BAKING PERFORMANCE OF ASCORBYL-6-PALMITATE

IN PUP LOAVES

by

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INTRODUCTION

In the last century, the food industry has undergone many significant changes in the way food items are formulated, preserved, packaged, and distributed. Products, which were primarily produced and consumed at home earlier in this century, are now being produced commercially in large volume and are being distributed over large geographical regions. The use of food additives has allowed food scientists to improve the texture, flavor, appearance, and shelf life stability of products.

A major segment of the food industry, the baking industry, has been greatly affected in recent years by additives commonly called dough conditioners, dough strengtheners, and crumb softeners. These materials are all surfactants, which means they reduce the surface tension of water. Surfactants are organic molecules containing two distinct functional groups; a hydrocarbon hydrophobic entity and a hydrophilic entity, which can be either ionic or nonionic (Greene, 1975).

Surfactants are used in the baking industry to improve loaf volume of bread doughs, to replace or reduce the amount or type of fat used in a formulation, to improve the shelf life of a product, to improve machine handling performance, and to allow the inclusion of foreign proteins in a bread dough (Pomeranz, Shogren, and Finney, 1969; Tsen, Hoover, and Phillips, 1971; Favor and Johnson, 1947; Tsen and Hoover; 1971; Garti, 1980; Tenney, 1978; Hoseney, Finney, Shogren, 1972; Hoseney, Hsu, and Ling, 1976; Chung, Pomeranz, Goforth, and Shogren, 1976).

Food additives are indispensable in the baking industry's food-delivery system. But additives must be safe to be useful, therefore food scientists are continually searching for the least innocuous materials to be used in foods. With the advent of changes in food-labeling laws, manufacturers are continually under pressure to remove chemical additives from food.

In the baking industry, one fairly well known oxidizing agent, ascorbic acid (Vitamin C), has been used to provide maturing action to flour. After baking and at the levels used in bread, however, only a small fraction of the ascorbic acid (AA) survives (Quadri, Liang, Seib, Deyoe, and Hoseney, 1975). Therefore, ascorbic acid used as a maturing agent imparts very little in nutritional gains to a loaf of bread. Mauro et al (1979) reported that 81% of ascorbyl 6-palmitate (AP) was recovered after baking. Inagaki et al (1968) indicated that growth curves of guinea pigs fed AP and those fed AA were comparable. Organ analysis indicated comparable levels of AA in each organ. These data indicate that animals are capable of utilizing AP as a source of vitamin C in their diets. If desired, AP could be used in bread to fortifying it with vitamin C.

The chemical structure of AP is presented in Figure 1. The molecule contains two distinct classes of structural groups. A hydrophobic group, in the form of an esterified fatty acid, is attached to C6. The hydroxyls on C2 and C5 add hydrophilic character to the molecule because they can engage in hydrogen bonding. The C3 hydroxyl adds to the hydrophilic character via ionization (pK_a 4.15). Thus, structurally AP has the potential to act as an anionic surfactant. AP is a GRAS additive with no limit set on its level in food usage except good manufacturing practice (Cort, 1974).

Figure 1. Structure of ascorbyl 6-palmitate.

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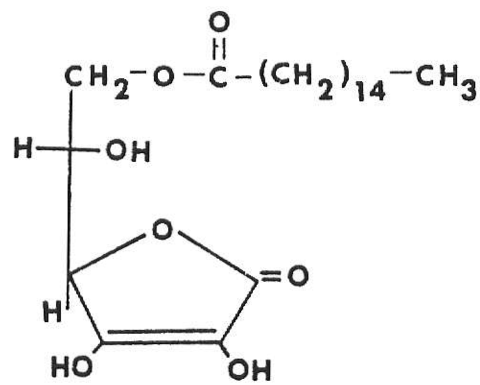

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In 1958, Ofelt et al investigated a number of surfactants in an attempt to relate structural differences with their antifirming action in bread. AP was comparable to distilled monoglycerides in antifirming action. From data on glycerides at differing chain lengths, Ofelt et al concluded that the chain length of the fatty acid moiety on a surfactant molecule affected the antifirming action of the additive. However, other structural differences were also important.

Hoseney et al (1977) published data on the baking properties of salts of L-ascorbic and D-isoascorbic acid esters. Table I presents a series of different chain-length ascorbic acid esters and their baking performance in replacing shortening. The sodium salts of the 6-laurate, 6-myristate, 6-palmitate, and 6-stearate esters, but not the 6-caprate, 6-sebacate and 6-valerate demonstrated a shortening replacing effect in terms of loaf volume and grain. In addition, the long-chain fatty acid esters also gave dough strengthening since the doughs felt drier and stronger at molding. It was also found that the position of substitution on AA was important in breadmaking. For example, the 2-palmitate ester of ascorbic acid was detrimental to the quality of a loaf and was worse than a nonshortening control (Table I).

Hoseney et al (1977) also examined the crumb softening effect of sodium ascorbate 6-palmitate (SAP). Those authors reported that 0.5% SAP gave softer bread than shortening or 0.5% AP plus shortening (Table II). The salts of the 6-laurate, 6-myristate, and 6-sterate esters also gave softer bread than a monoglyceride. However, SAP gave the best antifirming action of the four compounds.

Table I. Effect of Structure of L-Ascorbic Acid Esters on Dough Conditioning in a No-Shortening Bread Formula[a] (Taken from Hoseney, Seib, and Deyoe, 1977).

Additive	Absorption g	Volume cc	Dough Conditioning
None	65	905	-2
None (shortening control)	63	998	0
6-valerate[b]	65	740	-2
6-sebacate	64	720	-2
6-caprate	65	740	-2
6-laurate	66	1015	+4
6-myristate	66	995	+3
6-palmitate	66	997	+3
6-stearate	66	968	+2
2-palmitate[c]	65	740	-2
2-oleate[c]	66	793	-2
6-palmitate (iso)[d]	66	975	+3

[a]Quantity of all ingredients given in amount per 100 g of flour. All doughs contained 20 ppm of potassium bromate and no shortening except the control loaf (3 g of shortening). All additives tested at 0.5 g/100 g flour.

[b]All C-6 esters tested as sodium salts.

[c]Free acid form of ester ground with flour before dough mixing. Potassium bromate 30 ppm.

[d]Sodium 6-O-palmitoyl-D-isoascorbate.

Table II. Crumb-Softening by Sodium 6-O-Palmitoyl-L-Ascorbate (Taken from Hoseney, Seib, Deyoe, 1977).

Additive[a]	Shortening g	Gelometer Readings,[b] g		
		Day 1	Day 3	Day 5
None	3.0	108	179	275
Monoglyceride[c]	3.0	99	147	251
6-palmitate	3.0	86	162	248
6-palmitate	0	78	132	206

[a]All additives used at 0.5 g/100 g of flour.

[b]A reading in the table is the average determined for duplicate loaves.

[c]"Myverol", Distillation Products Industries, Rochester, N.Y.

Sodium 6-O-myristoyl-L-ascorbate has also been shown to improve the volume of bread containing 8% defatted soy flour (Hoseney, Seib, Deyoe, 1977). Thus ascorbic acid esters are capable of reversing the detrimental effects of addition of nonwheat protein to a bread dough.

In summary, the salts of a number of fatty acid esters of ascorbic acid are capable of several functions in bread dough. They replace shortening, improve loaf volume, provide antifirming action, improve machine handling, and permit the addition of foreign protein to bread.

Most of the work done to date on the use of ascorbyl 6-palmitate in breadmaking has been done with the salt form. The salt form is more readily dispersed in water and in a dough. However, Hoseney et al (1977) did show the free acid form of AP could be incorporated into a dough by pregrinding AP with flour in a high speed mill. A salt of AP would be more expensive than the free acid form and would add to the cost of using AP in bread. AP is also a readily available commercial product whereas the salt is not. The salt form would be less stable during storage than the free acid form. Moisture absorption by the salt form would lead to saponification during storage and destruction of the surfactant. Finally, and perhaps most importantly, AP is approved for food use whereas salt forms are not.

The objectives of the present investigation were; (1) to find convenient and reliable methods of adding AP to a bread dough, (2) to compare AP with sodium stearoyl-2 lactylate (SSL) in replacing shortening, strengthening dough, and crumb softening, (3) to determine why ascorbyl 2-palmitate (A-2-P) failed to function in bread (Hoseney, Seib, and Deyoe, 1977), and (4) to determine why ascorbyl 6-caprate was incapable of replacing shortening (Hoseney, Seib, and Deyoe, 1977).

MATERIALS AND METHODS

Flours

During the course of this investigation, several different flours were used. The BCS79 was a composite of hard winter wheat flours harvested throughout the Great Plains. It contained 12.4% protein (N x 5.7), 0.43% ash, and a moisture content of 12.2%. The KSU flour was milled at Kansas State University and was treated with benzoyl peroxide. Its protein content was 11.4% (N x 5.7), moisture 13.9%, and an ash value of 0.41%. The Ross Bake Flour was a commercially obtained sample (Ross Industries, PO Box 2696, Wichita, KS.). Protein level was 11.44% (N x 5.7), moisture 13.0%, and ash 0.44%.

Shortenings, Oils, and Surfactants

Two different plastic shortenings were used. Crisco vegetable shortening is produced by Procter and Gamble, Cincinnati, Ohio. It is made from partially hydrogenated soybean or palm oil and contains some mono- and diglycerides. Creamtex is a product of Durkee Food Service Group, SCM Corp, 900 Union Commerce, Cleveland, Ohio, and is partially hydrogenated vegetable oil with no emulsifier added.

Corn oil (Mazola) was obtained from a local supermarket and is a product of Best Foods, CPC International Inc., International Plaza, Englewood Cliff, New Jersey. Samples of soybean oil, cottonseed oil, palm oil, and peanut oil were donated by a large commercial company which requested anonymity.

The surfactants, their commercial names and their sources were:

ascorbyl-6-palmitate (AP) - Hoffman-La Roche, Nutley, N. J.;

mono- and diglycerides (MDG) - Dur-Em 114 K # 40% Mono, Durkee Food Service Group, SCM Corp., 900 Union Commerce, Cleveland, Ohio;

distilled monoglycerides (D. Mono.) - Dimodan PV (minimum 90% 1-monoglyceride), Grindsted Products, 201 Industrial Parkway, P.O. Box 26, Industrial Airport, Kansas;

sodium stearoyl 2-lactylate (SSL) - Stearolac S(444), ITT Paniplus, 100 Paniplus Roadway, Olathe, Kansas;

a mixture of soy oil, SSL, mono- and diglycerides, and ethoxylated mono- and diglycerides, Beta-Plus manufactured by Durkee Food Service Group, SCM Corp, 900 Union Commerce, Cleveland, Ohio;

ascorbyl-2-palmitate (A-2-P) - Sharon P. W. Lu, research assistant, Dept. of Grain Science and Industry, Kansas State University, Manhattan, Kansas;

ascorbyl-6-octanoate (A-6-0), ascorbyl-6-decanoate (A-6-DE), ascorbyl-6-undecanoate (A-6-U), and ascorbyl-6-dodecanoate (A-6-Dod) - Dr. Y. T. Liang, research associate, Dept. of Grain Science and Industry, Kansas State University, Manhattan, Kansas.

Premixes of AP and Surfactants

Premixes were made with 9 parts of AP and 1 part of another surfactant such as mono-diglycerides, Tween 60, or SSL. These materials were blended in a Tekmar micro mill (20,000 rpm) by milling ten seconds, scraping down the sides of the mill bowl, and then milling another 10 seconds to complete the process. This premix can then be added to the dry ingredients and incorporated into a dough system (Seib, 1977).

