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(54) MOISTURE INDICATOR

(71) We, VIRGINIA CHEMICALS, INC., a Corporation organised under the laws of the State of Maine, United States of America, of Portsmouth, Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In refrigerant systems and related liquid systems, a great deal of recent attention has been given to the detection of water or moisture content which has a deleterious effect upon system capabilities. Cobaltous bromide has been employed as an impregnant for glass fiber or paper. Cobaltous bromide itself undergoes a dominant colour change from green to pink, as it becomes saturated with water. However, the colour change of cobaltous bromide is fairly finite with respect to the percentage of water detected, that is the cobaltous bromide rapidly completes its colour change within a narrow percentage range of moisture. Accordingly, attention has been given to developing related compositions which would have variant colour indicating characteristics as system needs dictate.

Cobaltous bromide moisture indicators may be positioned in a moisture indicator housing, of the type illustrated and claimed in U.S. patent Specification No. 3,085,424 and assigned to ourselves. The liquid phase indicator may be of a cobaltous bromide type applied to a mat of inert fibers, as disclosed in U.S. patent Specification no. 2,836,974 or, as applied to a cellulosic paper, as set forth in U.S. patent Specification no. 2,761,312. In both cases the colour indicators were used in refrigerant systems having a refrigerant liquid of low water solubility.

A principal prior art teaching of the employment of salts such as magnesium chloride, calcium chloride and aluminum chloride together with cobalt chloride is set forth in Applied Biology (M.E. Solomon): "The Use of Cobalt Salts As Indicators of Humidity and Moisture", pages 75—85.

According to the present invention the colour indicating characteristics of the cobalt salt are considerably varied by employing dual indicating compositions comprising a cellulosic paper impregnated with cobaltous bromide characterised in that

the bromide impregnated paper is further impregnated with,

(i) a bromide of cadmium, mercury or zinc,
(ii) a bromide or chloride of calcium, barium or magnesium, or
(iii) another water soluble cobaltous salt.

The colour changes exhibited by these compositions are indicated in the accompanying drawings, in which:

Figure 1 is a graph depicting approximate colour changes by hue of the dual bromide salts; cobaltous bromide and bromides of zinc, cadmium and mercury, as affected by water content of a refrigerant;

Figure 2 is a like graph of the dual bromide salts; cobaltous bromide and bromide of barium, magnesium and calcium;

Figure 3 is a graph depicting approximate color change by hue with the increasing of the ratio of cadmium bromide to cobalt bromide;

Figure 4 is a graph depicting approximate color change by hue with increasing of salt concentration of ratio 2 in Fig. 3; and

Figure 5 is a graph depicting approximate colour changes of the cobaltous bromide-cadmium bromide indicator in operating refrigeration units. (The "Refrigerant-22" is a commercial chlorofluorocarbon refrigerant manufactured by the Ansul Chemical Company.)

Free and dissolved water in refrigeration systems has always been a major problem.

[Price 25p]

The presence of moisture in these systems can lead to some undesirable effects such as:

1. Chemical reaction with oil or refrigerant to form acidic materials, tars and varnishes.
2. Clogging of metering devices due to "freeze up".
3. Lowering of the dielectric of motor insulation in hermetic and semihermetic motors resulting in motor failure.
4. Enhanced probability for copper plating.

As a result, manufacturers of refrigeration equipment as well as the installing contractor and service engineer carry out expensive and/or time consuming procedures to obtain the degree of internal dryness which leads to reliable and prolonged system operation. These procedures generally consist of high vacuum techniques combined with elevated temperatures. However, even when these techniques are followed, the concentration of moisture in the system cannot be specifically determined unless expensive and time consuming analytical techniques are used. Some manufacturers carry out these procedures on a small segment of their daily production to assure themselves that their manufacturing procedures are conforming to expectations. Further, dehydrators containing desiccating materials are installed for further protection.

Since analysis of each assembly is economically unfeasible to the manufacture and impossible for field assembled equipment, moisture indicators have been used. These indicators reversibly change color with changes in relative saturation of water dissolved in a particular refrigerant.

The working portion of these indicators generally consist of a cobalt salt, preferably cobalt bromide, deposited on paper or some other material such as a polyester or fibreglass.

The relative concentration of the cobalt salt to the cellulose or paper base material is held so that a significant change in color is obtained when the relative saturation of water in refrigerant reaches 4 to 5% of complete saturation. Generally no further color change occurs after the relative saturation reaches about 17%. The color obtained below 5% relative saturation is considered the "dry" color while that obtained above 17% is considered the "wet" color. It is postulated that the cellulose—cobalt bromide forms a complex salt with different characteristics to the cobalt salt alone.

