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BEVERAGE ANTIOXIDANT SYSTEM

This invention relates to an antioxidant system for beverages; especially beverages in ready-to-drink form. The invention also relates to beverages and beverage precursors which contain the antioxidant system and to processes for removing oxygen using the antioxidant system.

5 Many beverages suffer adverse effects from exposure to oxygen. This is particularly the case with ready-to-drink beverages; especially ready-to-drink coffee beverages. Ready-to-drink coffee beverages are produced by extracting soluble coffee solids from roasted and ground coffee beans using hot water. The extract obtained may then be diluted to a desired concentration, usually to contain
10 about 1% by weight of soluble coffee solids. Various additives are added to the diluted extract which is then filled into containers. The containers are then sealed and subjected to retorting. Certain intermediate steps may also be carried out. For example, the extract may be concentrated and dried to powder prior to formation of the dilute extract. This is usually done when the coffee is filled into
15 the containers at a site different than the site at which the extraction is carried out.

During this process, the coffee may be exposed to oxygen several times. For example, oxygen may be present in the hot water which is used to extract the soluble coffee solids from the roasted and ground coffee beans. Also, the coffee may be exposed to oxygen during extraction or subsequent processing such as
20 concentration and drying. Further, oxygen may get into the container during filling. No matter where in the process the coffee is exposed to oxygen, it is now recognised that the oxygen adversely effects the flavour and aroma of the coffee beverage. In particular, the beverage loses its fresh, clean flavour and aroma; the flavour and aroma which characterises freshly brewed coffee. Often, bitter, acid
25 flavours develop.

Various measures have been taken in the past to reduce the influence of oxygen. Usually these methods have centred on preventing ingress of oxygen. For example, Japanese patent application 6-141776 discloses extracting coffee grounds using deoxygenated water in an inert gas atmosphere. Further, all
30 subsequent steps, including filling of the dilute extract into containers, is done under inert gas atmosphere. The patent application describes the resulting product to have a good, fresh flavour. The inert gas recommended is nitrogen. The primary problem with this technique is its cost. Carrying out an entire extraction and filling process in a nitrogen gas atmosphere is extremely
35 expensive. Also, deoxygenating water is not a perfect process and not all oxygen is removed.



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Another approach which has been attempted is to use antioxidants during the process. For example, US patent 5,384,143 describes a process in which the coffee extract is rapidly cooled to below 20°C and then an antioxidant selected from erythorbic acid, ascorbic acid, and their water soluble salts, is added to the cooled extract. The extract is then filled into cans under oxygen free conditions. This technique is less expensive than carrying out the entire process under inert gas atmosphere but there are problems. In particular, coffee is a potent antioxidant which is able to scavenge oxygen faster than most antioxidants commonly used in foods. Therefore, although the antioxidants described in this patent remove some of the oxygen, they are not potent enough to prevent the coffee from scavenging a large portion of the oxygen present. Consequently, the coffee undergoes some oxidative damage.

A further approach has been the use of enzyme systems. For example, the use of systems based upon glucose oxidase and alcohol oxidase have been suggested. However these systems have not proved to be adequate since degradation due to oxygen still occurs. Also, these enzyme systems often produce hydrogen peroxide which is undesirable.

Therefore it is an object of this invention to provide an antioxidant system which is relatively inexpensive and which is sufficiently potent to remove oxygen from beverage components which are themselves antioxidants.

Accordingly, in one aspect, this invention provides an antioxidant system for ready-to-drink beverages, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

It has been surprisingly found that the combination glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger is a sufficiently potent antioxidant such that small amounts are able to adequately compete with beverage components which are potent antioxidants, such as coffee. Since small amounts are required, the system therefore offers the advantage of being an inexpensive and effective antioxidant. Also, the system is food grade; especially at the small amounts required.

In another aspect, this invention provides a ready-to-drink beverage which includes an antioxidant system, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

The ready-to-drink beverage is preferably a coffee beverage; especially a black coffee beverage. The ready-to-drink beverage may be retorted.

In a yet further aspect, this invention provides a beverage concentrate which includes an antioxidant system, the system comprising glucose oxidase, a catalase, a glucose oxidase substrate and an inorganic oxygen scavenger.

The inorganic oxygen scavenger is preferably a sulphite; for example
5 sodium sulphite.

In another aspect, this invention provides a process for reducing oxygen in a beverage, the process comprising:

adding an antioxidant system comprising glucose oxidase, a catalase, a
glucose oxidase substrate and an inorganic oxygen scavenger to the beverage;
10 filling the beverage into containers; and
sealing the containers.

