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CHEMICAL MAXIMUM HUMIDITY
INDICATOR UPDATE REPORT

By W. B. Abel

Published November 1978

Topical Report

Prepared for the United States Department of Energy
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MASTER

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By W. B. Abel

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Topical Report
W. B. Abel, Project Leader

Communications Services

**Kansas City
Division**

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CHEMICAL MAXIMUM HUMIDITY INDICATOR UPDATE REPORT

BDX-613-1989 (Rev.), Topical Report, Published November 1978

Prepared by W. B. Abel

Raw materials and manufactured parts sometimes must be kept in a controlled-humidity environment. The use of moisture-sensitive systems to indicate the maximum level of humidity exposure is discussed. A chemical indicator made from deliquescent salts and water-soluble dyes provides an irreversible color change at discrete levels of relative humidity. The performance and long-term-stability characteristics of the indicator are described.

WPC-TR5/a

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SUMMARY

Accurate moisture monitors are available to evaluate and control the atmosphere surrounding a part; however, those monitors are both expensive and too large to accompany individual piece parts. Conventional color-change indicators have the disadvantage that they record only the current moisture content of the atmosphere, and they will reverse when the humidity changes. A small, inexpensive device therefore is needed which will provide a permanent record of the maximum relative humidity to which it has been exposed.

A simple color-change, maximum-humidity indicator, composed of deliquescent salts and water-soluble dyes, was developed through a contract with Battelle Columbus Laboratories. This indicator provides an irreversible change in color when discrete levels of relative humidity are exceeded. The relative humidity at which the system reacts depends upon the formulation of the salt. Prototypes of the device were evaluated, and a patent was applied for and granted.

Continued observation of the prototypes has shown excellent stability characteristics with no loss in response over a 5-year period.

DISCUSSION

SCOPE AND PURPOSE

This project was initiated to develop a humidity indicator for recording the maximum relative humidity to which a material or part has been exposed. This capability is needed when moisture-sensitive materials are transported from one controlled environment to another, when they are stored, and when humidity failures occur within a controlled area.

A variety of mechanical, electrical, and chemical approaches were investigated to develop a small, portable, rugged, and inexpensive device having the sensitivity and precision necessary to distinguish 1-percent relative-humidity (RH) changes in the range from 5 to 25 percent, and the capability of providing a warning when the specified limit has been exceeded.

PRIOR WORK

Studies have indicated that a small moisture indicator to irreversibly record the maximum moisture content of an environment, while unavailable, would have useful applications as a warning device to complement the overall humidity-control program.

ACTIVITY

As compared to other types of humidity indicators, the chemical color-change indicator provides the advantages of simplicity, low cost, and small size. In addition, the dramatic change in color does not require interpretation by the observer to discern that a specific level of relative humidity has been exceeded.

The basic indicating system is the result of research and development conducted, under contract, by the Battelle Columbus Laboratories. Each indicator is composed of a deliquescent salt which is deposited on a glass surface and dusted with a water-soluble dye. The level of relative humidity at which the system will react and change color is dependent upon the formulation of the salt.

Figure 1 shows a typical prototype of the indicators before and after exposure to a humid atmosphere. The samples are sealed in a glass container with a desiccant to demonstrate the irreversible character of the exposed indicators. Each of the three spots represents a different level of relative humidity.

Figure 1. Chemical Maximum Humidity Indicator

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Figure 2 indicates the relative humidity point at which, and the manner in which, each of the three spots changed color under controlled conditions in the Bendix Kansas City humidity test facility. The color development for each spot occurred within an increase in relative humidity of approximately 1 percent.

Separate experiments conducted in a special test chamber that was built for this project showed the reaction time of the indicator to be less than 60 seconds when exposed to an atmospheric relative humidity 1 percent higher than its reaction level. The reaction level for each specific spot, as tested in the Bendix humidity test facility, was from 5 to 6 percent RH lower than that reported by the Battelle Columbus Laboratories. The discrepancy was traced to a probable error in the calibration of the Battelle test facility which was referenced to the atmosphere over saturated salt solutions. Examination revealed that these reference solutions may not have been totally saturated as required to agree with published handbook values.¹

Theory of Operation

The operation of the deliquescent-chemical color-indicator system is based on the facts that (1) certain salts absorb moisture from the air to form concentrated salt solutions, and (2) dissolution of a powdered dye develops the color of the dye and produces a readily observable color change. When the dye is mixed with a deliquescent salt in the absence of water, a stable system results. However, when the system is exposed to humid air, the deliquescent salt absorbs moisture and forms a solution which dissolves the dye and produces a color change that is characteristic of the specific material used.

