Cysteine is unique among the protein amino acids because it has a sulfhydryl group at the end of the molecule. Cysteine is important to dough reduction chemistry because it occurs in the gluten protein from flour, in the tripeptide glutathione from yeast, and in free amino acid form as a synthetic reducing agent.

\[
\begin{align*}
\text{HSCH}_2\text{CHCOH} & \quad \text{O} \\
\text{NH}_2 & \\
\text{L-cysteine} \\
\text{HSCH}_{2}\text{CHC}–\text{NHCH}_2\text{COH} & \quad \text{O} \\
\text{O} & \\
\text{Glutathione}
\end{align*}
\]

The significance of cysteine’s sulfhydryl group is that two of them from different proteins can be oxidized to one molecule of cystine, with the creation of a disulfide bond between them. When gluten molecules become linked (oxidized) during breadmaking, the dough strength increases but its extensibility decreases. During mixing, these linkages are broken mechanically to provide the needed strength and structure. Reducing agents act like mixing to reversibly break down gluten so that once they have been used up the gluten reforms. This mechanism is the opposite of oxidizing agents, which build up gluten.

Reducing and oxidizing agents can be used separately, or a reducing agent can be used with a slow oxidizing agent (like potassium bromate) to increase gluten breakdown early in the process and gluten reformation later in the process. When reducing agents are used with fast oxidizing agents (like iodate or azodicarbonamide), they counteract each other.

Bread dough requires a combination of strength, extensibility, and tolerance that depends mostly on flour quality, water absorption, and mixing conditions. Reducing agents are used especially with high-strength flour and high-speed processes to reduce mix time, lower energy input, improve machinability, and improve loaf volume. Frozen bread dough is a special case where short mix time is especially important because it helps improve yeast stability.

Extensibility is important in other yeast and chemically leavened applications including pizza, tortillas, cookies, saltines, and other crackers. Reducing agents decrease the elasticity that can cause shrinkage or curling after these products are formed.

### Characteristics

**Protein-based** reducing agents include cysteine, glutathione, and yeast. Cysteine is the most commonly used reducing agent in bread. It is an amino acid that is usually produced synthetically as L-cysteine hydrochloride, is usually added at the mixer, and acts quickly. Glutathione is a peptide that contains cysteine but is not generally available in its pure form. It functions similarly to L-cysteine but is potentially more effective because it can react more times.

Yeast is a natural source of glutathione. Special nonleavening yeasts are used as reducing agents in the same applications as L-cysteine.

**Sulfites** are commonly used reducing agents in cookies and crackers. Their active ingredient is the bisulfite ion that is obtained from sulfur dioxide or from one of its salts, such as sodium bisulfite. Sulfites

### Reducing Agents and Mix-Time Reducers

<table>
<thead>
<tr>
<th>Compound</th>
<th>Use Level</th>
<th>Considerations</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-cysteine</td>
<td>10–90 ppm</td>
<td>Most-common reducing agent</td>
</tr>
<tr>
<td>Glutathione</td>
<td></td>
<td>Not commercially available</td>
</tr>
<tr>
<td>Nonleavening yeast</td>
<td>0.25–1.0%</td>
<td>Natural source of glutathione</td>
</tr>
<tr>
<td>Bisulfite</td>
<td>20–100 ppm</td>
<td>May require finished product labeling</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>100–200 ppm</td>
<td>For closed system continuous mix</td>
</tr>
<tr>
<td>Sorbic and fumaric acids</td>
<td>10–90 ppm</td>
<td>Limited use as reducing agent</td>
</tr>
<tr>
<td>Protease</td>
<td></td>
<td>Not a true reducing agent</td>
</tr>
</tbody>
</table>

Continued
Dough Reduction Chemistry (Continued)

Known as disulfide interchange. The reactions are shown here, with R and R’ representing the two gluten molecules and with cysteine as the reducing agent:

\[
R-S-S-R' + cys-SH \rightarrow R-S-S-cys + R'-SH
\]

These reactions reduce the number of cross-links between the gluten subunits proportional to the number of cysteine or glutathione molecules added and are reversible so that the degree of relaxation can be controlled. The reaction is similar with either cysteine or glutathione, except that with glutathione less is required. This is because an enzyme present in flour converts glutathione disulfide into two glutathiones with free SH groups that can participate in further disulfide reactions. Because no analogous enzyme exists for cysteine sulfide, each cysteine SH can be used only once.

