. 5. (a) illustrates relatively small impact of acetone. The marginal impact is increasing of the level of impedance. It is caused by decreasing in the level of remaining humidity (10 % RH) in measuring apparatus. Acetone has not big impact on sensing properties of organic humidity sensor element.

The impact of toluene and chloroform were placed in Fig. 5. (b). Their impacts are very similar. When the sensor element is exposed to the analyte for the first time, the level of impedance rapidly decreases. This effect was not observed in next measuring cycles. It is probably caused by a presence of residual humidity in apparatus.

## 6. Conclusion

All tested sensor elements were exposed to the impact of relative humidity after their exposure to organic vapour analytes. It was done in order to verify the functionality of sensing layer of humidity sensor element. The sensing properties were not changed. The impact of tested organic vapours on the sensor element is small in comparison to the impact of water vapour.

The next step in the research of organic humidity sensors is to find out a negative impact of organic vapour combined with different concentration of water vapour.

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