Stabilization of Frozen Milk Concentrates with Polyphosphates

A. LEVITON, J. H. VESTAL, H. E. VETTEL and B. H. WEBB

Dairy Products Laboratory; Eastern Utilization Research and Development Division
Agricultural Research Service, U. S. Department of Agriculture
Washington, D. C. 20250, U. S. A.

Polyphosphates have been reported to increase the storage life of sterile, sweetened and frozen milk concentrates (1). In frozen milk concentrates the polyphosphates owe their effectiveness not to one but rather to a combination of properties. For this reason, among stabilizing salts the polyphosphates are unique. There are, however, limitations to their usefulness. Our experimental program was designed to disclose both advantages and limitations. It embraces the study over a 255 day experimental period of control and polyphosphate-containing concentrates, and includes the study of lactose crystallization, protein and emulsion destabilization, and viscosity. It includes moreover the study of the effect on stability of seeding, and "in-can" heating (a denucleation step), and the effect on stability tests of the time-temperature conditions used in thawing and reconstitution.

EXPERIMENTAL

The polyphosphate glass used was a commercial product with an average of 4.8 phosphorous atoms per chain. A single lot of milk containing 4.1% fat and 12.86% solids was obtained from the USDA Beltsville herd.

The milk pasteurized at 72° C. for 15 seconds in a Mallory[1] coiled-tube heat exchanger was concentrated to 37% solids in a Harris-Wiegand falling-film evaporator. The concentrate was divided into three parts; one part was adjusted with water, the others with polyphosphate solution to bring the milk solids concentration to 35% and the additive concentration to 0.8 g. per 100 g. milk solids in one batch and to 1.6 g. per 100 g. solids in the other. The concentrates warmed to 66° C. were homogenized in two stages at 2500 and 500 p. s. i., respectively, and cooled to 21° C.

Each of the three concentrates was subdivided to yield four concentrates. Thus, twelve sets of canned samples were prepared differing as indicated in Table 1. The cans were held quiescent for 24 hours at −18° C., then transferred to a room maintained at −12° C.

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[1] Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

Viscosity was measured at 30° C. with a transpiration type viscometer (maximum shearing stress of 175 dynes/cm.^{2}). Thawing was conducted at 4.4° C. for 24 hours. The melted samples were stirred, aliquots were taken and held at 30° C. for 1 hour, then stirred 30 seconds with a vortex type mixer to achieve a basic viscosity value, and finally equilibrated at 30° C. for 15 minutes prior to measurement.

TABLE 1

Identification of concentrates with respect to treatments. All samples were derived from the same batch of milk

Concentrate	*Polyphosphate Concentration (g. per 100 g. milk solids)*	*Seeded*[1]	*Heated after concentration*[2]
1	None	No	No
2	"	Yes	"
3	"	No	Yes
4	"	Yes[3]	"
5	0.8	No	No
6	"	Yes	"
7	"	No	Yes
8	"	Yes[3]	"
9	1.6	No	No
10	"	Yes	"
11	"	No	Yes
12	"	Yes[3]	"

[1] 0.2 g. lactose powder per 100 g. concentrate.
[2] In Fort Wayne revolving reel sterilizer at 68° C. for 25 min., cooled in situ to 24° C.
[3] Seeded after heat treatment and cooling.

Sediment was determined at 4.4° C. in 10 ml. aliquots of reconstituted milks (12.6% solids). The milks (70 g.) in 208x208 cans were mxed by swirling, held 24 hours at 4.4° C., swirled again and then introduced into 10 ml. graduated centrifuge tubes. The quantity of sediment was measured after the tube had been spun 5 minutes at 1000 r. p. m. (222xG) in an International Centrifuge, Size 2, Model V. Storage life was considered to end when more than 2% sediment was present in the reconstituted milks. Control samples were reconstituted at times with polyphosphate solution to yield milks containing the same concentrations of polyphosphate as milks reconstituted from the polyphosphate-containing concentrates with water.

