

SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

División de Nuevas Creaciones

E. S. D.

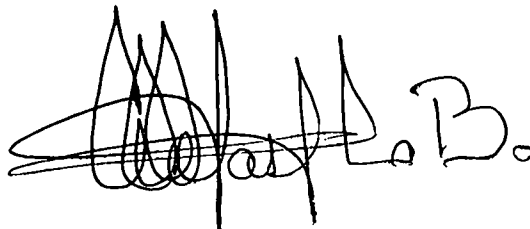
Ref: EXPEDIENTE No 01-007443

Solicitud de patente a nombre de STOKELY-VAN CAMP, INC

Como es de conocimiento de ese Despacho, el extracto de la solicitud indicada en la referencia se publicó en la Gaceta de Propiedad Industrial N° 522 del 28 de Noviembre de 2002.

Para dar cumplimiento al artículo 44 de la Decisión 486, pido se examine si la invención es patentable.

Atentamente,



JERONIMO CASTILLO BONILLA
C.C. 79.462.057 Bogotá
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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO

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Adjunto el recibo N° por la tasa correspondiente, según la Resolución 41687 del 24 de diciembre del 2002.

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RADICACIÓN EXPEDIENTE No 01-007443

EL EXTRACTO DE LA PRESENTE SOLICITUD DE **PATENTE DE INVENCION**

FUE PUBLICADO EN LA GACETA DE PROPIEDAD INDUSTRIAL No **522** DE

FECHA **28 DE NOVIEMBRE DE 2002** EL TERMINO HABIL EÑALADO POR LA

LEY EXPIRA EL **25 DE FEBRERO DEL 2003**

NOTA: Dentro del plazo de los seis (6) meses siguientes a partir de la fecha de publicación en la gaceta de Propiedad Industrial, deberá solicitar y cancelar el examen de patentabilidad so pena de que la solicitud caiga en abandono, de acuerdo con lo establecido en el Artículo 44 de la Decisión 486/2000.

SE PRESENTARON OPOSICIONES POR PARTE DE TERCEROS.

SI _____

NO__ **X** _____



US005336510A

United States Patent [19]
Chang

[11] **Patent Number:** **5,336,510**
 [45] **Date of Patent:** **Aug. 9, 1994**

[54] **COLOR-STABLE SYRUP AND BEVERAGE COMPOSITIONS FORTIFIED WITH VITAMIN C, AND METHODS OF MAKING SUCH COMPOSITIONS**

[75] **Inventor:** **Pei K. Chang**, Montrose, N.Y.

[73] **Assignee:** **PepsiCo, Inc.**, Purchase, N.Y.

[21] **Appl. No.:** **40,592**

[22] **Filed:** **Mar. 31, 1993**

[51] **Int. Cl.⁵** **A23L 1/27**

[52] **U.S. Cl.** **426/72; 426/262; 426/266; 426/311; 426/321; 426/540; 426/547; 426/590; 426/599; 426/648**

[58] **Field of Search** **426/72, 262, 266, 311, 426/321, 540, 547, 590, 599, 648**

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,652,290 3/1972 Hammes et al. 99/28
 3,958,017 5/1976 Morse et al. 426/72

4,208,434 6/1980 Iacobucci et al. 426/72
 4,992,282 2/1991 Mehansho et al. 426/72
 5,002,779 3/1991 Mehansho et al. 426/72

Primary Examiner—Helen Pratt

Attorney, Agent, or Firm—Finnegan, Henderson, Farabow, Garrett & Dunner

[57]

ABSTRACT

The invention is directed to color-stable syrup and beverage compositions fortified with vitamin C (ascorbic acid) which contain an azo food dye, such as FD&C Yellow #6. Riboflavin (vitamin B2) is employed as a color stabilizer and effectively prevents decoloring of the compositions, even upon prolonged periods of storage. The syrup and beverage formulations may optionally contain a glassy sodium polyphosphate, vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate, biotin, flavoring agents, sweeteners, acidic agents, etc.

20 Claims, No Drawings

COLOR-STABLE SYRUP AND BEVERAGE COMPOSITIONS FORTIFIED WITH VITAMIN C, AND METHODS OF MAKING SUCH COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to formulations for and a method of making color-stable syrup concentrates and beverages. More particularly, the invention relates to preventing decoloring or fading of syrups and beverages containing vitamin C (L-ascorbic acid) and an azo food dye using riboflavin (vitamin B2) as a color stabilizer.

2. Description of Related Art

Depending on the ingredients employed, beverage formulators in the past have experienced color stability problems, such as decoloring or discoloring of beverage compositions. As used herein, "decoloring" means causing the fading or loss of color imparted by a dye to a solution, for example, bleaching of the dye. This term, "decoloring," is to be distinguished from "discoloring" as used herein, which means imparting an undesired color to a formulation.

Various approaches have been tried in the past to solve different problems relating to the color stability of beverage formulations, especially beverage compositions fortified with vitamins and/or minerals.

U.S. Pat. No. 4,992,282 to Mehansho et al. is directed to problems caused by the presence of both vitamins and minerals, such as iron, in beverages. Iron supplements tend to discolor foodstuffs, i.e., iron sources tend to impart an undesirable color to beverage compositions (see also U.S. Pat. No. 5,002,779 to Mehansho et al.). The Mehansho et al. ('282) beverages are fortified with vitamin C, riboflavin, vitamin A, iron and calcium compounds, and may include other vitamins, such as vitamin B6, niacin and vitamin B12. The vitamin and mineral ingredients can be formulated in concentrated syrups which may contain, in addition to water, sugars, flavors and colors. The syrup compositions are diluted with water to make the final low-pH beverages.

Mehansho et al. ('282) discuss the problem of discoloration of beverages fortified with iron, rather than the problem of decoloring of beverage compositions fortified with vitamin C. However, others have attempted to solve the color instability problem, i.e., the fading of the dyes in beverages, resulting from the chemical incompatibility of certain food dyes in the presence of vitamin C.

For example, U.S. Pat. No. 4,208,434 to Iacobucci et al. is directed to forming color-stable food compositions which contain an anthocyanin pigment and vitamin C. Anthocyanin pigments are incompatible with ascorbic acid. Iacobucci et al. attempt to solve this problem by using certain ascorbic acid derivatives which do not bleach anthocyanin pigments as rapidly as ascorbic acid. Thus, Iacobucci et al. deal with a color-stability problem caused by the use of anthocyanin pigments in combination with ascorbic acid, rather than the use of azo dyes in combination with vitamin C.

Solutions containing vitamin C and azo dyes have been known to discolor over time. Difficulty has been encountered in maintaining the color over long periods of time of beverages fortified with ascorbic acid, such as sport-type drinks formulated to help optimize the performance of athletes. Ethylenediaminetetraacetic acid

(EDTA) helps stabilize the color of beverages containing an azo dye and vitamin C. However, under current U.S. regulations, EDTA cannot be used in still beverages. Thus, other ways to stabilize the color of beverages fortified with vitamin C are needed.

U.S. Pat. No. 3,958,017 to Morse et al. is directed to the use of cysteine to form color-stable beverages containing vitamin C, a food dye such as an azo dye, and optionally, iron. U.S. Pat. No. 3,652,290 to Hammes et al. discloses the use of histidine, glycine or methionine similarly to protect vitamin C in beverages containing a food dye such as an azo dye, and thus improve color stability.

Although Morse et al. and Hammes et al. suggest an approach to forming color-stable compositions containing both an azo dye and vitamin C, it would be desirable to produce syrup and beverage formulations containing an azo dye and vitamin C with even better color stability. Moreover, it would be desirable to form colorfast syrup and beverage formulations containing an azo dye and vitamin C without the necessity of using cysteine, histidine, glycine or methionine amino acids. It would also be desirable to find a color stabilizer which provides for colorfast azo-dyed beverage formulations fortified with vitamin C which even contain an additive such as a glassy sodium polyphosphate (e.g. a compound of the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$ where $n=13$ to 21) which, in the absence of the color stabilizer, undesirably accelerates the fading or decoloring of the formulation.

