

ppm at the mill, 1,000 - 100,000 ppm at the bakery (0.1 - 10%). The continuous production of large amounts of flour at the mill requires additives with good flow properties as well as low dosages. This means that additives such as emulsifiers or fat powders that tend to form lumps are not suitable, and salt and sugar are not added at the mill either because of their high dosage. Flour mills generally apply single ingredients separately – only occasionally in premixes – whereas bakeries apply bread improvers composed of several additives. This chapter mentions the most common flour improvers. They may also be part of bread improvers.

18.3 Oxidation and Flour Maturation

The present necessity for oxidative treatment might be regarded as a disadvantage of the fast and gentle processing of grain into flour. Natural ageing of the flour by exposure to the atmosphere alone is no longer possible, so maturation has to be speeded up with oxidative preparations. Oxidation primarily affects sulphur containing amino acids that are constituents of the gluten. The oxidation of two adjacent hydrogen sulphide (thiol) groups results in the formation of a disulphide bridge between different sections of the long gluten molecule or between different gluten molecules. This causes a hardening of the protein.

18.3.1 Ascorbic Acid

By far the most important substance for this purpose is ascorbic acid (AA). Using a complex biochemical method starting with starch as the raw material it is produced in a very pure

form and sold as a fine or crystalline powder in various concentrations to facilitate dosing. Less often, AA of purely biological origin is used. The most common product is Acerola fruit powder, the dried juice of the Acerola cherry, with 17 - 19% pure AA. However, this more natural variant is up to 50 times more expensive than the synthetic product. Other substances on the market are AA obtained from rose hips and mixed preparations, some of them containing AA of biochemical origin.

At the mill, flour is treated with typically 0.5 - 3 g of pure AA per 100 kg. Very soft glens or flours for certain applications (mainly frozen dough) require a larger dose of 6 - 10 g. AA does not act on the protein directly; it may be seen rather as an agent protecting against the loss of protein stability by counteracting glutathione, a reducing (softening) agent, that occurs naturally in the flour. This is only possible if AA is oxidized to dehydroascorbic acid (DHAA) at the beginning of the kneading process with the aid of the flour's own enzymes (i.e. ascorbate oxidase and glutathione dehydrogenase). In this process, glutathione is oxidized to glutathione disulphide, thus eliminating the gluten-softening effect of glutathione (Grosch and Wieser, 1999; Fig. 107).

Proof of an adequate quantity and homogeneous distribution of the product in the flour can easily be obtained with Tauber's reagent in conjunction with a Pekar test (Fig. 108). A convenient and storable set with the two solutions required is available on the market. Titration with iodine, which is more accurate but less convenient, is still common practice as well. In biochemical laboratories, test kits with ascorbate oxidase and also HPLC are used to determine AA very accurately.

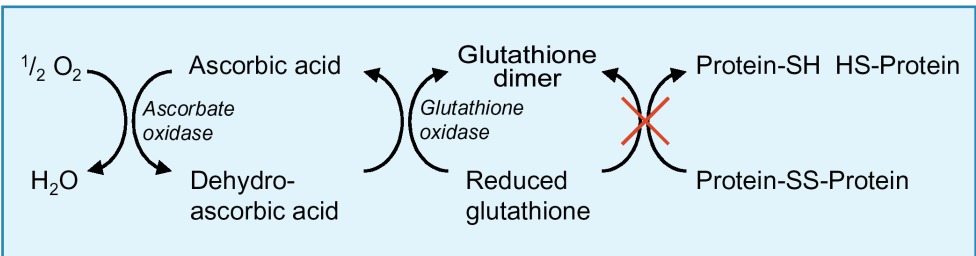


Fig. 107: Reaction of ascorbic acid in wheat dough (modified from Grosch and Wieser, 1999)



Fig. 108: Wet Pekar sample with Tauber's reagent for determination of ascorbic acid

18.3.2 Enzyme-Active Soy Flour

One enzyme from soy flour, lipoxygenase, also has an oxidative effect on the protein of the gluten. During the oxidation of the lipids by lipoxygenase, peroxides are formed that have a cross-linking effect on thiol groups. However, the gluten-strengthening effect of soy flour is comparatively slight; its bleaching effect is more important. There are several types of lipoxygenases with different action patterns. While type I lipoxygenase only acts on free unsaturated fatty acids, types II and III also oxidize unsaturated fatty acid bound to the glycerol backbone. Bean flour contains mostly types II and III, which makes it an efficient agent for oxidizing all unsaturated lipids in flour. The use of lipoxygenase is limited because the enzyme creates a "green" flavour that is not desirable in this application (see also chapter 18.8.2).

