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Module 17 Anti-browning/Bleaching agents and Anti-caking or Free-flow agents for the food industry

A] ANTI BROWNING AGENTS FOR FOOD INDUSTRY

1. Introduction

Many plant foods are subject to degradative reactions during handling, processing, or storage, collectively described as browning reactions, that result in the formation of brown, black, gray, or red colored pigments. Such reactions are generally grouped into two categories: enzymatic browning and nonenzymatic browning. Examples of the former include browning of cut apples or potatoes, while examples of the latter include browning of shelf-stable, pasteurized juices and dehydrated vegetables.

Enzymatic browning results from the oxidation of polyphenols to quinones, catalyzed by the enzyme polyphenol oxidase (also known as PPO, tyrosinase, *o*-diphenol oxidase, and catechol oxidase), and subsequent further reaction and polymerization of the quinones. This discoloration is generally a problem with raw fruit and vegetable products rather than blanched or thermally processed products since enzymes would be inactivated in the latter. Enzymatic browning of raw commodities may result from physiological injury; senescence; pre- or postharvest bruising; disruption of the fruit or vegetable flesh by peeling, coring, slicing, or juicing; tissue disruption from freeze–thaw cycling; and tissue disruption by bacterial growth. The occurrence of enzymatic browning can limit the shelf-life of fresh-cut fruits and salad vegetables, fresh mushrooms, prepeeled potatoes, and other fresh products of commercial importance. Enzymatic browning also may be a problem with some dehydrated and frozen fruits and vegetables. In addition to causing discoloration, enzymatic browning reactions in fruit and vegetable products also can result in loss of ascorbic acid (vitamin C) through reaction with quinones. Enzymatic browning is usually controlled by blanching, where applicable acidification; and application of sulfites (which are now subject to regulatory constraints with a number of commodities) or sulfite substitutes such as ascorbic acid or cysteine. These substitutes are generally less effective than sulfites.

Nonenzymatic browning reactions may result from the classic Maillard reaction between carbonyl and free amino groups, i.e., reducing sugars and amino acids, which produce melanoidin pigments in a wide variety of foods including dairy, cereal, fruit, and vegetable products. Such discolorations generally occur in products that are subjected to heat and/or prolonged storage. Nonenzymatic browning can be minimized by avoidance of excessive exposure to heat, control of moisture content in dehydrated products, and application of sulfites.

2. Regulatory Issues and Other Constraints

Sulfites have been associated with occurrence of allergic reactions, in some cases severe, with some individuals who are asthmatic. Consequently, the U.S. Food and Drug Administration has banned the use of sulfites in certain raw fruit and vegetable products. Other products such as wine and packaged dehydrated fruits and vegetables must be labeled to indicate the presence of sulfites. While a number of sulfite substitutes exist, there is a strong reluctance on the part of some food processors to use them since a label declaration would normally be required. Many consumers seek ‘‘natural’’ ingredients and might be expected to reject products in which ‘‘chemicals’’ are used as additives. Various plant extracts and other natural products have been found to possess antibrowning activity, but there is no assurance that such products are free of toxicants, and some form of regulatory approval would probably be required before they could be used.

3. Suphites as antibrowning agents

Sulfites are unique in their ability to perform a number of useful functions as food additives— control of both enzymatic and nonenzymatic browning, suppression of microbial growth, and bleaching. In the case of enzymatic browning, sulfites act as PPO inhibitors and also react with intermediates to prevent pigment formation. Sulfites inhibit nonenzymatic browning by reacting with carbonyl intermediates, thereby blocking pigment formation.

Treatment conditions vary widely. Sulfite may be applied as sulfur dioxide; sulphurous acid; or sodium (or potassium) sulfite, bisulfite, or metabisulfite. Treatment levels vary widely, but treatment residues usually do not exceed several hundred ppm, although some products may contain 1000 ppm. Among the products that are treated with sulfites are dehydrated fruits and vegetables, prepeeled potatoes, fresh grapes, and wine. Maximum levels of 300, 500, and 2000 ppm have been proposed for fruit juices, dehydrated potatoes, and dried fruit, respectively by FDA (1988).