Premixes of AP with Solid Shortening Using Mortar and Pestle

A premix of AP and shortening was made by placing incremental amounts of shortening with AP in a mortar and "creaming" the mixture with a pestle (Seib, 1977).

Premixes of AP and Oil

The amount of AP necessary was added to a small beaker and the oil added on top. The mixture was stirred thoroughly with a spatula and added to the flour right before mixing.

Pre-Melts of AP with Shortening

AP was weighed into a small beaker with shortening and both compounds heated to melting at ~120°C. This solution was either added to the dough in the liquid form or allowed to return to form a plastic state and then added.

Straight Dough Pup Loaf (100 g) Bake Test

The bread dough formulation was taken from Finney and Barmore (1945). Each loaf was composed of 100 g of flour on a 14% moisture basis, 4 g of nonfat dry milk, 6 g of sucrose, and 1.5 g of salt. Water absorption, oxidant, diastatic malt, shortening, and yeast varied with the treatments and flours utilized. The formulas for all loaves were optimized for comparison purposes.

Doughs were mixed individually using a 100 g National pin mixer (National Mfg. Co., Lincoln, Nebraska). Bread doughs were fermented three hours with two punches at 105 and 155 minutes, and panned at 180 minutes. After proofing 55 minutes, the dough was baked at 215°C for 24 minutes (Finney and Barmore, 1943).

Loaf volumes were measured by rape seed displacement with standard deviation generally ranging from 12 to 18 cc.

Spread Test

The spread test was used as described by Hoseney, Hsu, and Junge (1979) and by Elkassabany and Hoseney (1980).

Resistance Baking Oven

Some doughs were baked in a resistance oven as described by Junge (1980).

Anti-Firming Measurement

Antifirming action was measured by compressibility using a Precision Scientific penetometer, Chicago, Illinois. Maleki and Seibel (1972) found a correlation coefficient of 0.88 between penetrometer readings and softness as determined by organoleptic tests. The penetrometer was fitted with a hemi-spherical nose whose penetration into the crumb of bread was recorded in units of 0.1 mm. The nose of the plunger (204 g) was positioned until it just began to touch the crumb, at which point it was released for 10 sec.

To prepare bread for penetrometer measurements, the bread was cooled 1 hour after baking in the open bakery at 25°C, and then bagged and stored at 25°C. Two 1.75" cubes were cut from each loaf. The sidewalls were removed by marking a 1.75" lengthwise and center slice on the bottom of the loaf and cutting away the sidewalls with two verticle lengthwise cuts. One of the exposed sides was then marked starting from approximately the center of the loaf with two lines 1.75" apart and parallel to the bottom of the loaf. The top and bottom of the loaf were cut away with horizontal cuts. A verticle cut was then made 0.25" from the left hand side. Starting from the freshly cut left end, two more verticle cuts were made 1.75" apart. Careful cutting with the aid of a slicing guide produced the two 1.75" cubes.

Penetrometer measurements were taken on all six sides of both cubes. Thus, the softness of each loaf was the mean of 12 penetrometer readings. Quadruplicate loaves were used for each daily measurement for each treatment. Measurements were taken 24, 72, and 120 hours after baking. In each anti-firming experiment, bread softened with a non-emulsified, hydrogenated vegetable shortening (Creamtex) was used as a control. The anti-firming data was adjusted by subtracting the readings of the "Creamtex" loaves from those of the test loaves. The standard deviation on the penetrometer readings of the 84 control Creamtex loaves was ± 16.1 units.

RESULTS AND DISCUSSION

Incorporation of AP in Dough by Stein-Milling AP with Dry Ingredients by Premixing AP with Another Surfactant, and by Slurrying with Water.

Birnbaum (1977) states that the relative efficiency of a surfactant as a dough conditioner is related to its degree of dispersion in a dough. Sodium stearoyl 2-lactylate (SSL), which is a salt, is readily dispersed by the water in a dough system. For that reason, SSL may be preblended as a dry powder with other dry ingredients in a dough. However, distilled monoglycerides, which carry no charge and are more hydrophobic than SSL, must be premixed with fat or prehydrated with water before they will disperse efficiently.

Ofelt (1958) reported a blackening of the crust when ascorbyl 6-palmitate was added as a dry powder to a bread formula. This result is probably due to the inability of AP to totally disperse in a dough. As mentioned in the introduction, Hoseney, Seib, and Deyoe (1977) circumvented the dispersion problem by using salt forms of fatty acid esters of ascorbic acid.

Prior to this study, unpublished data (Seib, 1977), indicated the following:

(1) premixes could be prepared by high speed blending a 9:1 mixture of AP and a second surfactant such as Tandem 8, Tween 60, mono-diglycerides, diacetyl tartaric acid esters of monoglyceride, or ethoxylated monoglycerides.

(2) the premix of AP with either distilled monoglycerides or Tween-60 produced the best bread when used at 0.5% level.

(3) the AP pre-mixes produced breads with a softer crumb than shortening plus mono-diglycerides.

This preliminary data showed that a premix of AP with a second surfactant provides a means by which AP can be added as a dry ingredient to a bread dough.

In Table III several samples of premixes of AP with mono-diglycerides (MDG) were tested for reproducibility. High speed, Stein milling of AP with the dry ingredients in the bread formulation (loaf 3C, Table III) produced a loaf of bread comparable to a shortening control (1C), which again showed that AP is capable of sparing shortening. Loaf volume was comparable, grain was slightly improved, and no specks were present on loaf 3C. Speckling results when total AP incorporation is not achieved. The Stein milled loaf (3C) was superior in performance to a no-shortening group (2C). Premix samples 4C, 5C, 6C, and 7C gave comparable results in terms of volumes and grain to the Stein-milled AP control (3C). These results indicated that there was no difference between loaves 4C and 5C which were produced from two different batches of 9:1 premix of AP-MDG. Adding an extra milling period (6C) or increasing the level of MDG (7C) in the premix did not produce any noticable improvement in the bread.

A control loaf (8C) was baked using a sample of AP that was micromilled alone to determine if the grinding itself was responsible for the improving effect of the pre-mixes. Loaf (8C) was prepared from AP that was micromilled alone with a Tekmar 10 g mill for two twenty second periods. The milled AP was then added to the dry ingredients which was processed into the bread in the usual manner. Loaf 8C showed a noticable drop in loaf volume and specks were visible on the crust. Micromilling of AP without a suitable surfactant does not give particles of AP that totally disperse in a dough.

Table III. Pup Loaf Bake Test of Several Premix Samples of Ascorbyl Palmitate with Mono-Diglycerides Compared with Shortening Control and Stein-Milled Controls.

			Amount in dough								
No.	Treatment	N	AP g	Lipid g	Flour[b] g	Premix or Lipid g	Water absorption %	Potassium bromate ppm	Average loaf volume cc	Grain[e]	Specks
1C	Control	5	0	3[c]	100	3	61	5	906	Acceptable	-
2C	No shortening	1	0	0	100	0	63	5	835	Very poor	-
3C	AP Stein milled with dry ingredients	3	0.5[a]	0	100	0.5	65	5	888	Good	-
4C	AP-MDG	3	0.45	0.05[d]	100	0.5	65	5	893	Excellent	-
5C	AP-MDG	2	0.45	0.05[d]	100	0.5	65	5	887	Good	-
6C[f]	AP-MDG	2	0.45	0.05[d]	100	0.5	65	5	882	Good	-
7C	AP-MDG	2	0.45	0.12[d]	100	0.57	65	5	870	Good	-
8C	Tekmar micro-mill Control, no-MDG	2	0.5	0	100	0.5	65	5	850	Good	+

[a] AP = ascorbyl palmitate (Hoffman-La Roche Lot #144037).

[b] KSU flour protein 11.4%, moisture 13.9%, ash 0.41%.

[c] Durkee's Creamtex a hydrogenated vegetable oil.

[d] MDG = mixture of mono-diglycerides (Dur-Em 114 K#, 40% Mono Durkee's).

[e] Rating scale: very poor, poor, acceptable, good, excellent.

[f] Three ten second micro mill periods as opposed to the regular two 10 sec periods for treatments Nos. 4C, 5C, and 7C.

The authors results verify previous findings on AP incorporation in bread dough. Successful incorporation of AP can be achieved by using a dry premix blend of 9 parts of AP and 1 part of MDG.

Mr. Howard Gordon of Hoffmann-La Roche suggested that a water slurry of AP might be used to incorporate AP uniformly into a dough. Table IV presents baking data using a water-slurry of AP and two different flours. The shortening control loaves (1D and 5D), no shortening loaves (2D and 6D), and premix loaves (4D and 7D) all showed no sign of specks on the crust. On the other hand, loaves made with a water-slurry of AP (3D, 8D, and 9D) all showed specks on their crust.

Loaves 8D and 10D in Table IV were prepared using AP that had been passed through a 60 mesh sieve (particle sizes <0.246 mm). This fine material was obtained by hand sieving of the AP supplied by Hoffmann-La Roche. The finer AP was then added in the form of a slurry (8D) or added by pre-blending with the dry ingredients (10D). Each sample showed less of a tendency to speck, which indicates that particle-size reduction might be a feasible method of incorporation.

It should be noted the KSU flour used in Table IV gave inferior response to the addition of the AP-MDG premix (compare loaves 7D and 5D) as compared to the response with the BCS flour (compare loaves 4D and 1D). The somewhat low loaf volume for bread made with KSU flour and AP was consistent throughout the experimental baking. To the author's knowledge, the KSU flour was treated only with benzoyl peroxide, and was said to be free of oxidants. However, the loaves containing AP appear overoxidized,

Table IV. Pup Loaf Bake Tests Using a Water Slurry of Ascorbyl Palmitate.

No.	Treatment	N	Amount in dough AP g	Amount in dough Lipid g	Flour g	Premix or Lipid g	Water absorption %	Potassium bromate ppm	Average loaf volume cc	Grain[g]	Specks
1D	Control	2	0	3.0[e]	97.95[a]	3.0	63	20	920	Good	-
2D	No short.	1	0	0	97.95[a]	0	65	20	805	Very poor	-
3D	AP water slurry	2	0.38[c]	0	97.95[a]	0.38	65	20	918	Good	+
4D	AP-MDG	2	0.342	0.038[d]	97.95[a]	0.38	65	20	978	Good	-
5D	Control	5	0	3.0[f]	100.0[b]	3.0	61	5	894	Good	-
6D	No short.	2	0	0	100.0[b]	0	63	5	818	Very poor	-
7D	AP-MDG	2	0.45	0.05[d]	100.0[b]	0.5	65	5	870	Good	-
8D	Water slurry, 60 Mesh - AP	1	0.5	0	100.0[b]	0.5	65	5	870	Good	+[h]
9D	Water slurry, AP	2	0.5	0	100.0[b]	0.5	65	5	825	Good	+
10D	60 mesh-AP, Dry blend with flour	2	0.5	0	100.0	0.5	65	5	880	Good	+[h]

[a] Flour BCS 79, protein 12.4%; moisture 12.2%.

[b] KSU flour protein, 11.4%; moisture, 13.9%; ash, 0.41%.

[c] AP = ascorbyl palmitate (Hoffman-La Roche Lot #144037).

[d] MDG = mono-diglycerides (Dur Em 114 K# 40% mono Durkee).

[e] Shortening = Crisco vegetable shortening, Proctor and Gamble)

[f] Shortening = Durkee's Creamtex hydrogenated vegetable oil.

[g] Grain rating: Excellent, good, acceptable, poor, very poor.