In another aspect, this invention provides a process for reducing oxygen in a beverage containing extracted solids, the process comprising:

adding an antioxidant system comprising glucose oxidase, a catalase, a
15 glucose oxidase substrate and an inorganic oxygen scavenger to an extraction
liquid;

extracting solids from an extraction substrate using the extraction liquid to
provide a beverage;

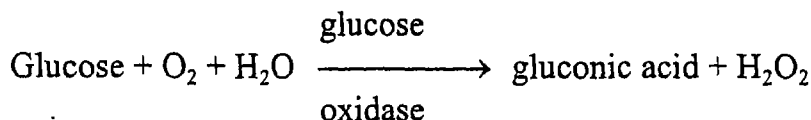
filling the beverage into containers; and
20 sealing the containers.

Preferably, the beverage is filled into containers under oxygen reduced or oxygen free conditions. Further, further amounts of the antioxidant system may be added to the beverage prior to sealing of the containers.

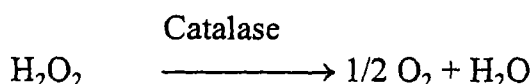
Embodiments of the invention are now described, by way of example only.
25 This invention provides an antioxidant system which is useful for removing
oxygen from beverages and beverage concentrates. The antioxidant system may
be used, for example, during the processing of the beverage, in a pre-cursor to the
beverage such as a beverage concentrate, or in ready-to-drink beverages. The
antioxidant system is particularly suitable for use in connection with ready-to-
30 drink, coffee beverages and will be described primarily in this context. It is to be
appreciated however that this is done for simplicity of description and the
antioxidant system is not limited to this application.

The antioxidant system includes a glucose oxidase (EC 1.1.3.4). The
glucose oxidase catalyses the oxidation of glucose to gluconic acid according to
35 the following reaction scheme:

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5 The antioxidant system also includes a catalase (EC 1.11.1.6). Then, the catalase degrades the peroxide according to the following reaction scheme:



10 The glucose oxidase and the catalase are preferably provided in the form of an enzyme mixture. A suitable enzyme mixture is the Novozym® 358 enzyme preparation commercialised by Novo Nordisk AS of Novo Allé, 2880 Bagsvaerd, Denmark. This enzyme preparation is prepared from *Aspergillus niger* and is
15 generally recognised as safe.

 The antioxidant system also includes a glucose oxidase substrate. This takes the form of glucose. The glucose oxidase substrate may be an inherent part of the beverage itself, may be added to the beverage, or both. In the case of coffee beverages, the glucose oxidase substrate is ordinarily added to the
20 beverage mix because coffee contains little or no glucose. However, for other beverages which inherently contain glucose, further glucose need not be added.

 The antioxidant system further includes an inorganic oxygen scavenger. Sulphites are particularly useful as inorganic oxygen scavengers. Suitable sulphites include sulphur dioxide, sodium sulphite, sodium metabisulphite, anhydrous sodium bisulphite, potassium metabisulphite, anhydrous potassium
25 bisulphite, and mixtures of these agents. Sodium sulphite is particularly preferred. Apart from further removing oxygen, the inorganic oxygen scavenger removes hydrogen peroxide generated by the glucose oxidase.

30 The amount of the antioxidant system used will depend upon the substance to be treated and the level of oxygen present. Also, the amounts used of the various components in the antioxidant system will depend upon the substance to be treated and the level of oxygen present. Further, the amount of enzyme used will depend upon the activity of the enzyme. These amounts will be readily determined for each situation.

35 However, in general, the amount of glucose oxidase used is less than about 0.5% by weight of the total weight of the substance to be treated. For example, the amount of glucose oxidase used is preferably in the range of about 0.001% to

about 0.1% by weight of the total weight of the substance to be treated. An amount in the range of about 0.005% to about 0.05% by weight is especially preferred for coffee beverages. The activity of the glucose oxidase is preferably about 1500 units/ml to about 2500 units/ml; for example about 2000 units/ml. A unit is the amount of enzyme which, at a temperature of 25°C and a pH of 5.1, catalyses the formation of 1 μmol of H_2O_2 .

The amount of glucose oxidase substrate which is used is conveniently less than about 1% by weight of the total weight of the substance to be treated. For example, the amount of glucose oxidase substrate used is preferably in the range of about 0.005% to about 0.5% by weight of the total weight of the substance to be treated. An amount in the range of about 0.01% to about 0.3% by weight is especially preferred for coffee beverages; for example about 0.05% by weight. The glucose oxidase substrate may be present in the substance to be treated or may be added to the substance, or both. Usually, for coffee beverages, the glucose oxidase substrate is added. For beverages which must undergo heat treatment, the amount of glucose oxidase substrate used is preferably kept to the minimum necessary to obtain the required glucose oxidase activity. In this way, the formation of undesirable Maillard reactions may be avoided.