The value of this type of system as a humidity indicator lies in the fact that the absorption of water by a deliquescent salt is dependent upon the relative humidity to which the salt is exposed. Once the dye dissolves or the chemicals react, the change in color is permanent; removal of the water at a later time will not reverse the color change. The system therefore provides a permanent record of exposure to moisture at the level necessary to dissolve the salt.

Different deliquescent salts absorb moisture at different relative-humidity levels. Normally, by diffusion, water molecules in the air impact on the surface of the deliquescent salt. A loss of water molecules from the surface of the salt also occurs by evaporation into the air. Ordinarily, the water in the air has a vapor pressure (P_v) which is a function of the amount of water in the air and is related to the relative humidity. The water on the surface of the salt tends to form a saturated salt solution

Figure 2. Bendix Humidity-Test-Facility Results for the Chemical Maximum Humidity Indicator

which also has a vapor pressure (P_s). At relative-humidity levels at which the vapor pressure of the water in the air is less than the vapor pressure of the water in the saturated salt solution ($P_a < P_s$), the water molecules will evaporate from the surface of the deliquescent salt more readily than they will be deposited. Thus the salt remains essentially dry. However, when the relative humidity increases to the extent that the vapor pressure in the air exceeds the vapor pressure of the saturated salt solution ($P_a > P_s$), water molecules will be deposited more rapidly than they will evaporate, and the deliquescent salt will dissolve.

Saturated salt solutions have been used for a number of years to produce constant-humidity conditions. Constant humidity is maintained by the vapor pressure in the air over the salt being regulated by the vapor pressure of the saturated salt solution through the described mechanism. The development of a color-humidity-indicator system is a novel application of this same principle.

Experimental Work

At the beginning of this project, two methods were considered for making a low-cost color-indicator system using either dyes or color-reactive chemicals that would be triggered by the moisture absorbed by a salt which deliquesces at a specific relative humidity. Prior work had shown that a reaction of dry chemicals can occur, apparently by ion diffusion, and that special water-soluble moisture barriers would be necessary to prevent a premature, dry reaction.

To avoid this problem, work was concentrated on the dye-deliquescent-salt system, based on the principle that dry dyes do not have high tinctoral strength. Thus a small amount of dye mixed with a deliquescent salt will show very little color. However, when the salt absorbs water, the full tinctoral strength of the dye is utilized as the dye goes into solution to produce a dramatic and easily recognizable change in color. The color change of some dyes is dependent upon the pH of the saturated solution formed by the salt.

The initial work on the program involved setting up test apparatus that would provide for exposing the salts to relative humidities ranging from 8 to 15 percent. Simultaneously, a search for dyes that are soluble in saturated salt solutions was begun, and this was followed by a search for salts that deliquesce in the desired range. Once candidate materials had been located, prototype indicators were prepared and tested.

Test Apparatus

In the initial phase of the program, the relative humidity in a 61- by 91- by 152-mm dry box was maintained at or near zero percent by circulating the air from the box through desiccant pads in an auxiliary, external duct system. Atmospheres of various relative humidities were provided in desiccators containing saturated salt solutions within the dry box. Relative humidity was monitored primarily with a commercial relative-humidity indicator.

The information obtained with this apparatus was limited because opening the desiccators to introduce a test sample dumped essentially all of the conditioned air, and the time necessary for the test environment to recover prevented a determination of the response time of the experimental humidity indicators. To avoid this problem, and to provide a wide range of test conditions, a system was devised which was based on mixing continuous flows of dry air and moist air to produce the desired relative humidity.

A schematic of the new test system is shown in Figure 3. Dry air is provided by one of the input lines by passing the air through two chambers (3.785-l or 1-gallon, wide-mouthed polyethylene bottles) containing a desiccant. Moist air is provided in a parallel supply which bubbles the air through a water bath. The airflow is controlled with a pressure regulator and needle valves, and it is monitored in each line with a flow gauge. The streams of conditioned air then are mixed and introduced into a test chamber in the dry box. Passing the air through baffles made from 6.35-mm sheets of 100-pore polyurethane foam in each end of the test chamber distributes the flow uniformly in the box. The air leaving the box passes through a wet-dry-bulb humidity-monitoring unit before it is exhausted to the atmosphere.