18.3.3 Glucose Oxidase

The enzyme glucose oxidase (GOD) is usually derived from the mould *Aspergillus* (in a similar manner to amylase) and sometimes *Penicillium*. Honey is also a rich source of GOD, where the enzyme enters the honey from the pharyngeal glands of the bees (Molan, 1992). However, its suitability is greatly restricted by its taste.

One effect of GOD in the dough is to oxidize glucose into gluconic acid with the aid of atmospheric oxygen (the slight souring that occurs in the process is negligible); its other effect is to transform water into hydrogen peroxide (Fig. 109). This oxidizing agent is not very specific and acts, for example, on the thiol groups of the gluten, on glutathione, or on ascorbic acid, all reactions resulting in tightening – or protection – of the gluten. The limiting factor in this process is the availability of oxygen.

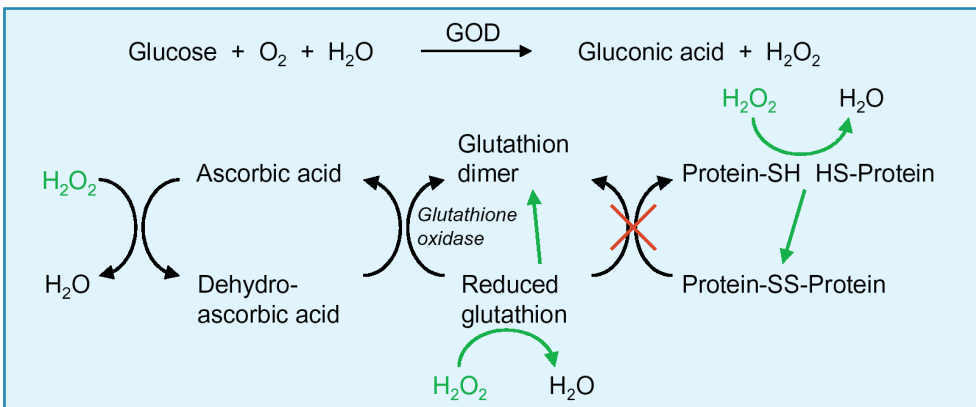


Fig. 109: Hypothetical reactions of glucose oxidase in wheat dough

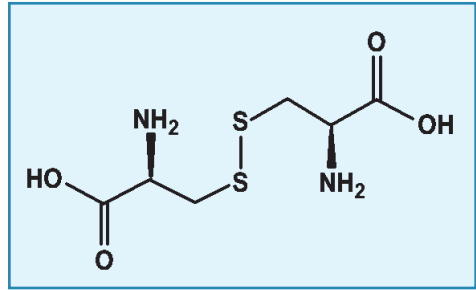
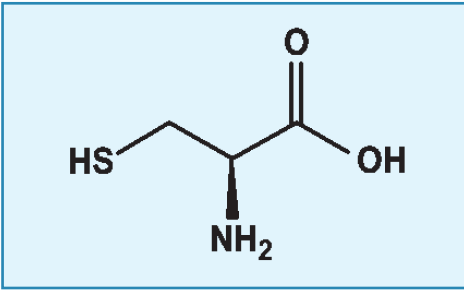


Fig. 110: Chemical structure of cysteine (left) and cystine (right)

Besides other chemical reactions that consume oxygen, yeast also takes up oxygen before starting its actual fermenting activity as it initially breathes instead of fermenting. This means that the conditions for GOD are really only good on the surface of the dough, as plenty of oxygen is always available there. The problem can be solved by technical measures during dough preparation, for example overpressure or the supply of extra oxygen (Lösche, 1996). The addition of an oxygen source, e.g. calcium peroxide, does not have sufficient effect within reasonable dosage limits. Saturation of the water with air by agitation at low temperatures improves the oxygen supply to a limited extent.