The amount of the inorganic oxygen scavenger which is used is conveniently less than about 0.1% by weight of the total weight of the substance to be treated. For example, the amount of inorganic oxygen scavenger used is preferably in the range of about 0.001% to about 0.05% by weight of the total weight of the substance to be treated. An amount in the range of about 0.002% to about 0.03% by weight is especially preferred for coffee beverages; for example about 0.005% by weight. Further, relevant regulatory requirements concerning the maximum residual levels of inorganic oxygen scavengers in foodstuffs should be respected.

If a catalase is used, the amount used is not critical. Usually the catalase will be provided in a mixture with the glucose oxidase and hence the catalase levels will be determined by the amount of glucose oxidase used.

The antioxidant system may be used at various points during the processing of a beverage. For example, for coffee and tea beverages, the antioxidant system may be added to the water which is to be used to extract soluble solids from the coffee or tea. In this way, the water which is used for extraction may be efficiently deoxygenated. However, because the glucose oxidase denatures at

temperatures above about 60°C, the treatment should be carried out prior to heating the extraction water.

The antioxidant system may also be added to the extract obtained after extraction. At the time of addition of the enzyme of the antioxidant system, the temperature of the extract should be below about 60°C. After the extract has been deoxygenated, the extract may be thermally treated; for example during concentration or drying or both. The inorganic oxygen scavenger continues to operate at temperatures above 60°C. Of course, for best effect, all further processing of the extract should be carried out under oxygen reduced or oxygen free conditions. The various techniques described in the art may be used. In this way, a beverage, beverage concentrate or beverage powder which contains the antioxidant system and low levels of oxygen may be obtained.

The antioxidant system may also be added to the beverage prior to filling of the beverage into containers. At the time of addition of the enzyme of the antioxidant system, the temperature of the beverage should be below about 60°C. After the beverage has been deoxygenated, the beverage may be retorted in the usual manner. For best effect, the subsequent filling of the beverage into containers may be carried out under oxygen reduced or oxygen free conditions. The various techniques described in the art may be used. The beverage obtained preferably contains less than about 1 ppm of dissolved oxygen; more preferably less than about 0.5 ppm dissolved oxygen.

The antioxidant system may be used in combination with any type of beverage such as tea beverages, coffee beverages, chocolate beverages, malted beverages, and the like. However the system is particularly suited for use in coffee beverages since the system is able to compete with the potent antioxidant effects of coffee. Black coffee beverages, which are intended to have a clean, fresh flavour and aroma, are especially suitable. These beverages ordinarily contain about 0.5% to about 1.5% by weight of soluble coffee solids. They may also contain a sweetener.

Specific examples are now described to further illustrate the invention.

Example 1

Three beverages are prepared and are standardised to contain about 8 ppm of dissolved oxygen. The first beverage (beverage 1) is freshly brewed coffee which contains 1% by weight of soluble coffee solids. The second beverage

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(beverage 2) is prepared from a commercially available instant coffee and contains 1% by weight of soluble coffee solids. The third beverage (beverage 3) is freshly brewed coffee which contains 1% by weight of soluble coffee solids, 0.1% by weight of Novozym® 358 enzyme preparation, 0.1% by weight of glucose, and 0.008% by weight of sodium sulphite. The beverages are held in containers open to the ingress of air and the concentration of dissolved oxygen is determined at regular intervals.

The results are as follows:

Time (minutes)	Dissolved O ₂ (ppm) Beverage 1	Dissolved O ₂ (ppm) Beverage 2	Dissolved O ₂ (ppm) Beverage 3
0	8	8	8
5	4.7	7.5	2
10	4.3	7.0	0.4
15	4.1	6.6	0.5
20	3.9	6.4	0.5
25	3.6	6.1	0.5
30	3.4	6.0	0.5
35	3.3	6.0	0.5
40	3.2	5.9	0.5
45	3.1	5.9	0.5
50	3.0	5.9	0.5
55	3.0	5.9	0.5
60	3.0	5.9	0.5

The results indicate the antioxidant system in beverage 3 removes dissolved oxygen much faster than freshly brewed and instant coffee. Therefore the antioxidant system is able to adequately compete with the coffee for oxygen; hence protecting the coffee from oxygen damage.