SUMMARY OF THE INVENTION

Thus, an object of the present invention is to provide improved color-stable syrups and beverages which contain an azo food dye and vitamin C.

Additionally, an object of this invention is to provide colorfast syrup and beverage formulations fortified with vitamin C and colored with an azo food dye, without using EDTA, cysteine, histidine, glycine or methionine in the formulation.

It is still another object of the present invention to provide color-stable syrup and beverage compositions comprising water, vitamin C, an azo food dye and, optionally, one or more conventional additives such as sweeteners and flavorings.

It is an additional object of the instant invention to provide a method of formulating improved colorfast syrup and beverage compositions comprising water, vitamin C and at least one azo dye and a color stabilizer.

It is a further object of this invention is to provide color-stable syrup and beverage formulations containing water, an azo dye, vitamin C and a glassy sodium polyphosphate having an average chain length 13-21, i.e. a compound of the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$ where $n=13-21$ such as sodium hexametaphosphate.

The foregoing objects and advantages have been achieved in accordance with the present invention by adding a color stabilizer containing or consisting essentially of riboflavin to syrup and beverage compositions containing an azo food dye and vitamin C. In one aspect, the present invention is directed to compositions for formulating syrups and beverages fortified with vitamin C and containing an azo dye and riboflavin. In accordance with the present invention, the riboflavin can be added to a syrup or a beverage alone or in a premix containing other additives, such as vitamins, minerals and azo food dyes, to stabilize the color of the

syrup or beverage. For example, the riboflavin can be added to the syrup or beverage in a vitamin premix containing vitamins and minerals.

In another aspect, the present invention is directed to a method for formulating a color-stable beverage, comprising forming a syrup composition containing water, vitamin C, an azo food dye and a color-stabilizing amount of riboflavin, and diluting the syrup composition with water.

Additional objects and advantages of the invention will be set forth in part in the detailed description of exemplary embodiments which follows, and in part will be apparent from the description, or may be learned through routine practice of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

Azo dyes are a class of synthetic dyes having $-N=N-$ as a chromophore group. These dyes are produced by reacting diazonium salts with tertiary amines or phenols (hydroxy-benzenes). By varying the chemical composition, acidic, basic, direct or mordant azo dyes may be produced. Exemplary azo dyes usable in the inventive syrups and beverages are FDA-approved food dyes such as FD&C Yellow #5 (trisodium salt of 3-carboxy-5-hydroxy-1-p-sulfophenyl-4-sulfophenylazopyrazole), FD&C Yellow #6 (disodium salt of 1-p-sulfophenylazo-2-naphthol-6-sulfonic acid) and FD&C Red #40 (disodium salt of 6-hydroxy-5[(2-methoxy-5-methyl-4-sulfophenyl)azo]-2-naphthalene-sulfonic acid) and the like.

In accordance with the present invention, it has been discovered that the addition of riboflavin (vitamin B2) or a color-stabilizing composition containing riboflavin, counteracts the decoloring effect of vitamin C when combined in solution with azo dyes.

Although there is no intention to be bound by any theory, a redox mechanism may explain the decoloring of solutions containing vitamin C and an azo dye. Riboflavin may, therefore, enhance color stability by protecting the azo dye from being chemically reduced by vitamin C.

Azo compounds are prone to chemical reduction at the nitrogen-nitrogen double bond by reducing agents, such as stannous chloride with concentrated hydrochloric acid and sodium hydrosulfide dihydrate. Vitamin C is a strong reducing agent due to the enediol group. Therefore, a possible mechanism explaining the bleaching effect of vitamin C on azo dyes is that the hydrogen ions of the vitamin C molecule chemically reduce the nitrogen-nitrogen double bond of the azo dye, rendering it colorless.

According to this possible mechanism, when riboflavin is added to the medium, the riboflavin accepts the hydrogen ions from the vitamin C molecule, and then transfers the hydrogen ions to oxygen, forming water, dehydro-L-ascorbic acid and reduced riboflavin. The reduced riboflavin then combines with residual oxygen to form water and regenerated riboflavin. Therefore, as long as there is about a stoichiometric or excess amount of riboflavin present in relation to the amount of vitamin C, the combination of riboflavin with vitamin C should minimize decolorization of the azo dye.

Again, the present invention as defined by the appended claims is not intended to be limited in scope by the above-described possible theory of operation of the chemical constituents.

Reference will now be made in detail to the present preferred embodiments which are exemplary of the invention.

In a preferred embodiment, the color stabilizer consists essentially of riboflavin. In an alternative embodiment, the color-stabilizing riboflavin may be premixed with at least one member selected from vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate and biotin. Preferably, the color-stabilizing premix contains riboflavin, vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate and biotin.

In general, a color-stabilizing amount, i.e., an amount sufficient to substantially lessen or prevent the fading or loss of color imparted by the azo food dye to the syrup or beverage containing vitamin C, of riboflavin is used. As explained above, a preferred amount of riboflavin is the stoichiometric amount of riboflavin relative to the amount of vitamin C. However, an excess of riboflavin may be used in accordance with the present invention, as long as there is no adverse effect on taste and like properties of the syrup or beverage formulation.

Preferred azo dyes which may be used in accordance with the present invention are the FDA-approved azo food dyes, such as FD&C Yellow #5, FD&C Yellow #6 and FD&C Red #40 and the like. Other azo food dyes which are unstable in the presence of vitamin C, suitable for the intended use, may also be selected by those skilled in the art. Additionally, a mixture of azo food dyes or an azo food dye in combination with other conventional food dyes and food colorants may be used in the present invention. The amount of azo food dye used is generally selected based on the intensity of the color desired for the particular syrup or beverage, and can be readily determined by one skilled in the art.

The amount of vitamin C is selected to meet the desired RDA percentage. Preferably, an amount of vitamin C which yields at least 100% of the RDA for vitamin C in 8 fluid ounces of the final beverage product is used.

Although preservatives may be used if desired, it is preferred that the syrup and beverage compositions are free of conventional preservatives.

According to the present invention, the syrup and beverage formulations contain water, azo food dye, vitamin C and riboflavin. Other ingredients in the syrups and beverages of the present invention can vary to suit the particular type of end product desired. The following listing of exemplary syrup and beverage ingredients is illustrative of the present invention.

Preferred syrups in accordance with the invention contain: 0.1% to 0.17% by wt. of vitamin C; 30 ppm to 350 ppm (parts per million) of an azo dye; 4 ppm to 6 ppm of riboflavin; and 92% to 97% by wt. water.

In addition, the syrups may contain the following: 5-10 ppm vitamin B6, 15-30 ppb (parts per billion) vitamin B12, 45-65 ppm niacinamide, 1-3 ppm folic acid, 20-40 ppm calcium pantothenate and 0.5-1.5 ppm biotin. Preferably, these ingredients are mixed with the riboflavin to form a color-stabilizing premix which is added to the syrup prior to dilution to the final beverage product.

Other optional syrup ingredients include: 0.1-0.25% w/w of a glassy sodium polyphosphate (average chain length, n, of 13-21 in the formula $(HPO_3)_n \cdot Na_2O$), such as sodium hexametaphosphate; 0.3-1.5% based on the volume of the syrup of one or more acidic agents approved for food use, such as phosphoric acid, citric acid and malic acid; a natural or artificial sweetening agent,

such as high-fructose corn syrup and/or sucrose (40–50% solids w/w), or aspartame (0.2–0.3% w/w); 0.5–1.0% w/w of a natural or artificial flavoring agent; 0.03–0.3% w/w of a mineral salt such as calcium chloride or sodium chloride; and 0.1–0.2% w/w of an electrolyte such as monopotassium phosphate.