A typical GOD preparation is dosed in similar quantities to other enzymes, for example 100 - 500 ppm on flour (about 1,500 to 7,500 units of GOD per 100 kg of flour), but this depends to a very great extent on the product and process. In long fermentation and sheeted dough applications, GOD is more effective due to prolonged exposure to atmospheric oxygen.

18.3.4 Cystine

Cystine is the dimer of the amino acid cysteine in which two molecules of cysteine are linked by a disulphide bridge (Fig. 110). This sulphur bridge gives the molecule a certain oxidative effect. But at low doses it is possible that the gluten may soften, as reducing cysteine is released when cystine reacts with thiol groups of the protein. Although this has yet to be thoroughly investigated, cystine is used in spite of its high price compared to AA because it is occasionally found to have a positive effect on the properties of the dough.

18.3.5 Dehydroascorbic Acid

DHAA is the oxidized form of AA (Fig. 111). This means that if DHAA were used instead of AA it would be possible to dispense with the initial step of oxidation. Tests have shown that this is quite possible. One reason why it is so rarely used, however, is its instability, but this could be improved by coating. A further problem is that it is more difficult, and thus more expensive, to synthesize.

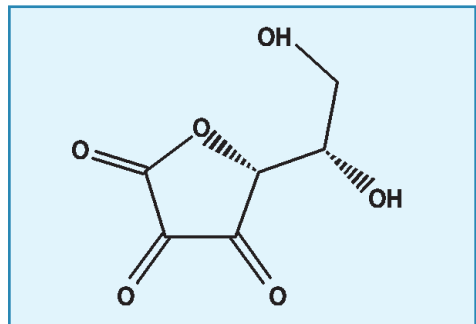
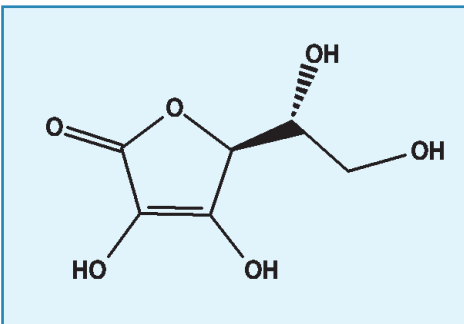


Fig. 111: Chemical structure of ascorbic acid (left) and dehydroascorbic (right)

18.3.6 Bromate

The powerful oxidizing agent bromate (more precisely: potassium bromate, KBrO_3) is still being used as a flour improver in many countries. Although it has a very long-lasting effect, this effect starts later than that of AA and allows better processing of the doughs, for bromate clearly oxidizes glutathione only very slowly without the need for an enzyme (cf. ascorbic acid). It results in very good fermentation tolerance and a high volume yield. In the main, bromate acts directly on the gluten. Because of doubts about its effects on health it has gradually been replaced by AA since the 1950s. A further problem is that it accelerates fire and explosion (bromate is a constituent of fireworks, especially rockets; Fig. 112).



Fig. 112: Laboratory waste bin that caught fire because of mixed residues of potassium bromate and ascorbic acid

In countries that are now replacing bromate, combinations of AA and enzymes offer good alternative ways of achieving satisfactory dough and baking properties. Because of the low doses required (similar to AA or less) and its lower price, bromate can hardly be replaced without intervention by public authorities. Bromate is easily detected and determined semi-quantitatively with a kit in a similar manner to AA.

18.3.7 Azodicarbonamide (ADA)

This chemical foaming agent (Fig. 113) used in the manufacture of expanded plastics (not only does it have an oxidative effect; it also decomposes into large-volume gases upwards

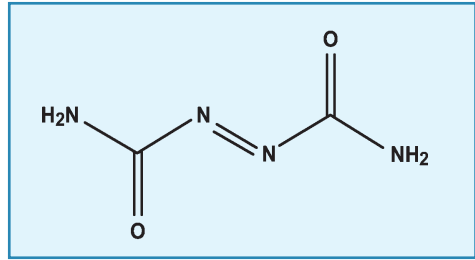


Fig. 113: Chemical structure of azodicarbonamide

of 120 °C) has been used as a temporary replacement for bromate and in some cases still is. A great disadvantage is its low dosing tolerance; a slight overdose causes the bread to split badly. The dosage is roughly the same as that of AA or bromate. The product most often used – in a correspondingly larger dose – is azodicarbonamide mixed with calcium sulphate to reduce its inflammability, usually with 23% of the pure substance.