[h] Specks hardly noticable.

which depressed the loaf volume. SSL in this same flour did not show any reduction in loaf volume.

Mixtures of AP and Solid Fats in Breadmaking

AP can be successfully added to bread dough if it is first dispersed in fat. If the fat is a shortening, then AP can be creamed with the shortening by adding incremental amounts of shortening to AP and mixing them with a mortar and pestle (Seib, 1977). Previous data showed that AP in the creamed blend was beneficial to grain and no specks were observed on the loaves.

Another method of preparing pre-blends of AP and solid fat is to heat the AP with the shortening to ~120^{o}C. This melt may be cooled to ~60^{o}C, and then added as a fluid at the mixer, or it may be cooled to a solid plastic fat and added at the mixer. Table V gives baking data on the use of pre-melts of shortening and AP. When the premelt was cooled to the plastic state, the loaves (6E and 7E) were comparable in grain and volume to the shortening control loaf (1E), and no specks were observed. However, when the premelt was added in a fluid state the loaves (4E and 5E) gave comparable volumes and grain to the shortening control (1E), but specks were observed on the crust.

AP melted with shortening is capable of producing a relatively stable mixture with the fat that allows incorporation of AP into bread dough. From the data in Table V, it appears that better dispersion of AP is achieved if the pre-melt is cooled so the shortening sets to a plastic state before the premelt is added to a dough.

Table V. Pup Loaf Bake Test on Incorporation Using Pre-melts (Loaves 4E, 5E, 6E, and 7E) of Ascorbyl-6-Palmitate with Shortening.

No.	Treatment	N	Amount in dough AP g	Amount in dough Lipid g	Flour g	Premix or Lipid g	Water absorption %	Potassium bromate ppm	Average loaf volume cc	Grain[e]	Specks
1E	Control	5	0	3.0[c]	100.0[a]	3.0	61	5	894	Good	-
2E	No short.	2	0	0	100.0	0	63	5	818	Very poor	-
3E	AP MDG premix	2	0.45[b]	0.05[b]	100.0	0.5	65	5	850	Good	-
4E	60 Mesh AP[f]	2	0.5	3.0[c]	100.0	3.5	61[h]	5	863	Good	+
5E	AP[f]	1	0.5	3.0[c]	100.0	3.5	61	5	885	Good	+
6E	60 Mesh AP[g]	3	0.5	3.0[c]	100.0	3.5	61	5	862	Good	-
7E	AP[g]	3	0.5	3.0[c]	100.0	3.5	61	5	885	Excellent	-

[a] KSU flour protein, 11.4%; moisture, 13.9%; ash 0.41%.

[b] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037).

[c] Creamtex - a hydrogenated vegetable oil, Durkee.

[d] MDG = monodiglycerides (Durkee Dur Em 114 K# 40% Mono).

[e] Grain rating: Very poor, poor, acceptable, good, excellent.

[f] Pre-melt of shortening and AP added to dry formulation in warm liquid state.

[g] Pre-melt of shortening and AP added to dry formulation in solid plastic state.

[h] Absorption kept at 61% because of presence of 3% shortening.

A premix of AP and plastic shortening could be a convenient and economical method of incorporating AP into bread. The fat might also help prevent breakdown of AP due to oxidation or hydrolysis. Commercial combinations of SSL and plastic shortening are already used by bakers.

One important function of surfactants is their ability to replace or reduce shortening levels in bread. The levels of shortening and AP were varied in breadbaking, and the results given in Table VI. When as little as 0.1 g of AP (12F) and 3.0 g of shortening were added to a loaf, the volume was improved over a 3.0 g shortening control (1F). Volumes comparable to the optimum level of 0.38 g of AP alone (4F) were obtained by adding 0.15 g of AP to 3.0 g of shortening (13F). Results superior to the shortening control (1F) group were obtained when 0.38 g of AP and 0.5 g of shortening were added (6F). With additions of 0.38 and 0.25 g of AP in combination with 1.0 and 1.5 g of shortening (7F, 8F, 9F, 10F), volumes and grains superior to control loaves (1F) were obtained. A baker could replace shortening in a bread dough with approximately 0.38 g of AP/100 g flour or he could reduce his shortening level by two-thirds and use a combination of 1.0 g of shortening and 0.25 g of AP. When used in combination with 3.0 g of shortening, very low levels of AP can be used to improve the volume and crumb characteristics of bread. AP alone at 0.135% or 0.045% is not sufficient to replace shortening (16F and 17F).

Also of interest in Table VI was the fact that adding 3.0 g of shortening to the optimum level of 0.38% AP gave no further improvement in loaf volume or grain over that achieved by the AP alone. Similar results were found by Hoseney, Finney, and Shogren (1972) when they tested

Table VI. Pup Loaf Baking Test Results of Mixtures of Ascorbyl-6-Palmitate and Shortening.

No.	Treatment	N	in dough AP g	in dough Lipid g	Flour g	Premix or Lipid g	Water absorp-tion %	Potas-sium Bromate ppm	Average loaf volume cc	Grain[g]	Specks
1F	Control	4	0	3.0[e]	97.95[a]	3.0	63	20	935	Acceptable	-
2F	No short.	1	0	0	97.95	0	65	20	875	Very poor	-
3F	AP[c]	2	0.25[d]	0	97.95	0.25	65	20	918	Acceptable	-
4F	AP[c]	1	0.38	0	97.95	0.38	65	20	975	Good	-
5F	AP & short.[b]	1	0.25	0.5[e]	97.95	0.75	65	20	920	Good	-
6F	AP & short.[b]	3	0.38	0.5[e]	97.95	0.88	65	20	986	Good	-
7F	AP & short.[b]	2	0.25	1.0[e]	97.95	1.25	65	20	953	Good	-
8F	AP & short.[b]	3	0.38	1.0[e]	97.95	1.38	65	20	963	Good	-
9F	AP & short.[b]	1	0.25	1.50[e]	97.95	1.75	65	20	965	Good	-
10F	AP & short.[b]	2	0.38	1.50[e]	97.95	1.88	65	20	970	Good	-
11F	AP & short.[b]	3	0.05	3.0[e]	97.95	3.05	65	20	943	Acceptable	-
12F	AP & short.[b]	3	0.10	3.0[e]	97.95	3.10	67	20	962	Acceptable	-
13F	AP & short.[b]	3	0.15	3.0[e]	97.95	3.15	67	20	972	Good	-
14F	AP & short.[b]	3	0.25	3.0[e]	97.95	3.25	67	20	960	Good	-
15F	AP & short.[b]	3	0.38	3.0[e]	97.95	3.38	67	20	973	Excellent	-
16F	AP MDG (premix)	1	0.045	0.005[f]	97.95	0.05	67	20	855	Poor	-
17F	AP MDG (premix)	1	0.135	0.015[f]	97.95	0.15	67	20	875	Poor	-
18F	AP MDG (premix)	2	0.342	0.038[f]	97.95	0.38	67	20	973	Excellent	-

[a] BCS 79, protein, 12.4%; moisture, 12.2%.

[b] AP and shortening combinations prepared by preblending solid shortening with AP using a mortar and pestle.

[c] AP Stein-milled 15 sec with all dry ingredients.

[d] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037.

[e] Crisco vegetable shortening, Proctor and Gamble.

[f] MDG = mono-diglyceride (Dur Em 114 K# 40% mono Durkee).

[g] Grain ranking: very poor, poor, acceptable, good, excellent.

sucrose monotallowate with shortening. Tsen and Hoover (1971), however, reported that the addition of a mixture of shortening and SSL gave a higher specific volume than SSL or shortening alone. But Tsen and Hoover (1971) tested SSL with 1 and 2% shortening and not with 3% shortening. The data in Table VI indicates that maximum loaf volume was achieved with the optimum level of 0.38 g of AP (4F and 18F) added alone. Other combinations of AP and shortening could match the loaf volume performance but did not exceed it.

Solid fats can thus be used as a carrier for AP into bread doughs. Furthermore, 0.25% AP can be used to replace 2/3 of the shortening normally used in bread. A loaf made with 0.25% AP and 1% shortening was equivalent to a loaf made with 3% shortening.

Mixtures of AP and Oils in Breadmaking

In baking formulations for bread, one area of change in recent years has been the type and amount of lipid or fat used in doughs. Early in this century lard was the main lipid ingredient added to bread doughs. With the discovery of hydrogenation of vegetable oils to form plastic fats, hydrogenated oils became an attractive alternative to lard. Del Vecchio (1977) reported that over 50% of the 333 million pounds of fat products used for edible and inedible consumption is soybean based.

Simon Jackel (1980) recently pointed out a new trend in lipids used by bakers. He reported that bakers are generally reducing the levels of lipids used in baked goods and that as much as 80% of the wholesale production of bread and rolls is now carried out using liquid vegetable oils. He credits the switch to oils to the increased use of surfactants.

Soybean is the primary oil used and the lipid levels have been reduced from 3% as a standard to 2% based on flour weight. With this trend in mind, the use of mixtures of AP in oil was tested in breadmaking.

Table VII presents data using corn oil and soy oil in combination with AP. Corn oil (3G) and soy oil (4G) by themselves are incapable of replacing shortening. The loaf volumes of loaves 3G and 4G are better than a no shortening loaf (2G), but the grain of the bread is open and poor. Generally, the loaf volume loss when an oil is substituted for lard or shortening is more substantial than that reported in Table VII. Additional data on the loaf-volume depressing effect of soy oil was reported in Table VIII, loaf 4H. Several bake tests with corn oil, cottonseed oil, and peanut oil also gave poor volume and grain, although the results are not reported here.

AP used in combination with corn oil (5G and 6G) and soy oil (9G) improved loaf volume and grain over the shortening control loaf (1G) and AP-shortening premix loaves (7G and 8G). A sample of AP suspended in melted shortening (10G, $60^{\circ}C$) did not perform as well as AP in oil.

Surfactants are commonly used with oils to reduce the amount of lipid necessary for a formula and to improve grain and loaf volume. Garton (1978) presented evidence that the fluid shortening "Beta Plus" was able to cut fat levels by 10-25% in bread. "Beta Plus" is a commercial product manufactured by Durkee Foods Service Group. It is a mixture of soy oil, SSL, mono- and diglycerides, and ethoxylated monoglycerides.

Table VII. Pup Loaf Bake Test Samples of Ascorbyl-6-Palmitate Incorporation Using Oil.

No.	Treatment	N	Amount in dough AP g	Amount in dough Lipid g	Flour[a] g	Premix or Lipid g	Water absporption %	Potassium Bromate ppm	Average loaf volume cc	Grain	Specks
1G	Control	4	0	3.0[c]	97.95	3.0	63	20	935	Acceptable	-
2G	No. short.	2	0	0	97.95	0	65	20	890	Very poor	-
3G	Corn oil	1	0	3.0[d]	97.95	3.0	63	20	925	Poor	-
4G	Soy oil	2	0	3.0[e]	97.95	3.0	63	20	945	Poor	-
5G	AP and corn oil	3	0.25[b]	3.0[d]	97.95	3.25	67	20	1015	Good	-
6G	AP and corn oil	3	0.38	3.0[d]	97.95	3.38	67	20	1008	Good	-
7G	Premix AP-Crisco[f]	3	0.25	3.0[c]	97.95	3.25	67	20	960	Good	-
8G	Premix AP-Crisco	3	0.38	3.0[c]	97.95	3.38	67	20	973	Excellent	-
9G	AP & soy oil	2	0.25	3.0[e]	97.95	3.25	67	20	1000	Acceptable	-
10G	Melt (75°C) AP-Crisco[g]	3	0.25	3.0	97.95	3.25	67	20	948	Good	+

[a]BCS 79, protein 12.4%, moisture 12.2%.

