BAKERY PROCESSES, CHEMICAL LEAVENING AGENTS

1. Introduction

Chemical leavening involves the action of an acid on bicarbonate to release carbon dioxide gas for aeration of a dough or batter during mixing and baking. The aeration provides a light, porous cell structure, fine grain, and a texture with desirable appearance along with palatability to baked goods.

Leavening of a dough with carbon dioxide from yeast fermentation was known to ancient civilization before the advent of recorded history. In contrast, the first use of chemical leavening dates back only to the early nineteenth century. Sodium bicarbonate [144-55-8] was used either alone or with sour milk in home baking $\sim$1830 (1). At about the same time, alum was used as baking acid. Monocalcium phosphate was introduced in the form of an impure baking acid in 1856 (2,3). Almost 80 years later, in 1937, the first free-flowing powdered monocalcium phosphate monohydrate (MCP) was introduced, followed by a milestone discovery of slow-acting coated anhydrous monocalcium phosphate (AMCP) in 1939 (4). Meanwhile, anhydrous sodium aluminum sulfate (SAS) was developed $\sim$1892 (2). Used in combination with the fast-acting monocalcium phosphate, it forms a double-acting baking powder. Sodium acid pyrophosphate (SAPP) was introduced in the early 1900s, and sodium aluminum phosphates (SALP) also joined the list of dry food-grade leavening acids in 1951 (5). More recently, leavening acids based on magnesium orthophosphates (6) and calcium pyrophosphates (7–12) have appeared. These leavening agents are responding to new needs in the marketplace for controlled baking performance and also for low sodium baked goods (Table 1).

2. Composition of Chemical Leavening Systems

There are essentially two components in a chemical leavening system: bicarbonate that supplies carbon dioxide gas, and an acid that triggers the liberation of carbon dioxide from bicarbonate upon contact with moisture.

Sodium bicarbonate (baking soda) is the primary source of carbon dioxide gas in practically all chemical leavening systems. This compound is stable and is obtainable as a highly purified dry powder at relatively low cost. Three types of baking soda differing in granulation are available to cover practically all applications. Powdered soda is preferred for self-rising flour and prepared biscuit mixes. A fine granular soda is used for baking powders and prepared cake mixes. Coarse granular soda is mainly used for frozen or refrigerated dough products or any product subject to storage for 6 months or longer.

Other bicarbonates of considerable commercial importance are ammonium bicarbonate [1066-33-7] and potassium bicarbonate [298-14-6]. These compounds are decomposed by the oven heat, liberating carbon dioxide, and water, as well as ammonia in the case of ammonium bicarbonate, to facilitate leavening action. Their uses are limited to low moisture products such as cookies and crackers or where reduced sodium levels are desired.

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The prevalent baking acids in modern chemical leavening systems are sodium, calcium, or magnesium salts of ortho, pyro, and complex phosphoric acids in which at least one active hydrogen ion is attached to the molecule (Table 1). Alum, although not a protonic acid, is used in retail baking powder formulations. Some organic acids are also used in refrigerated dough products. The discussion here focuses mainly on systems involving acidic phosphates and baking soda, since practically all chemical leavening systems today contain these components.

3. Characteristics of Leavening Agents

The evolution of carbon dioxide essentially follows the stoichiometry of acid–base reactions. The amount of baking soda determines the amount of carbon dioxide evolved, whereas the type of acid controls the speed of its liberation. Idealized reaction equations for some acids with baking soda are as follows:

$$\begin{aligned} &5\,Ca(H_2PO_4)_2H_2O + 14\,NaHCO_3 \longrightarrow 14\,CO_2 + Ca_5(PO_4)_3OH \\ &\quad + 7\,Na_2HPO_4 + 18\,H_2O \end{aligned} \tag{1}$$

$$Na_2H_2P_2O_7 + NaHCO_3 \longrightarrow CO_2 + Na_3HP_2O_7 + H_2O \tag{2}$$

$$Na_2H_2P_2O_7 + 2\,NaHCO_3 \longrightarrow 2\,CO_2 + Na_4P_2O_7 + 2\,H_2O \tag{3}$$

$$\begin{aligned} &2\,NaAl_3H_{14}(PO_4)_8 \cdot 4\,H_2O + 23\,NaHCO_3 \longrightarrow 23\,CO_2 \\ &\quad + Na_5Al_6(PO_4)_6(OH)_5 \cdot 12\,H_2O + 10\,Na_2HPO_4 + 14\,H_2O \end{aligned} \tag{4}$$

$$Na_2SO_4 \cdot Al_2(SO_4)_3 + 6\,NaHCO_3 \longrightarrow 6\,CO_2 + Al_2O_3 \cdot 3\,H_2O + 4\,Na_2\,SO_4 \tag{5}$$