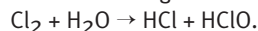
The ADA concentration of a premix can be determined by titration if no other oxidizing agent is present (AACC Method 48.71A), or by the Kjeldahl method if the carrier does not contain nitrogen. Another restriction on the use of the Kjeldahl method is the azo group ($\text{N}\equiv\text{N}$) which is not fully accessible. In flour, only determination by HPLC seems to be a reliable procedure (Ahrenholz and Neumeister, 1987).

18.3.8 Chlorine and Chlorine Dioxide

These oxidizing agents have been banned in many countries because of their possible harmful effects on health and the technical risks they involve. There is no doubt that with certain baked goods (for example cake with a high proportion of fat and sugar) chlorination of the flour – that can only be carried out at the mill – produces the best results. Products:

Cl_2 , ClO_2 (typical dosage 20 - 250 ppm), hypochlorite (NaOCl , $\text{Ca}(\text{OCl})_2$)

Chlorine reduces the pH because it is converted into hypochloric acid through reaction with water according to the following equation:



The pH usually drops to 4.5 - 4.7, and in flour for certain cookie applications it even falls as

low as 3.5. But the acidity is not responsible for the improving effect, since the latter is retained even after neutralization (Kulp *et al.*, 1985).

The resulting hypochloride is a strong oxidant, reacting with flour pigments and other components.

ClO₂ is a green gas that dissolves in water. It does not react with water, but with unsaturated chemical bonds and other reducing groups.

Chlorine and its derivatives affect pigments (bleaching), starch (partial breakdown of amylose and amylopectin that alters the pasting properties), proteins (improved solubility), fats (saturation) and pentosans (degradation, and hence reduced water absorption) (Kulp *et al.*, 1985).

Heat-treated flours have a certain similarity to chlorinated flour when combined with wheat starch, but chlorinated flour still achieves much better results (Seibel *et al.*, 1984).

18.3.9 Calcium Peroxide

Calcium peroxide is yet another commonly used oxidizing agent. Upon heating, CaO₂ releases oxygen that can be used in various oxidation reactions, for instance oxidation of ascorbic acid or water to hydrogen peroxide with the help of glucose oxidase. The effect of calcium peroxide is not very pronounced, but it is appreciated for its surface-drying property. For this reason it is always used in conjunction with more effective oxidizing agents. Calcium peroxide increases the pH of the dough. In certain limits this can be beneficial, particularly if the flour has high amylase activity. Larger amounts reduce the volume yield and cause excessive browning.

18.3.10 Other Oxidizing Agents

Tab. 86 summarizes the oxidizing agents that have been suggested for use in flour improvement. The "action in the dough" is based on the author's experience. For some of the substances, different information can be found in the literature. Some substances are rather risky, for instance acetone peroxide that tends to explode when exposed to even slight shock or friction. The substances not mentioned in the text above do not offer any considerable benefit as compared to the standard oxidizing agents.

Tab. 86: *Oxidizing agents suggested for flour treatment, and their typical reaction pattern*

Oxidizing agent	Action in dough	Remarks
Potassium bromate	Slow	
Potassium iodate	Fast	
Calcium bromate	Fast	
Calcium iodate	Fast	
Azodicarbonamide	Very fast	
Calcium peroxide	Slow	
Ammonium persulfate	Fast	
Potassium persulfate	Fast	
Acetone peroxide	Very fast	Highly explosive
Chlorine & chlorine dioxide		Reacts in flour
Hypochlorite		Reacts in flour
Benzoyl peroxide	Slow	Reacts in flour and dough
Ascorbic acid	Fast	Over-dosage: softening
Dehydroascorbic acid	Fast	
Cystine	Slow	Over-dosage: softening
Hydrogen peroxide	Fast	
Oxygen	Slow	

18.4 Reduction and Dough Softening

Gluten that is too short is difficult to process and results in a low volume yield, since the gas formed by the yeast is not able to expand the dough as it should. The problem can be solved by using substances with reducing properties that break down surplus disulphide bridges and thus give the protein molecules more room to move. Short gluten properties may result from the varieties used, but they are sometimes caused by the storage and processing of the grain (overheating) or the