[b]AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037.

[c]Shortening = Crisco vegetable shortening, Proctor and Gamble.

[d]Corn oil = Mazola corn oil, Best Foods, A division of CPC International, Inc., General Offices, Englewood, Cliffs, NJ.

[e]Soy oil = pure cold pressed soy oil, Hain Pure Food Co., Inc., Los Angelas, California.

[f]Plastic shortening and AP combined using mortar and pestle.

[g]AP was added by placing it in melted shortening; AP itself did not melt in the mixture.

Table VIII. Pup Loaf Bake Test Samples of Combinations of Soy Oil and Ascorbyl-6-Palmitate.

No.	Treatment	N	Amount in dough AP g	Amount in dough Lipid g	Flour[a] g	Premix or Lipid g	Water absorption %	Average loaf volume cc	Grain
1H	Control	6	0	3.0[c]	98.85	3.0	64	932	Good
2H	No short.	2	0	0	98.85	0	68	850	Very poor
3H	AP-Stein-Mill.	3	0.38[b]	0	98.85	0.38	68	952	Good
4H	Soy oil	3	0	3.0[d]	98.85	3.0	68	888	Poor
5H	Soy oil + AP	2	0.15[b]	3.0[d]	98.85	3.15	68	945	Poor; open grain
6H	Soy oil + AP	3	0.25[b]	3.0[d]	98.85	3.25	68	952	Acceptable
7H	Soy oil + AP	3	0.38[b]	3.0[d]	98.85	3.38	68	967	Acceptable
8H	Soy oil + AP	3	0.50[b]	3.0[d]	98.85	3.50	68	958	Good
9H	Soy oil + AP	3	0.75[b]	3.0[d]	98.85	3.75	68	947	Good
10H	Soy oil + AP	4	0.38[b]	2.0[d]	98.85	2.38	68	925	Good
11H	Soy oil + AP	4	0.38[b]	1.5[d]	98.85	1.88	68	945	Excellent
12H	Soy oil + AP	4	0.38[b]	1.0[d]	98.85	1.38	68	925	Excellent
13H	SSL	3	0.38[f]	0	98.85	0.38	68	963	Excellent
14H	Soy oil + SSL	3	0.38[f]	3.0[d]	98.85	3.38	68	965	Excellent
15H	Beta plus[e]	1	-	-	98.85	0.5	68	890	Poor
16H	Beta plus[e]	2	-	-	98.85	1.5	68	965	Good
17H	Beta plus[e]	2	-	-	98.85	3.0	68	1008	Good

[a] Ross bake flour, protein 11.44%, moisture 13.0%.

[b] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037).

[c] Shortening = Creamtex vegetable shortening, Durkee Foods.

[d] Soy oil = Donated sample

[e] Durkee Beta plus

[f] SSL = sodium stearoyl-2 lactylate = ITT Paniplus.

Table VIII contains data collected on pup loaves in which the levels of soy oil and AP were varied. Soy oil (4H) alone gave inferior grain and volume when compared with the shortening control (1H). The soy oil results were comparable to a no-shortening loaf (2H). The addition of as little as 0.15 g of AP (5H) produced a loaf volume comparable to an optimum stein milled loaf (3H) and better than a shortening (1H) loaf. However, 0.25 g of AP (6H) was necessary to improve the grain to an acceptable level using soy oil. The best results were obtained with 0.38 g of AP added with 3.0 g of soy oil (7H). Additions of larger amounts of AP (8H and 9H) gave no further improvement over the 0.38 g level. In fact, the loaves with a mixture of 0.38 g AP and 3% soy oil (7H) were comparable to loaves containing 0.38% AP alone (3H). When an optimum level of AP (0.38 g) was used and the level of soy oil reduced (7H, 10H, 11H, 12H), the grain tended to improve while the volume remained essentially unchanged.

Sodium stearoyl-2-lactylate (SSL) alone (13H) and in combination with soy oil (14H) gave slightly better volume and superior grain compared to loaves made with mixtures of AP and soy oil. A commercial product composed of SSL and soy oil ("Beta Plus"; 15H, 16H, 17H) showed, at a level of 1.5%, volume and grain in bread comparable to 0.38% SSL (13H), 0.38% AP (3H), or mixtures of oil and AP or SSL (7H, 14H). A 3.0% level of "Beta Plus" gave a larger volume than AP with or without oil.

The data tends to indicate that a surfactant is needed in dough made with oil. The oil system requires a surfactant to produce an acceptable grain. In contrast, when bread is made with sufficient amounts of shortening (~3%), no surfactant is needed to produce a desirable grain. It could be that when no surfactant is used plastic shortening is needed to entrain the fine nuclei bubbles during mixing.

AP alone at 0.38% produced bread with better grain than that obtained with mixtures of 1.0, 1.5, and 2.0% of oil. Although loaf volumes were comparable for mixtures of AP and soy oil, SSL and soy oil, and "Beta Plus," the latter two mixtures gave bread with better grain.

Comparison of AP and SSL

As mentioned earlier, SSL is a widely used surfactant in the baking industry. It is capable of replacing or reducing shortening levels, it is economical, it is easily dispersible, it improves volume and grain, and it has antifirming properties.

Table IX presents optimization data on levels of AP and SSL. Both compounds at a level of 0.25% are capable of replacing shortening (compare 7J and 3J to 1J). The SSL loaves (7J, 8J, 9J, 10J) tended to give higher volume and had better grain than the comparable AP loaves (3J, 4J, 5J, 6J). Higher levels of AP (5J and 6J) tended to be more detrimental to the loaf volume than higher levels of SSL (9J and 10J). Visual examination of the loaves indicates that AP has more of a "strengthening" effect than SSL. Therefore, high levels of AP appear to give doughs that are too strong and these do not expand properly.

Another useful property of surfactants is their "water-carrying" capacity in a dough, which could be useful as tolerance to too much water in a dough as well as higher moisture in the baked bread. Figure 2

Table IX. Loaf Volume Effects of Replacing Shortening with Various Levels of Ascorbyl-6-Palmitate and Sodium Stearoyl 2-Lactylate in Pup Loaves.

No.	Treatment[a]	N	Shortening g	Additive g	Absorption %	Average loaf volume cc	Grain
1J	Control	5	3.0[d]	0	64	948	Good
2J	No. Short.	2	0	0	68	878	Poor
3J	AP	2	0	.25[b]	68	955	Poor
4J	AP	2	0	.38[b]	68	958	Good
5J	AP	1	-	.50[b]	68	905	Acceptable
6J	AP	2	0	.75[b]	68	908	Good
7J	SSL	2	0	.25[c]	68	960	Excellent
8J	SSL	2	0	.38[c]	68	998	Excellent
9J	SSL	2	0	.50[c]	68	965	Excellent
10J	SSL	2	0	.75[c]	68	950	Good

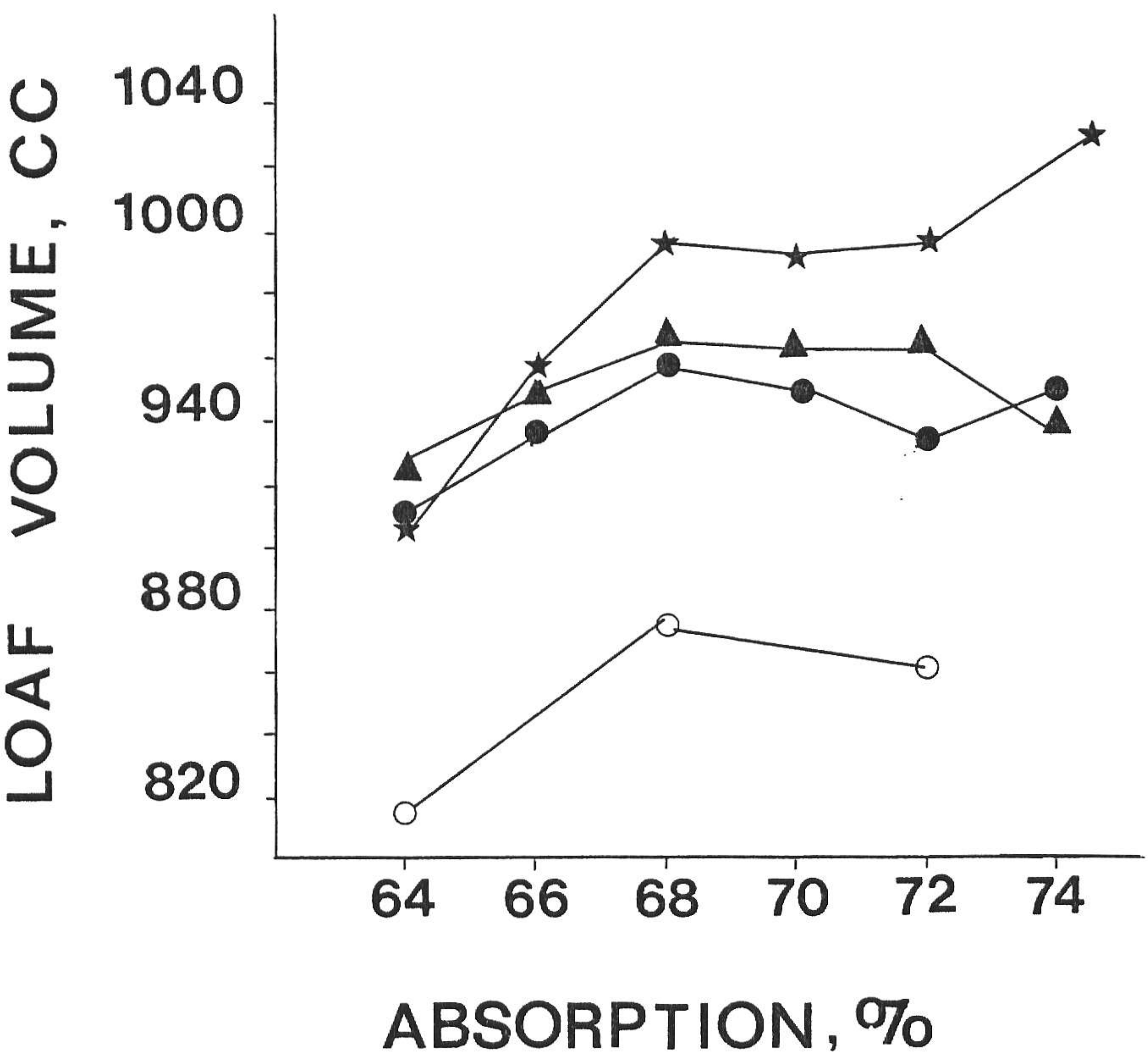
[a] Ross bake flour, protein 11.44%, moisture 13.0%.

[b] AP = ascorbyl 6-palmitate (Hoffman-LaRoche Lot #144037).

[c] SSL = sodium stearoyl 2-lactylate (ITT Paniplus).

[d] Shortening = Creamtex vegetable shortening, Durkee Foods.

Figure 2. Effects of absorption on loaf volume for loaves with different lipids. AP (0.38 g/100 g flour) ● ; SSL (0.38 g/100 g flour) ★ ; shortening control (3.0 g/100 g flour) ▲ ; no shortening ○ .


LOAF VOLUME, CC
1040
1000
940
880
820
64
66
68
70
72
74
ABSORPTION, %

presents loaf volumes at different absorption levels for 0.38% SSL, 0.38% AP, 3% shortening, and a no-shortening control. Confidence intervals ($p<.05$) indicated no significant difference between loaf volumes at each absorption level for AP, SSL, and shortening. All the groups were significantly different from the no-shortening control. Both SSL and AP were capable of carrying an increase in absorption of 10 percentage points, although the doughs were rather sticky at 74% absorption.

