

Peroxide Increase in Fat of Milk During Foam-Spray-Dried Powder Manufacture 3078

A. KONTSON, A. TAMSMA, and M. J. PALLANSCH

Dairy Products Laboratory, Eastern Utilization Research and Development Division
USDA, Washington, D.C. 20250

Abstract

Fresh milk contains low levels of peroxides which increase in concentration during its conversion to whole milk powder by spray drying. Analysis of peroxide increase during 20 foam-spray-drying runs showed the average peroxide value (meq O₂/kg fat) of fresh milk taken from bulk tanks to be .019; on concentrating to 50% total solids in a falling film evaporator this value rose to .024; after drying with nitrogen injection, the fat in the finished powders had an average peroxide value of .036. The peroxide content of fat in milk powders produced by conventional spray drying was approximately one-half that in the foam-spray-dried products. Further increases in peroxide of both types of powders could be detected after one to three days of holding in air after manufacture. The low peroxide values were measured using minor modifications of Horgan's method, in which peroxides convert the reduced leuco form of Brilliant Cresyl Blue to its oxidized blue form.

Hanrahan and his associates (2) have shown that injection of a small quantity of inert gas into a concentrate moving in the high-pressure line of a conventional spray dryer produced a whole milk powder having excellent initial flavor and good dispersibility. This powder has a relatively high level of its fat in the free, or easily extractable form.

In an earlier study of oxidation in powders produced by drying whole milk foams under vacuum, Greenbank and Pallansch (1) reported that the free fat was particularly subject to oxidation.

Since the foam-spray-dried product was dehydrated in air and contained at least 10% of its fat in the free form, we became concerned with the extent to which fat oxidation had proceeded during its manufacture. Even though the initial flavor of the product led us to be-

lieve that minimum oxidation has occurred during drying, a quantitative measure of the extent of oxidation during drying would allow specification of handling procedures necessary during packaging and use.

Therefore, we made a comparative study of the changes in the peroxide content of milk fat during the manufacture of dried whole milk by using conventional and foam-spray-drying techniques. Also noted was the evidence for further oxidation during holding periods after production consistent with packaging and use.

Previous work in our laboratories by Kliman and associates (5) has shown that the peroxide values of some fresh whole milk powders are comparatively low and approach or possibly exceed the limits of the favored Hills and Thiel (3) analytical procedure. We, therefore, sought a more sensitive method of peroxide determination for our work.

Data reported in this paper were obtained using a slight variation of the method developed by Horgan et al. (4).

Since the method is not well known, we will present a few details of the analytical procedure, as well as the results obtained by its use in determining the contribution of the various manufacturing steps to the peroxide value of the fat in whole milk powders.

Materials and Methods¹

All powders were made from milk obtained from a herd maintained at the Agricultural Research Center, Beltsville, Maryland. The milk was collected in bulk tanks over a three-day period before drying.

Powders were made from milk standardized to 3.3% fat. Subsequent pasteurization, homogenization, concentration, and foam-spray drying were done with equipment and techniques described by Hanrahan et al. (2). The same equipment was used without gas injection to produce the conventional spray-dried samples.

The peroxide content of milk fat isolated from samples of milk, concentrate, and powder by the method of Pont (6) was measured using a procedure described by Horgan et al. (4). According to this procedure, the reduced leuco form of the dye Brilliant Cresyl Blue (Allied Chemical Company, National Aniline Division,

Received for publication December 16, 1968.

¹Mention of brand or firm name does not constitute an endorsement by the Department of Agriculture over others of a similar nature not mentioned.