The neutralizing value (NV) of a leavening acid determines the number of parts by weight of baking soda that will be neutralized by 100 parts of the acid to impart neutral pH in baked goods:

$$NV = a/b \times 100$$

where a = grams of baking soda and b = grams of leavening acid required to complete the reaction.

These equations are based on the reactions that occur when the materials are placed in boiling water. In a dough or batter there appear to be complicated reactions of phosphate, involving ion exchange with ingredients such as milk and calcium salts, and formation of complexes with proteins and starch. In the case of a blend containing different types of leavening acid, the reactions are complex and cannot be expressed in NV equations. Note, eg, that more than one chemical equation can be written for a given phosphate acid, yielding different by-products. For this reason the neutralizing values given are often empirically determined.

Most of the acids react with baking soda, instantly liberating all the available carbon dioxide within a minute. Leavening of baked goods, however, requires both fast and slow liberation of carbon dioxide at a controlled speed; and the action must continue until just before the crumb structure of the baked goods is set by the heat of the oven. The required volume of carbon dioxide to be liberated at a particular stage during baking varies depending on the type of bakery product and processing conditions involved.

A number of acidic phosphates that vary in their rate of reaction are available for use in a wide variety of bakery applications. These acids, which include monocalcium phosphate, SALP, and SAPP, release carbon dioxide at a controlled rate to give a certain fraction prior to baking; the remaining fraction is released at a specific time during baking. Controlled release of carbon dioxide at the time it is needed can also be achieved by a mixture of different types of leavening acids.

The dough rate of reaction (DRR) is a term that defines the speed of carbon dioxide evolved during mixing and holding of a dough at bench prior to baking. It is determined by measuring the volume of carbon dioxide evolved from a standard dough formula containing known quantities of leavening acid and baking soda under a constant temperature of 27°C (Fig. 1). The DRR is often used as a guide for selecting the type of leavening acid that is best suited for a particular product application.

4. Leavening Agents for Preleavened Mixes

By far, the greatest use of leavening in the home is in preleavened mixes. Pancake, biscuit, and cake and muffin mixes have long been established as consumer products. The advent of powerful emulsifiers coupled with components produced in rapidly dispersible forms produce bakery mixes that require very little mixing and have a wide tolerance for variability in handling. Most of the mixes on the market require the consumer to add only water, sometimes oil, and possibly eggs. Certain types of cake mixes may be given a final treatment through a high speed shearing to disperse the fat properly. This provides the consumer with easy, quick preparation even for the novice consumer.

Many mixes are also produced for commercial use. Because of the complexity of the doughnut system, many commercial bakeries buy preformulated doughnut mixes. This approach has spread to commercial use of various types of cake, muffin, and brownie mixes and mix concentrate and has been adopted by both retail and wholesale bakeries. This approach saves scaling time and reduces scaling errors.

5. Leavening Agents for Refrigerated and Frozen Batters and Doughs

Sales of frozen or refrigerated doughs and batters have increased rapidly in recent years. This is attributed to changing demographics and consumer demand for easy to prepare home baked products. In the commercial sector, the demand is driven by retail bakeries, food service providers, and in-store bakeries. This convenience allows for increased product offerings without adding employees. These changes have challenged the food ingredient industry to develop new or improved ingredients, eg, leavening acids, emulsifiers, gums, and starches, which provide greater dough and batter stability during refrigerated or frozen storage. For many of these products, leavening is the most critical component. The type, quantity, and combination are all tailored to each product to give maximum stability, tolerance, performance, and quality. Leavening acids that are slow reacting or heat reactive are commonly used in these types of applications. Practically all of the leavening acids used in the commercial mix industry today are of the phosphate type.

6. Nutritional Aspects of Leavening Agents

With increasing health concerns about their diets, consumers are becoming more aware of the ingredients in food products. With the general awareness of the benefits of increasing calcium and the need to decrease sodium in their diets, consumers are increasingly reading the nutritional labels and making choices based on sodium and calcium levels in their foods.