To obtain optimum effectiveness of the air driers, the flow rate through the test chamber was reduced progressively to $0.472 \text{ l}^3/\text{s}$, and finally to $0.236 \text{ l}^3/\text{s}$. As a result, the wet-dry-bulb apparatus was sized to maintain a velocity of 0.305 m/s , which is necessary to produce evaporation at the wet bulb. Provision was made to isolate the test chamber with solenoid valves in the air lines on each side of the chamber, and a bypass line was provided to permit adjusting the relative humidity in the air lines before the conditioned air is introduced into the box.

After difficulty developed in maintaining a relative humidity of less than approximately 10 percent in the dry box during extended periods of operation, the external circulation system was disconnected and the inlet and outlet ports on the test chamber were sealed. Circulating the air through the same desiccant filter

Figure 3. Schematic of Humidity Test System

beds inside the dry box with a small fan then maintained a relative humidity of approximately 5 percent in the dry box.

In an effort to obtain greater accuracy in the dry-box relative-humidity readings, the wet-dry-bulb indicator used on the test chamber was installed on the box as indicated in Figure 3. The dry box was pressurized with ambient room air to exhaust air through the indicator. However, because of air leaks in the external circulating system, the airflow through the indicator was not sufficient to provide a reading. Consequently, relative-humidity measurements in the dry box were made with the commercial instrument. The calibration of this instrument was checked frequently in the test chamber to assure that its readings were accurate.

The thermometers used with the wet-dry-bulb humidity-monitoring unit were calibrated with a standard thermometer certified by the National Bureau of Standards, Washington, D. C. Of the four thermometers that were standardized, two deviated less than 0.003°C and two deviated approximately 0.03°C from the standard. By reading these thermometers to 0.15°C and using standard wet-dry-bulb tables, relative humidity can be readily monitored to within 1 percent in the 8- to 15-percent range. Obviously, greater precision could be attained by calculating additional points closer than 0.15°C .

Materials Studies

The procurement of suitable materials was a crucial part of this study. A major search therefore was made for deliquescent salts for use in the indicator system, and for dyes which are soluble in saturated solutions of the deliquescent salts.

Solubility of Dyes in Saturated Salt Solutions

To evaluate the solubility of dyes, saturated solutions were prepared from the following salts, all of which are known to be deliquescent.

Calcium chloride (CaCl_2)

Lithium chloride (LiCl)

Potassium acetate (CH_3COOK)

Zinc chloride (ZnCl_2)

Magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$]

A total of 71 water-soluble dyes having the following colors were evaluated in the solubility tests: 19 blue, 29 red, 11 black, 6 green, 3 yellow, 2 violet, and 1 turquoise. Of these, 3 were soluble in saturated CaCl_2 (1 blue and 2 red), 4 were soluble in saturated LiCl (3 blue and 1 red), 4 (all blue) were soluble in saturated $\text{Mg}(\text{ClO}_4)_2$, 6 were soluble in saturated CH_3COOK (5 blue and 1 yellow), and 36 were soluble in saturated ZnCl_2 , many with remarkable changes in color--mostly to yellow, presumably because of the low pH (less than 2.0) of the solution. Red-to-blue and blue-to-red color changes also were found. Thus a good supply of dyes is available to provide a variety of color effects in saturated salt solutions. These effects include both increases in color saturation and changes from one color to a totally different color.

Deliquescent Salts

The search for deliquescent salts was concentrated on a list of approximately 450 hygroscopic or deliquescent materials that had been prepared from the Handbook of Chemistry and the Handbook of Chemistry and Physics.² Approximately 350 of these materials are inorganic salts, while approximately 100 are organic compounds.

Preliminary Screening. More than 50 salts were tested with dyes at an ambient humidity of 30 to 45 percent. These tests convincingly demonstrated that the water-absorbing material must deliquesce to produce color intensification. Calcium sulfate, while a good desiccant, is not very soluble in water and does not deliquesce. Crystals of a dye (Acid Magenta 0, for example), when placed on a piece of anhydrous CaSO_4 and exposed to room humidity, showed no evidence of the dye bleeding. When the dye was placed on a piece of anhydrous, deliquescent CaCl_2 , bleeding was rapid. Other deliquescent solids behaved similarly to the CaCl_2 when spotted with dye crystals and exposed to room humidity.