Optimum absorption level for the 3% shortening control was 64%, and higher levels of water improved volume but also tended to open the grain. Optimum absorption levels for SSL and AP was 68%. It was generally found in bake tests using several different flours, a 4% increase in absorption over a shortening control loaf produced the best overall results in terms of volume and grain appearance when 0.25 - 0.38% AP or SSL were added to the loaf.

Combinations of SSL and AP were compared in Table X to determine if synergistic effects occur when both surfactants are added to dough. A 9:1 premix of AP with MDG was used in this part of the investigation. The ratio of the premix to SSL in the bread was varied from 1:1 to 9:1. No synergistic action of the two surfactants was observed. The loaves with a larger proportion of AP were slightly lower in loaf volume than those with a larger proportion of SSL (compare loaves 5K, 6K, and 7K). We did find that SSL could be used in place of a mono-diglyceride as the dispensing surfactant in preparing AP premixes for use in bread. Loaf 9K was prepared using a 1:1 premix of AP-SSL. The pre-mix was

Table X. Pup Loaf Bake Tests with Mixtures of Ascorbyl-6-Palmitate and SSL.

No.	Treatment	N	Amount in dough: Premix AP g	Amount in dough: Premix Lipid g	SSL g	Ratio of $\frac{\text{AP Premix}}{\text{SSL}}$	Flour g	Water Absorption %	Potassium bromate ppm	Ave. loaf volume cc	Grain
1K	Control	3	0	3.0	0	-	100.0[a]	61	5	845	Good
2K	No short.	2	0	0	0	-	100.0	63	5	765	Very poor
3K	AP MDG premix	1	0.45	0.05	0	-	100.0	65	5	825	Excellent
4K	SSL	1	0	0	0.5[c]	-	100.0	65	5	885	Cood
5K	SSL + APMDG[d] premix	3	0.027	0.003	0.27	1:9	100.0	65	5	842	Acceptable
6K	SSL = APMDG premix	1	0.081	0.009	0.21	3:7	100.0	65	5	835	Good
7K	SSL = APMDG premix	2	0.135	0.015	0.15	1:1	100.0	65	5	823	Good
8K	SSL + APMDG premix	3	0.225	0.025	0.25	1:1	100.0	65	5	828	Excellent
9K	Premix of SSL-AP	1	0.25	0	0.25	1:1	100.0	65	5	840	Excellent

[a]KSU flour, protein 11.4%; moisture, 13.9%; ash, 0.41%.

[b]AP - ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037).

[c]SSL = sodium stearoyl lactylate (ITT, Paniplus, Olathe, KS).

[d]APMDG is a 9:1 premix of AP with MDG = mono-diglyceride (Dur EM 114 K# 40% Mono Durkee).

prepared as usual by high-speed blending in a micro-mill for two 10 second mixing periods. Loaf 9K gave good loaf volume and excellent grain.

Figure 3 confirms, by a different method, the loaf volume results of Figure 2 (page 31). The graph in Fig. 3 shows a plot of loaf height with time as dough is baked by resistance heating. In this type of baking procedure, a dough piece is placed between two plates. When an AC voltage is applied across the plate, the dough is heated uniformly and expands. The height of the dough is proportional to loaf volume. As Junge (1980) has stated, the shape and height of the resistance-heating curve is related to the gelatinization of starch which controls the set temperature of the loaf.

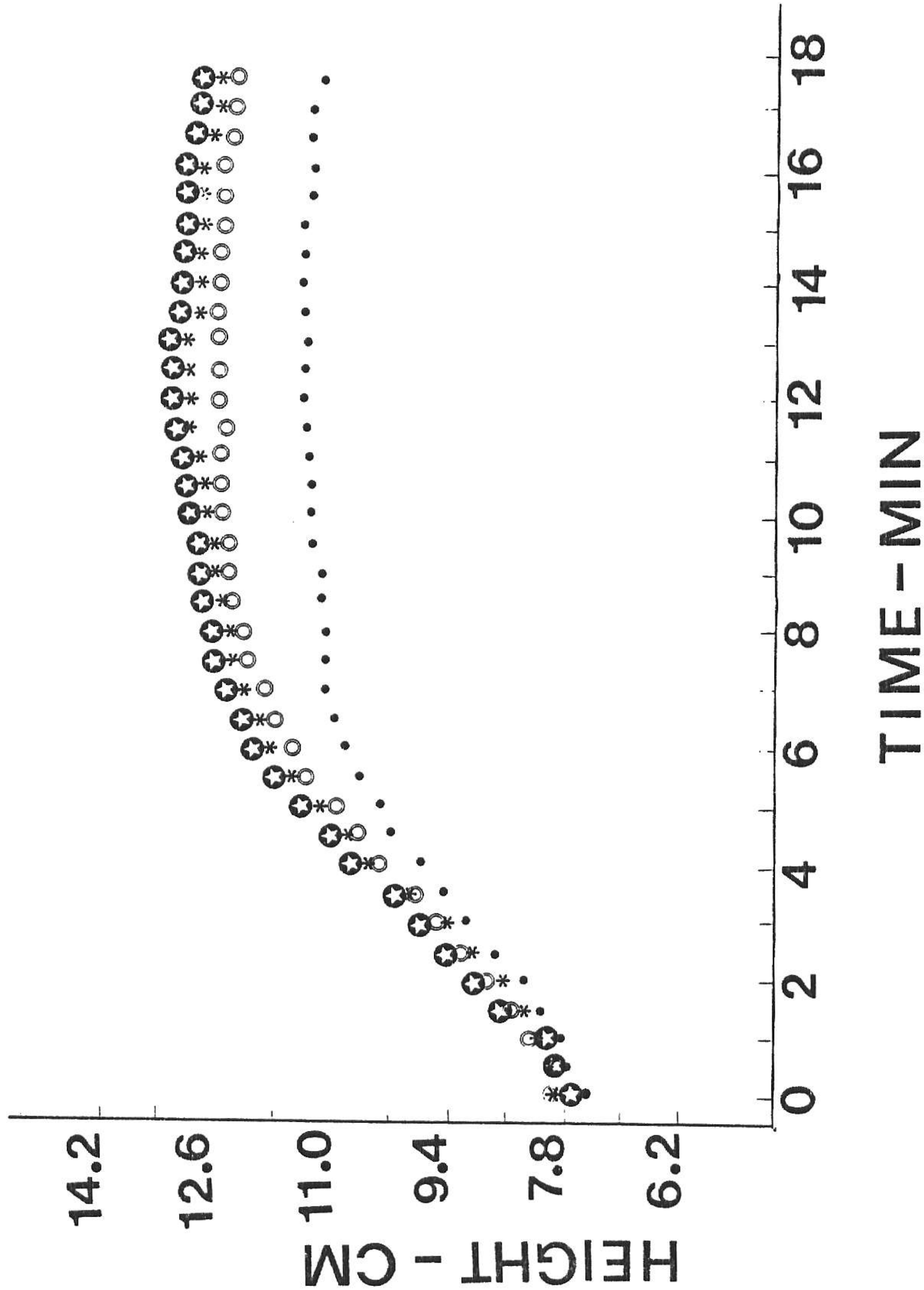
As shown in Fig. 3, the curves for a shortening control, SSL, and AP are all similar. The three doughs show a longer set time (higher set temperature) than the no shortening control, and they also show a more rapid rise in volume with time.

Comparison of Anti-firming Action

One very important property of certain surfactants is their ability to soften the crumb of bread. The anti-firming action of several crumb softeners were compared, including SSL (0.38%), AP (0.38%), a mixture of distilled monoglyceride (0.5%) and "Creamtex" (3%), a mixture of SSL (0.38%) and "Creamtex," (3.0%).

Anti-firming measurements were taken on quadruplicate loaves by slicing two cubes from a loaf and measuring the softness of each cube from all

Figure 3. Resistance oven data. No shortening (●), shortening (◎), SSL (✪), and AP (*).


HEIGHT - CM
14.2
12.6
11.0
9.4
7.8
6.2
TIME - MIN
0
2
4
6
8
10
12
14
16
18

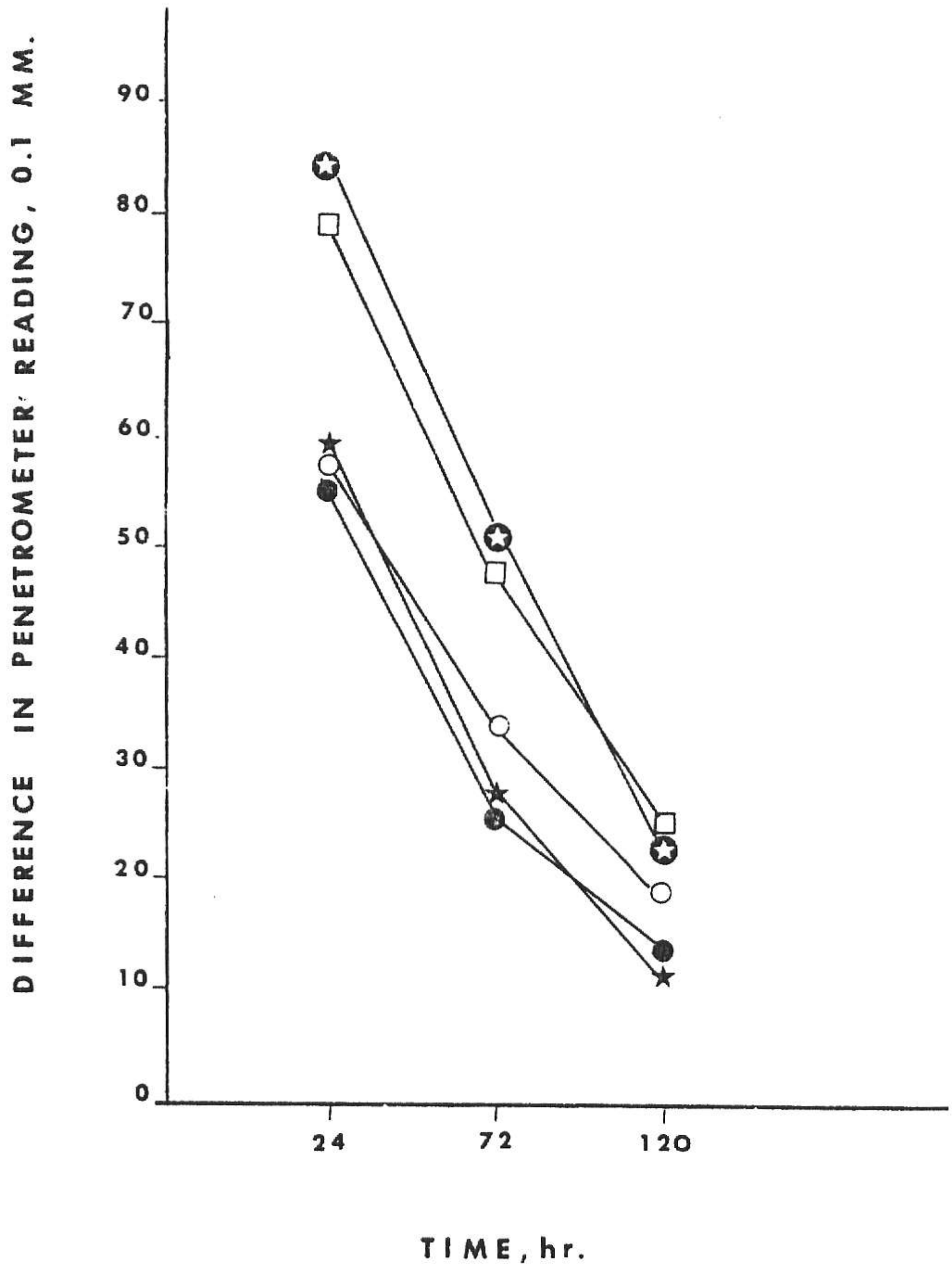
six sides with a penetrometer. In that manner, the penetrometer reading for a given softener at a given staling time represents the mean of 48 observations.