Preferably, the above-listed ingredients are added to the syrup formulation prior to its dilution with water to form the final beverage product. However, the ingredients may be added to the beverage after the concentrated syrup has been diluted with water to the final concentration. Alternatively, the ingredients may be added together in a single batch to produce the final beverage composition without formulating a syrup concentrate. Conventional mixing and blending techniques may be used to blend, mix and/or dilute the syrups and beverages of the present invention.

In embodiments of the present invention employing a dry premixture of ingredients for admixture with other ingredients and dilution with water to form a syrup or beverage, the premix ingredients may be ground or pulverized and/or mixed together using any suitable equipment known in the art.

Preferred beverage compositions according to the invention contain the preferred concentrated syrups diluted with water at a volume ratio of from about 1:3.5 to 1:4.5. More preferably, the beverages are prepared by adding about 1 part syrup to 4 parts water on a volume basis.

Exemplary fortified sport-type beverages in accordance with the invention may be prepared from the following 5000-ml syrup formulations:

TABLE I

Sport Drink Formulations

Ingredient	(grams)		
	Syrup A	Syrup B	Syrup C
Orange flavor	53.43	—	—
Fruit punch flavor	—	33.64	—
Lemon-lime flavor	—	—	43.74
Cloud*	28.98	28.98	28.98
Phosphoric acid	14.80	14.80	14.80
Malic acid	2.50	2.50	2.50
Citric acid	1.66	1.66	1.66
Sodium chloride	11.65	11.65	11.65
Calcium chloride	1.56	1.56	1.56
Monopotassium phosphate	7.99	7.99	7.99
High-fructose corn syrup (HFCS), 77° Brix	2636.0	2944.0	2636.0
FD&C Yellow #5	—	—	0.17
FD&C Yellow #6	0.625	—	—
FD&C Red #40	—	1.65	—
Treated Water	Q.S.	Q.S.	Q.S.
	to 5000 ml	to 5000 ml	to 5000 ml

*suitable cloud agent added to provide turbidity

Syrup A in Table I is a base formulation for orange syrup. A base formulation for fruit punch syrup is Syrup B. Syrup C is a base composition for lemon-lime syrup.

To 5000 ml of one of the above base syrup formulations, a sufficient amount of vitamin C is added to meet the desired RDA percentage upon storage. Preferably, 6.76 g ascorbic acid are added to a 5000-ml batch of syrup base prior to formulating into the final beverage to yield a vitamin C content of 270 ppm in the beverage.

Additionally, 24.80 mg riboflavin is added to the 5000-ml batch of the syrup fortified with vitamin C to form a color-stabilized syrup. In an alternative embodiment, 10.42 g of a premix containing 24.80 mg riboflavin, 41.5 mg vitamin B6, 112.5 µg vitamin B12, 291.5 mg niacinamide, 8.25 mg folic acid, 156.25 mg calcium pantothenate and 3.75 mg biotin is added to the 5000-ml

batch of the syrup fortified with vitamin C to form a color-stabilized syrup.

If desired, 5.00 g of a glassy sodium polyphosphate compound (spp) can be added to 5000 ml of a base syrup formulation.

A glassy sodium polyphosphate compound (spp) with an average chain length (n in the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$) of from 13 to 21; e.g. sodium hexametaphosphate, is preferably added to increase the microstability of the acidic beverage. In the absence of vitamin C, spp causes no decolorization of beverage and syrup formulations containing azo food dyes. However, in the presence of ascorbic acid, spp accelerates the fading or decoloring of the beverage or syrup containing an azo dye. The addition of the riboflavin color stabilizer to azo-dyed syrups and beverages containing spp and vitamin C negates the adverse decoloring effects of the spp/vitamin C combination.

Ethylenediaminetetraacetic acid (EDTA) may be added to the azo-dyed syrup and beverage formulations, e.g., at about 25 ppm, to chelate or sequester copper ions and thus prevent the formation of copper-ascorbate complexes which can cause color problems. However, EDTA is preferably absent from still beverage formulations because of current FDA regulations.

A preferred low-pH (e.g., pH=2.5, titratable acidity=15) still beverage may be prepared by diluting one volume of syrup with four volumes of treated (i.e., purified) water. Such a beverage is colorfast, even when spp is added. The following Examples illustrate beverages in accordance with the present invention.

Example 1A

Example 1A of the invention was prepared by adding vitamin C at a level yielding 270 ppm in the final beverage composition and 24.80 mg riboflavin (vitamin B2) to 5000 ml of Syrup A, and then diluting 1 part by volume of the syrup with 4 parts by volume of treated water.

Example 1B

Inventive Example 1B was prepared in the same manner as Example 1A, except Syrup B was used instead of Syrup A.

Example 1C

Similarly, Example 1C of the invention was prepared in the same manner as Example 1A, except Syrup C was used in place of Syrup A.

Example 2A

Example 2A was prepared in a manner similar to that for Example 1A, except instead of riboflavin alone, a premix was used which contained 24.80 mg riboflavin, 41.5 mg vitamin B6, 112.5 µg vitamin B12, 291.5 mg niacinamide, 8.25 mg folic acid, 156.25 mg calcium pantothenate and 3.75 mg biotin.

Example 2B

Inventive Example 2B was prepared in the same manner as Example 2A, except Syrup B was used instead of Syrup A.

Example 2C

Similarly, Example 2C was prepared in the same manner as Example 2A, except Syrup C was used in place of Syrup A.

Example 3A

Inventive Example 3A was prepared as in Example 1A, except HEXAPHOS® (a sodium hexametaphosphate product manufactured by FMC) was also added to the syrup prior to dilution to yield 300 ppm of spp in the beverage.

Example 3B

Example 3B of the invention was prepared in the same manner as Example 3A, except Syrup B was used instead of Syrup A.

Example 3C

Example 3C was prepared in the same manner as Example 3A, except Syrup C was used in place of Syrup A.

Example 4A

Inventive Example 4A was prepared as in Example 2A using the same multi-vitamin premix containing riboflavin, except HEXAPHOS® was added to the syrup prior to dilution to yield 300 ppm of spp in the beverage.

Example 4B

Example 4B of the invention was prepared in the same manner as Example 4A, except Syrup B was used instead of Syrup A.

Example 4C

Example 4C was prepared in the same manner as Example 4A, except Syrup C was used in place of Syrup A.

For comparison with the inventive examples, comparative examples were prepared as described below.

Examples IA-IC

Examples IA, IB and IC were prepared without vitamin C to serve as color controls. To prepare control Example IA, 5000 ml of Syrup A were diluted with purified water at a ratio of 1 part by volume syrup to 4 parts by volume water. Example IB was analogously prepared, except 1 part by volume of Syrup B was diluted with 4 parts by volume of water. Similarly, control Example IC was prepared by diluting 1 part by volume of the base Syrup C with 4 parts by volume of water.

Examples IIA-IIC

Examples IIA, IIB and IIC were prepared with vitamin C for comparative purposes. Specifically, Examples IIA, IIB and IIC were prepared in a manner similar to that used for Examples IA, IB and IC, respectively, except vitamin C was added to the syrups, yielding beverage compositions containing 270 ppm of vitamin C.

Example IIIA-IIIC

Examples IIIA-IIIC are beverage formulations containing a vitamin C/spp combination. Examples IIIA, IIB and IIC were prepared as in Examples IIA, IIB and IIC, respectively, except HEXAPHOS® was additionally added to the syrups to yield 300 ppm of spp in the beverage compositions.

Example IVA

For comparison with the color stabilities of the examples in accordance with the present invention, Example IVA was prepared in a manner analogous to Examples 1A, except cysteine was used in place of riboflavin. The amount of cysteine in each of these beverage compositions was approximately 2.7 to 5.4 ppm.

The above-noted inventive and comparative examples were stored at 90° F. After storage periods of one month and three months, the examples were visually compared with the corresponding control examples to determine the extent of color fading.

