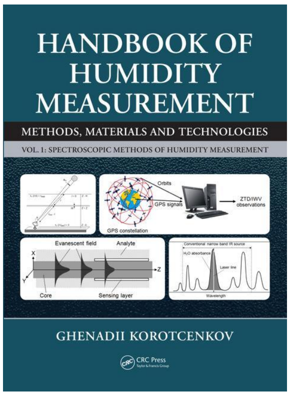

# Handbook of Humidity Measurement Methods, Materials and Technologies: Spectroscopic Methods of Humidity Measurement

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## Moisture Indicators

Publication details
https://test.routledgehandbooks.com/doi/10.1201/b22369-13
Ghenadii Korotcenkov
**Published online on: 26 Mar 2018**

**How to cite :-** Ghenadii Korotcenkov. 26 Mar 2018, *Moisture Indicators from:* Handbook of Humidity Measurement, Methods, Materials and Technologies: Spectroscopic Methods of Humidity Measurement CRC Press
Accessed on: 03 Dec 2023
https://test.routledgehandbooks.com/doi/10.1201/b22369-13

# 13 Moisture Indicators

In the truest sense of the word, moisture indicators are not the sensors. However, their concept of operation is based on the same physical and chemical principles that have been discussed in Chapter 12. Therefore, we decided to include a description of moisture indicators in the current chapter.

## 13.1 PRINCIPLES AND MATERIALS

Sometimes it is desirable to detect only a change in the amount of moisture in the sample, whereas the exact concentration is of only secondary importance. Such may be the case on the outlet of drying beds where the moisture breakthrough will indicate the need for regeneration. In other cases, for example, we must be sure that the relative humidity (RH) does not exceed 30%–35%. RH in the range of 30%–35% was the concern because this is when corrosion can begin.

Research has shown that indicated problem can be solved by using certain salt crystals, which change color with the appearance of moisture. It has been found that the use of this effect is the most economical method for detecting changes of moisture level (Blinn 1965). Experiments have shown that cobalt chloride, discussed in the previous Chapter 12, is the material most suitable for such applications (Katzin and Ferraro 1952). One should note that *chemical compounds of the element cobalt have been used for thousands of years as coloring agents in paint, ink, ceramics, and glass.* The color change is a result of chemical reactions taking place with the participation of cobalt chloride and water. As the humidity increases, and water is absorbed by $CoCl_2$, the crystal structure rearranges itself to make room for water molecules. The *hydration* reaction may be represented by the chemical reaction in Equation 13.1. Two water molecules surround each cobalt atom, forming the *dehydrate*. Cobalt chloride dehydrate is purple.

$$CoCl_2\ (\text{blue}) + 2H_2O \rightarrow CoCl_2 \cdot 2H_2O\ (\text{purple}) \qquad (13.1)$$

Chemists use the raised dot "·" symbol before the $H_2O$ to indicate the number of water molecules that have become incorporated into a compound at the atomic level. As the humidity increases further, the crystal structure again changes, this time rearranging itself to let four more water molecules in to surround each cobalt atom, forming the *hexahydrate*:

$$\begin{aligned} &CoCl_2 \cdot 2H_2O\ (\text{purple}) + \\ &\quad 4H_2O \rightarrow CoCl_2 \cdot 6H_2O\ (\text{pink}) \end{aligned} \qquad (13.2)$$

In reality, cobalt chloride has six states of hydration and exhibits progressive color changes with corresponding changes in hydration state. Several reports indicate that with excess exposure to moisture cobalt chloride can exist in even higher states of hydration (Russell and Fletcher 1985), although no further color change can be noted. As the initially anhydrous cobalt salt bonds with each water molecule, it exhibits a color change from blue to a fully hydrated pink (Katzin and Ferraro 1952). Heating the hydrated forms of cobalt chloride reverses the above-mentioned reactions, returning cobalt chloride to the blue, water-free, or *anhydrous*, state. Water is *liberated* in these reactions, known as *dehydration* reactions. Thus, indicated property allows creation of a color-change element, which turns from blue to lavender to pink as the humidity increases, and turns back to blue when the humidity decreases. It was established that this characteristic enables these elements to be reused as long as they have not been exposed to humidity in excess of 90% for periods of 36 h or longer, which tend to wash out the element.

It was found that on the basis of cobalt chloride nonreversible humidity indicators can be made. For these purposes, ammonia salts are added in the element. In the presence of vapors of ammonia, the elements lose the reversibility of the color. Such nonreversible elements or maximum humidity indicator cards are needed to prevent the fact when certain humidity levels have been exceeded, or when the desiccant may need to be recharged or replaced. For example, these cards can indicate the highest level of humidity experienced by cargo during its voyage, regardless of current (potentially lower) humidity levels. Maximum humidity indicator cards provide a clear, unmistakable means of determining if goods have been exposed to damaging humidity levels during their journey. If the card indicates high levels of humidity, users know how to check their products to avoid a possible damage or modify their packaging regimen accordingly.

