Control of Gelation in Evaporated Milk

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Gelation of evaporated milk in storage can be controlled by preheating milk in the concentrated state, followed by dilution to standard composition, if necessary, and sterilization. This treatment does not affect the color and flavor of the finished product. The optimum time and temperature of the preheating treatment vary with the concentration of the milk at the time it is preheated. Because of variations in the colloidal characteristics of milk, optimum conditions of the preheating treatment also vary seasonally and with milk from different areas.

HIGH-TEMPERATURE SHORT-TIME (HT-ST) STERILIZATION is at present the most feasible method of improving evaporated milk quality with respect to brown discoloration and cooked or caramelized flavor (*2*, *3*, *5*). However, HT-ST-sterilized milk has a limited shelf life because of a rapid fat separation and gel formation in storage. These defects—especially gel formation—impede a general adoption of the process by the industry. Gelation in stored evaporated milk is, therefore, a problem of both theoretical and commercial importance.

Gel formation in stored evaporated milk is not spontaneous. The initial change in storage in the body of evaporated milk is a loss of viscosity. In rare batches of conventionally sterilized milk, and frequently in milk sterilized by HT-ST method, the initial thinning is followed up by a gradual thickening, a spotty formation of lumpiness, and, finally, complete immobilization of fluidity. The gelation is not accompanied by syneresis, and is clearly a different phenomenon from coagulation of milk by heat, rennet, or other agents. Gel formation in evaporated milk is accelerated by storage at elevated temperatures (*3*).

The basic factors underlying this type of gelation defect in evaporated milk are not known other than the evidence that it is not of bacteriological origin (*6*). The gel in its initial stages is characterized by thixotropy—i.e., gel-sol isothermal reversibility. Only a relatively mild shaking is necessary for changing gel into sol, which suggests that the structural network is held by rather weak secondary attractive forces. At the stage of partial gelation in a can of milk, a limited analysis of gel and sol with respect to content of fat, total nitrogen, calcium, and phosphorus gave no significant difference in distribution of the above constituents in the phases, except that the gel phase was a little higher in fat content (*4*). The absence of any difference between gel and sol in the distribution of calcium and phosphorus indicates that the gel's network is formed and held by direct interaction between the enfolded (denaturated) protein molecules rather than through divalent cations as calcium that can provide bridges between free carboxyl groups. Physicochemical data available on the protein gels of stored sterilized milk are very meager, and no conclusions can be drawn concerning the mechanism of formation or the structure of the gel's network.

One approach to this problem would be the acquisition of basic knowledge on the colloidal changes in sterilized milk that gels—changes in the size and asymmetry of protein particles, the reactive groups of proteins involved, and interaction of these groups with the water phase. The specific groups concerned in the gelation process and their mode of linkage would be rewarding objectives in such a study. Simplified model systems would be a logical starting point in elucidating what constituents of milk, if any, besides calcium caseinate are involved in and necessary for gelation.

The authors' experimental approach to the problem of gelation was a practical one. It was based on the fact, first pointed out by Bell, Curran, and Evans in 1944 (*2*), that the length of continuing fluidity of milk in storage is associated with severity of heat sterilization treatment.

Experimental

According to Ferry (*1*), "denatured protein gels can be formed only under highly specific conditions." The evidence that the HT-ST sterilization treatment is much more conducive to gel formation than is the more severe heat treatment of conventional sterilization implies that the state of milk proteins as affected by heat denaturation passes through "a critical" zone for gelation during conventional sterilization. In the case of HT-ST sterilization—i.e., milder heat treatment—an additional thermal denaturation is necessary to avoid gelation in storage. Additional heat treatment in the sterilizer will produce a more severe browning and caramelized flavor, thus nullifying the advantages of the HT-ST process. Greater denaturation without deleterious effects of browning reaction can be accomplished by increasing the protein particle concentration and preheating at temperatures below 100° C.—i.e., preheating the concentrated milk prior to HT-ST sterilization treatment.

