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ACID-BASE TEST MATERIALS

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This invention relates to novel acid-base test materials. More particularly this invention relates to acid-base test materials that are adaptable for use in non-aqueous, water insoluble systems.

Acid-base test papers such as Congo Red, Litmus, Brilliant Yellow and the like are old and well known for testing aqueous systems or systems which are soluble in water for the presence of acids or bases. However, they have little or no use when testing for the presence of acids in oils, solvents and the like which are water insoluble. This is primarily due to the fact that the oil is absorbed on the paper, masking whatever effect the presence of acid in the oil might have on the test paper. Also, some of the indicators used in the test papers are soluble in oils and are partially extracted from the paper with the result that the effect of acids or bases is more difficult to observe.

Acids may occur in oils or other water-insoluble materials for several reasons. One is the oils contained as lubricants in internal combustion engines where a certain amount of acid is formed. Another is in refrigeration equipment when a motor burnout has occurred with resulting decomposition of part of the refrigerant, particularly when the refrigerant is one of the halogenated hydrocarbon types which are so widely used at present. In cleaning such engines or refrigeration equipment, it is generally desired to remove all of the acid present because of the severe corrosion it causes. This is done by washing the equipment with solvent, oil or the refrigerant until the system is free of acid. It is immediately found however that testing for the presence of acid when oil is present, as it will be both in engines and refrigeration equipment being repaired, can be a very time consuming affair. This is because oil is absorbed on ordinary test papers, which otherwise detect acid quite rapidly, giving the paper the color of the oil and masking the color change which may occur in the paper. It has been necessary therefore to resort to more laborious methods for detecting acids in the presence of oils. One such method is described by Bergstrom et al. in U.S. Patent 2,770,530.

It is an objective of this invention therefore to provide a series of acid-base test materials for testing for the presence of acids in non-aqueous systems. It is a further object to provide acid-base test materials for detection of acids in oils and other water-insoluble liquids. Other objects will appear hereinafter.

These and other objects are accomplished by using an acid-base test material containing from about 5% to about 50% by weight of a hygroscopic, neutral sensitizer chosen from the strong acid salts of strong bases and polyhydroxy aliphatic organic compounds.

The present invention consists of improved acid-base test papers or other cellulosic materials into which has been incorporated from about 5% to about 50% by weight of a sensitizer chosen from polyhydroxy aliphatic organic compounds and the strong acid salts of strong bases. The polyhydroxy compounds may be relatively simple compounds such as glycerine, ethylene glycol, di, tri and other ethylene glycols, propylene glycol, more complicated structures such as some of the naturally occurring sugars, e.g. glucose, sucrose, soluble starches and the like or synthetic compounds such as sorbitol, penta-

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erythritol, erythritol and the like. As a practical matter, there is no limitation on the number of carbon atoms in the polyhydroxy compounds. The strong acid salts of strong bases include the salts of the alkali metal or alkaline earth metal hydroxides. The acid portion of these compounds include hydrogen chloride, hydrogen bromide, hydrogen iodide, sulfuric acid and nitric acid.

Acid-base indicators which are used in test papers are organic dyes which change color with a change in the concentration of hydrogen ion. Usually these dyes contain either basic groups, e.g. amino groups, or acidic groups which can react with the acid or base present. Some typical examples of such dyes which are used are: Congo Red, Brilliant Yellow, Litmus, Neutral Red, Bromphenol Red, Phenol Red, Thymol Blue, Methyl Red and the like. These dyes are substantive to other cellulosic material substrates as well as to paper. Usually, however, they are also somewhat oil soluble and can be extracted from the paper with organic solvents such as oils. A large number of such types of test papers are used. Certain test papers also contain more than one indicator and these also may be used.

Although the present invention is directed primarily to paper test strips, other materials can be used in place of paper. Examples are cotton cloth, felt and the like as well as inert, porous materials which are inert to acids and bases as well as organic solvents.

