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INDICATOR FOR WATER CONTENT OF LIQUIDS

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This invention relates to an indicator element for indicating excessive quantities of water in liquids of extremely low water solubilities. More specifically, this invention relates to the indication of excessive quantities of water in halogenated refrigerants, gasoline, oils, and other organic liquids having low water solubility and having low chemical activity.

This invention resides essentially in an indicating material consisting of matted inert fiber prepared in such a manner that it has the appearance of filter paper upon which is deposited uniformly predetermined amounts of pure anhydrous cobaltous bromide.

The mechanical refrigeration industry has been continually plagued by the presence of moisture in the refrigerant system. The industry spends large sums of money and takes great pains in attempting to dry the working system as much as possible. Manufacturers of refrigerants and oils with which these systems are charged also dry their products as much as possible. This can be seen by the fact that commercially available dichlorodifluoromethane (refrigerant 12), monochlorodifluoromethane (refrigerant 22), and trichloromonofluoromethane (refrigerant 11) contain 10 parts per million or less of water.

However, water still is present or can enter into these systems causing an undue amount of damage. It may enter into the system if it is necessary to recharge the system with oil or refrigerant if the charging lines are wet, or in some cases the oil may be contaminated with excessive amounts of water. If precautions are not taken when a part is being replaced moist air may enter the system. The replacement part can have adsorbed moisture on it and with a slight rise in temperature some of this water will be desorbed thereby raising the water content of the refrigerant stream.

Excessive quantities of dissolved water in the refrigerant stream can lead to accelerated corrosion of component parts and the formation of corrosion solids which may plug up the refrigerant metering device or lead to the failure of other moving parts thereby leading to the failure of the entire unit. Furthermore, due to the large temperature differential between the liquid line and the metering device the solubility of the dissolved water can be reduced to such an extent, due to the temperature decrease, that water can crystallize out and plug the metering device leading to complete failure of the unit. For example, at a 125° F. liquid line temperature refrigerant 22 can dissolve about 2550 parts per million of water while at a 20° F. evaporator temperature refrigerant 22 can dissolve only approximately 500 parts per million. Under these conditions separated water will then form ice which can plug the metering device.

It is the general consensus in the refrigeration industry that most refrigeration units containing 15 parts per million or less by weight of dissolved water in refrigerant 12 or 60 parts per million or less by weight of dissolved water in refrigerant 22 will run trouble-free and no accelerated corrosion or oil sludging will occur.

There are various methods employed in the determination of small quantities of water in liquids. These methods are described in the literature, but in most cases expensive equipment is required and/or the services of a skilled analyst are necessary. This equipment or these services are generally unavailable to the refrigeration service man.

A simple and inexpensive means of water determination is therefore desirable. The device described in U. S. Patent 2,761,312 September 4, 1956 is such a means, but it only partially fulfills the need because of certain limitations. As stated above, it is the general consensus in the refrigeration industry that equipment using refrigerant 12 will run trouble-free if this refrigerant contains 15 parts per million or less of dissolved water. Certain equipment manufacturers are now striving to reduce this dissolved water content to 5 parts per million. With equipment operating with refrigerant 22 a dissolved water content of 60 parts per million or less is desirable.

The liquid phase water indicator disclosed in U. S. Patent 2,761,312 goes through various shades of blue and purple, each shade corresponding to a specific degree of relative saturation. For example, when a Munsell color value of Purple [5.0 P] 8/2 is attained the relative saturation of dissolved water in refrigerant 12, refrigerant 22 and various other halogenated hydrocarbons is 20 percent. At 10 percent relative saturation the Munsell color is Purple Blue [5.0 PB] 7/6. However, at a relative saturation of 6.0 percent the indicating element attains a slightly darker Munsell color value of Purple Blue [5.0 PB] 6/6 and does not change with any further reduction in relative saturation. When this indicating device is used in operating refrigeration equipment it is the common policy to keep the indicating device as blue as possible, that is, at Munsell color value Purple Blue [5.0 PB] 6/6. As can be seen from Table I when this color is indicated by the device and the refrigerant temperature rises above approximately 117° F. (shaded area of table) with refrigerant 12 there is no reasonable assurance that the unit is operating with a dissolved water concentration of 15 parts per million or less, which is considered safe with this type of refrigerant. The table shows similar lack of assurance with other refrigerants.

Table I

	40° F.	60° F.	75° F.	100° F.	125° F.	140° F.	160° F.
Refrigerant 11	2.6	4.2	6	10.1	16.2	21.3	29.7
Refrigerant 12	1.9	3.5	5.2	9.9	18.3	24.6	38.1
Refrigerant 22	41.4	58.2	76	109	153	185.4	287

Furthermore, Table I shows that when this indicating device is used in a refrigeration unit using refrigerant 22, the refrigerant temperature would have to be less than approximately 60° F. for the operator to be reasonably sure that the unit is operating with a moisture level of 60 parts per million or less of dissolved water. A liquid line temperature of 60° F. is very rare. Normal operating conditions tend to give refrigerant temperatures of at least 90° F. and higher.

It should be evident, therefore, that a liquid phase water indicator which changes color at a lower relative saturation of water in liquids is necessary to give the operator adequate indication that the system does not contain excessive quantities of dissolved water.