The experimental processing of milk was essentially the same as that used in commercial practice, with respect to preheating before condensing, concentration in vacuum pan, homogenization, and standardization. Preheating of milk in the concentrated state before sterilization was done in a steam-jacketed vat equipped with a motor-driven agitator and designed for a rapid transfer of heat. Sterilization was done in a Fort Wayne batch sterilizer with the reel continuously operating. The sterilization temperatures were 127° C. (260° F.) for 2 minutes or 129° C. (265° F.) for 1 minute for HT-ST process, and 117° C. (243° F.) for 13 minutes for conventional sterilization as described previously (*5*).

Processed samples were stored under the conditions indicated in the figures. Viscosity determinations were made with the Fisher electroviscometer at 25° C. after mixing the milk by pouring it back and forth four times. The critical

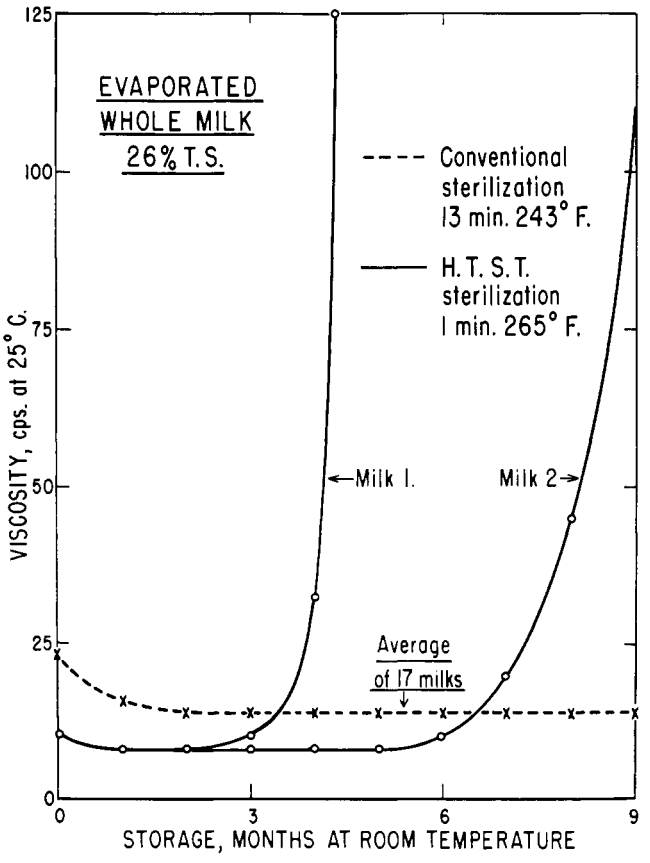

Figure 1. Viscosity of evaporated milk in storage

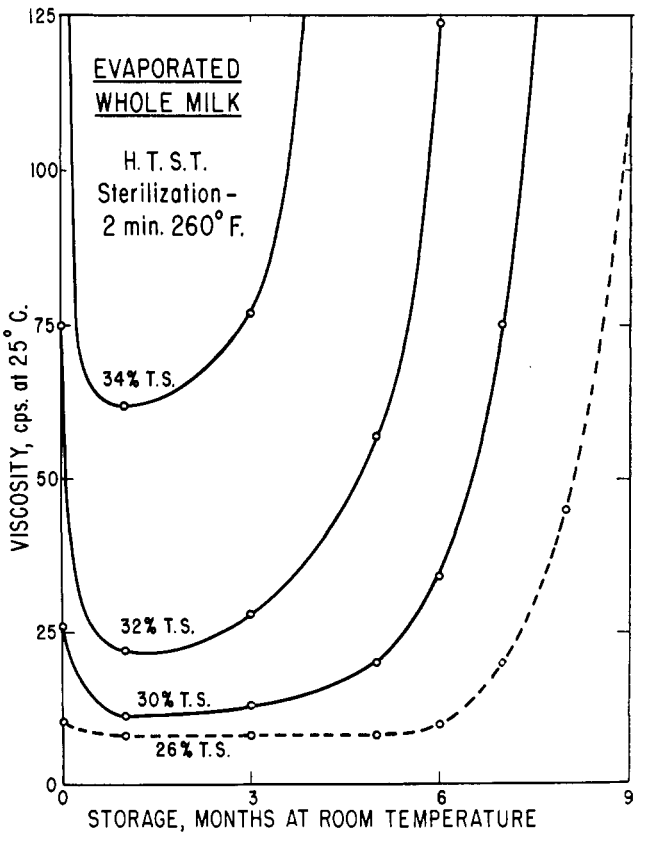

Figure 2. Effect of solids concentration on the rate of gelation

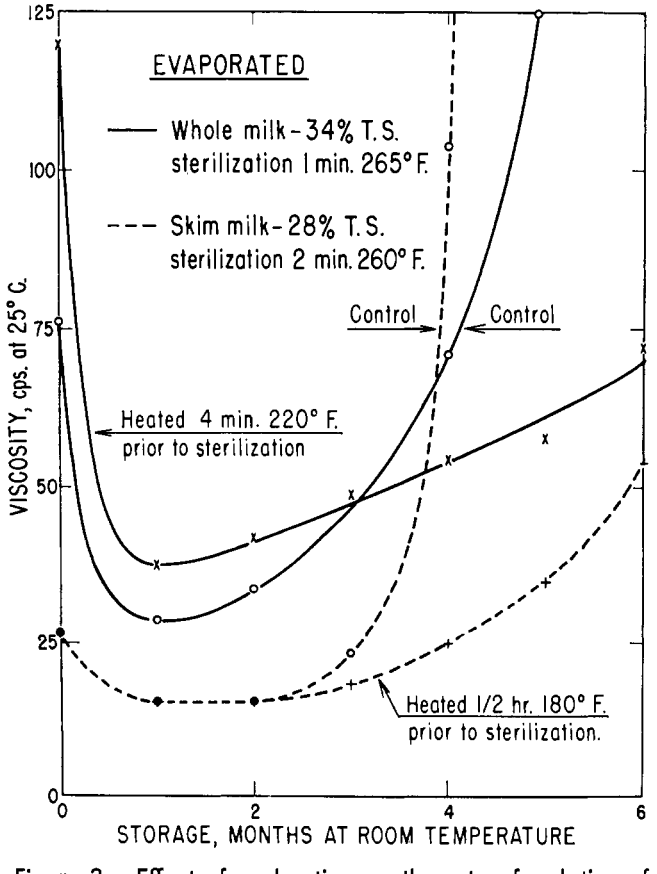

Figure 3. Effect of preheating on the rate of gelation of high solids concentrated milk

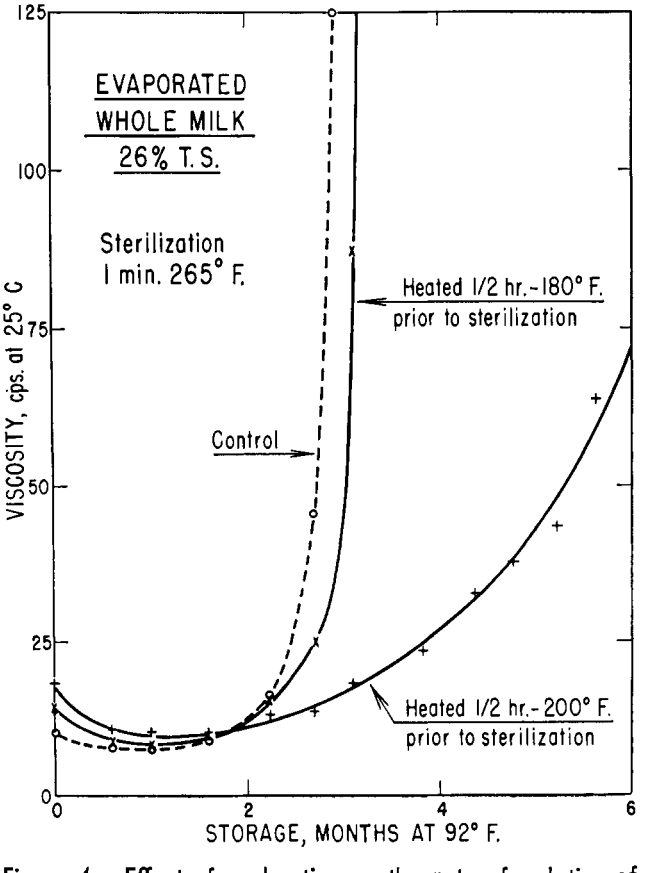

Figure 4. Effect of preheating on the rate of gelation of evaporated milk

zone of viscosity that coincided with the first and partial appearance of gel formation was in the range of magnitude of 90 to 100 cps.