The results of the color stability tests are summarized in Table II below. In the table, "a" means no fading of color observed, "b" means very slight fading of color observed, "c" means slight fading of color observed, "d" means moderate fading of color observed and "e" means extreme fading of color observed.

TABLE II

Example	Color Stability Tests	
	Fading after 1 mo.	Fading after 3 mos.
1A	a	a
1B	a	a
1C	a	a
2A	a	a
2B	a	a
2C	a	a
3A	a	a
3B	a	a
3C	a	a
4A	a	a
4B	a	a
4C	a	a
IA	a	a
IB	a	a
IC	a	a
IIA	c	c
IIB	a	a
IIC	d	d
IIIA	d	d
IIIB	b	b
IIIC	e	e
IVA	c	c

The above-tabulated results show that the present invention achieves highly color-stable beverage formulations. Moreover, as evident from a comparison of Examples 1A and 2A with Example IVA, the inventive color stabilizers are more effective than cysteine. When an azo dye highly incompatible with vitamin C is utilized, such as FD&C Yellow #6, the use of riboflavin in accordance with the invention advantageously achieves color stability, whereas the use of cysteine results in color fading.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For example, still or carbonated beverages may be made in accordance with the invention. In addition to sport-type drinks or beverages, other types of beverages may be color-stabilized by means of the present invention. Further, the color-stabilized compositions of the invention may be used to produce foodstuffs fortified with vitamin C and colored with an azo dye other than beverages or drinks, such as Popsicle-type confections, gelatins and the like.

Thus, other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples

be considered as exemplary only, with the true scope and spirit of the invention being indicated by the following claims.

What is claimed is:

1. A composition for formulating a colored syrup or beverage, the composition comprising vitamin C, an azo food dye and a color-stabilizing amount of riboflavin.

2. A composition as recited in claim 1, further comprising an ingredient selected from the group consisting of vitamin B6 and vitamin B12.

3. A composition as recited in claim 1, further comprising and ingredient selected from the group consisting of a sweetener, a flavoring agent and phosphoric acid.

4. A composition as recited in claim 1, further comprising a glassy sodium polyphosphate compound of the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$, wherein n is an integer of from 13 to 21.

5. A composition as recited in claim 1, further comprising an ingredient selected from the group consisting of vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate and biotin.

6. A composition as recited in claim 1, wherein the azo food dye is selected from the group consisting of FD&C Yellow #5, FD&C Yellow #6 and FD&C Red #40.

7. A composition as recited in claim 1, further comprising water in an amount of from 92 to 97 percent by weight, wherein the vitamin C is present in an amount of from 0.1 to 0.17 percent by weight, the azo food dye is present in an amount of from 30 to 350 ppm, and the color-stabilizing amount of riboflavin is from 4 to 6 ppm.

8. A composition as recited in claim 7, further comprising 5 to 10 ppm of vitamin B6, 15 to 30 ppb of vitamin B12, 45 to 65 ppm of niacinamide, 1 to 3 ppm of folic acid, 20 to 40 ppm of calcium pantothenate, and 0.5 to 1.5 ppm of biotin.

9. A composition for preparing a color-stable food-stuff, the composition comprising water, vitamin C, an

azo food dye and a color stabilizer, consisting essentially of riboflavin.

10. A composition as recited in claim 9, further comprising a member selected from the group consisting of vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate and biotin.

11. A composition as recited in claim 9, further comprising a glassy sodium polyphosphate compound of the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$, wherein n is an integer of from 13 to 21.

12. A composition as recited in claim 9, further comprising a sweetener.

13. A composition as recited in claim 9, further comprising a flavoring agent.

14. A composition as recited in claim 9, wherein the azo food dye is selected from the group consisting of FD&C Yellow #5, FD&C Yellow #6 and FD&C Red #40.

15. A composition as recited in claim 9, wherein the composition is acidic.

16. A method for formulating a color-stable beverage, comprising forming a syrup composition comprising water, vitamin C, an azo food dye and a color-stabilizing amount of riboflavin, and diluting the syrup composition with water.

17. A method as recited in claim 16, wherein the syrup composition further comprises a glassy sodium polyphosphate compound of the formula $(\text{HPO}_3)_n \cdot \text{Na}_2\text{O}$, wherein n is an integer of from 13 to 21.

18. A method as recited in claim 16, wherein the syrup composition further comprises an ingredient selected from the group consisting of vitamin B6, vitamin B12, niacinamide, folic acid, calcium pantothenate and biotin.

19. A method as recited in claim 18, wherein the azo food dye is selected from the group consisting of FD&C Yellow #5, FD&C Yellow #6 and FD&C Red #40.

20. A method as recited in claim 16, wherein the syrup composition further comprises an ingredient selected from the group consisting of a sweetener, a flavoring agent and phosphoric acid.

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1000-1700ppm

United States Patent [19]

Cherry et al.

[11] Patent Number: 4,937,085

[45] Date of Patent: Jun. 26, 1990

[54] DISCOLORATION PREVENTING FOOD PRESERVATIVE AND METHOD

[75] Inventors: Joe H. Cherry, Lafayette; Sheo S. Singh, West Lafayette, both of Ind.

[73] Assignee: Agra-Research, Inc., West Lafayette, Ind.

[21] Appl. No.: 240,414

[22] Filed: Sep. 1, 1988

Related U.S. Application Data

[63] Continuation of Ser. No. 896,970, Aug. 15, 1986, abandoned.

[51] Int. Cl.³ A23B 7/10; A23B 7/154

[52] U.S. Cl. 426/269; 426/310; 426/321; 426/637; 426/654

[58] Field of Search 426/269, 268, 262, 321, 426/637, 654, 259, 310, 615; 252/400.20, 400.21, 400.23, 402

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Primary Examiner—Kenneth M. Schor

Attorney, Agent, or Firm—Woodard, Emhardt, Naughton, Moriarty & McNett

[57] ABSTRACT

A food preservation composition comprising a combination of safe chemicals is effective in low concentrations and imparts no off-color taste to the foods with which it is used, yet effectively prevents the discoloration of vegetables such as potatoes. Citric acid and cysteine, combined in the ratio of about 1 part cysteine to about 25 to 30 parts citric-acid, may effectively prevent the blackening of potatoes when applied in solutions of about 0.5 to 0.7 percent by weight in water. A water solution of cysteine and citric acid in which the citric acid does not exceed 1 percent by weight, and the cysteine does not exceed 0.05 percent by weight of the solution, effectively prevents such blackening. Citric acid/cysteine compositions are rendered even more effective in the presence of very low concentrations of ascorbic acid; for example, about 0.1 percent to about 0.3 percent by weight in the water solution. The further addition of essentially trace amounts of ethylenediamine tetraacetic acid; for example, about 0.01 percent to about 0.05 percent by weight in the solution, will permit the reduction of the weight percentage of cysteine in the solution to about 0.01 percent, and will further improve the efficacy of the composition.

3 Claims, No Drawings

DISCOLORATION PREVENTING FOOD PRESERVATIVE AND METHOD

This application is a division of application Ser. No. 5 896,970, filed Aug. 15, 1986.

BACKGROUND OF THE INVENTION

This invention relates to food preservatives to prevent the discoloration of physiologically injured fruits and vegetables, and is more particularly related to a food preservative which is effective to prevent the discoloration of cut potatoes prior to serving.