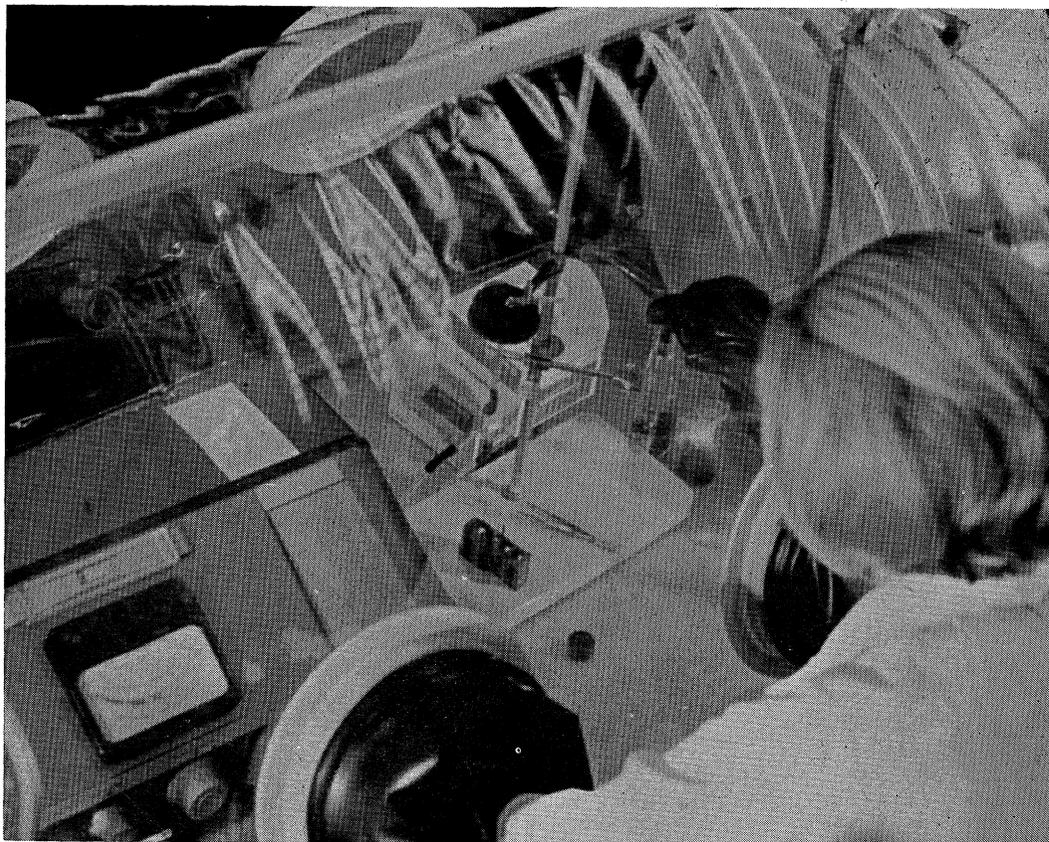


FIG. 1. Equipment used for determining peroxide concentration in milk fat using Horgan's procedure. The spectrophotometer is to the left of the analyst and the dye-reducing equipment to the right.

New York, New York) reacts stoichiometrically with peroxides to produce the colored oxidized form of the dye. However, the reaction is not specific and the reagent is easily attacked by atmospheric oxygen. To overcome this difficulty we did all peroxide determinations under nitrogen in a plastic glove-box. A slight positive pressure was maintained on the gas in the interior of the compartment and the oxygen content of the atmosphere in the glove-box was continuously monitored by allowing a small quantity of interior gas through a Beckman Model E2 paramagnetic oxygen analyzer. A photograph showing the general layout of the equipment as used is presented in Figure 1.

In doing the analysis, fat extraction from samples investigated was done outside the glove-box. A 0.22-ml aliquot of the extracted fat sample was measured into a spectrophotometer cell followed by adding 1.3 ml *n*-butanol. A 1.5 ml sample of *n*-butanol served as the control.