When the anti-firming action of a softener was tested, a bake was done in which loaves contained either the softener in question or a "creamtex" control group. Penetrometer readings were taken on the test loaves and the "creamtex" loaves 24, 72, and 120 hours after baking. The penetrometer readings were normalized by subtracting the "creamtex" control group from the softener group readings. Figure 4 shows a graph of the adjusted penetrometer reading for each of the five softeners tested.

The adjusted penetrometer values were analized statistically using analysis of variance and Duncan's multiple range tests. No significant difference was found between the adjusted values of SSL and AP both of which were used at 0.38%. As the positive values in Fig. 4 indicate, all the loaves baked with the five test softeners were significantly softer than those containing "creamtex" shortening alone (mean data for penetrometer values are presented in Table I-A page 61). However, SSL and AP both gave significantly softer bread crumb than a mixture of distilled monoglycerides (0.5%) and "creamtex" shortening (3%), as well as the mixtures of AP (0.38%) or SSL (0.38%) with "creamtex" (3%). As anti-firming agents, SSL and AP were more effective when used alone than when used in combination with shortening. This observation on the salt form of AP had been previously made by Hoseney et al (1977). A distilled monoglyceride group alone was not tested because distilled monoglycerides are incapable of replacing shortening.

Figure 4. Adjusted penetrometer values for bread containing various softeners. The adjusted values were obtained by subtracting penetrometer readings for loaves containing a "creamtex" shortening from readings on loaves containing a test softener. SSL (0.38%)✪, AP (0.38%)□, distilled monoglycerides (0.5%) and "creamtex" (3.0%)○, SSL (0.38%) and "creamtex" (3.0%)★, and AP (0.38%) and "creamtex" (3.0%)●

DIFFERENCE OF MEAN PENETROMETER READINGS



In summary, AP appears to function comparably to SSL in breadmaking. Both materials are better anti-firming agents when used alone than when used together with shortening. They both replace shortening at ~0.38%. They improve crumb grain and increase absorption by 4%. SSL has advantages over AP in that it is easier to incorporate, it is cheaper, and it tends to give more consistent volumes and a somewhat finer grain. However, AP provides a source of vitamin C in bread. FDA approval of AP as a source of vitamin C would allow the compound to be labeled vitamin C palmitate. On the ingredient legend of a loaf, that name might provide a labeling advantage over surfactants with "chemical names" in bread doughs.

EFFECTS OF CHAIN LENGTH AND STRUCTURE ON BAKING PROPERTIES OF FATTY ACID ESTERS OF ASCORBIC ACID

Ofelt et al (1958) reported that both chain length and structural differences were important factors in a surfactants antifirming properties. Hoseney, Seib, and Deyoe (1977), also indicated that the ten carbon fatty acid ester of ascorbic acid (6-caprate) and the palmitic ester on the 2-position (2-palmitate) would not replace shortening in bread doughs (Table I, page 6). We undertook a series of bakes with ascorbyl 2-palmitate, ascorbyl 6-octanoate, ascorbyl 6-decanoate, ascorbyl 6-undecanoate, and ascorbyl 6-dodecanoate in order to determine which compounds were effective shortening replacers.

Ascorbyl 2-Palmitate (A-2-P)

Ascorbyl 2-palmitate (A-2-P) did not function to replace shortening in bread (Table I; page 6). In order to determine if A-2-P is hydrolyzed to ascorbic acid (AA) in a dough, the spread test was used. This method was developed by Hoseney, Hsu, and Junge (1979) to determine the effects of various fast, medium, and slow acting oxidants in doughs. Lillard (1980) used this method recently to determine that AA is a moderately rapid oxidant in dough. Elkassabany and Hoseney (1980) showed that as little as 15 ppm of AA is required to produce the maximum effect of that oxidant on dough flour. If AA is released by hydrolysis of A-2-P, then the spread test might be used to detect AA.

Table XI is a list of spread test results taken after 180 minutes fermentation time. Oxidizing effects are evidenced by lower spread ratios. A lower ratio indicates the dough has more resistance to flow

Table XI. Spread Ratios at 180 Minutes Fermentation of Flour-Water Doughs Containing A-2-P, AP, Ascorbic Acid, $KBrO_3$, and Palmitic Acid.

Treatment	Level, g	Spread ratio
Flour	-	3.6
Palmitic acid	0.29	4.1
Ascorbyl 6-palmitate	0.5	3.0
Ascorbyl 2-palmitate	0.5	2.4
Ascorbic acid	0.19	2.6
$KBrO_3$	0.002	2.3
$KBrO_3$ + ascorbic acid	0.002 + 0.19	2.3

than a dough with a higher spread ratio. The palmitic acid, AP, and A-2-P were added to the flour via the 9:1 MDG premix method described earlier in this paper.

The control dough and a dough containing palmitic acid gave the greatest flow properties (spread ratios, 3.6 and 4.1, respectively). Palmitic acid was added in amounts equivalent to that in a dough containing 0.5% AP. AP showed a slight oxidizing effect by reducing the spread ratio to 3.0. A-2-P, however, lowered the ratio to 2.4 which was comparable to the value of 2.6 observed for addition of an equal molar quantity of AA. Potassium bromate and a combination of potassium bromate and ascorbic acid gave the lowest spread ratio of ~2.3. This data indicates that A-2-P is not replacing shortening in a loaf of bread because it hydrolyzes in the dough to give AA and palmitic acids.

Baking data for A-2-P is given in Table XII. In this bake test, the shortening control (1M), AP without shortening (3M), and AP with shortening (4M) all produced loaves with comparable volume and grain. A-2-P at the same level with and without shortening (7M and 8M) produced loaves with reduced volume and unsatisfactory grain. Those loaves had a strong, well oxidized appearance, so reduced levels of A-2-P were used in 9M thru 12M. But the volume and grain of loaves 9M through 12M showed no sign of improvement. It should be noted that ascorbic acid at a concentration comparable to that in 0.5 g of A-2-P produced unacceptable loaves of bread with and without shortening (5M and 6M).

Table XII. Effects of Level, Absorption and Shortening on Bread Baking Capacity of Ascorbyl-2-Palmitate in Pup Loaves Based on 100 Grams of KSU FLour.

No.	Treatment[a]	N	Shortening g	Additive g	Absorption %	Potassium bromate	Average loaf volume cc	Grain[e]
1M	Control	6	3.0[b]	0.0	61	5	898	S
2M	No shortening	3	0.0	0.0	63	5	836	U
3M	AP-6-premix	3	0.0	0.5[c]	65	5	908	S
4M	AP-6-premix	1	3.0[b]	0.5[c]	61	5	908	S
5M	Ascorbic acid	1	0.0	0.19	65	5	895	U
6M	Ascorbic acid	2	3.0[b]	0.19	61	5	900	U
7M	A-2-P premix	1	0.0	0.5[d]	65	5	860	U
8M	A-2-P premix	1	3.0[b]	0.5[d]	61	5	860	U
9M	A-2-P premix	1	0.0	0.25[d]	65	5	810	U
10M	A-2-P premix	1	0.0	0.12[d]	65	5	745	U
11M	A-2-P premix	1	0.0	0.06[d]	65	5	775	U
12M	A-2-P premix	1	0.0	0.01[d]	65	5	810	U

[a] KSU flour protein 11%, moisture 13.9%.

[b] Creamtex = Durkee's hydrogenated vegetable oil.

[c] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037.

[d] A-2-P = ascorbyl-2-palmitate; laboratory manufactured.

[e] Satisfactory, S; unsatisfactory, U.

Dough systems can tolerate high amounts of ascorbic acid without detrimental overoxidizing effects. In Table XII, the ascorbic acid samples (5M and 6M) both produced loaves with poor grain. The addition of shortening in 6M should have produced acceptable bread. Therefore, it appeared the problem with loaf 6M was due to overoxidation caused by the use of potassium bromate in the loaf.

If A-2-P is hydrolyzing in dough and releasing large amounts of ascorbic acid, then an acceptable loaf of bread should be obtained with A-2-P by adding 3.0 g of shortening and removing the potassium bromate from the formula. Removal of potassium bromate should prevent any overoxidation, while addition of shortening should prevent a "no shortening" appearance to the grain.

This hypothesis was tested in a baking experiment and the results are given in Table XIII. The control group with 3% shortening (1N) produced unacceptable loaves (2N) when bromate was removed. The no shortening controls (3N and 4N) were unacceptable whether bromate was present or not. The effect of no bromate in the shortening control group (2N) was detrimental in terms of loaf volume and grain. Since palmitic acid exhibits neither an oxidizing nor a shortening sparing effect, acceptable loaves should have been produced with adequate oxidant and shortening. Loaves 16N - 19N demonstrated the expected results. Loaf 19N, which contained adequate oxidant and shortening along with the palmitic acid, produced an acceptable loaf of bread. Removing the oxidant (18N) and the shortening (16N and 17N) produced loaves with low volume and inferior grain.

Table XIII. Effects of Shortening and Bromate on the Bread Baking Capacity of Ascorbyl-2-Palmitate, Ascorbic Acid, and Palmitic Acid in BCS 78 Flour.

No.	Treatment[a]	N	Shortening g	Additive g	$KBrO_3$ ppm	Water absorption %	Average loaf volume cc	Grain comments[e]
1N	Control	5	3.0[b]	0	20	64	922	Acceptable
2N	Control	2	3.0[b]	0	0	64	873	Unacceptable; weak
3N	No short	3	0	0	20	66	907	Unacceptable; weak
4N	No short	3	0	0	0	66	854	Unacceptable; weak
5N	AP-6-premix	2	0	0.5[c]	20	66	935	Excellent
6N	AP-6-premix	3	3.0[b]	0.5[c]	20	64	932	Excellent
7N	A-P-2 premix	3	0	0.5[d]	0	66	955	Unacceptable
8N	A-P-2 premix	3	0	0.5[d]	20	66	930	Unacceptable; over oxidation
9N	A-P-2 premix	3	3.0[b]	0.5[d]	0	64	897	Acceptable
10N	A-P-2 premix	3	3.0[b]	0.5[d]	20	64	898[+]	Unacceptable; over oxidation
12N	Ascorbic acid	3	0	0.19	0	66	912	Unacceptable
13N	Ascorbic acid	3	0	0.19	20	66	868[+]	Unacceptable; over oxidation
14N	Ascorbic acid	3	3.0[b]	0.19	0	64	937	Acceptable
15N	Ascorbic acid	3	3.0[b]	0.19	20	64	932	Unacceptable; over oxidation
16N	Palmitic acid	3	0	0.29	0	66	888	Unacceptable; weak
17N	Palmitic acid	1	0	0.29	20	66	910	Unacceptable; weak
18N	Palmitic acid	3	3.0[b]	0.29	0	64	863	Unacceptable; weak
19N	Palmitic acid	2	3.0[b]	0.29	20	64	956	Acceptable

[+] Includes volumes of several wrong side break loaves.

[a] BCS 78 flour protein 12.2%, moisture 12.3%.

[b] Creamtex: Durkee's hydrogenated vegetable oil.