When no complex is formed, such as when using a polyester/cobalt bromide indicator, color changes occur at a lower relative saturation of water in refrigerants. This change occurs at about 1.2 to 2.4% relative saturation with the "wet" colour occurring above 2.4% and the "dry" color below 1.2% relative saturation. The degree of sensitivity to low dissolved moisture levels is desirable in many cases. This is especially true when proper dehydration of equipment has been carried out. These systems, then, have an extremely low concentration of moisture in the circulating refrigerant when first placed into operation. Later, through normal or only slightly adverse operating conditions deterioration of the organic constituents such as oil or motor insulation water is formed and the concentration of dissolved water rises. If deterioration should continue equipment extremely low concentration of moisture in system such as a moisture indicator changing color at low moisture levels is vital. Should a color change be observed the necessary steps can be taken to correct the adverse conditions.

Under a given set of operating conditions, system sensitivity to chemical or thermal deterioration varies with selection of components making up the motor compressor. Some components are more sensitive than others to the environment and depending upon their chemical nature contribute more or less water to the system during deterioration. The amount of material used also bears on the quantity of water contributed to the system.

Considering moisture increase in a system as an indication of chemical deterioration, a moisture indicator changing from a "dry" to a "wet" color would signal that this deterioration is occurring. With systems of varying sensitivities and ability to create water, moisture indicators should be designed for specific refrigeration systems. Rather, standardized moisture indicators are applied to any and all systems. By changing the ratio of cobaltous bromide to the paper base the standard indicators can be made to show color shifts between narrow limits.

Indicators can be prepared that will show color changes at high moisture levels or at low moisture levels. This can be done by the addition of water soluble salts of metals in Groups II A and II B in the periodic table to cobaltous bromide. Furthermore, other cobaltous salts such as the nitrate, acetate and sulfate with cobalt bromide have a color change shifting effect. Addition of Group II B salts to the cobaltous bromide sensitizes the moisture indicator—that is—colour shifts from "dry" to "wet" occur at a lower water concentration level. On the other hand, salts of Group II A have the opposite effect.

By varying the ratio of one salt to another and/or by varying the ratio of salt mixture to the paper base one can obtain moisture indicators, with color shifts in any desired range depending upon the requirements of the refrigeration system to which it is applied.

The moisture indicators are prepared by immersing unsized paper, such as Whatman no. 1 laboratory grade filter paper in the solution of the salts. The solutions are controlled very specifically with regard to normal concentrations of the salts as well as the ratio of concentration of one salt to another.

After drying the treated paper, the paper can be cut to various geometric configurations to be mounted in a hermetic device having a sight glass and proper fittings for installation in refrigeration systems. The color change of the indicator with changing concentrations of dissolved water in the refrigerant can be observed through the sight glass.

Examples of some of the various types of moisture indicator combinations are shown in the graphs FIGS. 1—5. For simplicity purposes the color changes are shown as change by hue rather than specific colors since the "dry" color is not always at the same hue. For example, the "dry" color for a cobaltous bromide based indicator has a Color Harmony Value of 15 ic while an indicator prepared with cobalt chloride mercuric chloride has a Color Harmony Value of 12 1/2 gc in its "dry" state.

The base line of the graphs is considered as the color of the indicator in its "dry" state. This color is generally a blue color. The graph shows the indicator going through its intermediate stages of lavendar, lilac, etc. The termination point of each graph line is that point at which a definite pink or "wet" color is reached. This is generally equivalent to a Color Harmony Value of 11 ca.

The addition of salts of Group II B to "sensitize" these indicators appears to eliminate the "dry" anhydrous color so that one continuously approaches the "intermediate" colors with increasing amounts (based on the ratio of the two salts) of the II B salts. In this way the number of hues the indicator must go through to reach the pink or "wet" color, is constantly reduced.

The effect of the addition of the dual salts on the color change characteristics of Whatman No. 1 filter paper are set forth in the Tables below. In Tables 1 and 2 the filter paper was dipped in an aproximately 0.1M solution of the listed compounds. Color calibration of a dual salt system involving cobaltous bromide and cadmium bromide is set forth in Table 3, color change points of this dual salt indicator are set forth in Table 4. In these Tables, H—151, R—12 and R—22 are chlorofluorocarbon refrigerants manufactured by the Aluminum Company of America (H—151) and the Ansul Chemical Company (R—12 and R—22).