From those materials which deliquesced at the higher relative humidities, candidates were picked for more extensive study at relative humidities in the desired trigger range. These materials included AlCl_3 , As_2O_5 , CaCl_2 , CoBr_2 , CoI_2 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, CuCl_2 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, FeCl_3 , H_3PO_3 , $\text{KC}_2\text{H}_3\text{O}_2$, KOH , LiBr , LiCl , $\text{KF} \cdot 2\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{ClO}_4)_2$, $\text{NaPO}_3/\text{HPO}_3$, $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$, NaI , NaOH , NH_4SCN , P_2O_5 , $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, TMAC (tetramethylammonium chloride), ZnBr , ZnCl_2 , and ZnI_2 .

These candidate deliquescent salts and dyes were screened further in the dry box. Selected dyes were sprinkled on a small pile of the deliquescent salts at a relative humidity of 6 percent, and then placed in the test chamber where the relative humidity was raised to 8, 10, 15, and 20 percent at 30-minute intervals. Several materials, principally CoBr_2 , CoI_2 , LiBr , LiCl , ZnBr_2 ,

and ZnCl_2 , produced a bleeding of the dye in the desired range up to a relative humidity of approximately 15 percent. $\text{NaOH}\cdot\text{H}_2\text{O}$ and $\text{KOH}\cdot\text{H}_2\text{O}$ also produced bleeding at a relative humidity of about 10 percent, but their caustic nature made them undesirable. The other materials produced bleeding at a relative humidity of 20 percent, or higher.

A few stoichiometrically prepared hydrates, including $\text{LiCl}\cdot\text{H}_2\text{O}$, $\text{ZnCl}_2\cdot 1\text{-}1/2\text{H}_2\text{O}$, $4\text{ZnBr}_2\cdot 3\text{H}_2\text{O}$, and $4\text{NaI}\cdot 5\text{H}_2\text{O}$ also were tested, but the dyes bled instantly at 6-percent relative humidity.

Color-Changing Hydrates. Salts that deliquesce and change color as a result of hydration were studied as a possible method for eliminating the use of dyes. The hydrate systems that were considered are shown in Table 1.

Seven of the anhydrous salts were placed in the test chamber, and the relative humidity gradually was increased from 6 to 23 percent. Of the salts tested, only CoBr_2 showed any evidence of hydrating; it began to turn from green to pink at a relative humidity of 15 percent. Unfortunately, when it was over P_2O_5 (which provides a bone-dry atmosphere), the hydrate lost its water, and the salt reverted to its original color. Thus, although hydrates can be used as humidity indicators, they probably will not permanently record the maximum exposure.

Tests of Indicator Systems

Fourteen different indicator systems were prepared on glass slides and evaluated in the test chamber, starting at a relative humidity of 6 percent and a temperature of 28.9°C . The relative humidity was increased in 2-percent steps every 30 minutes. The results that were obtained are shown in Table 2.

Nine of these systems produced indications in the range of 8- to 16-percent relative humidity at 28.9°C . ZnCl_2 , ZnBr_2 , LiBr , LiCl , CoBr_2 , and CoI_2 were selected for further study in prototypes.

Effect of Temperature on Trigger Point

Because the equilibrium humidity of saturated solutions of deliquescent salts is known to decrease with increasing temperature, a temperature effect on the trigger point of the deliquescent-salt indicator system was expected. The trigger points of the six selected salt systems therefore were measured at temperatures of approximately 15.6, 21.1, 26.7, and 37.8°C . Cooling to 15.6 to 21.1°C was achieved by passing the test air through a coil immersed in ice water, and by cooling the dry box with dry ice on the back, outside wall. The dry box was warmed to approximately