[c] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot #144037.

[d] A-P-2 = ascoryl-2-palmitate; laboratory manufactured.

[e] Acceptable; unacceptable.

Ascorbic acid with shortening and no potassium bromate (14N) produced an acceptable loaf of bread in terms of volume and grain. Removing the shortening (12N and 13N) or adding the potassium bromate (15N) were detrimental. The same results were obtained with A-2-P, shortening removal (7N and 8N) and potassium bromate addition (10N) were unacceptable. Removal of potassium bromate (9N) produced an acceptable loaf of bread.

The data indicates that ascorbyl 2-palmitate is an unstable compound in a dough system. It splits within the system releasing ascorbic acid which in combination with potassium bromate overoxidizes the dough.

Effects of Chain Length of Fatty Acid on 6-Acyl Esters of Ascorbic Acid

Samples of ascorbyl-6-octanoate (A-6-0), ascorbyl 6-decanoate (A-6-De), ascorbyl 6-undecanoate (A-6-U), and ascorbyl 6-dodecanoate (A-6-Dod) were prepared in the laboratory by Dr. Y. T. Liang and Ms. S.P.W. Lu. Preliminary baking data (Hoseney et al, 1977) had indicated that A-6-De was incapable of replacing shortening (Table I, page 6). Thus it appeared that fatty acid esters with more than 10 carbons were needed for functionality of 6-acyl esters of ascorbic acid.

Table XIV gives the baking results of A-6-0, A-6-De, A-6-U, A-6-Dod, and AP at different levels. As loaf 6Q indicates, A-6-0 was able to replace shortening when 0.75 g/100 g of flour was added. The optimum level for A-6-De was 0.75 g (11Q). A-6-U and A-6-Dod showed optimum levels of 0.5 g (15Q and 20Q). AP optimum was 0.38 g (24Q). This baking data indicated two important conclusions. As the chain length decreased, more compound was necessary to replace shortening. Also, as the chain length decreased, the grain tended to open. AP gave a finer grain than any of the other esters.

Table XIV. Shortening Replacing Ability of Different Chain Length Ascorbic Acid Esters in Bread Doughs.

No.	Treatment[a]	N	Shortening g	Additive g	Water absorption %	Average loaf volume cc	Grain
1Q	Control	10	3.0[b]	0	64	947	Good
2Q	No shortening	1	0	0	68	840	Poor
3Q	Ascorbyl-6-octanoate	2	0	0.25	68	818	Poor
4Q	Ascorbyl-6-octanoate	2	0	0.38	68	823	Poor
5Q	Ascorbyl-6-octanoate	2	0	0.50	68	810	Very poor
6Q	Ascorbyl-6-octanoate	1	0	0.75	68	940	Acceptable
7Q	Ascorbyl-6-octanoate	2	0	1.0	68	885	Poor
8Q	Ascorbyl-6-decanoate	2	0	0.25	68	815	Very poor
9Q	Ascorbyl-6-decanoate	2	0	0.38	68	803	Very poor
10Q	Ascorbyl-6-decanoate	2	0	0.50	68	888	Poor
11Q	Ascorbyl-6-decanoate	2	0	0.75	68	990	Good
12Q	Ascorbyl-6-decanoate	2	0	1.0	68	975	Acceptable
13Q	Ascorbyl-6-undecanoate	1	0	0.25	68	830	Very poor
14Q	Ascorbyl-6-undecanoate	2	0	0.38	68	910	Acceptable
15Q	Ascorbyl-6-undecanoate	1	0	0.50	68	1005	Acceptable
16Q	Ascorbyl-6-undecanoate	2	0	0.75	68	1015	Acceptable
17Q	Ascorbyl-6-undecanoate	1	0	1.0	68	988	Poor
18Q	Ascorbyl-6-dodecanoate	1	0	0.25	68	850	Very poor
19Q	Ascorbyl-6-dodecanoate	1	0	0.38	68	935	Poor
20Q	Ascorbyl-6-dodecanoate	2	0	0.50	68	978	Acceptable
21Q	Ascorbyl-6-dodecanoate	1	0	0.75	68	995	Acceptable
22Q	Ascorbyl-6-dodecanoate	2	0	1.0	68	997	Acceptable
23Q	Ascorbyl-6-palmitate	2	0	0.25	68	955	Poor
24Q	Ascorbyl-6-palmitate	2	0	0.38	68	958	Good
25Q	Ascorbyl-6-palmitate	1	0	0.50	68	905	Acceptable
26Q	Ascorbyl-6-palmitate	2	0	0.75	68	908	Good

[a]Ross bake flour, protein 11.44%, moisture 13.0%.

[b]Durkee Creamtex, hydrogenated vegetable shortening.

The baking data was verified by resistance oven graphs in Figure 5, Figure 6, and Figure 7. All three figures demonstrate no significant difference between dough height and gelatinization temperature of A-6-0, A-6-Dod, AP, and a shortening control. All appear capable of replacing shortening.

It can be concluded that ascorbic acid esters with fatty acid chains as short as eight carbons can replace shortening in a dough system. However, when compared to the 16-carbon ester (AP), more ascorbyl 6-octanoate must be used in the dough to replace shortening and to achieve a satisfactory crumb grain.

Figure 5. Resistance oven data of no shortening (✱), shortening (○) and 6-palmitate (★).

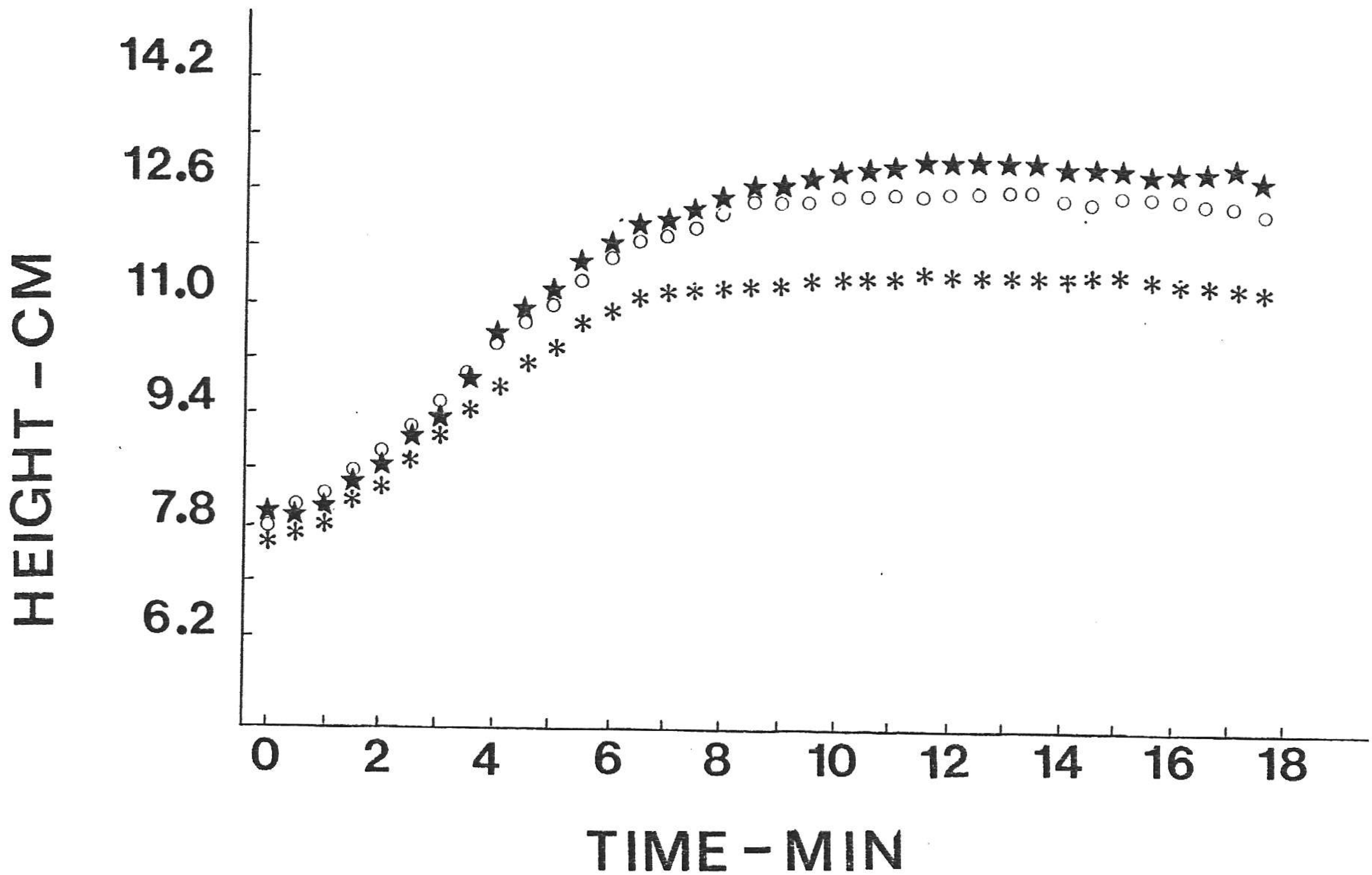

HEIGHT - CM
14.2
12.6
11.0
9.4
7.8
6.2
0
2
4
6
8
10
12
14
16
18
TIME - MIN

Figure 6. Resistance oven data of 6-palmitate (*) and 6-octanoate (●).