Leavening acid choice is becoming more important as food scientists realize the impact it will have on the nutritional make up of baked goods (see Table 2). The calcium-based leavening acids can contain up to 18% calcium and no sodium, while sodium based leavenings have up to 21% sodium and only a trace of calcium (see Table 3). The choice of proper leavening acids can dramatically effect the sodium and calcium concentrations on the nutritional label and for some baked goods provide a “reduced” sodium claim or a “good source” of calcium claim.

6.1. Monocalcium Phosphate. The monohydrate of monocalcium phosphate (MCP) was the first of the phosphates to be used as a leavening acid, and has since been in commercial use for more than a century. Used alone, it reacts with baking soda very rapidly, releasing 60–70% of the available carbon dioxide in a 2-min mixing of dough. The remaining gas is not evolved at room temperature since the reaction generates some dicalcium phosphate [7789-77-7], and the heat of baking is required to complete the reaction. Because of its fast reaction, MCP is used at low concentration in combination with a slow-acting acid, eg, SAPP in double-acting baking powder.

The primary advantage of MCP is to create a large number of gas cells rapidly during mixing. These gas cells serve as nuclei for a greater expansion later in the oven. The MCP also finds many uses in the products in which fast release of carbon dioxide and a low bench action are required. Examples are pancake, cookie, and angel food cake mixes. The milling industry uses MCP in the manufacture of phosphated flour.

A coated anhydrous monocalcium phosphate (AMCP) was developed in 1939 (3). The reaction with baking soda at room temperature is delayed by coating each AMCP crystal with a relatively insoluble condensed phosphate element. Retardation of the reaction (3–5 min) at onset enables the dough or batter to develop a greater resilience for a sustained oven spring. This is especially advantageous in developing desirable tenderness in biscuits and pancakes prepared from self-rising flour and in corn bread prepared from self-rising corn meal.

6.2. Sodium Acid Pyrophosphate. Sodium acid pyrophosphate is prepared by thermal dehydration of monosodium phosphate. By varying processing conditions, a product with a wide range of reactivity can be prepared. Various manufacturing techniques are used to adjust the reactivity of SAPP for use in widely differing applications (13–18). The SAPP is classified as a slow-reacting acid, but its function is dependent on its secondary reaction with calcium ion and protein in flour and milk and is also the only leavening acid that can be affected by granulation. In a batter, the finer the size of SAPP particles, the slower the reaction with baking soda. When treated with water and baking soda in the absence of a flour ingredient, all of the SAPP grades are fast and similar, releasing 60–70% of carbon dioxide from baking soda in a few minutes. This interference in reactivity is presumably caused by *in situ* coating of SAPP particles by relatively insoluble calcium pyrophosphate from the reaction of SAPP with calcium ions from batter ingredients. A number of grades of SAPP, ranging from fast to very slow reactivity, are available for a wide range of baking applications (see Fig. 1).

The fast-acting SAPP releases 40–43% of carbon dioxide during 2 min of mixing. It is often blended with a slower acting SAPP to provide intermediate reaction. The SAPP for cake doughnut production requires a certain quantity of gas to be released during mixing of the batter, followed by a rapid and uniform response to heating for proper expansion of the doughnut during frying. A special grade of SAPP is available to meet rigid specifications for cake doughnut production.

Refrigerated dough or batter for canned biscuits, muffins, and cakes requires a SAPP with very slow reactivity at room temperature. A slow reactivity is needed before and during mixing, make-up, and packing processes; but a rapid and controlled gassing during proofing is essential to fill and seal the can with dough to prevent the entrance of air into the can. A specially designed, very slow-acting grade of SAPP that conforms to the most rigid specifications is available for this particular application.

A SAPP with intermediate reactivity is used in combination with fast-acting MCP for the manufacturer of industrial baking powder and for retail and wholesale prepared cake mixes. Sodium acid pyrophosphate imparts a bitter aftertaste that is often characterized as a mild burning sensation, especially when used in a product of low sweetness. The SAPP is normally used at an NV of 72. However, it may be used at slightly higher or lower NV to obtain specific effects in certain types of baked goods.