Table 1. Hydrate Systems Considered for Maximum Humidity Indicator

Hydrate System	Color Sequence	Temperature* (°C)
$\text{Co}(\text{OOCCH}_3)_2 + 4\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$	Purple, Pink	140
$\text{CoBr}_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{CoBr}_2 \cdot 6\text{H}_2\text{O}$	Green, Pink	130
$\text{CoCl}_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Blue, Red	110
$\text{CoI}_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{CoI}_2 \cdot 4\text{H}_2\text{O} + 2\text{H}_2\text{O} \rightleftharpoons \text{CoI}_2 \cdot 6\text{H}_2\text{O}$	Black, Green, Red	135
$\text{Co}(\text{NO}_3)_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Pink, Red	
$\text{NiCl}_2 + 6\text{H}_2\text{O} \rightleftharpoons \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Yellow, Green	
$\text{NiBr}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{NiBr}_2 \cdot 3\text{H}_2\text{O}$	Yellow, Green	200
$\text{NiI}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NiI}_2 \cdot \text{H}_2\text{O}$	Black, Green	
$\text{CuCl}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Brown-Yellow, Blue-Green	110
$\text{Cu}(\text{NO}_3)_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Pale Blue, Blue	
$\text{CuSO}_4 \cdot \text{H}_2\text{O} + 4\text{H}_2\text{O} \rightleftharpoons \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Green-White, Blue	110
$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	Yellow-Orange, Orange	85
*Temperature at which hydrate loses all water of hydration. (From Lange, <u>Handbook of Chemistry</u>)		

Table 2. Results of Indicator-System Tests

Deli- quescent Salt	Dye	Original Color	Trigger-Point Relative Humidity (Percent)	Trigger Color
ZnCl ₂	Alphazurine 2G	Bluish Gray	8	Yellow → Green
ZnBr ₂	Alphazurine 2G	Bluish Gray	10 to 11	Yellow → Green
ZnI ₂	Alphazurine 2G	Bluish Gray	20	Yellow
LiBr	Acid Magenta 0	Reddish Gray	12	Magenta
LiCl	Acid Magenta 0	Reddish Gray	15	Magenta
LiI	Acid Magenta 0	Reddish Gray	16	Magenta
CoBr ₂	None	Green	14 to 15	Pink
CoI ₂	None	Black	14 to 15	Yellow-Green
NiI ₂	None	Black	>20	
CuCl ₂	None	Brown-Yellow	>20	
ZnCl ₂	Acid Magenta 0	Reddish Gray	8	Magenta
ZnBr ₂	Acid Magenta 0	Reddish Gray	10 to 11	Magenta
ZnI ₂	Acid Magenta 0	Reddish Gray	20	Magenta
TMAC	Acid Magenta 0	Reddish Gray	>20	

37.8°C by means of a hot plate inside the box. The relative humidity was raised in 1-percent increments until the indicators triggered.

Table 3 summarizes the results of experiments that were conducted with prototypes of four deliquescent salt-dye systems and two color-changing-salt systems. The prototypes were prepared by coating abrasion-frosted microscope slides with a solution of the salt, heating them at 121.1°C in the dry box until they were dry, and then placing them in a desiccator until they had cooled. After cooling, the dyes were dusted or brushed onto the salt films.

The data shown in Table 3 are plotted in Figure 4. As expected, the humidity trigger points decreased with an increase in temperature. The curves show that ZnCl_2 , ZnBr_2 , LiBr , and LiCl can be used to produce prototypes that will trigger at approximately 11-, 13-, 14-, and 18.5-percent relative humidity at a temperature of approximately 21°C. CoBr_2 and CoI_2 provide indications at relative humidities of approximately 14.5 and 15.5 percent for the same temperature.

Indicators for Low Relative Humidity

Because none of the salts deliquesced at a relative humidity lower than about 11 percent at 21.1°C, the possibility of reaching a lower range with salt mixtures and hydrates was studied only briefly.

Higher Humidity Levels

Although the humidity-indicating devices that actually have been developed to date are designed for low-humidity applications in the range of 8 to 20 percent, salts that deliquesce at higher humidities are abundant. A few salts that cover the range from 20- to 90-percent relative humidity are listed in Table 4. Although these systems have not been tested, there is no reason to believe that they would not perform in the same manner as the lower-humidity salts.

Indicator Prototypes

The technique of sprinkling dye on the salt crystals was satisfactory for the rough screening of materials, but a practical method of combining the materials on a simple supporting substrate is necessary to provide maximum sensitivity and reproducibility of the indicators. A thin film of the deliquescent salt containing a small amount of dye is believed to be the best approach.