When a plant material such as fruit or vegetables is cut or physiologically injured, a brown or black discoloration appears at the site of the cut or injury within a few minutes. The discoloration of fruits and vegetables as a result of cutting and other preparation for human consumption is a problem of great economic importance in the food industry. The discoloration of such vegetable matter is unsightly and unappetizing, and is associated by the public with distastefully old food. This problem has become more acute with the popularity of fresh salad bars, commonly found at fast food outlets and restaurants in all price ranges. In order to satisfy the demand for fresh fruits and vegetables at salad bars, it is frequently necessary to cut the fruits and vegetables to edible size many hours before they may be consumed. The discoloration of such pre-prepared fruits and vegetables has required that they be treated to prevent their discoloration so that the restaurant customer will perceive an appetizing selection at the salad bar. The discoloration problem has been the subject of much study because of its great economic importance in the food industry. In fruits and vegetables, tyrosine or one of its oxidation products are the substrates most often implicated in the blackening of the injury site. The browning reaction of injured fruit and vegetables is more often attributed to o-hydroxyphenols, such as chlorogenic acid. Phenol oxidase or polyphenol oxidase enzymes have been reported to cause the discoloration in peaches, grapes, pears, avocados, apples and potatoes.

In 1979, it was reported that the total annual potato market was as much as 2.4 billion pounds. Because of their importance as a foodstuff, particular attention has been directed to the problem of discoloration of potatoes when they are cut. Both chlorogenic acid and tyrosine are present in potatoes, and tyrosine is thought to be responsible for the enzymatic blackening of potatoes.

The enzymatic blackening of potatoes and the effect of inhibitors of enzymatic oxidation were reported in "Comparisons of Inhibitors of Tyrosine Oxidation in the Enzymatic Blackening of Potatoes", Muneta, P., 1981, *Am. Pot. J.* 58, 85. Muneta indicates that the blackening of potatoes results from the enzymatic oxidation of tyrosine by polyphenol oxidase, a copper-containing enzyme, and that in the presence of oxygen, the enzyme oxidizes tyrosine to 3,4-dihydroxyphenylalanine (dopa), which is then rapidly oxidized by the enzyme to dopaquinone; and further that the dopaquinone cyclizes to 5,6-dihydroxyindole derivatives which are oxidized to a reddish-brown orange "dopachrome" pigment which is seen in the early stages of enzymatic blackening. After the dopachrome formation, a series of non-enzymatic polymerizations, oxidations and reactions with protein form brown to purple, and finally the black melanin pigment. Enzymatic browning in fruit

usually involves oxidation of o-hydroxyphenols such as chlorogenic acid instead of tyrosine.

Muneta reports that the chemical control of enzymatic blackening or browning involves the inhibition of the polyphenol oxidase activity by adjusting the pH, adding bisulfite or sulfhydryl compounds; the chelation of the copper from the polyphenol oxidase; the use of reducing compounds which reduce the wholequinones to the o-hydroxyphenol state; or chemicals which react with o-quinone to give colorless addition products.

Muneta tested and reported the effects of chemical inhibitors on the enzymatic oxidation of tyrosine using polyphenol oxidase obtained from potatoes. Muneta removed the polyphenol oxidase enzyme from potatoes by acetone precipitation, dialyzed and buffered the solution and measured the oxygen uptake to determine the rate at which the polyphenol oxidase enzyme oxidized a tyrosine substrate. As a result of his testing, Muneta reported that bisulfite was a very effective inhibitor of tyrosine oxidation. Muneta also indicated that cysteine, dithiothreitol and two sulfhydryl compounds temporarily inhibited the blackening. Muneta found that partial inhibition required twenty times the concentration of cysteine as dithiothreitol on a molar basis.

Muneta reported, however, that potatoes pose special problems because of the natural occurrence of o-hydroxyphenol such as chlorogenic acid, along with the tyrosine. The chlorogenic acid, without sufficient bisulfite and sulfhydryl compounds present, is oxidized to quinone which reacts with the inhibitor to reduce the effective inhibitor concentration, and permits the tyrosine oxidation to proceed. Thus, in order to inhibit the melanin blackening formation in the presence of chlorogenic acid and tyrosine, higher inhibitor concentrations are required.

Muneta also tested the effect of ascorbic acid on tyrosine oxidation, and reported that oxygen uptake was more rapid in the presence of ascorbic acid than when only tyrosine was oxidized. Muneta noted that the ascorbic acid inhibited blackening only temporarily by reducing the dopaquinone back to dopa.

Muneta summarized that from a food processor's standpoint, bisulfite is preferred to other chemical inhibitors, that cost and flavor problems are deterrents to the use of sulfhydryl groups such as dithiothreitol and cysteine, and that inhibitors such as ascorbic acid are not desirable because blackening will occur when the ascorbic acid is oxidized.

Although bisulfites have proven to be the most popular and widely used preservatives for fresh fruits and vegetables, the United States Food and Drug Administration has recently banned their use on fruits and vegetables including the use in restaurant salad bars effective August 8, 1986.

Other studies have been made of the problem of discoloration of fruits and vegetables. Among the studies, there is one reported by Cheryll Reitmeier and R. W. Buescher in *Arkansas Farm Research*, Vol. 24, 1975. The study by Reitmeier and Buescher indicated that carbon dioxide atmospheres of 10 to 20 percent could reduce the black and brown discoloration of snap beans at 75 degrees Fahrenheit and effectively prevent it for 48 hours at 60 degrees Fahrenheit, and suggested shipping snap beans with dry ice in commercial systems to both reduce the temperature and increase the carbon dioxide levels.

Reitmeier and Buescher also studied the effect of chemical materials in delaying the rate and intensity of

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the browning discoloration. Snap beans, which were washed and cut into sections, were sprayed or washed with solutions for 1 to 30 seconds. Browning discoloration was then evaluated on the residue from cut end tissues after the tissues had been homogenized and centrifuged. Reitmeier and Buescher tested a number of materials on the prepared bean residue. Citric acid in a 5 percent concentration was reported as providing a 67 percent inhibition after 24 hours, but a 13 percent inhibition after 48 hours. Cysteine in a 0.02 percent concentration was reported as demonstrating 100 percent inhibition after 24 hours, but 50 percent inhibition after 48 hours. Treatment with enriched carbon dioxide atmospheres and low temperatures was preferred because of the clearances needed for chemical treatments.

Commercially available food preservatives include compositions combining citric acid, calcium chloride, erythorbic acid, tricalcium phosphate, monocalcium phosphate, and materials for preventing the conversion of starch to sugar in sweet corn such as those disclosed in U.S. Pat. Nos. 3,837,837 and 3,876,412.

SUMMARY OF THE INVENTION

We have discovered a food preservation composition comprising a combination of safe chemicals which is effective in such low concentrations that the chemicals impart no off-color taste to the foods with which they are used, yet effectively prevent the discoloration of vegetables such as potatoes. It has been discovered that while both citric acid and cysteine themselves are ineffective to prevent the blackening of potatoes unless used in such high concentration levels as to lend their offensive tastes to the potatoes, they may be combined in the ratio of about 1 part cysteine to about 25 to 30 parts citric acid and may effectively prevent the blackening of potatoes when applied in solutions of about 0.5 to 0.7 percent in water. The invention permits a water solution of cysteine and citric acid in which the citric acid does not exceed 1 percent by weight, and the cysteine does not exceed 0.05 percent by weight of the solution to effectively prevent such blackening. We have further discovered that the citric acid/cysteine composition is rendered even more effective in the presence of very low concentrations of ascorbic acid; for example, about 0.1 percent to about 0.3 percent by weight in the water solution; and further, that the addition of essentially trace amounts of ethylenediamine tetraacetic acid; for example, about 0.01 percent to about 0.05 percent by weight in the solution, will permit the reduction of the weight percentage of cysteine in the solution to about 0.01 percent and will further improve the efficacy of the composition.

An effective food preservative composition adapted for water solution and application to potatoes can comprise citric acid in weight percentage of about 60 to about 80 percent, cysteine in weight percentage of about 2 to about 4 percent, and ascorbic acid in weight percentage of about 10 to about 40 percent. Such a composition may be dissolved in water so that it provides about 0.5 to 0.7 percent by weight of the solution. Potatoes may be treated with the water solution of this composition and prevented from blackening significantly for up to six days, thus providing an effective method of preserving the appearance of cut potatoes.