The test papers of this invention are prepared by addition of one of the sensitizing agents to the indicator dye, paper combination during some stage of manufacture. Being essentially nonvolatile, the sensitizing agents do not evaporate from the test paper after manufacture. This is, of course, a prime requirement of the sensitizing agent for the whole purpose is defeated if the sensitizing agent is lost from the test paper. Glycerine is the preferred polyhydroxy compound because it is relatively cheap, does not evaporate and seems to give the best results. The limits of concentration of the sensitizing agents is determined, on the lower limit, by the minimum amount of material which must be present to obtain the desired results. This minimum appears to be about 5% by weight. The upper limit is determined by how much of the agent the test paper can hold. Paper, and the other useful substrates, are highly absorbent, but about 50% by weight appears to be a practical upper limit. There is certainly no advantage gained from using more than 50%. The preferred concentration is about 25–50% by weight of the total indicator mass.

The presence of the sensitizing agents in the test papers serves two purposes. First, they prevent oils and other water-insoluble organic materials from being absorbed in the paper and/or from extracting the indicator dye from the paper. Second, the polyhydroxy compounds increase the sensitivity of the test papers to acids present in oils or other water-insoluble organic solvents. This latter point is demonstrated by the following comparison. A sample of trichlorofluoromethane used to wash out a burned out, hermetically sealed refrigeration unit, and thus containing acids formed from the refrigerant during the burn-out, was tested with three types of Congo Red acid test paper. Congo Red paper which had been previously wetted with water was found to be the least sensitive to acids present in the organic material; in other words, it took the highest concentrations of acid to cause the color change. Paper which was not pretreated in any way was somewhat more sensitive, detecting somewhat lower concentrations of acid. Surprisingly, test papers containing glycerine are the most sensitive, detecting the lowest concentrations of acids in the organic material.

The color change of most of these novel test papers containing one of the polyhydroxy organic compounds is most readily observed at the torn, rough edge of a piece of test paper. It has been observed that a torn edge will undergo the color change while the body of the test paper is unaffected. This is particularly true when the concentration is low. This phenomenon has a great advantage in detecting the presence of low concentrations of acid because the changed color along the torn edge stands out in sharp contrast to the unaltered color of the body of the test paper. This is the recommended method for using most of the test papers of this invention, particularly with low acid concentrations. Of course, when the concentration of acids is high, the color of the body of the test paper changes color also.

Oils, particularly when they have been used for a period of time, are highly colored. While solvents such as trichlorofluoromethane, which are used to wash out burned-out refrigeration units, are not colored in themselves, they usually pick up enough oil or other colored materials during the washing process to give them some color also. Thus materials such as those just mentioned may be colored and, if absorbed in the presently available test paper, would mask any color change which might occur in the dye indicator. This is particularly true when the concentration of acid is low.

The acid-base test papers of this invention can be used for testing liquids which are water soluble or contain water but there appears to be no advantage gained under such conditions in using these papers. The primary advantage of these new acid-base test papers is for the acid-base testing of oils or water-insoluble liquids. These papers can also be used to test gases for the presence of acidic or basic materials and there is an advantage gained over ordinary wetted test papers.

The following examples will better illustrate the practice of the present invention; however, the invention is not intended to be limited to these examples. Parts are by weight unless otherwise indicated.

Example 1

Congo Red test paper strips were dipped in a solution of 20 volume percent glycerine, 80 volume percent anhydrous methanol, then air dried. The dried paper strips contained 35-40% by weight glycerine. The dried papers still had a slightly damp feeling.

For test purposes, two sets of solutions were made up, one by dissolving anhydrous hydrogen chloride in trichlorofluoromethane and the other by dissolving anhydrous hydrogen chloride in a solution of one volume of refrigeration grade oil in two volumes of trichlorofluoromethane. Solutions of acid numbers of 0.04 and 0.02 mg. KOH/g. were prepared in each case.

Treated and untreated test paper strips were torn across the narrow dimension to give a rough, torn edge. The torn edge of both treated and untreated test strips was dipped into the acid solutions and the adhering solution was allowed to drain and evaporate. The edges of the test strips were then examined.

It was found that the torn edge of the glycerine treated test strip which was dipped into the oil-containing solution of acid number 0.04 was a strong blue color, standing out in sharp contrast to the bright red side of the paper. The blue edge of the untreated paper, although present, was much more difficult to see. Glycerine treated paper which was dipped into the oil-containing solution of acid number 0.02 gave a clear blue edge but the blue of the edge of the untreated test paper was doubtful at best.