Safety & regulatory Issues

Sulfite residues in foods have been responsible for some severe allergic reactions in susceptible individuals, usually asthmatics. Fatal anaphylactic reactions have been reported. The FDA has restricted use of sulfites in certain categories of foods where there is no means of alerting sensitive consumers to their presence (FDA, 1986). Fruit and vegetable products that are consumed raw and sold unlabeled in salad bars, restaurants, or from bulk containers so that the consumer cannot be alerted to their presence fall in this category.

4. Alternatives to Sulphites

Fear that use of sulfites as browning inhibitors for fruit and vegetable products might be restricted prompted the food industry to seek alternatives. During the 1980s, this was an area of great research activity, and a number of new browning inhibitors were developed.

The search for alternatives to sulfite has been complicated by the fact that sulfites are extremely potent as browning inhibitors, inexpensive to use, and multifunctional, exhibiting antimicrobial activity as well as anti-browning activity. Ideally, sulfite substitutes should exhibit similar properties. Moreover, sulfite substitutes should be safe and free of regulatory constraints. Unfortunately, most alternatives to sulfites do not meet these criteria, so that the choice of agent must represent a compromise. Furthermore, since individual anti-browning agents may be deficient in some respects, most alternatives to sulfite represent combinations of agents that act synergistically or at the very least have an additive effect. Even so, there is no ‘‘magic bullet’’ to control browning in commercial use or under development. Perhaps the eventual development of genetically engineered commodities lacking PPO or with reduced levels of this enzyme will eliminate the need for browning inhibitors.

4.1 Conventional Alternatives to Sulfite

4.1.1 Ascorbic Acid–Based Formulations

Ascorbic acid (vitamin C) has been used as an antibrowning agent for more than five decades and is still the most widely used alternative to sulfiting agents. This may be an outgrowth of the common kitchen practice of using lemon juice to delay browning during food preparation.

The pioneering investigations reporting ascorbic acid as antibrowning agents included experiments wherein investigators added ascorbic acid or its isomer erythorbic (*d*-isoascorbic) acid to syrups or dips to control browning of fresh sliced and frozen apples and peaches. In some cases, an organic acid such as citric acid and a firming agent such as calcium chloride were added along with the ascorbic acid. To improve the uptake of these agents and at the same time remove oxygen from the product void spaces, vacuum infiltration was sometimes used in conjunction with browning inhibitor treatment.

The chemical basis for the efficacy of ascorbic acid treatments is the ability of ascorbic acid to reduce quinones, produced by PPO-catalyzed oxidation of polyphenols, back to dihydroxy polyphenols. As long as quinones do not accumulate, further reactions leading to pigment formation are avoided. When the added ascorbic acid is depleted quinines will accumulate, and browning will result. Thus, the primary effect of ascorbic acid is as an inhibitor of the enzymatic browning reaction, not as an inhibitor of PPO per se. However, ascorbic acid does have some direct inhibitory effect against PPO. Dehydroascorbic acid, the oxidation product of ascorbic acid that is formed during quinone reduction, can itself undergo nonenzymatic browning, leading to product discoloration. This treatment thus can be used to permanently eliminate the capacity of juices to undergo enzymatic browning. However the efficacy of ascorbic acid as antibrowning agent was reported to be far less than sulphites.

4.1.2 Cysteine

The ability of cysteine to inhibit enzymatic browning is well established and has been used commercially for a number of years (Cherry and Singh, 1990). This alternative to sulfites is a key ingredient of browning inhibitor formulations for apples and prepeeled potatoes supplied by EPL Technologies, Inc. Cysteine reacts with quinone intermediates, formed by PPO-catalyzed oxidation of polyphenols, to yield stable, colorless compounds, thereby blocking pigment formation. Cysteine also directly inhibits the enzyme. It was observed that cysteine-based inhibitors are particularly effective against browning of apple core tissue. However, under some conditions, cut pears and potatoes treated with cysteine show pink discolorations. At high treatment levels, a noticeable sulfury odor can result. Some studies suggests that reduced glutathione and N-acetylcysteine are nearly as effective as sulfites in controlling browning of apple, potato, and fresh fruit juices. However, only cysteine is approved for food use.