Humidity indicators designed on the basis of above-mentioned principle are a special kind of hygrometer (humidity indicator strips) that use the blotting paper impregnated with cobalt salts, blue cobalt(II)chloride or cobalt thiocyanate (Balköse et al. 1998, 1999). These indicators are inexpensive, easily stored, not easily damaged, and may be used in many variants. Humidity indications can be determined by comparison with a color guide printed next to indicating color spots for easy reading. As a rule, a series of patches are labeled with RH, usually in 10% increments, from 10% to 80% RH, as well as various combinations of these humidities. Emerson reported that Emerson's moisture indicator can detect moisture at 3% RH. Usually the humidity-sensitive elements have long-term calibration and accuracy to within ±5% when read at 24°C. Indicators have a temperature-caused error of 2.5% per 5°C deviation from a base of 24°C (Spomer and Tibbitts 1997). At other temperatures a small correction factor for each 5.5°C higher or lower than 24°C must be taken into consideration. For example, at high temperatures the element will indicate a lower humidity than is actually the case, and conversely, a higher humidity will be indicated at low temperatures. As indicated above, these elements are water soluble and should not be placed in direct contact with water or steam or exposed to extremely high humidity for protracted periods of time. If these indicators are used in a moist environment, they can become inaccurate. They are damaged by excessive humidity or condensation, which dilutes the spots and results in nonuniform chemical distribution and inconsistent color response (Spomer and Tibbitts 1997). Strong solvents such as ammonia fumes, which cause the bleaching of the color change dye and lose color reversibility, should not be present in the atmosphere.

Other substrates such as cellulose, cellulose acetate, polyvinyl pyrollidon, wool, calcium sulphate, silica gel, zeolites, and alumina can also be used. Usually the substrate type does not affect the color change: the color is blue at low RH levels and pink at high RH levels. But wool impregnated with cobaltous chloride is blue in dry form and converts to yellow on moisture adsorption (Balköse and Ülkü 2007). It was established that decreasing the amount of cobalt chloride in the matrix decreased both hysteresis effects and the effective RH range over which the salt/substrate combination could be used for RH measurement. It was also found that acetylation of the cellulose extended the effective RH range, increased reproducibility, and decreased hysteresis effects (Boltinghouse and Abel 1989). Moreover, optimizing the type of the substrate and the type and concentration of the cobalt salt, it is possible to produce indicators, which show a sharp color change in a small humidity range (Balköse et al. 1998).

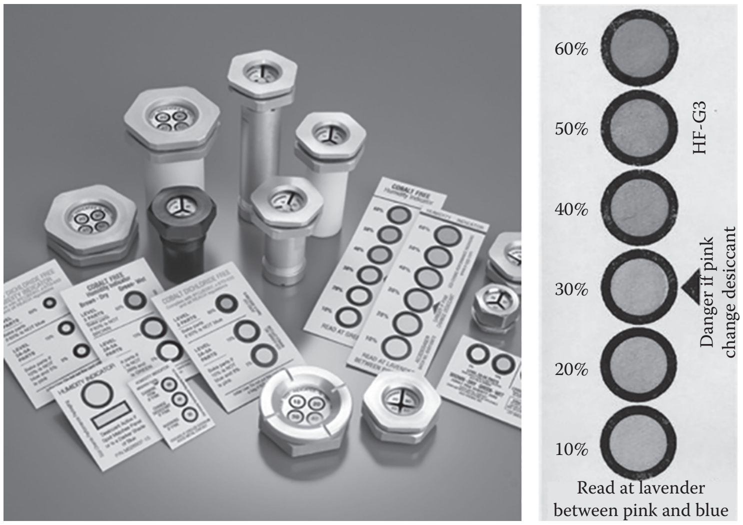
## 13.2 MARKET OF MOISTURE INDICATORS

Currently various companies (Table 13.1) offer a big variety of humidity indicators. Humidity indicators can be manufactured as strips, cards, and in the form of elements embedded in the gas main. In particular, the crystals and humidity-sensitive elements, which change the color under the influence of water, can be packed into a small chamber with a glass window for observation of the color. A sample side stream is piped through the chamber, and increase of moisture in the sample is indicated to the operator by a color change.

At that both types of elements, reversible, and nonreversible, may be installed in the same plug-type housing, which is leak-proof and will withstand shock and vibration. Examples of humidity indicator cards and components from different manufacturers are shown in Figures 13.1 and 13.2. Humidity indicators are often incorporated into plug-type desiccators for small enclosures. The plugs can be quickly installed with common hand tools, and are suitable for almost all applications. Of course, these cards are not precision indicators. In addition, these cards indicate only the RH. However, they are very good at telling you the RH in a container. For example, if all of the dots are deep blue on a card which is a 10%–60% card then you can be assured that the humidity in that container is below 10%. Humidity indicator strips or cards are also designed for mounting in moisture-sensitive electronic or electro-optic equipment, or any other humidity controlled enclosure.