Tests with oil free trichlorofluoromethane of acid number 0.02 gave a blue edge on the glycerine treated paper which was clearly discernible (there was no change in the color of the body of the paper) but there was no clear indication of acidity with the untreated paper.

Example 2

Strips of Congo Red paper were dipped into the following liquids and hung up to drain and/or dry: glycerine, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, 19 wt. percent aqueous dextrose, 20 wt. percent aqueous sorbitol, 38 wt. percent aqueous sucrose and 6 wt. percent aqueous, soluble starch. The treated papers contained 25-35% by weight of the agent in each case.

The strips were torn and the torn edges dipped in a solution of hydrogen chloride in trichlorofluoromethane of acid number of about 0.02 mg. KOH/g. After draining and drying, they were compared with untreated strips which had been dipped in the same solution.

All of the treated test papers showed greater sensitivity than the untreated paper, giving a readily recognizable blue color at the torn edge.

The test papers treated with glycerine and the glycols retained a damp feeling but the papers treated with solids such as dextrose, sorbitol, sucrose and starch did not. The dry-feeling treated test papers were more sensitive by visual observation than the untreated test papers.

Example 3

Strips of Congo Red test paper were dipped in a 30 wt. percent aqueous solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and others in a 20 wt. percent aqueous solution of LiBr. The strips were then dried by hanging in air, giving papers containing about 25-35 wt. percent of additive. The strips retained a quite damp feeling and were darker red than glycerine-treated or untreated dry strips.

On testing as in Example 2, the treated test papers were found to be more sensitive than the untreated strips but were less sensitive than the glycerine treated strips.

Example 4

Strips of Brilliant Yellow, red litmus, and blue litmus test papers were immersed in a 20 volume percent solution of glycerine in anhydrous methanol as in Example 1. The strips were then dried overnight. The treated strips of Brilliant Yellow and red litmus test papers proved to be more sensitive than the corresponding untreated test papers when exposed simultaneously to weak ammonia fumes.

The blue litmus was tested by immersion in a hydrogen chloride solution in trichlorofluoromethane with an acid number of 0.04 mg. KOH/g. The treated test paper was more sensitive than the untreated paper, the former giving a strong, clear test while the latter gave a weak and doubtful color change.

In the case of red and blue litmus, the color change was most clearly observed on the rough edge of a torn strip of the paper. With Brilliant Yellow however, better results are obtained using the flat side of the test strip rather than an edge of the test paper. At a higher but undetermined concentration, the same results are obtained with acetic acid.

However, weak organic acids, viz. acetic, propionic, butyric and hexanoic acids, in trichlorofluoromethane (acid No. 0.2 mg. KOH/g.) give only a weak test on the flat side of glycerine treated Congo Red test paper. No clear development of color was obtained on the torn edge.

The above examples clearly demonstrate that the novel test papers prepared according to this invention are superior to untreated test papers for detecting the presence of strong acids in nonaqueous, water-insoluble systems. These acid-base test papers offer a cheap, efficient and rapid method for detecting the presence of acids in such systems which does not require more than ordinary skill, and the ability to detect color changes, on the part of the user. For these reasons, the new test papers of this invention are a valuable contribution to the art.

As many widely different embodiments of this invention may be made without departing from the spirit and scope

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thereof, it is to be understood that this invention is not limited to the specific embodiments thereof except as defined in the appended claims.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. An acid indicator consisting of a porous cellulosic material substrate containing an organic dye which is capable of undergoing a color change at a pH of less than 7.0 and from about 5% to about 50% by weight of a neutral, water soluble, saturated aliphatic polyhydroxy compound composed entirely of carbon, hydrogen and oxygen.

2. An acid indicator as defined in claim 1 wherein said polyhydroxy aliphatic compound is glycerine.

3. An acid indicator as defined in claim 1 wherein said polyhydroxy aliphatic compound is ethylene glycol.

4. An acid indicator as defined in claim 1 wherein the amount of said polyhydroxy aliphatic compound is 25% to 50% by weight.

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5. An acid indicator as defined in claim 1 wherein said cellulosic material substrate is paper and wherein the amount of said polyhydroxy aliphatic compound is 25-50% by weight.

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