4.1.3 4-Hexylresorcinol

This PPO inhibitor is used commercially to control discoloration of unpeeled shrimp and is highly effective as a browning inhibitor for some fruits and vegetables. While 4-hexylresorcinol has a long history of human consumption, it is only approved for use on shrimp (where the application is to the peel, which is not usually eaten). Regulatory approval for other applications where it might be consumed in quantity is uncertain. 4-hexylresorcinol is known to be particularly effective against core browning in fresh-cut pears. However, some reports suggest that 4-hexylresorcinol was responsible for darkening and tissue breakdown in fresh mushrooms at concentrations greater than 50 ppm.

4.2 Other PPO inhibitors

Various PPO inhibitors have been proposed as alternatives to sulfites, but they lack regulatory approval at this time. Scientists Walker and Wilson investigated inhibition of apple PPO by a number of phenolic acids. Walker reported that cinnamic acid at concentrations greater than 0.5 mM prevented browning of Granny Smith apple juice for 7 hours.

Kojic acid [5-hydroxy-2-(hydroxymethyl)-γ-pyrone] has been considered for use as an alternative to sulfite. This compound can reduce quinones to polyphenols, thereby preventing browning by the same mechanism as ascorbic acid (Chen et al., 1991). It is not clear whether this compound acts as a true PPO inhibitor. The regulatory status of kojic acid is in doubt because of reported mutagenic activity

Some experiments indicates carrageenans and other sulfated polysaccharides as having browning inhibitor activity in apple juice and diced apples; citric acid acting synergistically with these compounds in inhibiting browning. The mechanism of browning inhibition by the sulfated polysaccharides is not known. Even maltodextrin is reported to inhibit browning of ground apple.

Natural PPO inhibitors have been found in honey, pineapple, fig latex, and a large number of botanical products. The view is probably misguided since their purity and composition may be unknown, and consumption patterns of these products as browning inhibitors may be substantially different than their use as herbs or traditional medicinal agents. In any event, FDA approval would be required if the products were to be isolated, concentrated, and applied to foods as browning inhibitors.

4.3 Complexing agents

In various studies conducted, β-cyclodextrin was found to be an effective browning inhibitor for fruit and vegetable juices. β-cyclodextrin has been shown to form inclusion complexes with chlorogenic acid and presumably other PPO substrates, thereby effectively removing them from contact with PPO in fresh juices. Although there has been commercial interest in this antibrowning agent, regulatory approval has not been forthcoming. Fruit and vegetable juices treated with insoluble polymerized forms of β-cyclodextrin is known to resist browning indefinitely.

PVPP, an insoluble product used as a fining agent for juices, can bind the polyphenol substrates of PPO and thus prevent browning. PVPP can be separated from juices by decanting or centrifugation so that there are no treatment residues.

Sodium acid pyrophosphate (SAPP) is widely used as a chelating agent in potato products. Its primary purpose is to prevent after-cooking darkening by chelating ferrous ion, thus preventing formation of dark-colored iron-chlorogenic acid complexes.

One of the complexing agent, a proprietary polyphosphate marketed as Sporix, was found that this product was highly effective in controlling browning of cut apple and apple juice when used in combination with ascorbic acid. This polyphosphate product is highly acidic and is reputed to be a powerful chelating agent.

While polyphosphates and cyclodextrins each provide browning inhibition in fresh juices, use of these complexing agents in combination leads to even more effective (synergistic) results. Combinations of β-cyclodextrin with SAPP, Sporix, sodium hexametaphosphate, or phytic acid resulted in greater browning inhibition than predicted from the effects of each component tested separately. This synergistic effect allows greater inhibition of browning and use of lower levels of additives to achieve control of browning.

