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METHOD FOR STABILIZING REFINED ETHANOL AGAINST DEGRADATION CAUSED BY POLYVALENT METAL IONS

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ABSTRACT OF THE DISCLOSURE

Refined ethanol is stabilized against the formation of odor and color, caused by the presence of free copper ions, by the addition of a small amount of a metallic salt of an acid derivative of an ethylene polyamine.

Commercially-produced ethyl alcohol or ethanol, as it is commonly called, ordinarily contains a small quantity of easily oxidized impurities all of which have not been identified heretofore. The level of these impurities present is usually determined qualitatively by the permanganate time test. In this test, two milliliters of a solution containing 0.2 gram of potassium permanganate per liter of distilled water is added to 50 milliliters of ethanol in a 50 milliliter glass-stoppered graduated cylinder. This mixture is stored in the dark at 15° C. with a Barbet color standard. The time, in seconds, required for the color to change to that of the standard is recorded as the permanganate time. The standard is an aqueous solution containing 0.5 percent by weight of cobaltous chloride ($CoCl_2.6H_2O$) and 0.56 percent by weight uranyl nitrate [$UO_2(NO_3)_2.6H_2O$].

Materials which oxidized more easily than ethanol lower the time required for permanganate consumption as indicated by color change. Among these are unsaturated compounds (—C=C—) and carbonyls (—CHO) whose detrimental effects have been minimized by their more complete removal in modern refining facilities. We have found that reduced, multivalent metal ions, particularly copper, are also present as impurities and have an immediate and a greater reducing effect than organic impurities inherent in high-quality ethanol. The problem seems to arise in part from the fact that the equipment used for the production of ethanol is commonly made of copper and production procedures include use of reagents such as chloroform which can yield acidic degradation products which, in turn, solubilize the metal of the production equipment.

The presence of the metal ion contaminants, while undesirable in ethanol destined for any use, is a particular problem when the ethanol is to be used for medicinal or cosmetic purposes. For such uses even a few parts per million of metal ions can cause serious problems of product degradation which affect purity and color. In addition, a color problem arises when ethanol containing these impurities is reacted with silicon tetrachloride to make tetraorthosilicates for use in the metal die-casting industry. Even a few parts per million of impurities can cause sufficient discoloration to make the material unsatisfactory for use. It is an object of the present invention, therefore, to provide a simple, safe and inexpensive way of eliminating the adverse effects of metal ions present in ethanol.

Ethanol with essentially no foreign odors is required for cosmetic formulations containing blends of perfumes. It has been found that reduction of the metal ion content unexpectedly reduces the odor intensity of ethanol, thus making it more suitable for cosmetic use. Odor intensity is measured by a group of trained people called an odor panel who are expert in detecting the presence of foreign odors and in determining the overall level of odor intensity. Intensity as reported here is measured on a numerical scale of 1 through 6, with a rating of 1 denoting the lowest level of intensity. Odor intensity is such an important factor in cosmetic formulations that an improvement of only a few tenths of a point on the 1 through 6 scale can be critical.

To determine odor intensity an individual sample is diluted to about 20 percent ethanol with odor-free water, and a number of odor experts, one at a time, rate the sample on the intensity scale. Sometimes they are asked to compare samples and rate them most or least intense. The samples are coded so that the odor panel members know only that they contain 200 proof ethanol.

We have found that the quality of ethanol can be greatly improved by reducing the quantity of free metal ions present through the addition of the ethanol of a few parts per million of a metallic salt of an acid derivative of an ethylene polyamine. This not only improves purity, as evidenced by the permanganate time test, and color, as shown by tests of the orthosilicate, but also confers the unexpected benefit of greatly improved odor. Our preferred salts are the trisodium salt of hydroxyethylethylenediaminetriacetic acid which is commercially available under the trademark "Versenol," the tetrasodium salt of ethylenediaminetetraacetic acid available as "Versene," the pentasodium salt of diethylenetriaminepentaacetic acid sold as "Versenex" and the calcium chelate of disodium ethylenediaminetetraacetic acid available under the trademark "Versene CA."

We have found that the quality of the ethanol is noticeably improved by the addition of as little as 1.0 part per million of one of these salts. The improvement is quite pronounced as 5 parts per million while the addition of at least 10 parts per million will about double the permanganate time in most cases. While there is no specific upper limit on the quantity to be added, the addition of more than about 50 parts per million has not been found to have sufficient beneficial effect in most cases to make such addition desirable. Thus, our preferred range for the addition is between about 5 and 50 parts per million. It should be recognized, however, that in the case of badly-contaminated ethanol much larger quantities might be desirable.