TABLE 1

Effect of the addition of Various Salts on the Color Change Characteristics of Whatman No. 1 Filter Paper Treated with $CoBr_2$

Percent H_2O in H—151	Color Harmony Value							
	No salt Added	$2nBr_2$	$CdBr_2$	$HgBr_2$	$MgBr_2$	$CaBr_2$	$BaBr_2$	$Co(NO_3)_2$
0	15 lc	13½ gc	13½ ic	13½ ic	16 la	17 la	16 la	13 lc
1	15 lc	13½ gc	13½ ic	13½ ic	16 la	17 la	16 la	13 lc
2	15 lc	13 gc	13½ ic	13½ ic	16 la	17 la	16 la	13 la
3	15 ic	12½ ec	12½ ge	12½ ge	16 la	17 la	16 la	13 ic
3.25	15 ic	12½ ec	12½ ec	12½ ec	16 la	17 la	16 la	13 ic
3.50	15 ic	12½ ec	12½ ec	12½ ec	16 la	17 la	16 la	13 ic
3.75	15 ic	12 ec	11 ec	11 ec	16 ia	17 ia	16 ia	13 ic
4.00	15 gc	12 ec	11 ec	11 ec	16 ia	17 ia	16 ia	13 ic
4.50	15 gc	11 ca	10 ec	10 ec	16 ga	17 ga	16 ga	13 ie
5.00	15 gc	11 ca	10 ec	10 ec	16 ga	17 ga	16 ga	13 ie
6.00	14 ec	7 ca	7 ca	7 ca	16 ga	17 ga	16 ga	13 gc
7.00	13 ca	7 ca	7 ca	7 ca	17 ec	17 ga	16 ec	12 ec
8.00	10 cb	7 ca	7 ca	7 ca	16 ec	16 ga	14 ec	10 ca
9.00					14 ec	17 ea	13½ ca	
10.00					13 ca	17 ca	12½ ca	
11.00					12 ca	17 ca	12 ca	
12.00					12 ca	14 ca	12 ca	
13.00					12 ca	12½ ca	12 ca	
14.00					12 ca	12 ca	12 ca	

TABLE 2

Effect of Increasing the Ratio of Cadmium Bromide to Cobalt Bromide on the Color Change Characteristics of Treated Whatman No. 1 Filter Paper

H_2O in H—151 Percent by wt.	Color Harmony Value							
	Molar Ratio of $CoBr_2$ to $CdBr_2$ $CoBr_2 = 1$							
	½	¾	1	1½	2	3	4	5
0	14 ic	14 gc	13½ ic	13½ gc	13½ gc	13½ ic	13 ic	13 ga
1	14 ic	14 gc	13½ ic	13½ gc	13½ gc	13 ic	13 ic	13 ga
2	14 ic	14 gc	13½ gc	14 ec	14 ec	12½ ec	12 ca	12½ ga
3	14 gc	12½ ec	12 ec	12½ ca	12 ca	12½ ec	12 ca	12 ca
3.25	14 gc	12 ec	12½ ca	7 cb	7 cb			
3.50	14 gc	12 ec	12½ ca	7 cb	7 cb			
3.75	14 ec	12½ ca	10 cb	7 cb	7 cb			
4.00	14 ca	12½ ca	7 cb	7 cb	7 cb	10 ca	9 ec	11 ca
4.50	12½ ca	7 cb	7 cb	7 cb	7 cb			
5.00	12½ ca	7 cb	7 cb	7 cb	7 cb	10 ca	9 ec	11 ca
6.00	7 cb	7 cb	7 cb	7 cb	7 cb	9 ca	9 ec	11 ca

TABLE 3

Effect of Increasing the Salt Concentration in the Color Characteristics of Whatman No. 1 Filter Paper Treated With $CoBr_2$ and $CdBr_2$

	Color Harmony Value		
	Amount Salt in 100 cc. H_2O, g.		
Percent H_2O in H-151	5.00 g. $CoBr_2$ 7.85 g. $CdBr_2$	10.00 g. $CoBr_2$ 15.70 g. $CdBr_2$	20.00 g. $CoBr_2$ 31.40 g. $CdBr_2$
0	13½ ic	14 lc	15 nc
1.00	13½ ic	14 lc	15 nc
2.00	13½ gc	13 ic	15 nc
3.00	12 ec	13 ic	15 nc
3.25	12½ ca	13 ic	15 nc
3.50	12½ ca	13 ic	15 nc
3.75	10 cb	12½ gc	15 nc
4.00	7 cb	12½ gc	15 nc
4.50	7 cb	11 gc	12½ ic
5.00	7 cb	11 ec	12½ ic
6.00	7 cb	9 gc	12 gc

TABLE 4

Color Calibration of Dual System Paper Base Moisture Indicators Treated with $CoBr_2$ and $CdBr_2$
$CoBr_2$ = 0.023M/Liter = 1

R—12

0.75 $CdBr_2$	0.825 $CdBr_2$	1.00 $CdBr_2$	H_2O, p.p.m.	T., °F.
14 gc	13½ gc	13½ gc	2.6	88
14 gc	13½ gc	13½ gc	2.5	84
14 gc	13 gc	13 gc	2.9	84
12½ ec	12½ ec	12½ ec	3.6	83
13 ec	11 ec	11 ec	6.1	76
12 ca	11 ec	11 ec	11.5	78

TABLE 4—cont.