A combination of citric acid, cysteine, ascorbic acid and ethylenediamine tetraacetic acid effectively prevents the blackening of potatoes. Individually, none of these chemicals either prevents the blackening of pota-

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toes over a period of a week, or effectively prevents the blackening of potatoes for more than one day at best. The synergistic combination of citric acid and cysteine lies at the heart of this effective composition, but the addition of the ascorbic acid and ethylenediamine tetraacetic acid has a further synergistic effect in the long-term prevention of blackening. The combination permits each of these chemicals to be used at very low concentrations, well below levels where chemicals effect the taste of the food or have any other deleterious effect.

DETAILED DESCRIPTION OF THE INVENTION

The effect of citric acid was tested by making solutions of 0.25 percent by weight, 0.5 percent by weight, 1 percent by weight and 2 percent by weight of citric acid in deionized water. The solutions of 0.25 percent and 0.5 percent of citric acid in deionized water demonstrated no effect in preventing the blackening of the potatoes. The 1 percent solution of citric acid in deionized water showed a slight effect, and a 2 percent solution of citric acid in deionized water was required before effective prevention of blackening was obtained. Concentrations of 2 percent citric acid, however, create taste problems in the treated potatoes, and may not be used commercially.

In testing the effect of cysteine, solutions of 0.005 percent by weight through 0.1 percent by weight of cysteine in deionized and tap water were tested. The cysteine-deionized water solution produced an observable effect on the blackening of potatoes only at and above concentrations of 0.05 percent by weight of cysteine. Even at these concentrations of cysteine, its effect diminishes with time and the potatoes resume their blackening. Cysteine concentrations of 0.05 percent by weight, however, provide an off flavor and would be costly in use. In all these studies, it is important to note that cysteine in tap water gave the same results as with deionized water.

Ascorbic acid and ethylenediamine tetraacetic acid were also tested for their effectiveness in preventing the blackening of potatoes. Ascorbic acid was tested in solutions of up to about 0.5 percent by weight in deionized water, and ethylenediamine tetraacetic acid was tested in solutions of up to about 0.1 percent by weight in deionized water. Both ascorbic acid and ethylenediamine tetraacetic acid were ineffective in such concentrations in preventing the blackening of potatoes.

Surprisingly, it was discovered that low concentrations of cysteine and citric acid, when combined, were particularly effective in preventing the blackening of potatoes. Cysteine, in concentrations of 0.0125 percent by weight in deionized water, was combined with citric acid concentrations of from 0.025 percent to 1 percent by weight. The synergistic effect of cysteine and citric acid was demonstrated with citric acid concentrations at about the 0.1 percent level. However, the cysteine/citric acid combination was most effective when the citric acid in concentrations of about 0.5 percent to about 1 percent by weight were combined with cysteine at about 0.0125 percent by weight.

We further discovered that ascorbic acid in low concentrations, when combined with the cysteine/citric acid combination, substantially increased the long-term prevention of blackening, and particularly when combined with ethylenediamine tetraacetic acid, which permitted a further reduction in the cysteine concentra-

tion. We discovered that up to about 0.3 percent by weight of ascorbic acid increased the effectiveness of the composition in combination with cysteine concentrations of 0.01 to 0.04 percent by weight and citric acid concentrations of 0.5 percent by weight. The best results were obtained when the ascorbic acid and cysteine were present in the solution in 0.3 percent and 0.01 percent by weight, respectively; or 0.1 percent and 0.02 percent by weight, respectively. Adding ethylenediamine tetraacetic acid to the solution in concentrations of only up to 0.05 percent by weight/volume, and preferably about 0.02 percent by weight/volume, permitted a reduction in the cysteine concentration to 0.01 percent.

To test the invention, potatoes were purchased from local grocery stores. The potatoes were washed and cut into small pieces, 2×1 cm. in size and 2 to 4 mm. thick. The cut potatoes were thoroughly mixed and were used for testing various compositions and their individual components as set forth below. The food preservative compositions and chemicals being tested were dissolved in deionized water.

The cut potatoes were divided into test samples and control samples. The test samples were exposed to the compositions and components being tested by immersing them in the compositions and components for about five minutes. The control samples were immersed in deionized water. It was found that if the cut potatoes were exposed to the material solutions for a time duration of about 5 minutes, further exposure time had no effect on the effectiveness of the material solutions in preventing blackening in the potatoes. After exposure to the composition and component solutions, the potatoes were collected and stored either at room temperature or at 4 degrees Centigrade. Thus, each cut potato sample was divided into two samples, one control sample with only deionized water treatment, and the other sample treated with the composition or component being tested. Visual observation of the control samples and test samples were made every day to determine the extent of discoloration of the cut potato tissue.

In a parallel experiment, an objective test of whiteness was also measured by using a Hunterlab colorimeter, Model No. D-25. A white tile was selected as a standard, having an L value of +92.9. An L value of 100 represents extreme whiteness, and an L value of 0 represents extreme blackness. The natural potatoes without any discoloration measured an L value of 73 immediately upon being cut.

Table 1 presents the measurement of the degree of whiteness of the potato samples immediately after cutting and at one day, two days and six days following treatment with the solution of deionized water, and each of the compositions and components included in Table 1. Table 1 reflects the testing of the percentage concentration indicated in the table of each of the chemicals and chemical compositions in deionized water. All percentages used in Table 1 and in this application indicate percentage weight to volume concentrations. Table 1 reflects an accurate comparison of the effect of each of the chemical materials upon the blackening of the potato slices. The numerical information presented in Table 1 corresponds in degree to the visual observations of the potatoes following their treatment. Untreated potatoes turned brown after a few hours, and by 24 hours they are black. The L value for black potatoes after one day is about 40 and stays at that level thereafter. (See Test No. 1) The difference in L values between

naturally white and blackened potatoes has a value of about 30, and a difference in L values of 3 units is significant and detectable visually.

TABLE 1

Test	Treatment Material, Concentration in Deionized Water ¹	Days			
		0	1	2	6
1.	No treatment	73	41	38	38
2.	Deionized water	73	52	50	48
3.	Citric acid, 0.5%	73	62	58	54
4.	Ascorbic acid, 0.1%	73	53	52	48
5.	EDTA, 0.02%	73	54	50	48
6.	Cysteine, 0.02%	73	53	53	52
7.	Cysteine, 0.02% - Ascorbic acid, 0.1%	73	59	55	50
8.	Cysteine, 0.02% - EDTA, 0.02%	73	57	55	51
9.	Ascorbic acid, 0.1% - EDTA, 0.02%	73	55	52	47
10.	Cysteine, 0.02% - Citric acid, 0.5%	73	71	67	59
11.	Formulation 1 ²	73	72	67	64
12.	Ascorbic acid, 0.1% - Citric acid, 0.5%	73	68	63	55
13.	EDTA, 0.02% - Citric acid, 0.5%	73	67	62	54

¹percent = weight to volume

²Citric acid, 0.5%; Ascorbic acid, 0.1%; Cysteine, 0.02%; and EDTA, 0.02%

As noted from Table 1, potato samples treated with only deionized water blackened from an L reading of 73 to an L reading of 52 after one day, and further blackened to L readings of 50 and 48 after two and six days, respectively. (See Test No. 2).

Treatment of the potatoes with a solution of 0.5 percent by weight/volume of citric acid in deionized water reduced the blackening and increased the L reading to 62 after one day, compared to control, but the blackening of the potatoes then continued, and the L value fell to 58 after two days and to 54 after six days. (See Test No. 3). Treatment of the potatoes with individual solutions of ascorbic acid, cysteine and ethylenediamine tetraacetic acid, respectively, in 0.1, 0.02, and 0.02 percents, respectively, by weight/volume in deionized water appeared to be no more effective in preventing the blackening of the potatoes than deionized water alone. (See Test Nos. 4-6). None of these three materials in solutions of deionized water prevented blackening or a reduction in the L value from 72 to about 53 after 24 hours.