Table 3. Effect of Temperature on Humidity Indicator Systems

Salt	Dye	Color Change	Relative-Humidity Trigger Point for Indicated Temperatures			
			15°C (Percent)	20 to 25°C (Percent)	25 to 30°C (Percent)	35 to 40°C (Percent)
ZnCl ₂	Alphazurine 2G	Bluish Gray to Yellow-Green	16.0	10.0	8.0	6.0
ZnBr ₂	Alphazurine 2G	Bluish Gray to Yellow-Green	18.0	12.0	9.0	7.0
CoBr ₂	None	Green to Pink	19.0	13.0	11.0	9.0
CoI ₂	None	Black to Olive	19.0	14.0	12.0	10.0
LiBr	Acid Magenta 0	Reddish Gray to Magenta	19.0	14.0	11.0	8.0
LiCl	Acid Magenta 0	Reddish Gray to Magenta	21.0	17.0	16.0	13.0

Figure 4. Temperature-Humidity Relationship of Trigger Points

Substrate Studies

Initially, filter paper was selected as the supporting substrate for the indicators. Solutions of various deliquescent salts were

Table 4. Relative Humidity
of Saturated Salt
Solutions at
25.56°C²

Salt	Relative Humidity (Percent)
KC ₂ H ₃ O ₂	20
CaCl	32.3
CrO ₃	35
Zn(NO ₃) ₂	42
KNO ₂	45
KCNS	47
NaHSO ₄	52
NaBr	58
Mg(C ₂ H ₃ O ₂) ₂	65
NaNO ₂	66
NaClO ₂	75
NaC ₂ H ₃ O ₂	76
Na ₂ S ₂ O ₃	78
NH ₄ Cl	79.5
(NH ₄) ₂ SO ₄	81
KBr	84
KHSO ₄	86
K ₂ CrO ₄	88
ZnSO ₄	90
NaBrO ₃	92

Table 4 Continued.
Relative Humidity
of Saturated Salt
Solutions at
25.56°C²

Salt	Relative Humidity (Percent)
Na ₂ SO ₄	93
Na ₂ SO ₃	95
Pb(NO ₃) ₂	98

applied to the paper, dried at 130°C, and desiccated at 6-percent relative humidity. Dyes then were dusted on the dried salt films. Indicators prepared from ZnBr₂, ZnCl₂, ZnI₂, LiCl₂, TMAC, NaOH, CuCl₂, CoCl₂, and NiI₂ failed to respond after 20-minute exposures at each of several increased humidity levels in the range of 6 to 29 percent. Apparently, the paper interfered with the response of the indicator system. Work with paper supports therefore was abandoned in favor of glass or plastic substrates which do not absorb water as does the paper.

Thin salt films were prepared on glass slides by spreading a drop of each salt solution on the glass, drying the slides at 130°C in the dry box at a relative humidity of 6 percent, and dusting each indicator with an appropriate dye. Most of the indicator systems prepared in this manner triggered at specific relative humidities in the 6- to 20-percent range in less than 1 minute of exposure time.

Plastics and ceramics, including polystyrene, polycarbonate, Mylar, nylon, and polyurethane films (commercial films 0.076 to 0.102 mm in thickness), and 0.792-mm-thick sheets of alumina were considered for use as substrates. The polystyrene, polycarbonate, and Mylar became badly distorted by the heat used to dry the salt solution.

Indicators prepared with ZnCl₂ on nylon and polyurethane failed to trigger when exposed in the 7- to 12-percent relative-humidity range. However, ZnCl₂ produced a satisfactory indication at a relative humidity of 8 percent and a temperature of approximately

28.9°C when it was placed on an alumina substrate. The alumina substrate offers the advantage that the moisture picked up by the salt is largely absorbed by the porous ceramic.

Dusting a mixture of powdered dye and salt on a pressure-sensitive adhesive coating was considered as an alternate method for obtaining a thin indicator film. However, grinding the deliquescent salts with a mortar and pestle in the dry box proved to be an unsatisfactory technique for producing the powders. Although special grinding techniques might be developed, the handling of the premixed powders would require special care to avoid their being triggered prior to use. With the preferred production method, precautions would be unnecessary until the actual assembly of the indicator.

Prototype Preparation

Prototype indicators were prepared with ZnCl_2 , ZnBr_2 , and LiCl on glass microscope slides which are approximately 1.6 by 25.4 by 76.2 mm. The three indicator spots were applied on 12.7-mm-diameter areas on slides that had been roughened with 400-grit abrasive paper to provide uniform wetting of the glass. As a further aid to wetting, a 1-percent solution of a wetting agent was added to the salt solutions after tests had confirmed that the wetting agent did not affect the trigger point of the indicator system. The salt solutions were brushed on the roughened spots, the slides were dried in the dry box at a temperature of 130°C and a relative humidity of 6 percent, and the spots were dusted with the appropriate dye.