6.3. Sodium Aluminum Phosphate. This leavening acid was introduced in 1951, somewhat later than SAPP and MCP (5). It quickly gained a dominant position in self-rising flour, prepared cake mixes, pancakes, waffles, and refrigerated and frozen dough or batter products because of a number of outstanding features (19–22). The SALP has a relatively low initial release of carbon dioxide. It exhibits retarded reaction when cold, even with extended holding of dough or batter. It has a bland flavor in baked goods and an excellent buffering action that provides greater tolerance of dough or batter against the influence of other ingredients and flour variety. Sodium aluminum Phosphate has a high neutralizing value of 100, which is an advantage for bakers. The baked products made from SALP or its blends are notable for firm yet tender crumb texture due to the great number of thin-walled cells that are formed.

One modified form is especially efficient in improving the tolerance of retail cake mixes containing highly emulsified shortening (23). A mixture of SALP and a small amount of coated AMCP has been adopted by the self-rising flour industry for the production of biscuit mixes ever since the introduction of SALP in the early 1960s (24). This system offers increased shelf-life for the flour, and it enables one to hold biscuit dough and pancake batters for extended periods without loss in baking response or change in viscosity. This imparts considerable versatility and convenience to the use of self-rising flour. This development has been further extended to frozen and refrigerated pancake batters with an extended stability in the refrigerated state. These batters may be conveniently marketed in dairy or frozen food cases. The relatively inactive state of this acid in batter and dough and its efficient response to oven heat make it ideally suited for this application.

6.4. Dicalcium Phosphate Dihydrate. Dicalcium phosphate dihydrate (DCPD) is completely nonreactive at room temperature. At 65–71°C and in the presence of water, it dehydrates and decomposes into hydroxyapatite and acidic monocalcium phosphate, or free phosphoric acid (25). It is used to some extent in cake mixes in combination with faster acting acid. Its primary function is to provide acidity late in the baking cycle and thus produce a neutral and palatable product. The DCPD has an NV of 33. It provides sufficient acidity only in products requiring long baking times.

6.5. Dimagnesium Phosphate Trihydrate. Like DPD, dimagnesium phosphate trihydrate is a heat triggered leavening agent that only provides leavening during baking. Commercial products with optimized performance have been developed by partially dehydrating the DMP-3, leading to amorphous dimagnesium phosphates as an intimate mixture with the trihydrate. The retarded leavening action leads to a consistent leavening acid improving control in doughs and batters. The baked products are moist and have a uniform cell structure consistent with the delayed leavening. The NV of 40 generally requires that DMP-3 be mixed with a faster leavening agent in commercial applications.

6.6. Calcium Acid Pyrophosphate. Calcium acid pyrophosphate is a relatively slow leavening acid. It provides controlled release of carbon dioxide under almost all applications. Pure CAPP has a relatively low NV of 67, but many commercial varieties have been optimized to increase the NV to 72. The CAPP is a multifunctional leavening acid. It plays a role in augmenting the viscosity of a batter and acts as a dough conditioner. The high concentration of calcium ions strengthens the gluten network making the dough more elastic and better able to stand rough handling or freezing. The CAPP is a source of calcium and does not contain any sodium.

6.7. Sodium Aluminum Sulfate. Sodium aluminum sulfate is a dehydrated double salt of aluminum and sodium sulfate. It does not react with baking soda in the cold, but in the heat of an oven, 1 mol of SAS produces 6 mol of carbon dioxide from reacting with baking soda. Historically, SAS was one of the first materials used to liberate carbon dioxide from baking soda. Today its primary use is in household baking powder production. It is used either alone or in combination with MCP. The SAS is not recommended for use in prepared mixes due to its lack of compatibility with other ingredients in a mix.

6.8. Glucono-Delta-Lactone. Glucono-delta-lactone is an inner ester of gluconic acid. In a water solution, GDL slowly hydrates to become acidic and thus acts as a leavening acid. Hydrolysis is slow in the cold, but is accelerated by heat, making GDL ideal for refrigerated or frozen dough products (26). A drawback is the high cost, which, combined with a low NV of 47, make GDL prohibitive for use in most baked goods except in some refrigerated or frozen dough formulations.

6.9. Baking Powder. Modern baking powder consists of a mixture of baking soda, one or more acid components, and an inert ingredient that serves to keep the reactive components physically separated and thus minimizes premature reaction in dry mixtures. The inert ingredient is usually starch dried to 5–7% moisture. Calcium sulfate and calcium carbonate have sometimes been substituted for part of the starch. In addition to stabilizing the active ingredients, the inert substance provides a means for adjusting and standardizing the composition to a sodium bicarbonate concentration of $\sim$30%. Table 4 lists typical formulations for both household and commercial baking powders.