Example 2

Cans containing coffee solids are prepared. All cans contain about 1% by weight of coffee solids, about 5% by weight of sugar, about 0.065% by weight of sodium bicarbonate, and about 0.01% by weight of lysine. All cans are filled and

sealed under the same conditions. During filling, the contents of each can are exposed to air.

Certain of the cans (the "Test cans") also contain an antioxidant system of 0.1% by weight of glucose, 0.01% by weight of Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The other cans form a control (the "Control cans").

After 1 hour, 1 can from each group is opened and the dissolved oxygen is determined. The remaining cans of each group are then retorted and allowed to cool. After 12 days, a can of each group is opened and a sensory panel is used to analyse the aroma and flavour of the sample.

Group	Time (hours)	Dissolved O ₂ (ppm)	Aroma & Flavour
Test	1	0.9	Fresh, clean flavours and aroma with roasty notes. Less acidity.
Control	1	6.8	Acid notes present. Prune-like, bland flavour.

The beverage of the test group has much less dissolved oxygen and much improved flavour and aroma.

Unopened cans of each group are stored for 10 weeks at room temperature and are then opened. The pH is determined. The beverage of the Control cans has a pH of about 5.5 while the beverage of the Test cans has a pH of about 5.7. A sensory panel is used to analyse the aroma and flavour of the beverage of the Test cans and it is found to have fresh, clean flavours and aroma.

Example 3

Roast and ground coffee is placed in an extraction system. The conditions are not oxygen free. The coffee is then extracted with one of three different types of deionised water at a temperature of about 25°C to 40°C. The first type, Type A, is untreated deionised water. The second type, Type 1, is deionised water which is treated with an antioxidant system of 0.05% by weight of glucose, 0.01% by weight of Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The third type, Type 2, is deionised water which is treated with an antioxidant system of 0.05% by weight of glucose, 0.1% by weight of

Novozym® 358 enzyme preparation, and 0.005% by weight of sodium sulphite. The dissolved oxygen content of each type of deionised water and each extract is determined.

5 Each extract obtained is diluted with a sugar solution to provide a coffee beverage containing about 1% by weight of coffee solids. Each beverage is then filled into cans and the cans sealed. A can of each beverage is opened and the dissolved oxygen content of the beverage is determined. The remaining cans are retorted.

Water Type	O ₂ Conc (ppm) in Extraction Water	O ₂ Conc (ppm) in Extract	O ₂ Conc (ppm) in Beverage
A	7.79	2.54	0.81
1	2.96	0.86	0.08
2	0.04	0.15	0.07

10

The results indicate that reducing the oxygen content of the extraction liquid greatly reduces the oxygen content in the resultant beverage, despite the beverage being produced under conditions which are not oxygen free.

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Unopened cans of each group are stored for 10 weeks at room temperature and are then opened. A sensory panel is used to analyse the aroma and flavour of the beverages in the cans. The beverages produced using water Types 1 and 2 have a fresh, clean flavour and aroma. The beverages produced using water Type A have an unacceptable flavour and aroma.

Claims

1. A ready-to-drink coffee beverage which includes an antioxidant system, the system comprising an enzyme composition containing a glucose oxidase, a glucose oxidase substrate and a catalase, and an inorganic oxygen scavenger.
2. A beverage according to claim 1 which contains about 0.001% to about 0.1% by weight of glucose oxidase.
3. A beverage according to claim 1 or claim 2 which contains about 0.005% to about 0.5% by weight of glucose oxidase substrate.
4. A beverage according to any of claims 1 to 3 in which the inorganic oxygen scavenger is a sulphite.
5. A beverage according to claim 4 which contains about 0.001% to about 0.05% by weight of sulphite.
6. A beverage according to claim 4 or claim 5 in which the sulphite is sodium sulphite.
7. A beverage according to any of claims 1 to 6 which is a black coffee beverage.
8. A ready-to-drink coffee beverage concentrate which includes an antioxidant system, the system comprising an enzyme composition containing a glucose oxidase, a glucose oxidase substrate, and a catalase, and an inorganic oxygen scavenger.
9. A process for reducing oxygen in a ready-to-drink coffee beverage, the process comprising: adding an antioxidant system comprising glucose oxidase, a glucose oxidase substrate, a catalase and an inorganic oxygen scavenger to the beverage;
filling the beverage into containers; and
sealing the containers.
10. A process for reducing oxygen in a ready-to-drink coffee beverage containing extracted solids, the process comprising:

adding an antioxidant system comprising glucose oxidase, a glucose oxidase substrate, a catalase and an inorganic oxygen scavenger to an extraction liquid;

extracting solids from an extraction substrate using the extraction liquid to provide a beverage;

5 filling the beverage into containers; and
 sealing the containers.