B] ANTI CAKING AGENTS FOR FOOD INDUSTRY

1. Introduction

An anticaking agent is an additive placed in powdered or granulated materials, such as table salt, to prevent the formation of lumps and for easing packaging, transport, and consumption.

Processed foods often contain ingredients that are mixed as powders. Anti-caking agents are added to allow them to flow and mix evenly during the food production process. They rarely have nutritional value and only a small proportion of the additives find their way into the food.

Some anti-caking agents may be found in foods. For example, magnesium carbonate is used in table salt to improve its flow during manufacture. It is left in the salt so that it flows well when being sprinkled onto food.

Powders can form clumps because the particles become sticky when they absorb water. Lumpy powders do not flow evenly. Some powders, such as grated cheese for pizza toppings, can stick together and this again prevents them from being spread evenly. Anti-caking agents modify the contact between the powder's particles and are added to prevent these problems.

Without anti-caking agents, vending machine powders such as coffee or chocolate would not flow regularly. They could block the various tubes in the vending machine and the taste of the drinks would not be consistent enough. Powdered milk can clump together during processing, packing and storage. Sugar absorbs water and incorporating a free-flow aid before grinding prevents it sticking to the processing equipment.

Some anticaking agents are soluble in water; others are soluble in alcohols or other organic solvents. They function either by absorbing excess moisture, or by coating particles and making them water repellent. Calcium silicate ($CaSiO_3$), a commonly used anti-caking agent, added to e.g. table salt, absorbs both water and oil.

2. Examples of anti-caking agents

One of the most important anti-caking agents is silicon dioxide (E551). It is manufactured to have physical properties that are tailored to meet the food producer's specific requirements. Other manufactured anti-caking agents include: calcium silicate (E552), sodium aluminosilicate (E554) and dicalcium phosphate (E341). Natural products such as talc, kaolin, potato starch and microcrystalline cellulose (E460) are also used.

An anticaking agent in salt is denoted in the ingredients, for example, as "anti-caking agent (554)", which is sodium aluminosilicate, a man-made product. This product is present in many commercial table salts as well as dried milk, egg mixes, sugar products, and flours. In Europe, sodium ferrocyanide (535) and potassium ferrocyanide (536) are more common anticaking agents in table salt. Natural anticaking agents used in more expensive table salt include calcium carbonate and magnesium carbonate.

The following anticaking agents are listed in order by their E number.

1. E341 tricalcium phosphate
2. E460(ii) powdered cellulose
3. E470b magnesium stearate
4. E500 sodium bicarbonate
5. E535 sodium ferrocyanide
6. E536 potassium ferrocyanide
7. E538 calcium ferrocyanide
8. E542 bone phosphate
9. E550 sodium silicate
10. E551 silicon dioxide
11. E552 calcium silicate
12. E553a magnesium trisilicate
13. E553b talcum powder
14. E554 sodium aluminosilicate
15. E555 potassium aluminium silicate
16. E556 calcium aluminosilicate
17. E558 bentonite
18. E559 aluminium silicate
19. E570 stearic acid
20. E900 polydimethylsiloxane

3. List of some permitted anticaking agents and their applications

Additive	**Permitted in or Upon**	**Maximum Level of Use and Other Conditions**
Calcium Aluminum Silicate	(1) Salt	(1) 1.0%, except in the case of fine grained salt