Fermaid® Dough Relaxers

Fermaid® DOUGH RELAXERS are nonleavening yeast products that reduce mix time and improve dough extensibility. They are natural replacements for L-cysteine hydrochloride, sulfites, and other chemical reducing agents in breads, rolls, pizza, pretzels, tortillas, and crackers. Fermaid® dough relaxers are processed to maximize available glutathione—a naturally occurring yeast peptide that acts as a reducing agent. They function similarly to L-cysteine but with the added benefit of being label-friendly.

For breads and rolls, Fermaid® dough relaxers can be used to reduce the mix time required for high-strength flour or high water absorption. They give a dough that is smoother and easier to handle at the moulder, with good flow in the pan.

Finished volume is high and uniform, with a fine, uniform internal structure. Using Fermaid® dough relaxers to optimize mix time minimizes the effect of flour changes, improves machinability, and avoids both “bucky,” undermixed doughs and sticky, overmixed doughs.

Fermaid® dough relaxers are available in versions for a range of products and applications. Those with lower glutathione levels are used at higher doses so that they also contribute flavor and crust color. Those with higher glutathione levels are used at lower doses to provide dough relaxation without contributing taste or flavor.

Formulations with other dough conditioner ingredients are optimized for specific applications including pizza, pies, crackers, tortillas, and wraps.

International Perspective: FRENCH BREAD AND MODERN FLOUR

Parts of the French baking industry have modernized rapidly since the 1970s, with increased production of pan bread and frozen dough on high-speed lines with short processes. In response, French wheat growers and flour millers have selected wheat varieties for increased strength. But the increase in strength has come at the expense of extensibility and has made optimum mixing and moulding more difficult to achieve.

The problem of decreased extensibility is worsened by traditional product types and legal restrictions. Baguettes must be long and regular in shape with well-defined top cuts. Croissants and brioches require thin dough laminations without tearing. For these and other products, French regulations prohibit most reducing agents, including L-cysteine, sulfites, and sorbic acid. Techniques such as decreased dough temperature and reduced proofing time help somewhat by slowing oxidation reactions but create other problems.

Since 1990, French bakers have begun using increasing amounts of nonleavening yeast as a dough conditioner for high-strength/low-extensibility flour. The products have a high glutathione content so that they act as reducing agents and are permitted under French regulations as “deactivated fermentative agents.” Versions are available for artisanal and industrial applications and for a range of products including bread, pastry, puff pastry and retarded dough. The same products are used in other European countries with similar flour/product/regulatory requirements and in the U.S. and Canada for bromate replacement and other applications.

A Guide to Reducing Agents (Continued)

destroy the vitamin thiamine, are inhibitory to yeast, cause sensitivity reactions in some people, and require special label declarations if used in the U.S. at levels in the finished product above 10 parts per million.

Ascorbic acid (vitamin C) is used as a reducing agent only in certain closed continuous mix applications. In the presence of oxygen it functions as an oxidizing agent, but in the absence of oxygen, as a reducing agent. It can be used in coated form for increased stability as a component of bread improvers and dough conditioners.

Other acids that have been suggested as reducing agents, but are not commonly used, include sorbic acid and fumaric acid. They are part of a group of “activated double-bond compounds” and are more commonly used as preservatives. These acids are inhibitory to yeast and less economical than other synthetic reducing agents.

Proteases are used to decrease mix time and increase elasticity but are not reducing agents. They are natural enzymes that break down gluten irreversibly and must be used with careful attention to dose, time, and temperature to avoid overconversion.

Lallemand Baking Update is produced by Lallemand Inc. to provide bakers with a source of practical technology for solving problems. If you would like to be on our mailing list to receive future issues, or if you have questions or comments, please contact us at:

LALLEMAND Inc.
1620 Préfontaine
Montréal, QC H1W 2N8 CANADA
tel: (800) 840-4047 (514) 522-2133
tel: (514) 255-6861
e-mail: solutions@lallemand.com

To the best of our knowledge, the information in Lallemand Baking Update is true and accurate. However, any recommendations or suggestions are made without warranty or guarantee.