The following examples are illustrative of the invention.

EXAMPLE I

To a 1809 gram sample of 200 proof ethanol were added 0.018 gram of the trisodium salt of hydroxyethylethylenediaminetriacetic acid (Versenol), thereby providing a concentration of 10 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 46 minutes as compared to 23 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE II

To a 1346 gram sample of 200 proof ethanol were added 0.0254 gram of the trisodium salt of hydroxyethylethylenediamine triacetic acid (Versenol), thereby providing a concentration of 18.9 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 120 minutes as compared to 13 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE III

To a 693 gram sample of 200 proof ethanol were added 0.0173 gram of the trisodium salt of hydroxyethylethylenediaminetriacetic acid (Versenol), thereby providing a concentration of 25 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 180 minutes as compared to 12 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE IV

To a 1337 gram sample of 200 proof ethanol were added 0.0264 gram of the pontasodium salt of diethylenetriaminepentaacetic acid (Versenex), thereby providing a concentration of 19.7 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 39 minutes as compared to 13 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE V

To a 1356 gram sample of 200 proof ethanol were added 0.293 gram of the tetrasodium salt of ethylenediaminetetraacetic acid (Versene), thereby providing a concentration of 22 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 56 minutes as compared to 13 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE VI

To a 550 gram sample of 200 proof ethanol were added 0.0567 gram of the calcium chelate of disodium ethylenediaminetriacetic acid (Versene CA), thereby providing a concentration of 10 parts per million of the salt. The sample was then subjected to the permanganate time test and found to have a permanganate time of 72 minutes as compared to 23 minutes for a control sample of ethanol with no additive. The odor of the ethanol was greatly improved by the addition of the salt and no discoloration occurred.

EXAMPLE VII

A sample of 200 proof ethanol was diluted with 5 weight percent of distilled water to make 190 proof alcohol. To 160 gram aliquots of this 190 proof alcohol were added varying quantities of the trisodium salt of hydroxyethylethylenediamine triacetic acid (Versenol). Each aliquot was then subjected to the permanganate time test. The results were as follows:

Aliquot	Grams of salt Added	Parts per million of salt	Permanganate time
Control	0	0	13
A	0.00144	9	34
B	0.00240	15	39
C	0.00496	31	70
D	0.00800	50	120

EXAMPLE VIII

To a 1346 gram sample of 200 proof ethanol were added 0.0254 gram of the trisodium salt of hydroxyethylethylenediaminetriacetic acid (Versenol), thereby providing a concentration of 18.9 parts per million of the salt. A 195 milliliter portion of this sample was then reacted with 84 milliliters of silicon tetrachloride which had been prepared by redistilling commercial grade silicon tetrachloride at a reflux ratio of 20 to 1. The tetraethylorthosilicate thus produced had a color of 30 on the platinum-cobalt scale as compared with 60 for tetraethylorthosilicate made from ethanol containing no chelating salt.

EXAMPLE IX

To a 1356 gram sample of 200 proof ethanol were added 0.0271 gram of the tetrasodium salt of ethylenediaminetetraacetic acid (Versene), thereby providing a concentration of 22 parts per million of the salt. A 195 milliliter portion of this sample was then reacted with 84 milliliters of silicon tetrachloride which had been prepared by redistilling commercial grade silicon tetrachloride at a reflux ratio of 20 to 1. The tetraethylorthosilicate thus produced had a color of 30 on the platinum-cobalt scale as compared with 60 for tetraethylorthosilicate made from ethanol containing no chelating salt.

EXAMPLE X

To a 1337 gram sample of 200 proof ethanol were added 0.0264 gram of the pentasodium salt of diethylenetriaminepentaacetic acid (Versenex), thereby providing a concentration of 19.7 parts per million of the salt. A 195 milliliter portion of this sample was then reacted with 84 milliliters of silicon tetrachloride which had been prepared by redistilling commercial grade silicon tetrachloride at a reflux ratio of 20 to 1. The tetraethylorthosilicate thus produced had a color of 30 on the platinum-cobalt scale as compared with 60 for tetraethylorthosilicate made from ethanol containing no chelating salt.

Ethanol with essentially no foreign odors is required for cosmetic formulations containing blends of perfumes. It has been found that reduction of the metal in content unexpectedly reduces the odor intensity of ethanol, thus making it more suitable for cosmetic use.