		2.0%,
	(2) Garlic salt; Onion salt	(2) 2.0%
	(3) Unstandardized dry mixes	(3) Good Manufacturing Practice
Calcium Phosphate tribasic	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%
	(2) Garlic salt; Onion salt	(2) 2.0%
	(3) Dry curd	(3) Good Manufacturing Practice
	(4) Unstandardized dry mixes	(4) Good Manufacturing Practice
	(5) Oil-soluble annatto	(5) Good Manufacturing Practice
	(6) Icing sugar	(6) If used either singly or in combination with Calcium Silicate, Magnesium Carbonate, Magnesium Silicate, Magnesium Stearate, Silicon Dioxide or Sodium Aluminum Silicate the total must not exceed 1.5%
Calcium Silicate	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%
	(2) Garlic salt; Onion salt	(2) 2.0%
	(3) Baking Powder	(3) 5.0%
	(4) Dry cure	(4) Good Manufacturing Practice
	(5) Unstandardized dry mixes	(5) Good Manufacturing Practice
	(6) Icing sugar	(6) If used either singly or in combination with Calcium Phosphate tribasic, Magnesium Carbonate, Magnesium Silicate, Magnesium Stearate, Silicon Dioxide or Sodium Aluminum Silicate the total must not exceed 1.5%
	(7) Meat Binder or (naming the meat product) Binder	(7) 1.0%
	(8) Grated or shredded cheddar cheese; Grated or shredded (naming the variety) cheese; Unstandardized grated or shredded cheese preparations	(8) If used singly or in combination with Microcrystalline Cellulose or Cellulose, the total amount not to exceed 2.0%
	(9) Dried egg-white (dried albumen); Dried whole egg; Dried whole egg mix; Dried yolk; Dried yolk mix	(9) 2.0%
Calcium Stearate	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%,

	(2) Garlic salt; Onion salt	(2) 2.0%
	(3) Unstandardized dry mixes	(3) Good Manufacturing Practice
Cellulose	(1) Grated or shredded cheddar cheese; Grated or shredded (naming the variety) cheese; Unstandardized grated or shredded cheese preparations	(1) If used singly or in combination with Calcium silicate or Microcrystalline Cellulose, the total amount not to exceed 2.0%
	(2) Cheddar cheese curd; Varietal cheese curd	(2) If used singly or in combination with Microcrystalline Cellulose, the total amount not to exceed 1.0%
Magnesium Carbonate	(1) Salt (except when used in preparations of Meat and Meat By-products of Division 14)	(1) 1.0%, except in the case, of fine grained salt 2.0%
	(2) Garlic salt, Onion salt (except when used in preparations of Meat and Meat By-products of Division 14)	(2) 2.0%
	(3) Unstandardized Dry Mixes (Except when used in preparations of Meat and Meat by-products of Division 14)	(3) Good Manufacturing Practice
	(4) Icing sugar	(4) If used either singly or in combination with Calcium Phosphate tribasic, Calcium Silicate, Magnesium Silicate, Magnesium Stearate, Silicon Dioxide or Sodium Aluminum Silicate the total must not exceed 1.5%
Magnesium Oxide	Unstandardized dry mixes (Except when used in preparations of Meat and Meat by-products of Division 14)	Good Manufacturing Practice
Magnesium Silicate	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%
	(2) Garlic salt; Onion salt	(2) 2.0%
	(3) Unstandardized dry mixes	(3) Good Manufacturing Practice
	(4) Icing sugar	(4) If used either singly or in combination with Calcium Phosphate tribasic, Calcium Silicate, Magnesium Carbonate, Magnesium Stearate, Silicon Dioxide or Sodium Aluminum Silicate the total must not exceed 1.5%
Magnesium Stearate	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%
	(2) Garlic salt; Onion salt	(2) 2.0%