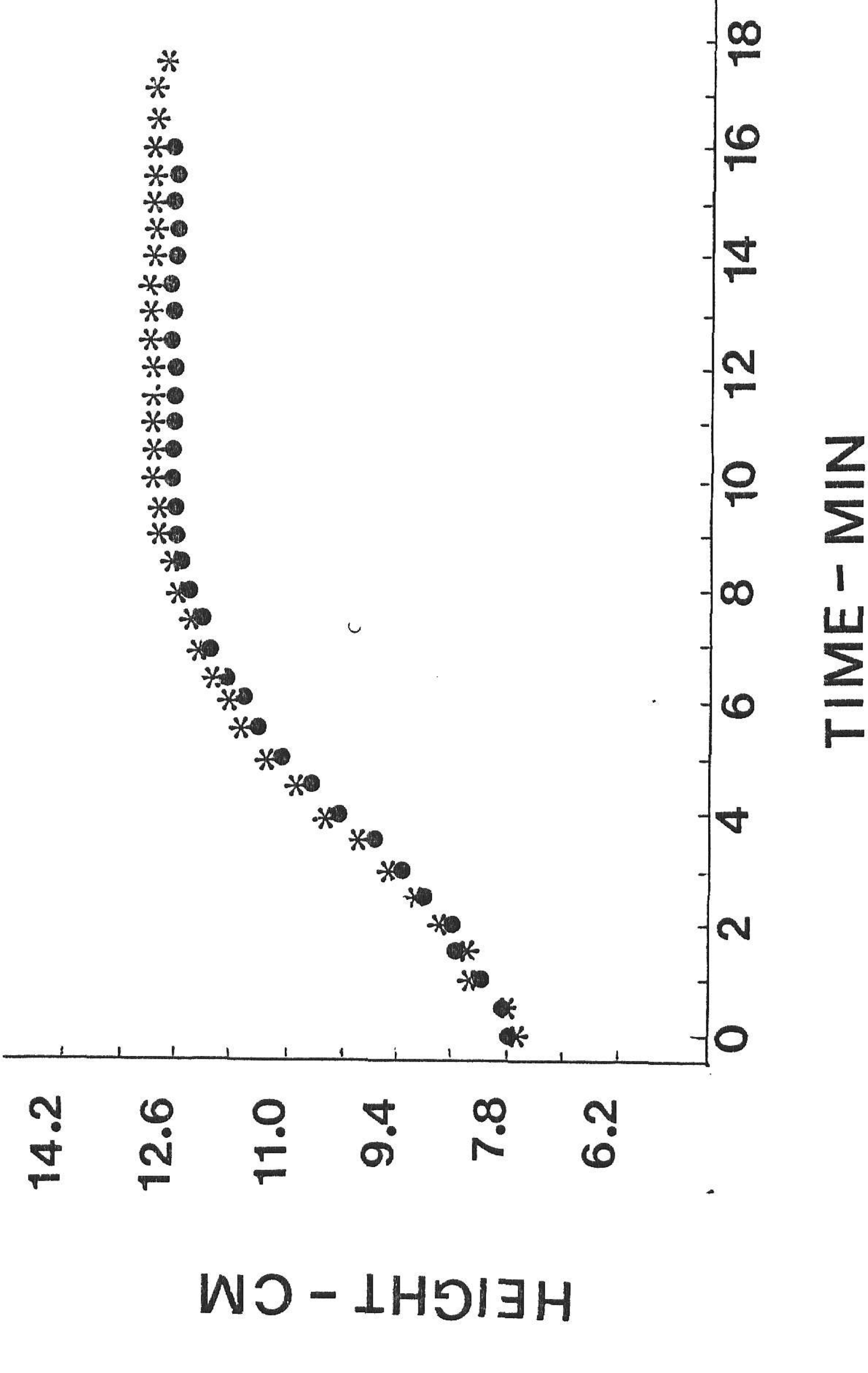
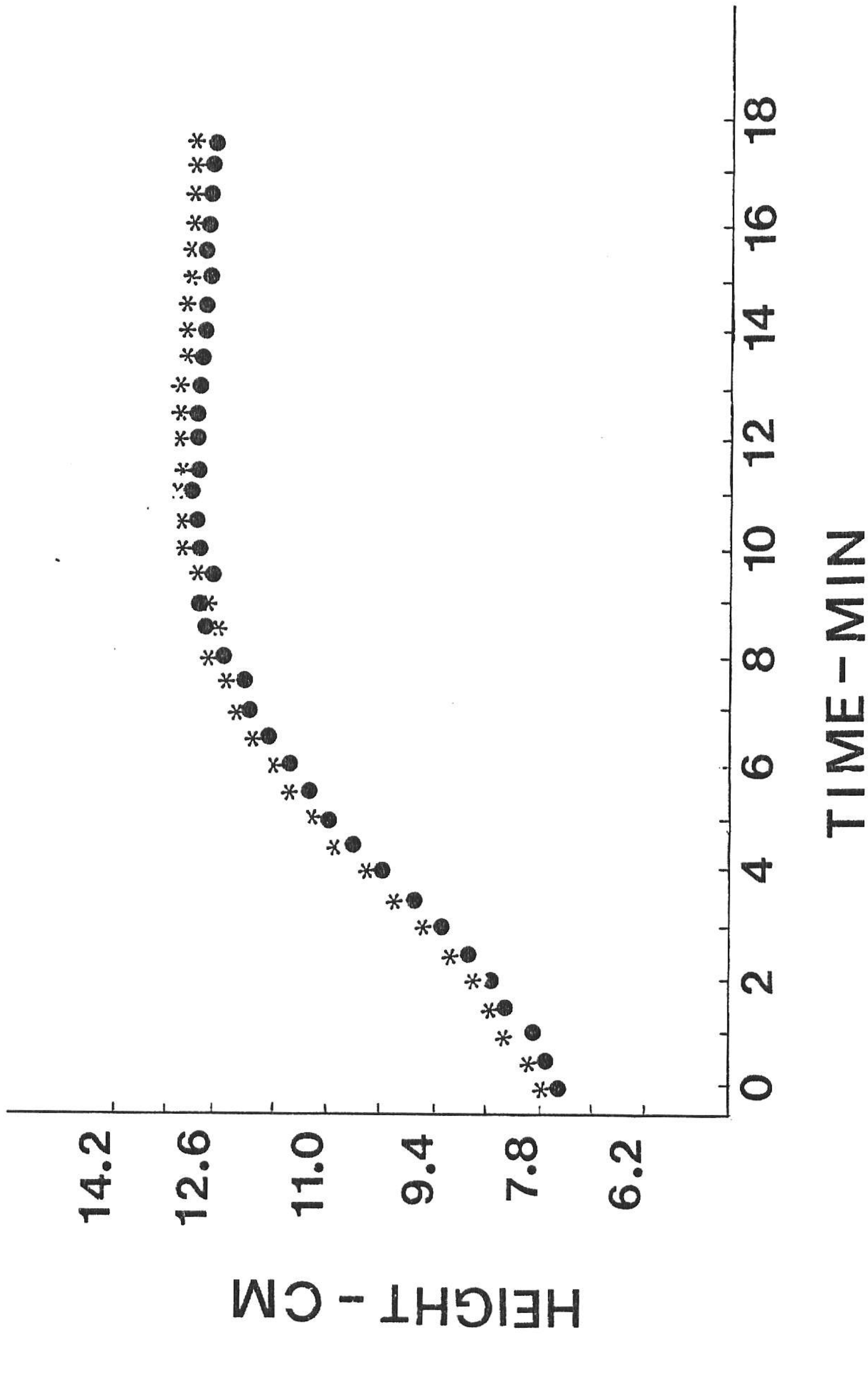

HEIGHT - CM
14.2
12.6
11.0
9.4
7.8
6.2
TIME - MIN
0
2
4
6
8
10
12
14
16
18

Figure 7. Resistant oven data of 6-palmitate (✱) and 6-dodecanoate (●).


HEIGHT - CM
14.2
12.6
11.0
9.4
7.8
6.2
TIME - MIN
0
2
4
6
8
10
12
14
16
18

SUMMARY

Ascorbyl 6-palmitate (AP) can be successfully added to bread dough by the use of premixes of AP with other lipids. When compared to SSL at the optimum level of usage, AP functions equally as well as a dough strengthener, shortening replacer, and crumb softeners. Ascorbic acid esters of chain lengths from 16 to 8 carbons are capable of replacing shortening in bread doughs. As the chain length decreases, the amount of compound necessary to replace shortening increases. Ascorbyl 2-palmitate was incapable of replacing shortening in bread dough because the molecule was unstable.

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APPENDIX

Table I-A. Pentometer Mean Measures by Days for Each Surfactant and Control Group and Normalized Pentrometer Readings.

No.	Treatment[a]	Surfactant g	Lipid g	Level g	Water absorption %	Mean loaf volume cc	Penetrometer units (0.1 mm)[f] Day 1	Day 3	Day 5	Normalized Data Day 1	Day 3	Days
1	Creamtex control (Overall mean)	0	3.0[c]	3.0	64	935	238	125	93	-	-	-
2	SSL	0.38[d]	0	0.38	68	964	304	165	112	79	48	25
3	Creamtex control	0	3.0[c]	3.0	64	945	225	117	86	-	-	-
4	AP	0.38[b]	0	0.38	68	935	306	162	110	83	51	23
5	Creamtex control	0	3.0[c]	3.0	64	931	223	111	88	-	-	-
6	D.Mono. + creamtex	0.5[e]	3.0[c]	3.5	64	928	309	187	118	53	35	19
7	Creamtex control	0	3.0[c]	3.0	64	942	251	153	99	-	-	-
8	SSL + creamtex	0.38[d]	3.0[c]	3.38	64	922	278	149	104	58	27	12
9	Creamtex control	0	3.0[c]	3.0	64	920	220	122	92	-	-	-
10	AP + creamtex	0.38[h]	3.0[c]	3.38	64	922	298	146	103	55	27	11
11	Creamtex control	0	3.0[c]	3.0	64	932	243	119	92	-	-	-
12	AP	0.5[b]	0	0.5	68	940	317	184	122	76	58	28
13	Creamtex control	0	3.0[c]	3.0	64	933	241	126	94	-	-	-
14	AP + creamtex	0.5[b]	3.0[c]	3.5	64	930	319	149	116	59	23	20
15	Creamtex control	-	3.0[c]	3.0	64	946	260	126	96	-	-	-

[a] Ross Bake Flour, Protein 11.44, Moisture 13.0.

[b] AP = ascorbyl-6-palmitate (Hoffman-La Roche Lot # 144037).

[c] Shortening = creamtex vegetable shortening, Durkee Foods.

[d] SSL = sodium stearoyl-2 lactylate (ITT Paniplus).

[e] D.Mono. = distilled monoglycerides (Grinsted).

[f] Depth of depression in tenths of a millimeter for 10 seconds by a constant weight (204 g) plunger having a hemispherical nose. Each reading is the average of four loaves except the creamtex control (Overall mean) group which is an average of 28 loaves.

BAKING PERFORMANCE OF ASCORBYL-6-PALMITATE

IN PUP LOAVES

by

Richard B. Koch
B.A., West Chester State College, 1976

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Grain Science and Industry

KANSAS STATE UNIVERSITY
Manhattan, Kansas
1981

ABSTRACT

Baking results have shown that AP can be incorporated in bread dough by addition of premixes of AP with another lipid. The premixes can be prepared by (1) dispersing 38 parts of AP in 100 parts of vegetable oil, (2) premelting AP (38 parts) in shortening (300 parts) at 120°C and allowing the mixture to solidify to a plastic fat, (3) dispersing 38 parts of AP in 100 parts of plastic shortening at 25°C using a mortar and pestle, and (4) mixing at very high speed 9 parts of AP with 1 part of mono-diglyceride or SSL. It was found that a premix of AP slurried in water did not give good dispersion of AP in bread dough. However, preliminary data indicate that AP with a particle size <0.246 mm could be slurried with water and successfully used in breadmaking.

In combination with other lipids, AP was found to reduce the amount of lipid needed in bread by two-thirds. A preblend of 0.25 g of AP in 1.0 g of shortening/100 g of flour or 0.38 g in 1.0 g of soy oil was found to be as effective as 3 g of a non-emulsified shortening in dough. A premix of 0.38 g AP with 3.0 g of soy, peanut, cottonseed, or corn oil gave excellent results in bread. It is possible to replace all shortening or oil in bread using the 9:1 premixes of AP with a hydrophilic surfactant. At optimum level (0.38%), grain and volume of bread made with 9:1 premixes of AP and mono-diglyceride were equal to those of bread made with shortening.

AP, when compared with SSL, gave comparable anti-firming action, comparable loaf volume, and comparable absorption increases. Combinations of AP and SSL produced no synergistic effects in breadmaking. Both surfactants gave softer bread when used alone at 0.38 g/100 g of flour than

when used at the same level in combination with 3 g of shortening. Both AP and SSL (0.38%) gave softer bread than the combination of distilled monoglycerides (0.5%) and shortening (3%). SSL tended to give more consistent volume and grain than did AP.

The amount of ascorbyl 6-fatty acid ester needed to spare shortening in bread increases as the fatty acid chain length decreases. Furthermore, the grain of bread tends to open more as the chain length decreases. When the fatty acid is substituted on C2 rather than C6 of ascorbic acid, the ester linkage appears to hydrolyze in the dough system. That hydrolysis not only destroys the possibility of the A-2-P to replace shortening, but also causes over-oxidation of the bread in the presence of potassium bromate.

Ascorbyl 6-palmitate (0.38%) like SSL, is capable of replacing shortening (3%) in bread because those materials delay the "setting" of the loaf structure compared to a no-shortening control. Those results were found by heating dough internally by placing it in an alternating electrical field between two charged parallel plates.