Solutions including cysteine and ascorbic acid in 0.02 and 0.1 percent, respectively, by weight/volume in deionized water, cysteine and ethylenediamine tetraacetic acid in 0.02 percent each, respectively, by weight/volume in deionized water, and ascorbic acid and ethylenediamine tetraacetic acid in 0.1 and 0.02 percent, respectively, by weight/volume in deionized water, were each only slightly more effective than deionized water alone. (See Test Nos. 7-9). None of these three compositions in deionized water prevented the blackening of potatoes after two to six days.

A composition including 0.02 percent by weight/volume of cysteine and 0.5 percent by weight/volume of citric acid in deionized water demonstrated an unexpected effectiveness in preventing blackening. Following treatment with this cysteine/citric acid combination, blackening of the potatoes was reduced, and an L value of 72 to an L value of 71 was obtained after one day, which compared favorably with the L value of 52 for deionized water and the L value of 62 after one day for the citric acid solution alone. After two days, the

samples treated with cysteine and citric acid solution demonstrated an L value of 67, compared with an L value of 50 for deionized water and an L value of 58 with citric acid alone; and after six days, the cysteine/citric acid treated samples demonstrated an L value of 59 compared with L values of 48 for deionized water and 54 for deionized water and citric acid. (See Test No. 10).

Addition of ascorbic acid and ethylenediamine tetraacetic acid to the cysteine/citric acid solution decreased even further the blackening after two days, and increased the L value of the cysteine/citric acid treatment from 59 to 64. (See Test No. 11). Erythorbic acid may be substituted for ascorbic acid in the same weight-/volume concentrations with no significant reduction in effectiveness.

We have found the following to be examples of particularly effective compositions which are adapted for solution in water and application to potatoes.

Example 1:

A composition includes 78.4 percent by weight of citric acid, 3 percent by weight of cysteine, 15.6 percent by weight of ascorbic acid, and 3 percent by weight of ethylenediamine tetraacetic acid. These four chemicals are mixed until uniformly distributed. When the composition is dissolved in deionized water in an amount from 0.5 to 0.6 percent by weight of the total formulation, it provides a food preservative which will prevent the blackening of potatoes so that the original L value of 73 is reduced to an L value of 72 after one day, an L value of 67 after two days, and an L value of 64 after six days, which is the most effective anti-blackening composition tested.

Example 2:

A composition was prepared by uniformly mixing together 70.5 percent by weight of citric acid, 2.4 percent by weight of cysteine, 11.8 percent by weight of ascorbic acid, 3.5 percent by weight of ethylenediamine tetraacetic acid, and 11.8 percent by weight of sodium acid pyrophosphate or tetrasodium acid pyrophosphate. A uniform mixture of these five chemicals is dissolved in deionized water to produce a 0.6 to 0.7 percent by weight solution. Cut potatoes immersed in the solution of Example 2 demonstrate the same L levels as obtained with Example 1, substantially preventing the blackening of potatoes for up to six days.

Potatoes treated with this invention maintain a natural white color, having L values of 64-72 for up to six

days after cutting. It is interesting to note that the ascorbic acid/citric acid composition, while decreasing blackening in the first day, did not provide a significant anti-blackening effect over a six-day period. (See Test No. 12). Likewise, while the ethylenediamine tetraacetic acid/citric acid composition decreased blackening after one day, it did not provide a significant anti-blackening effect over a six-day period. (See Test No. 13). Only the cysteine/citric acid combination of this invention, and particularly the cysteine/citric acid/ascorbic acid/ethylenediamine tetraacetic acid combination of this invention provided no blackening for 24 hours and no significant blackening over periods of up to six days. The invention is also effective in preventing blackening of frozen potatoes, and may prevent significant blackening of frozen potatoes.

The combination of this invention thus provides a particularly effective commercial food preservative which is usable in very small concentrations to safely, cheaply and effectively prevent the discoloration and blackening of vegetables and fruits such as potatoes for long periods of time. It also provides the food industry with a significant alternative to bisulfites and other food preservatives. Each of the ingredients of the invention is from the Food and Drug Administration's list of materials generally recognized as safe.

We claim:

1. A method of preventing the discoloration of potatoes comprising cutting the potatoes for consumption and exposing the cut potatoes to a solution consisting essentially of citric acid in a weight percentage concentration of from about 0.5 percent to about 1.00 percent of the solution and cysteine in a weight percentage of about 0.01 percent to about 0.04 percent of the solution, and the remainder water, said exposing including contacting said potatoes with said solution for a time sufficient such that the contacting of the potatoes with said solution prevents discoloration of said potatoes when said potatoes are exposed to an atmosphere which would cause discoloration in the absence of said contacting.

2. The method of claim 1 wherein said solution includes ascorbic acid in a weight concentration of from about 0.1 percent to about 0.3 percent of the solution.

3. The method of claim 2 wherein said solution includes ethylenediamine tetraacetic acid in a weight concentration from about 0.005 percent to about 0.02 percent of the solution.

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**SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISION DE NUEVAS CREACIONES**

202085

Bogotá, D.C., 19 de Octubre de 2007

Abogado

JERÓNIMO CASTILLO BONILLA

Solicitante

Stokely-Van Camp, INC

ASUNTO	Radicación	01007443
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	13763
	Folios	16

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

- 1.1. Capitulo descriptivo: Folios 4 a 12 como se radicó inicialmente
- 1.2. Capitulo reivindicatorio: Folios 13 a 18 como se radicó inicialmente.
- 1.3. Prioridad: Folios 32 a 48, US 09/495768, 1 de Febrero de 2000

2. Objeto de la invención

Título de la solicitud: Bebidas que contienen ácido L ascórbico con estabilidad de color y claridad. Folio 1.

Objeto de la invención: El objeto de la presente solicitud de patente de invención consiste una solución acuosa, para bebidas, que incluye ácido L-ascórbico y EDTA.

Reivindicaciones 1–28

Una solución acuosa para bebidas.

Reivindicaciones 29 – 54

Una solución acuosa para bebidas.

El problema técnico planteado en esta solicitud radica en la decoloración ó turbiedad de una bebida clara e incolora, fortificada con vitamina C, pues será poco atractiva para los consumidores. Para solucionar este problema técnico la solicitud plantea soluciones acuosas para bebidas que contienen ácido ascórbico y EDTA con un color estable, a pesar de la oxidación del ácido L-ascórbico.

El objeto de la solicitud definido anteriormente se clasificó en la IPC A23L 2/00.

3. De la solicitud de Patente (artículo 28 y 30 D. 486)

Durante todo el capítulo reivindicatorio se utilizaron los términos "aproximadamente" y "sustancialmente" que son imprecisos y no definen la materia, ni alcance de la invención. Sírvase utilizar términos precisos que precisen la invención.

La reivindicación 1 presenta una solución acuosa para bebidas que comprende: agua, ácido L-ascórbico y EDTA. Sin embargo la frase "no contiene un número suficiente de componentes que podrían disimular el cambio de color producido por la oxidación del ácido L-ascórbico" es confusa y no representa ninguna característica de la solución acuosa ó de alguno de sus componentes, solo corresponde a una posible ventaja del producto (la ventaja técnica no caracteriza al producto). En consecuencia esta frase es irrelevante y no define ni caracteriza el objeto de la invención. Se le recuerda al solicitante que una composición ó producto es caracterizado por sus componentes específicos y las proporciones de estos, y no los que no están presentes.