Free fat was determined by the method of Lagoni and Peters (2). Indices characterizing emulsion destabilization were determined on reconstituted milk diluted for analysis according to the methods of Deackoff and Rees (3). However, the transmittancy at 1020 millimicrons was not used as an index. A more suitable index was obtained by following changes in the ratio, R, between the absorbance at 1020 and 600 millimicrons as a function of time. Absorbance becomes nearly independent of wavelength for fat particles greater than 3 microns in diameter. Hence, the maximum possible change of the ratio between absorbances during the period of destabilization was equal to $1\text{-}R_0$, where R_0 is the value of the ratio prior to concentrate storage. The destabilization index (that is, the fraction of maximum possible change in the ratio) is given by the quotient $R_t\text{-}R_0/1\text{-}R_0$ where R_t is the value of the ratio at time t.

Alpha lactose was determined in 10 g. frozen milk according to the method of Sharp and Doob (4). However, the oxalic acid solution was modified to contain 2. g. oxalic acid dihydrate per liter. Since it is α-lactose which crystallizes in frozen milk, the change in α-lactose concentration during storage furnishes a measure of the degree of crystallization.

Thus: α-lactose (sol'n) $\rightleftharpoons$ β-lactose (sol'n)

$\downarrow\uparrow$

α-lactose (crystals)

and the total concentration of α-lactose (expressed as percentage of total lactose) increases with the degree of crystallization.

RESULTS

The three sets of graphs in the upper part of Fig. 1 refer to the effect of two levels of polyphosphate concentration on the various stability indices. The progress of lactose crystallization is indicated by the changes in percentage of α-lactose, the course of emulsion destabilization by changes in the emulsion destabilization index (expressed as percent) and the course of protein destabilization by changes in the viscosity of the thawed concentrate and by variations in the percent of sediment (percent of milk volume) observed in reconstituted milks. The graphs in the lower parts of Fig. 1 and Fig. 2 refer to seeded concentrates.

When the milks of Fig. 1 were subjected to a mild in-can heat treatment the results plotted in Fig. 2 were obtained. The values on the viscosity axis of Fig. 2 are double the values in Fig. 1.

In Table 2, Part I the sediment in milks from polyphosphate-containing concentrates (P) is compared with that in milks from control concentrates (C). Whereas water was used in reconstituting (P), polyphosphate solutions were used in reconstituting (C). Table 2, Part II, refers to the state of the fat emulsion in some of the milks.

Free fat determinations were made in an attempt to follow emulsion destabilization. Only small quantities were observed. The values (Table 3) ranged from 0.04 to 0.4%. Inasmuch as the correlation between these and the emulsion destabilization indices was poor, measurements were discontinued after 17 days. Emulsion deterioration could also be judged subjectively. Deteriorated concentrates had a pronounced yellow cast.

Time-temperature effects were observed at a number of polyphosphate concentrations (0.025 to 0.15%) in an experiment in which polyphosphate was used to disperse the colloids in a badly deteriorated 260 day old control concentrate (See Table 4).