Of the household baking powders in general use, the type containing SAS is most prevalent. A small amount of MCP is used in combination with the SAS to make a double-acting baking powder. The MCP serves to generate gas cells during the mixing of dough or batter so that uniform expansion can be attained in the oven. This is necessary since SAS is almost completely nonreactive until heat is applied. Commercial baking powders contain SAPP, which is superior to SAS in stability and performance. The SAPP has an inherent aftertaste that is effectively masked by the sweetness of sugar in cakes, doughnuts, cookies, and other sweet goods. Household baking powders are often used in biscuits, where the pyro taste precludes the use of SAPP. Considerable variation exists among baking powders produced by various manufacturers. The concentration of baking soda may vary 28–30%; the acids vary proportionately to provide neutralized products. The use of cream of tartar as an acid component in baking powder is quite minor today because acids of equal performance are available at a lower cost.

7. Manufacture of Baking Powders

The blending of baking powder is essentially a physical mixing of the various components in a large-scale batch mixer and is often carried out in automated plants. The order in which mixing occurs may influence the stability of the product. Mixing of starch or other inert components with individual reactive components tends to maintain the separation of reactive components so as to prevent premature reaction during storage. Rigid specifications for purity, granulation, and moisture content of the ingredients must be adhered to if a uniform, stable, and reliable product is to be obtained. The proper kind and speed of blending is essential to attain uniform distribution of ingredient particles. The baking powder is usually packaged in airtight metal or fiber cans. Hermetically sealed packages are not used because of the possibility of buildup of high internal pressures.

Baking powder has declined in home use since the 1940s. However, leavening acids are used in an increasing array of modern food products. These products include self-rising flour, self-rising corn meal, prepared cake mixes, pancake mixes, cookie mixes, doughnut mixes, and refrigerated or frozen doughs and batters.

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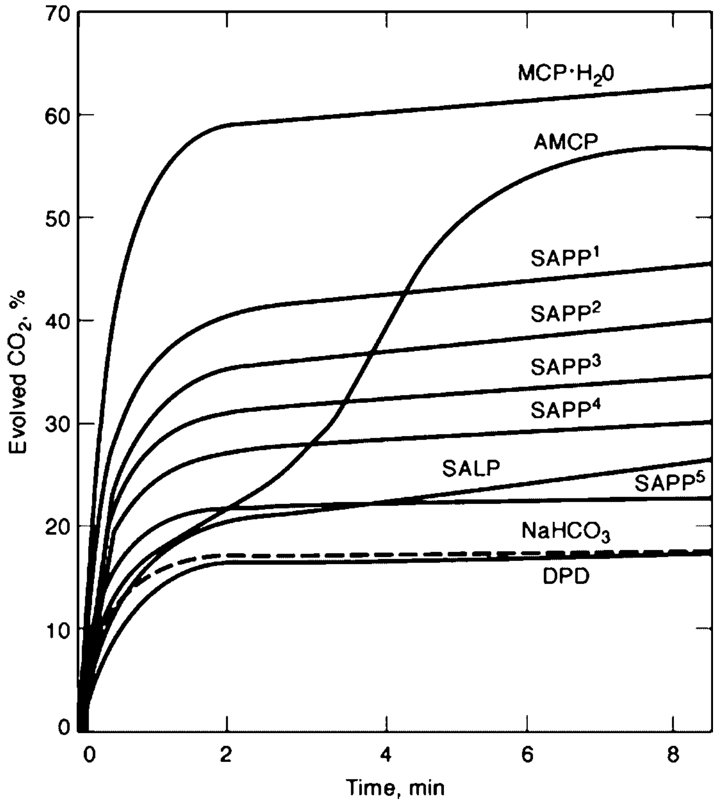

Fig. 1. Typical DRR of chemical leavening acids. The SAPP superscripts designate various speed grades: $SAPP^1$ = fastest; $SAPP^2$ = fast; $SAPP^3$ = medium fast; $SAPP^4$ = slow; $SAPP^5$ = slowest at 27°C. See Table 1 for definitions of abbreviations.