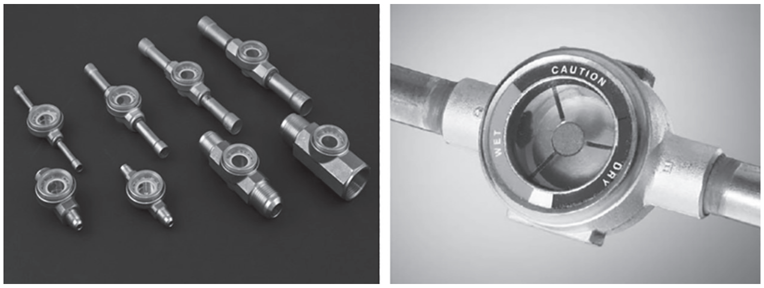
**TABLE 13.1**
**Examples of Manufacturers of Humidity Indicators**

| Company | Internet Site |
|---|---|
| Desiccare, Inc. | http://www.desiccare.com |
| Emerson Climate Technologies | http://www.emersonclimate.eu |
| Castel S.r.l. | http://www.castel.it |
| Parker Hannifin Corporation. Sporlan Division | http://www.sporlan.com |
| Henry Technologies Ltd. | http://www.henrytech.com |
| Texas Instruments Incorporated | http://www.ti.com |
| AGM Container Controls, Inc. | http://www.agmcontainer.com |
| IGLOO | http://www.igloo-refrigerazione.com |
| IMPAK Corporation. Sorbent Systems | http://www.sorbentsystems.com |
| Brownell Ltd. | http://www.brownell.co.uk |
| Clariant International Ltd. | http://www.clariant.com |



(a) (b)

**FIGURE 13.1** (a) Humidity indicators designed by Clariant International Ltd. (From http://www.clariant.com/.) (b) Reversible humidity indicator cards fabricated by Brownell Ltd. In this figure the bottom image shows a new card that is directly out of a sealed bag from the supplier. A lavender color usually indicates the relative humidity of the environment the card is placed within. (From http://www.brownell.co.uk/.)



(a) (b)

**FIGURE 13.2** Indicators with moisture sensitive element designed by different companies to monitor the condition of the refrigerant: (a) from http://www.igloo-refrigerazione.com and (b) from http://www.emersonclimate.eu.

For example, humidity indicator cards are present on many small electronic devices, ranging from cellular phones to laptop computers, for the purpose of alerting the manufacturer that the device has been exposed to high levels of moisture. In many cases, this voids or changes the terms of warranty coverage for the device.

One should note that in addition to cobalt salt indicators other salts can be also applied in humidity indicators. The need for such developments was due to the fact that in 1998, the European Community (EC) issued a directive which classified the items containing cobalt (II) chloride from 0.01% to 1% w/w as T (Toxic). Studies have shown that there is a sufficiently large set of materials that can also change color when exposed to moisture (Moreton 2002; Matsushima et al. 2000, 2002, 2003; Carmona et al. 2006; Fueda et al. 2007; Mackenzie and O'Leary 2008; Mills et al. 2010, 2017; Zhang et al. 2013). For example, Matsushima et al. (2000, 2002, 2003) presented a series of reports on reversible humidity-sensitive indicator films, formed from a combination of a dye with a sugar-based hydrogel (such as agarose or k-carrageenan), which undergo a reversible color change due to the formation of an aggregated form of the dye at high humidities, and its subsequent breakdown at low humidities. In these RH indicators, the color change is attributed to the humidity-promoted aggregation of the dye. In 2010 and 2017, Mills et al. (2010, 2017) published details of a humidity indicator based on the thiazine dye, (esp. methylene blue, MB), encapsulated in a film of hydroxyethyl cellulose (HEC) containing urea. In this system, the urea was present in a quantity that was roughly 20 times that of the dye. Under both dry (i.e., RH = 0%) and ambient conditions (RH~60%, at 23°C), the film was bright purple, but turned a deep blue after exposure to an ambient atmosphere with RH ≥ 85%. This discovery is unusual in such that it yields a sharp evident reversible color change at high RH, whereas this has been a problem in other investigations. Mills et al. (2017) believe that such a film is suitable for use as an indicator in the packaging of goods which cannot tolerate highly humid environments. Copper(II) chloride and potassium lead iodide can also be used in humidity indicators. Yellow lead iodide is obtained from potassium lead iodide upon moisture adsorption. Experiment has shown that *polymer–dye* systems also changed their color with air humidity (Kunzelman et al. 2007). Some studies have shown that polymer-based photonic crystals were also promising for these applications (Shi et al. 2008). The latter are interesting in view of the ways that ordered materials can interact with light to produce a variety of optical effects. A high sensitivity optical humidity probe was developed by using Nafion-crystal violet films. Reversible change in absorbance of the films at 650 nm with RH was linear in the 0% to 1% range (Dacres and Narayanaswamy 2006).

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