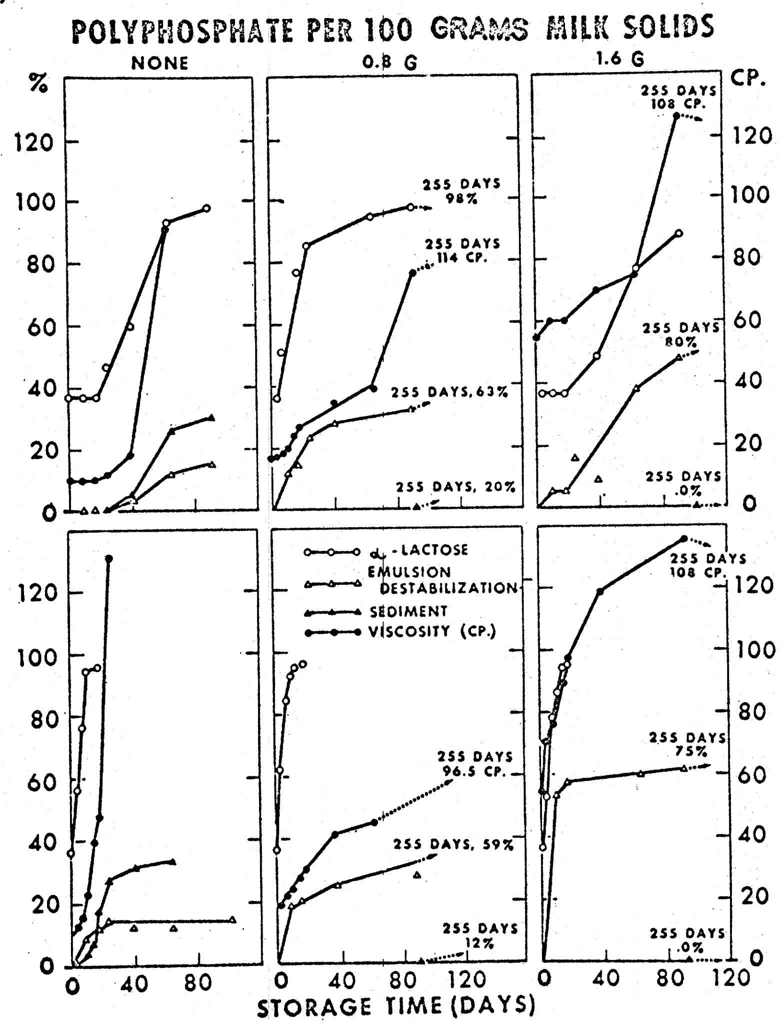

Fig. 1: *Influence of polyphosphate on some properties of frozen, 35% milk concentrates stored at —12° C. Milks represented in the lower curves were seeded before freezing; those in the upper sections were not seeded. Slopes of arrows show the average rate of change of various ordinates for the period 91 to 255 days.*

DISCUSSION

The effectiveness of polyphosphates against protein destabilization in fluid milks is greatest in sterile milk concentrates (5, 6). The problem of stabilizing frozen concentrates is complicated by the high ratio between solids and free water. Calculations based on freezing point and lactose solubility data show that this ratio in equilibrated frozen concentrates at −12° C. approaches that in milk powder. Aggregation and dehydration are associated with the decrease in free water and follow rapidly in the wake of maximum lactose crystallization. One of the virtues of polyphosphates is their ability to deflocculate highly intractable aggregates.