R—22

13½ ic	13½ ec	13½ ic	9.7	74
13½ gc	13½ gc	13½ gc	10.5	74
13½ gc	13½ gc	12½ gc	19.0	74
13½ ec	12½ ec	12½ ec	21.4	74
13½ ec	12½ ec	12½ ec	22.0	74
13½ ec	12½ ec	12½ ec	30.0	74
12½ ec	12 ec	12 ec	43.3	74
12½ ec	12 ec	12 ec	48.0	74
		11 ca	57.0	74

$CoBr_2 = 0.0196M = 1$

0.75 $CdBr_2$	1.00 $CdBr_2$	1.25 $CdBr_2$	H_2O, p.p.m.
13½ ie	13½ ie	13 gc	5.8
13½ ic	13½ gc	13 gc	7.0;7.0;7.1
13½ gc	13½ ic	13 gc	8.7;8.9;10.3
13 gc	12½ gc	12 ec	16.5;17.5;18.0
13 ca	12½ ea	12 ea	20.2;19.6;19.3
12½ ea	12 ec	11 ic	34.6;35.4;35.4
12½ ec	12 ec	11 ca	61.0;58.3:58.3
12 ca	11 ca	10 ca	64;64;64

WHAT WE CLAIM IS:—

1. A dual salt moisture indicating device comprising a cellulosic paper impregnated with cobaltous bromide characterised in that the bromide impregnated paper is further impregnated with,
   (i) a bromide of cadmium, mercury or zinc,
   (ii) a bromide or chloride of calcium, barium or magnesium, or
   (iii) another water soluble cobaltous salt.

2. An indicating device as claimed in claim 1, comprising a cellulosic paper impregnated with cobaltous bromide and cobaltous nitrate.

3. An indicating device as claimed in claim 1, comprising a cellulosic paper impregnated with cobaltous bromide and cadmium bromide, the cadmium bromide being in the molar proportion of ½ to 2 times the amount of cobaltous bromide.

4. An indicating device as claimed in claim 1 substantially as hereinbefore described.

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TABLE 4—cont.

R—22

13½ ic	13½ ec	13½ ic	9.7	74
13½ gc	13½ gc	13½ gc	10.5	74
13½ gc	13½ gc	12½ gc	19.0	74
13½ ec	12½ ec	12½ ec	21.4	74
13½ ec	12½ ec	12½ ec	22.0	74
13½ ec	12½ ec	12½ ec	30.0	74
12½ ec	12 ec	12 ec	43.3	74
12½ ec	12 ec	12 ec	48.0	74
		11 ca	57.0	74

$CoBr_2 = 0.0196M = 1$

0.75 $CdBr_2$	1.00 $CdBr_2$	1.25 $CdBr_2$	H_2O, p.p.m.
13½ ie	13½ ie	13 gc	5.8
13½ ic	13½ gc	13 gc	7.0;7.0;7.1
13½ gc	13½ ic	13 gc	8.7;8.9;10.3
13 gc	12½ gc	12 ec	16.5;17.5;18.0
13 ca	12½ ea	12 ea	20.2;19.6;19.3
12½ ea	12 ec	11 ic	34.6;35.4;35.4
12½ ec	12 ec	11 ca	61.0;58.3:58.3
12 ca	11 ca	10 ca	64;64;64

WHAT WE CLAIM IS:—

1. A dual salt moisture indicating device comprising a cellulosic paper impregnated with cobaltous bromide characterised in that the bromide impregnated paper is further impregnated with,
   (i) a bromide of cadmium, mercury or zinc,
   (ii) a bromide or chloride of calcium, barium or magnesium, or
   (iii) another water soluble cobaltous salt.

2. An indicating device as claimed in claim 1, comprising a cellulosic paper impregnated with cobaltous bromide and cobaltous nitrate.

3. An indicating device as claimed in claim 1, comprising a cellulosic paper impregnated with cobaltous bromide and cadmium bromide, the cadmium bromide being in the molar proportion of ½ to 2 times the amount of cobaltous bromide.

4. An indicating device as claimed in claim 1 substantially as hereinbefore described.

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