Indicators containing the wetting agent triggered as follows: ZnCl_2 , 7.25-percent relative humidity at 30.8°C; ZnBr_2 , 9.0-percent relative humidity at 30.8°C; and LiCl , 14.0-percent relative humidity at 31.1°C.

Prototype Storage

Sealing the prototypes in rubber-stoppered glass vials (200- by 32-mm extra-large test tubes) containing a small amount of desiccant was the only satisfactory storage method that was found. Heat-sealing the prototypes in envelopes made from 0.076- to 0.102-mm-thick (3- to 4-mil) films of polyethylene, Saran, polycarbonate, and wax paper also was tried, but upon removal from the dry box to ambient relative-humidity conditions, the indicators triggered in less than 1 hour.

Sensitivity and Stability

All of the exposure tests were conducted in the test box by raising the relative humidity in 1-percent increments. The indicated exposures therefore are within 1 percent of the indicated humidity. At the trigger point, the color changes began immediately, and the color development was nearly complete after 30 to 60 seconds.

The dye-salt systems proved to be stable while in storage at relative humidities below their trigger points for periods ranging up to several weeks. The LiCl (17-percent relative humidity) and LiBr (14-percent relative humidity) indicators did not trigger when stored at a relative humidity of approximately 11 percent over a saturated solution of ZnCl_2 for periods ranging from 3 to 8 weeks.

Drying the indicators by heating them or placing them over a desiccant for more than 6 weeks demonstrated that the coloring of the salt-dye systems is irreversible once the bleeding of the dye has been triggered. However, the CoBr_2 and CoI_2 indicators were reversible when dried over such desiccants as CaCl_2 or P_2O_5 . At the same time, $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ (pink) and $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$ (red) did not dehydrate when stored in a desiccator at a relative humidity of 5 percent over a 69.44-percent solution of H_2SO_4 for more than 6 weeks. Apparently, an extremely low humidity is needed to dehydrate these hydrated salts.

An attempt was made to measure the quantity of moisture required to trigger the indicator spots by exposing the indicators to a controlled amount of water vapor. For this purpose, the indicators were placed in a desiccator which then was evacuated to a vacuum of 73.7 mm of mercury. In general, when moist air, having a relative humidity above the trigger point, was introduced into the desiccator, the indicators triggered immediately.

One-hundred additional prototypes were prepared, and they have been retained for long-term stability studies. Sealed in test tubes with a desiccant, these samples have been checked at 6- to 8-month intervals for a period of 5 years. No change has been observed in the appearance of the unexposed samples. Samples that have been removed from the test tubes and exposed to moisture (ambient laboratory conditions) have shown no loss in response time or color development. Exposed samples which have been resealed in a dry atmosphere have not reversed their coloring, nor have they lost the indication that they have been exposed.

The results of this lengthy stability study are believed to conclusively demonstrate the adequacy of these humidity indicators

for storage with products which must be maintained at specified humidity levels.

ACCOMPLISHMENTS

The basic principle of the deliquescent-salt-and-dye indicator system has been convincingly shown to provide a permanent, irreversible indication of exposure to specific relative-humidity values. Although the prototype indicator does not trigger precisely at relative humidities of 8, 10, and 15 percent at a temperature of 20°C as desired, the relative-humidity trigger points of approximately 11, 13.5, and 18.5 percent that have been demonstrated provide a potentially useful range. A patent application was filed on the indicator, and a patent has been granted.³

The device that was developed in this program is small--about the size of a microscope slide, and it is simple to manufacture. The simplest method for manufacturing the indicator appears to be that of applying a thin film of the deliquescent salt solution to a frosted glass or alumina substrate, drying it, and dusting it with the appropriate dye.

FUTURE WORK

Should a need be found that requires production quantities of the described maximum humidity indicator, additional development activity would be necessary to define a large-scale production process. A more appropriate means of storing the indicators prior to their being put into service should be devised, and a method for both containing and preventing contamination of the saturated salt solutions that form on the surface of the exposed indicators would have to be developed.

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Raw materials and manufactured parts sometimes must be kept in a controlled-humidity environment. The use of moisture-sensitive systems to indicate the maximum level of humidity exposure is discussed. A chemical indicator made from deliquescent salts and water-soluble dyes provides an irreversible color change at discrete levels of relative humidity. The performance and long-term-stability characteristics of the indicator are described.

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