Spectrophotometer cells containing diluted fat samples and the controls were passed into the glove-box through appropriate ports. Residual oxygen was swept from the samples and controls by bubbling a fine stream of nitrogen through them for 5 min. A 0.5-ml aliquot of a solution of reduced Brilliant Cresyl Blue was then added to each cell and the intensity of the blue color developed by the peroxides present was measured, using a Model B Beckman spectrophotometer. Absorption of light having a wave length of $620\text{ m}\mu$ was measured. These absorption values were converted to peroxides by using a standard curve constructed from data obtained using solutions containing a known quantity of benzoyl peroxide. Due to the instability of the dye solutions, new standard curves were made for each series of analysis.

The precision of this method was excellent. The average difference between duplicate an-

alyses in 75 analyses was 0.003 meq O₂/kilo-gram fat.

Results

The effect of the concentrating and foam-drying steps on the peroxide values of milk fat is shown in Table 1. It can be seen from the average values obtained from analysis of 20 production runs that fresh milks contain low, but detectable, levels of peroxide which increase only slightly on concentration. Even though a more significant increase in peroxide concentration was noted during foam-spray drying, the average peroxide value of the fat in the finished product remained relatively low.

Even though the foam-spray-drying operation produces powders in which the milk fat has undergone relatively little oxidative change, the observed peroxide values are almost double those obtained from a study of conventionally spray-dried material. Shown in Figure 2 are typical data obtained in our comparative study of peroxide content of foam-spray and conventionally spray-dried products. Here we see evidence that the extent of oxidation of milk fat in conventionally spray-dried powder is less than in foam-spray-dried material. Also to be noted is the difference in oxidation rates of the two types of powders when stored in air. Conventionally spray-dried material exhibits greater stability against oxidaton when exposed to air. However, reducing the storage

Table 1. Changes in peroxide content of milk during concentrating and foam-spray drying.^a

Sample number	Milk	Concen- trate		Dried milk
		(meq O ₂ /kg fat)		
1	.010	.010	.020	
2	.010	.010	.020	
3	.010	.010	.025	
4	.010	.010	.025	
5	.010	.010	.030	
6	.010	.015	.020	
7	.010	.015	.030	
8	.010	.015	.040	
9	.010	.025	.030	
10	.010	.025	.030	
11	.015	.015	.030	
12	.015	.015	.030	
13	.015	.020	.025	
14	.015	.045	.050	
15	.025	.030	.040	
16	.025	.030	.040	
17	.040	.040	.045	
18	.040	.045	.050	
19	.040	.045	.055	
20	.040	.045	.110	
Average	.019	.024	.036	

^a All values are averages of duplicate analyses.