	(3) Unstandardized dry mixes	(3) Good Manufacturing Practice
	(4) Icing sugar	(4) If used either singly or in combination with Calcium Phosphate tribasic, Calcium Silicate, Magnesium Carbonate, Magnesium Silicate, Silicon Dioxide or Sodium Aluminum Silicate the total must not exceed 1.5%
Microcrystalline Cellulose	(1) Grated or shredded cheddar cheese; Grated or shredded (naming the variety) cheese; Unstandardized grated or shredded cheese preparations	(1) If used singly or in combination with Calcium Silicate or Cellulose, the total amount not to exceed 2.0%
	(2) Cheddar cheese curd; Varietal cheese curd	(2) If used singly or in combination with cellulose, the total amount not to exceed 1.0%
Propylene Glycol	Salt	0.035%
Potassium Ferrocyanide, Trihydrate	Salt	If used singly or in combination with Sodium Ferrocyanide, decahydrate, the total amount not to exceed 13 p.p.m., calculated as Anhydrous Sodium Ferrocyanide
Silicon Dioxide	(1) Garlic salt; Onion salt	(1) 1.0%
	(2) Celery Pepper; Celery Salt	(2) 0.5%
	(3) Unstandardized dry mixes	(3) Good Manufacturing Practice
	(4) Icing sugar	(4) If used either singly or in combination with Calcium Phosphate tribasic, Calcium Silicate, Magnesium Carbonate, Magnesium Silicate, Magnesium Stearate or Sodium Aluminum Silicate the total must not exceed 1.5%
	(5) Foods sold in tablet form	(5) Good Manufacturing Practice
	(6) Cayenne Pepper; Chili pepper; Chili Powder; Paprika; Red Pepper	(6) 2.0%
	(7) Salt	(7) 1.0%, except in the case of fine grained salt 2.0%
Sodium Aluminum Silicate	(1) Salt	(1) 1.0%, except in the case of fine grained salt 2.0%
	(2) Icing sugar	(2) If used either singly or in combination with Calcium Phosphate tribasic, Calcium Silicate, Magnesium Carbonate, Magnesium Silicate, Magnesium Stearate or Silicon Dioxide the total must not exceed 1.5%
	(3) Dried egg-white (dried albumen); Dried whole egg; Dried whole egg mix; Dried yolk; Dried yolk mix	(3) 2.0%

	(4) Garlic salt; Onion salt	(4) 2.0%
	(5) Unstandardized dry mixes	(5) Good Manufacturing Practice
Sodium Ferrocyanide, decahydrate	Salt	If used singly or in combination with Potassium Ferrocyanide, trihydrate, the total amount not to exceed 13 p.p.m., calculated as Anhydrous Sodium Ferrocyanide

4. Health Impact

Any Food additives when added in foods, they are always assessed for their health hazards. Most permitted anticaking agents are safe within the limits of their concentration present in various foods. However natural anticaking agents are safer as compared to synthesized additives and depending on the chemical nature they may have various health implications. Some of the anticaking agents also have other additional functionalities and along with that multiple health effects which may or may not be hazardous.
Magnesium carbonate is a mineral salt, anti-caking, pH adjusting, bleaching, modifying agent. Medically used as an antacid and laxative. Magnesium is used in the treatment of heart attack patients, and promotes the health of arteries, bones, nerves and teeth, low-sodium salt substitute, table salt.

Sodium aluminium silicate, produced from several natural minerals, is a mineral salt, anti-caking agent. It is used in salt, dried milk substitutes, egg mixes, sugar products and flours. Aluminium is known to cause placental problems in pregnancy and has been linked to Alzheimer's Parkinson's, bone loss.

Magnesium stearate has no known adverse effects in food use. It is used as stabiliser, anti-caking and release agent, emulsifier for artificial sweeteners and confectionary. But inhalation of the powder is harmful.

Sodium ferrocyanide is a crystal modifier and anti-caking agent prepared from hydrogen ferrocyanide and sodium hydroxide. No adverse effects are known for use in food. However, use is very limited, partly due to the strong yellow colour.

5. Conclusion

Recent advances in antibrowning agents and improved application methods, used in conjunction with antimicrobial treatments and modified atmosphere packaging, have yielded large improvements in control of browning in fresh-cut and other minimally processed fruit and vegetable products. However, whether such improvements can be translated into shelf-life extension will depend on the retention of other quality attributes such as flavour and texture as well as on the suppression of microbial spoilage. Anticaking agents are also considered important ingredient for shelf-life extension of many dried products especially to maintain their free-flowing characteristics but issues related to their probable health effects needs better technical insights.

Regulatory hurdles, labelling issues, lack of competitive advantage, and cost may limit the commercialization of promising treatments by use of antibrowning and anticaking agents. Thus, there is a continuing need for research to develop effective antibrowning treatments and anticaking agents that meet the requirements of technical and economic feasibility, safety, and consumer acceptance.