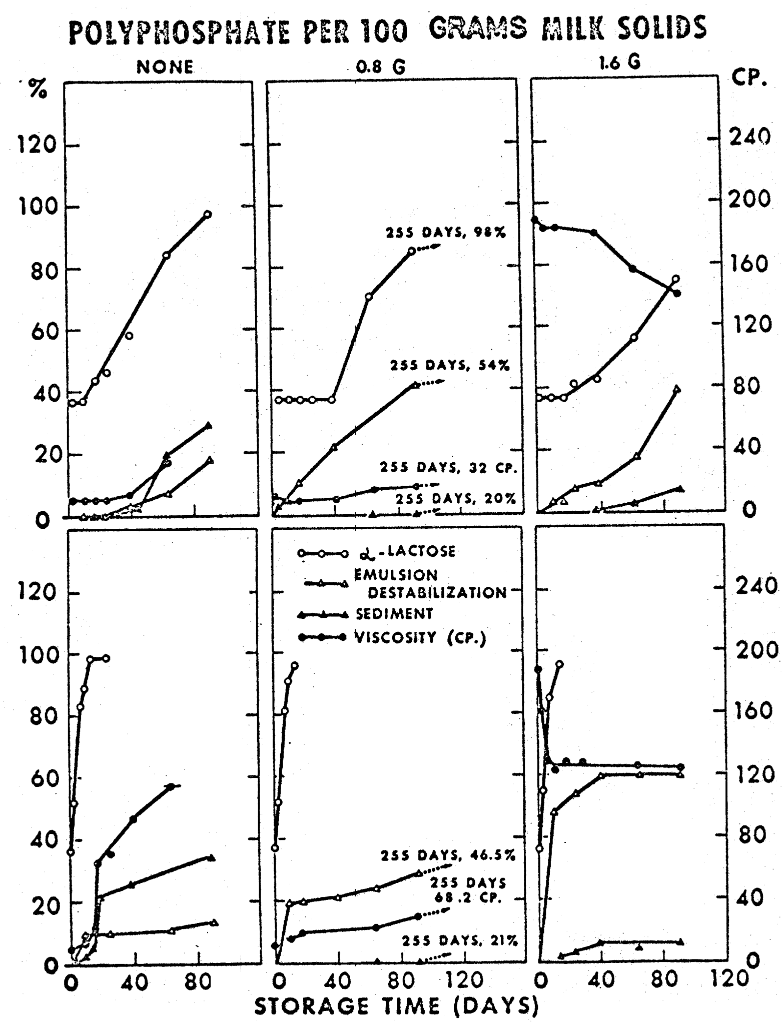

Fig. 2: Influence of polyphosphate on some properties of frozen 35% milk concentrates. The concentrates were heated to 68° C for 25 minutes then cooled quiescently to 21° C prior to storage at −12° C. Milks represented in the lower curves were seeded before freezing; those in the upper sections were not seeded. Slopes of arrows show the average rate of change of various ordinates for the period 91 to 255 days.

TABLE 2

Sediment and emulsion destabilization indices belonging to seeded polyphosphate-containing concentrates reconstituted at 4° C. with water, compared with corresponding indices for seeded control concentrates reconstituted with polyphosphate solutions

Time of storage at −12° C. Days	Indices (per cent) Control Concentrates (C) Polyphosphate used to reconstitute: 0	0.8 g.[1]	1.6 g.[1]	Experimental Concentrates (P) Polyphosphate in: 0.8 g.[2]	1.6 g.[2]
	Part I — Sediment				
3	0.5	—	—	0	0
7	2.0	0.5	0.2	0	0
10	2.5	0.5	0.1	0	0
14	10	1.5	0.3	0	0
17	18	1.5	0.3	0	0
24	28	13	0.8	0	0
39	31	23	1.0	0	0
64	30	30	1.0	0	0
91	34	42	1.5	0	0
	Part II — Emulsion destabilization				
64	12	12	12	26	60
91	15	15	15	29	60

[1] Quantity of polyphosphate added per 100 g. milk solids in concentrate.
[2] Polyphosphate per 100 g. milk solids added to concentrate before freezing.

TABLE 3

Free fat in milks reconstituted from frozen concentrates

Storage Time (days)	Free Fat (per cent) Concentrate number[1] 1	2	3	4	5	6	7	8	9	10	11	12
10	0.16	0.13	0.14	0.13	0.05	0.05	0.03	0.03	0.02	0.38	0.03	0.05
17	0.29	0.29	0.30	0.39	0.06	0.05	0.05	0.04	0.05	0.31	0.06	0.19

[1] See Table 1 for identification of concentrates. Concentrates 1—4 contain no additive, concentrates 5—8 contain 0.8 g. additive per 100 g. milk solids, concentrates 9—12 contain 1.6 g. additive per 100 g. milk solids.

This property together with several others accounts for the usefulness of polyphosphates in frozen concentrates.

With respect to control concentrates there was positive correlation between the degree of lactose crystallization and the degree of deterioration of the protein and fat dispersions. The results on protein destabilization agree generally with those in the literature (7, 8, 9). The lag reported by Desai et al. (7) between protein coagulation and lactose crystallization was not observed although the rate of destabilization was slow during the early stages of crystallization.