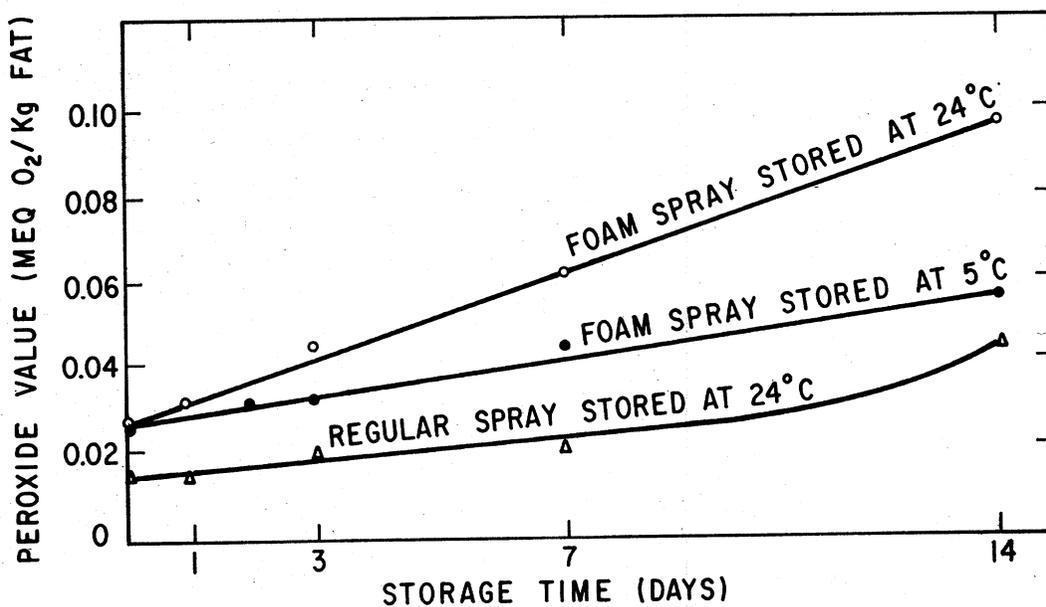


Fig. 2. Comparison of initial peroxide content and oxidative stability of foam-spray and conventionally spray-dried whole milk. Values represent average of duplicate analyses.

temperature of foam-spray-dried milk allows at least 14 days' storage in air with only minor increase in peroxide content.

Discussion

The peroxide values of fat isolated from fresh milk and determined by using the method of Horgan et al. (4) ranged from 0.010 to 0.040 meq O₂/kilogram fat. They agree well with those reported by Hills and Thiel (3) for peroxides in fat extracted from fresh milk taken from individual cows.

The small increase in peroxide content of milk fat during concentration to 50% total solids may be atypical, since the operation was done in custom-built equipment designed for aseptic concentration and leaked little or no air. The peroxide content of fats isolated from foam-spray-dried powders was similar to that observed in vacuum-dried milk foams by Kliman et al. (5). From the data presented by these authors, it is improbable that the fat oxidation occurring during foam-spray drying can be detected organoleptically.

Fat in foam-spray-dried powders obviously oxidizes more rapidly than in conventionally spray-dried material during manufacture and storage. However, the extent of oxidation during drying is relatively minor.

In consideration of the inherent oxidative instability of foam-spray-dried whole milk, due to its relatively high free fat content, it is advisable to package the product in an inert atmosphere soon after production.

After opening packaged foam-spray-dried material and exposing it to the air, it should be used within a week if kept at room tempera-

ture. This holding time can be doubled if the product is kept under refrigeration.

Even though foam-dried whole milk is inherently more unstable than conventional spray-dried material when exposed to air, its porous structure is highly advantageous in obtaining the low in-package oxygen levels necessary for long shelf life (7).

References

- (1) Greenbank, G. R., and M. J. Pallansch. 1962. The progress of oxidation in milk powder granules. XVIth Int. Dairy Congr., Rep. Section V: 2, p. 1002.
- (2) Hanrahan, F. P., A. Tamsma, K. K. Fox, and M. J. Pallansch. 1962. Production and properties of spray-dried whole milk foam. *J. Dairy Sci.*, 45: 27.
- (3) Hills, L., and C. C. Thiel. 1946. The ferric thiocyanate method of estimating peroxide in the fat of butter, milk and dried milk. *J. Dairy Res.*, 14: 340.
- (4) Horgan, V. J., J. St. L. Philpot, B. W. Porter, and D. B. Roodyn. 1957. Toxicity of autoxidized squalene and linoleic acid, and of simpler peroxides, in relation to toxicity of radiation. *Biochem. J.*, 67: 551.
- (5) Kliman, P. G., A. Tamsma, and M. J. Pallansch. 1952. Peroxide value-flavor score relationships in stored foam-dried whole milk. *Agr. Food Chem.*, 6: 496.
- (6) Pont, E. G. 1955. A deemulsification technique for use in the peroxide test on the fat of milk, cream, concentrated and dried milks. *Australian J. Dairy Technol.*, 10: 72.
- (7) Tamsma, A., F. E. Kurtz, and M. J. Pallansch. 1967. Effect of oxygen removal technique on flavor stability of low-heat foam-spray-dried whole milk. *J. Dairy Sci.*, 50: 1562.