Odor intensity is mesaured by a group of trained people called an odor panel who are expert in detecting the presence of foreign odors and in determining the overall level of odor intensity. Intensity as reported here is measured on a numerical scale of 1 through 6, with a rating of 1 denoting the lowest level of intensity. An individual sample is diluted to about 20 percent ethanol with odor-free water, and a number of odor experts, one at a time, rate the sample on the intensity scale. Sometimes they are asked to compare samples and rate them most or least intense. The samples are coded so that the odor panel members know only that they contain 200 proof ethanol.

EXAMPLE XI

To aliquots of a sample of 200 proof ethanol having an average intensity rating of 4.67 determined by six odor panel members were added 15 and 31 parts per million of the trisodium salt of hydroxyethylethylenediamine-triacetic acid (Versenol). The sample containing 15 parts per million was given an average intensity rating of 4.17. The sample containing 31 parts per million was given an average intensity rating of 3.83.

EXAMPLE XII

To a sample of 200 proof ethanol having an average intensity rating of 4.45 determined by nine odor panel members was added 10 parts per million of the calcium chelate of disodium ethylenediaminetetraacetic acid (Versene CA). The sample, after addition of the salt, was given an average intensity rating of 3.89 by the members. In addition, the treated and untreated samples were compared 48 different times; 38 of those times the treated samples were found by the odor panel members to have the least intense odor.

EXAMPLE XIII

To a sample of 200 proof ethanol having an average intensity rating of 5.22 determined by nine odor panel membres was added 20 parts per million of the trisodium salt of hydroxyethylethylenediaminetetraacetic acid (Versenol). The treated sample was given an average

intensity rating by the odor panel members of 4.56. In addition, on 12 consecutive days 7 to 9 odor panel members per day were asked to compare the two samples and rate them most or least in odor intensity. Out of a total of 94 individual votes over the 12-day period, 80 votes were for the treated sample having the least intense odor.

What is claimed is:

1. A method for stabilizing refined ethanol against the formation of odor and color caused by the presence of free multivalent metal ions which comprises adding to said refined ethanol at least 1 part per million of a metallic salt of an acid derivative of an ethylene polyamine selected from the group consisting of the trisodium salt of hydroxyethylethylenediaminetriacetic acid, the tetrasodium salt of ethylenediaminetetraacetic acid, the pentasodium salt of diethylenetriaminepentaacetic acid, and the calcium chelate of disodium ethylenediaminetetraacetic acid, whereby the quantity of said free multivalent metal ions is reduced.

2. The method of claim **1** wherein said metallic salt is the trisodium salt of hydroxyethylethylenediaminetriacetic acid.

3. The method of claim **1** wherein said metallic salt is the tetrasodium salt of ethylenediaminetetraacetic acid.

4. The method of claim **1** wherein said metallic salt is the pentasodium salt of diethylenetriaminepentaacetic acid.

5. The method of claim **1** wherein said metallic salt is the calcium chelate of disodium ethylenediaminetetraacetic acid.

6. The method of claim **1** wherein between about 5 and about 50 parts per million of the calcium chelate of disodium ethylenediaminetetraacetic acid is added to the refined ethanol.

7. A refined ethanol composition, stabilized against the formation of odor and color caused by the presence of free multivalent metal ions, containing an amount, sufficient to reduce the quantity of said free multivalent metal ions, of a metallic salt of an acid derivative of an ethylene polyamine selected from the group consisting of the trisodium salt of hydroxyethylenediaminetriacetic acid, the tetrasodium salt of ethylenediaminetetraacetic acid, the pentasodium salt of diethylenetriaminepentaacetic acid, and the calcium chelate of disodium ethylenediaminetetraacetic acid.

8. The composition of claim **7** wherein said metallic salt is the trisodium salt of hydroxyethylethylenediaminetriacetic acid.

9. The composition of claim **7** wherein said metallic salt is the tetrasodium salt of ethylenediaminetetraacetic acid.

10. The composition of claim **7** wherein said metallic salt is the pentasodium salt of diethylenetriaminepentaacetic acid.

11. The composition of claim **7** wherein said metallic salt is the calcium chelate of disodium ethylenediaminetetraacetic acid.

12. The refined ethanol composition of claim **7** containing between about 5 and about 50 parts per million of the calcium chelate of disodium ethylenediaminetetraacetic acid.

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