Destabilization of the fat and protein phases in control concentrates follow similar patterns with respect to lactose crystallization. Interaction is suggested. Thus the results in Fig. 1 and 2 with seeded samples suggest that as the rate of protein destabilization approaches a maximum the rate of fat destabilization approaches a minimum and vice versa. The system behaves as if the fat globules were trapped and protected by the destabilized protein.

TABLE 4

Sediment from 260 day old control concentrates. Milks reconstituted with water or polyphosphate solution, and held at various temperatures before measurement

Poly-phosphate concen-tration [1]	*Sediment after 15 min.* [2] *Peptizing temperature* 20° C.	30° C.	40° C.	49° C.
%	%	%	%	%
0	29	30	33	34
0.025	33	36	35	10
0.050	33	39	5	0 [5]
0.100	39	5	0 [3]	0 [6]
0.150	44	0	0 [4]	0 [7]

[1] Polyphosphate concentration based on 12.6% fluid milk reconstituted from seeded 35% concentrate which had been stored 260 days at —12° C.

[2] Samples inverted every 2 minutes; tube walls inspected for sign of sediment. Sediment measured at 5° C.

[3] [4] [5] [6] [7] No sediment at 6, 4, 10, 2 and 2 minutes, respectively.

In unseeded concentrates lactose crystallization continues for 2 to 3 months. Benefits of an in-can heat treatment in retarding lactose crystallization were not generally obtained. The in-can heating step, however, recommended by Braatz and Winder (10) has its place both in investigational work and in practice. It tends to overcome the capriciousness of the crystallizing system due to inadvertent nucleation. Another approach in investigational work is to swamp the system with nuclei (seeding).

The advantage in the use of polyphosphates under the conditions of these experiments was marked. Correlation between lactose crystallization and colloid destabilization was poor. In seeded samples lactose crystallization was complete in 10 days whereas sediment was not observed even after 88 days. Small amounts of a voluminous sediment observed during early storage in reconstituted milks from some polyphosphate-containing heat-treated concentrates may have been brought about by the conversion of polyphosphate into insoluble pyrophosphate (11). Moreover, the viscosity of the heat-treated thawed product tended to decrease rather than increase during storage. In unseeded concentrates the polyphosphate at the higher concentration level retarded lactose crystallization, pos-

sibly because of the heavy body of these concentrates. Part of the stabilizing in-
fluence of the polyphosphates must reside in their capacity to retard lactose cry-
stallization.

The stabilizing action of polyphosphate can be described partly, but not entirely, as one of deflocculation in the thawing and reconstitution steps.This is suggested by the data in Table 2. Thus reconstitution with polyphosphate solution (see Table 2 and 4) instead of water greatly reduced sediment but not to the degree observed in reconstituted polyphosphate-containing concentrates.

Emulsion stability was seriously impaired in polyphosphate-containing concen-
trates, a consequence perhaps of the inverse relationship noted earlier between the rates of emulsion and protein destabilization.

Once the degree of lactose crystallization reaches its maximum and the concen-
trate is aged further, increasingly drastic measures must be taken to deflocculate and rehydrate the proteins. The proteins in concentrates containing polyphopha-
tes are much more responsive to rehydration and deflocculation than those in control concentrates (see Table 4). Rehydration requires time and it is accelerated at higher temperatures and polyphosphate concentrations (Table 4).

These conclusions, based on experiments in which freshly prepared polyphos-
phate solutions acted on the intractable aggregates in control concentrates, also apply to frozen polyphosphate-containing concentrates reconstituted with water. Thus after 255 days, 12-20% sediment was found in milks from polyphosphate-
containing concentrates which had been reconstituted at 4.4° C. over a 24 hour period. No sediment was found if an additional 30 minutes was allowed at 30° C. for reconstitution (data not recorded). Solubilization occurs rapidly only after critical temperature and/or time values have been exceeded. The loss in "instant quality" at 4.4° C. was observed after 3 months only in seeded concentrates.

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