The color changes shown by the cellulose base indicating element of U. S. Patent 2,761,312 are specific for this base material. There is considerable evidence to indicate that cobaltous bromide forms a coordination

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complex with the hydroxyl groups of cellulose and that this complex forms colored hydrates different from that of pure cobaltous bromide. Numerous attempts to provide an inert carrier for cobaltous bromide were rather unsuccessful. For example, cobaltous bromide is deposited very unevenly on woven cloth made from such materials as glass, nylon (polyamides) and dynel (vinyl chloride-acrylonitrile copolymer). These uneven deposits are easily removed mechanically. I have discovered that matter glass fiber can retain a uniform deposit of cobaltous bromide, when the matter fiber is immersed in a water solution of cobaltous bromide and then dried in air.

I have found that this indicator prepared from matted glass fiber changes from Munsell color values Yellowish Green [2.5 G] 7/8 to Purple, Red-Purple [10.0 P] 7/8. This color change occurs between a relative saturation of 1.2 to 2.4 percent of dissolved water in halogenated hydrocarbons and other organic liquids having low water solubility and having low chemical activity.

A color change at this relative saturation range is extremely advantageous because when this indicating device is used in refrigeration systems using refrigerant 12 or refrigerant 22 it is reasonably certain that the system is adequately protected from troubles caused by amounts of water considered to be excessive. Table II gives the concentration of dissolved water in parts per million, for refrigerant 12 and 22 at four temperatures, at 1.2 and 2.4 percent of saturation. The Munsell color values corresponding to these percents of saturation are also given in the table.

Table II

	Yellowish Green	Purple Red-Purple	Yellowish Green	Purple Red-Purple
	90° F.		125° F.	
	[2.5 G]7/8	[10.0 P]7/8	[2.5 G]7/8	[10.0 P]7/8
Refrigerant 12	1.5	3.0	3.6	7.2
Refrigerant 22	19	38	31	62
	140° F.		160° F.	
Refrigerant 12	4.9	9.8	7.6	15.2
Refrigerant 22	37	74	47	94

As previously noted, the indicating element consists of pure anhydrous cobaltous bromide deposited on a mat of fibers chemically inert to an aqueous solution of cobaltous bromide, such as glass fibers, pure asbestos fibers, "fiberfrax," manufactured by Carborundum Co. which is a ceramic fiber made from alumina and silica, and "dacron," manufactured by E. I. du Pont de Nemours & Co. which is a synthetic polyester fiber made from a polymer of methyl terephthalate and ethylene glycol. The concentration of the anhydrous cobaltous bromide has no apparent effect upon the range where the color change occurs. However, the intensity of the color rises with increased concentration and increased amounts of the salt impart greater strength to the inert fiber.

The thickness of the inert fiber has no effect upon the indicating characteristics. A preferred indicator is a mat of glass fiber varying from 0.006 to 0.008 inch in thickness and having deposited on it 8 to 160% by weight pure anhydrous $CoBr_2$ based upon the weight of inert fiber so as to give an adequate intensity of color and additional strength to the fibers.

This liquid phase water indicator may be prepared by simply immersing the mat of inert fiber in an aqueous solution containing 1 gm. to 25 gm. pure anhydrous cobaltous bromide per 100 cc. After drying, the indicator so prepared can be immersed in the organic liquid to be tested. The indicator will then remain green (Munsell color value Yellowish Green [2.5 G] 7/8) if the relative saturation of water in the liquid is 1.2 percent or below and will turn red (Munsell color value Purple Red-Purple [10.0 P] 7/8) if the relative saturation is above 2.4 percent. The color change is reversible. That is, if the relative saturation is reduced from above 2.4 percent to 1.2 percent, or below, the indicator will turn green and if then again increased to 2.4 percent or above will again turn red.

I claim:

1. An indicating element for determining quantities of water just above or just below the range of 1.2 to 2.4 percent relative saturation in liquids of low water solubility selected from the group consisting of trichloromonofluoromethane, dichlorodifluoromethane, monochlorotrifluoromethane, monochlorodifluoromethane, methyl chloride, gasoline and kerosene adapted to be immersed in the said liquids, said indicating material comprising a mat of fibers chemically inert to cobaltous bromide having uniformly distributed therein 8 percent to 160 percent by weight pure anhydrous cobaltous bromide, the color of the indicating element just above the range of 1.2 to 2.4 percent relative saturation being Purple Red-Purple (Munsell color [10.0 P] 7/8) and the color just below said range being Yellow Green (Munsell color [2.5 G] 7/8).

2. An indicating element as defined in claim 1, wherein the mat of inert fibers is made of glass varying from 0.006 inch to 0.008 inch in thickness.

3. An indicating element as defined in claim 1, wherein the mat of inert fibers is made of a ceramic fiber of alumina and silica.

4. An indicating element as defined in claim 1, wherein the mat of inert fibers is made of a polymer of methyl terephthalate and ethylene glycol.

5. An indicating element as defined in claim 1, wherein the mat of inert fibers is asbestos.

6. An indicating element as defined in claim 1, wherein the concentration of uniformly deposited anhydrous cobaltous bromide varies from 20 percent to 130 percent by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

1,749,826	Lubach	Mar. 11, 1930
2,279,230	Frost	Apr. 7, 1942
2,636,962	Bouyoucos	Apr. 28, 1953
2,761,312	Line et al.	Sept. 4, 1956

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