As gelation progressed but was still in the stage so that a uniform fluidity would be obtained by pouring milk back and forth, viscosity increased to 150 to 200 cps. Beyond this stage of gelation the milk was lumpy after mixing and the viscosity values were in the range of several hundred centipoises. Viscosity measurements of heat-processed products like evaporated milk represent only relative values. It is not absolute viscosity, because there is yield value or structure even when product is entirely fluid and some of the structural viscosity is destroyed by mixing. These relative viscosity values, however, do reflect the consistency of the body of the product and are suitable for comparative purposes.

The data in Figures 1 to 4 show the general behavior of various concentrated milks in storage with respect to viscosity, and the marked retardation of gelation by certain preheating treatments of milk in a concentrated state.

The data of Figure 1 show that a more severe heat treatment (13 minutes at 243° F.) with conventional sterilization ensures the fluidity of milk in storage. The shelf life of HT-ST sterilized milks is limited by gelation, varying undoubtedly with differences in the colloidal properties of the original milks. Figure 2 illustrates that the rate of gelation in storage is a function of milk solids concentration. In separate experiments it was shown that the accelerated rate of gelation with increased concentration is entirely associated with increased concentration of solids-not-fat fraction. This can be seen also by comparing the rate of gelation of concentrated whole and skim milk controls in Figure 3.

The effectiveness of preheating milk in a concentrated state on the rate of gelation in storage of HT-ST-sterilized milk is shown in Figures 3 and 4. The data of Figure 4 indicate that preheating milk in the concentrated state before sterilization controls the gelation defect of HT-ST–sterilized evaporated milk. In other experiments milk was concentrated to contain 40% total solids, and the samples made by dilution and containing from 40% to 28% total solids were preheated. The preheated samples were all diluted to standard composition (26% total solids) and sterilized. The data on gelation of these samples in storage indicated that the optimum time and temperature of preheating treatment will vary with the concentration of the milk at the time it is preheated. For example, at 28% total solids, preheating treatment at 195° F. for 30 minutes gave greater retardation of gelation than preheating at 180° F. for 30 minutes, but at 35% total solids, the indicated optimum treatment was preheating at 180° F. for 30 minutes. At higher concentrations, preheating treatments of lesser severity are required for optimum retardation of gelation in storage.

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PESTICIDE ANALYSIS

Determination of Captan

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A specific and sensitive analytical method for the fungicide, captan, *N*-(trichloromethylthio)tetrahydrophthalimide is based on the reaction with alkaline resorcinol under reducing conditions. The method is most useful in the range of 3 to 30 γ, and a semiquantitative measure of as little as 0.4 γ is readily obtained. Good recoveries were obtained from various natural products.

Reactions of molten resorcinol with compounds containing the $-CCl_3$ group were investigated during work on analytical methods for chlorinated hydrocarbon pesticides, as these might be expected to give fluorescein derivatives (*3*). An example of such a reaction appeared in the analytical method developed by Kittleson (*4*) for the commonly used fungicide, *N*-(trichloromethylthio)tetrahydrophthalimide (captan) (*7*). It was found that certain of these pesticides gave fluorescein-like derivatives, and that the liberated hydrochloric acid contributed to the color formation. In alkaline medium, only captan gave a significant color with resorcinol. Addition of sodium hydrosulfite to the alkaline resorcinol minimized interference from air oxidation, making this a highly sensitive and specific analytical reagent for captan determination. This appears to have some advantages over the Kittleson method (*2, 4*), the only other method available.

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Experimental

Preparation of Sample. For firm-surfaced materials, the usual methods for stripping pesticides from the surface of food products appear to be suitable. Experiments have been carried out with apples, pears, tomatoes, and whole wheat. They were agitated with benzene for 5 minutes, the solvent was filtered through folded filter paper, and an