De otro lado, la frase "y el la cual un color de la bebida es sustancialmente estable durante un tiempo deseado predeterminado" también es ambigua y confusa y no define la materia de la invención. Además se presentan las expresiones "sustancialmente estables" y "un tiempo deseado predeterminado" que son subjetivas y no definen ningún parámetro. Lo mismo sucede en las reivindicaciones 9, 18 y 20, que además son repetitivas pues presentan la misma materia de la reivindicación 1 sin ninguna característica adicional.

La reivindicación 29, que es una reivindicación independiente, presenta una solución acuosa para bebidas que comprende: agua, ácido L-ascórbico y EDTA. Y que nuevamente enuncia que "no contiene un número suficiente de componentes..." que como se menciono anteriormente no caracteriza, ni define el objeto de la invención, pero además presenta "y en la cual una turbiedad es sustancialmente estable durante un tiempo deseado predeterminado." Sin embargo "un color" y "una turbiedad" puede representar el mismo concepto y no hay argumentos que muestren porque esta reivindicaciones son diferentes. Por lo tanto la reivindicación 1 y 29 son iguales. Y presenta los mismos problemas de claridad y concisión.

Hay que tener cuenta además, que la reivindicación 1 reclama una solución acuosa para bebidas, es decir, que se utiliza en bebidas. Y las reivindicaciones dependientes reclaman la bebida. Sírvase definir cual es el objeto de la invención, si la solución acuosa ó la bebida.

Las reivindicaciones 2 a 5, se presenta el período de tiempo durante el cual la bebida descrita en la reivindicación 1 es estable, no obstante este tiempo solo representa el objetivo a alcanzar y por lo tanto no caracteriza la composición acuosa. Lo mismo sucede con las reivindicaciones 25 a 28, 30 a 33.

Las reivindicaciones 6 a 8, 22 a 24 y 34 a 36 relacionan en intervalos muy amplios la concentración de ácido L-ascórbico en la solución.

Por otra parte, un inconveniente adicional que presenta el capítulo reivindicatorio radica en lo repetitivo que es. Por ejemplo:

Las reivindicaciones 25 y 26, repiten la materia de las reivindicaciones 2 y 5.

Las reivindicaciones 27 y 28 (donde además se presenta una falsa dependencia con la reivindicación 31 que es posterior y que demuestra el poco orden del capítulo reivindicatorio) son iguales a las reivindicaciones 2 y 5, 25 y 26, 30 y 33.

Las reivindicaciones 6 a 8 contienen la misma materia de las reivindicaciones 34 a 36, al igual que las reivindicaciones 8, 22, 23, 24 y 36.

Asimismo las reivindicaciones 10 a 15, 19, 21 y 38 a 43 son repetitivas puesto que muestran la inclusión de por lo menos una fuente de vitamina B al objeto de la invención.
Las reivindicaciones 16 y 50 repiten la materia de las reivindicaciones 17 y 51.
Las reivindicaciones 52 a 54 son iguales.

La reivindicación 44, que depende de la reivindicación 1 caracteriza al producto por su proceso, incurriendo en la falta de “falsa dependencia de las reivindicaciones” puesto que un producto no es caracterizado por su proceso de obtención. Lo mismo sucede con las reivindicaciones 45 a 49. Pero además, nótese que las reivindicaciones 44, 46 y 48 están repetidas, al igual que las reivindicaciones 45, 47 y 49. Sírvase definir exactamente cual es el objeto de la invención.

En resumen, el capítulo reivindicatorio es desordenado ambiguo, impreciso y poco claro y no define el alcance ni la materia de la invención.

En conclusión, estas reivindicaciones no cumplen con el requisito de claridad y concisión de acuerdo al art. 30 de la Decisión 486.

4. Determinación del Estado de la Técnica

Considerando que la fecha de prioridad de la solicitud internacional PCT es 2000-06-26, se encontraron los documentos relacionados a continuación, que pueden afectar la patentabilidad del objeto de la presente solicitud:

Nº	DOCUMENTO	TÍTULO	FECHA DE PUBLICACIÓN
D1	US5336510	Color-stable syrup and beverage compositions fortified with vitamin C, and methods of making such compositions	1994-08-11
D2	US4937085	Discoloration preventing food preservative and method	1990-06-26

Los documentos citados se anexan al expediente.

5. Evaluación de los requisitos de patentabilidad (artículo 14 D486)

5.1. Novedad (artículo 16 D486)

La presente Solicitud de Patente Colombiana No. 01007443 en su reivindicación 1 presenta una solución acuosa para bebidas, la cual comprende: agua, ácido L-ascórbico, EDTA.

La anterioridad D1 (columna 1 renglón 63 a columna 2 renglón 6) composiciones de color estable para jarabes y bebidas que contienen agua e incluye: un colorante, agua, vitamina C y otros aditivos entre los cuales se presentan EDTA, edulcorantes como aspártame y vitaminas como las vitaminas del complejo B. (columna 2 renglones 34 a 41, columna 4 renglones 54 a 60, columna 5 renglón 2). Este documento divulga además que el ácido etilendiaminotetraacético (EDTA) estabiliza el color de dichas bebidas.

En consecuencia, la reivindicación 1 no es nueva y las dependientes de ella tampoco lo son, pues no aportan otras características que las pudieran hacer nuevas, porque al comparar los elementos representativos de la invención con los elementos presentados en la anterioridad D1 resultan ser los iguales. En otras palabras, ya se habían divulgado composiciones que incluyen agua, vitamina C y EDTA, y por lo tanto la composición reivindicada carece de novedad.

Asimismo, la reivindicación 29 no es nueva y las reivindicaciones dependientes de ella tampoco lo son. Puesto que esta reivindicación presenta los mismos elementos representativos de la reivindicación 1.

5.2. Nivel Inventivo (artículo 16 D486)

El documento D2 presenta una composición acuosa para conservar el color de los alimentos que comprende el ácido cítrico/cisteína y la adición de ácido ascórbico y EDTA en bajas concentraciones (1000-3000 ppm) que mejora la efectividad de la composición. La anterioridad plantea además que aunque la combinación ácido cítrico/cisteína preserva el color de los alimentos, la adición de la combinación ácido ascórbico/EDTA le agrega otro efecto sinérgico en la preservación de color en alimentos. (Columna 3 renglones 43 a 52 y columna 4 renglones 5 a 7).

La presente Solicitud de Patente No. 01007443, presenta una solución acuosa para bebidas, la cual comprende: agua, ácido L-ascórbico, EDTA.

La diferencia de D2 con la solicitud en estudio radica en la presencia de la mezcla de ácido cítrico/cisteína, que como lo presenta la anterioridad, es el corazón de la composición y le atribuyen principalmente la conservación del color en alimentos. Sin embargo la anterioridad también divulga que la mezcla ácido ascórbico/EDTA también posee propiedades para preservar el color de los alimentos y más aún que existe un sinergismo entre estos compuestos.

En consecuencia, una persona versada en la materia, en vista del estado de la técnica y su conocimiento, hubiera sugerido sin mucho esfuerzo de su parte, formular una composición acuosa con EDTA y vitamina C para ser aplicada en una bebida, puesto que el documento D2 ya había divulgado que dicha mezcla en concentraciones bajas de ácido ascórbico evitaba en pardeamiento de los alimentos. Y que la adición EDTA tiene un efecto sinérgico que preserva el color.

En consecuencia las composiciones reivindicadas son obvias para el experto en la materia y en consecuencia carecen de nivel inventivo.

Conclusión:

La solicitud presenta problemas de claridad (*artículos 28 y 30*). Los requisitos de patentabilidad de la presente solicitud se encuentran afectados así:

N°	TÍTULO	REIVINDICACIONES AFECTADAS	REQUISITO QUE AFECTA
D1	US5336510	1-54	Novedad
D2	US4937085	1-54	Nivel Inventivo

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. **En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.**

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

3


ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones
El anterior requerimiento fue notificado por fijación en lista, de fecha
01 NOV. 2007

CONCEPTO TECNICO No. 1982	EXAMINADOR TECNICO Código No.202085
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722