Table 1. **Baking Acids Commercially Produced for Leavening Systems**

Common name (Chemical Abstracts name)	CAS Registry Number	Chemical Formula	Neutralizing value	Uses[a]
monocalcium phosphate monohydrate, MCP [phosphoric acid, calcium salt (2:1), monohydrate]	[10031-30-8]	$CaH_4(PO_4)_2 \cdot H_2O$	80	H, L, C
monocalcium phosphate anhydrous, AMCP coated [phosphoric acid, calcium salt (2:1)]	[7758-23-8]	$CaH_4(PO_4)_2$	83	(H)[b], L
sodium acid pyrophosphate, SAPP (diphosphoric acid, disodium salt)	[7758-16-9]	$Na_2H_2P_2O_7$	72	C, L
sodium aluminum phosphate, SALP			100	C, L
[phosphoric acid, aluminum sodium salt (8:3:1)]	[10305-76-7]	$NaH_{14}Al_3(PO_4)_8 \cdot 4H_2O$		
[phosphoric acid, aluminum sodium salt (8:2:3)]	[10279-59-1]	$Na_3H_{15}Al_2(PO_4)_8$		
(phosphoric acid, aluminum sodium salt)	[7785-88-8]	$Na_xAl_y(PO_4)_z$		
dicalcium phosphate dihydrate, DCPD [phosphoric acid calcium salt (1:1)]	[7789-77-7]	$CaHPO_4 \cdot 2H_2O$	33	L
sodium aluminum sulfate, SAS (soda alum) [sulfuric acid, aluminum sodium salt (2:1:1)]	[10102-71-3]	$Al_2(SO_4)_3 \cdot Na_2SO_4$	100	H
glucono-delta-lactone, GDL [D-gluconic acid–δ-lactone]	[90-80-2]	$C_6H_{10}O_6$	50	L
potassium hydrogen tartrate (cream of tartar) [butanedioic acid, 2,3-dihydroxy-, [*R*-(*R**, *R**)]-monopotassium salt	[868-14-4]	$KHC_4H_4O_6$	45	(H)[b]
dimagnesium phosphate trihydrate, DMP-3 [phosphoric acid magnesium salt (1:1)]	[7782-75-4]	$MgHPO_4 \cdot 3H_2O$	40	C, L
calcium acid pyrophosphate, CAPP (diphosphoric acid, monocalcium salt)	[14866-19-4]	$CaH_2P_2O_7$	72	C, L

[a] C = commercial baking powders; H = household baking powders; L = leavening agents for preleavened products.
[b] () = some use, but limited.

Table 2. **Quantity of Sodium and Calcium in Leavening Ingredients**

Ingredients	Sodium (mg) per 100 g	Calcium (mg) per 100 g
sodium bicarbonate	27,370	0
potassium bicarbonate	0	0
sodium acid pyrophosphate	21,000	90
sodium aluminum phosphate	2,100	400
monocalcium phosphate, monohydrate (MCP-M)	0	16,700
monocalcium phosphate anhydrous (MCP-A)	0	17,700
DOUGH-RISE	1,060	9,200
CAL-RISE	0	18,000

Table 3. **Sources of Sodium in Formulations**

Ingredient	Yellow cake (%)	Muffins (%)	Biscuits (%)
salt	42	29	52
sodium bicarbonate	26	33	23
SAPP	27	34	24
% of total sodium	95	96	99

Table 4. **Baking Powder Compositions, %**

Constituents	Pure phosphate[a]			Phosphate–SAS double-acting types[a]			Cream of tartar	Commercial baking powders			
	1	2	3	1	2	3		1	2	3	4
baking soda, fine granular	28.0	28.0	28.0	30.0	30.0	30.0	27.0	30.0	30.0	30.0	30.0
MCP	35.0			8.7	12.0	5.0		5.0		5.0	
AMCP		34.0									
SALP			30.5								32.7
corn starch, redried	37.0	38.0	36.5	26.6	37.0	19.0	20.0	24.5	26.0	27.0	32.3
SAS				21.0	21.0	26.0					
SAPP								38.0	44.0	38.0	
calcium sulfate 7778-18-9]				13.7							
calcium carbonate [471-34-1]						20.0					
cream of tartar							47.0				
tartaric acid [133-37-9]							6.0				
calcium lactate [814-80-2]								2.5			
tricalcium phosphate [7758-87-4]			5.0								5.0

[a]Household baking powders.