1834

Peroxide Value–Flavor Score Relationships in Stored Foam-Dried Whole Milk

PHYLLIS G. KLIMAN, ARJEN TAMSMA, and M. J. PALLANSCH

Dairy Products Laboratory, U. S. Department of Agriculture, Washington, D. C.

The possibility of determining the flavor score of stored vacuum-foam dried whole milk powders by determination of the peroxide content (P.V.) of the powders was studied. In both air packs and nitrogen packs, no useful correlation was found between P.V. and flavor scores. An interesting periodic fluctuation of P.V. with time was observed in nitrogen packs. It was concluded that information on the peroxide content of whole milk powders could not be used to establish flavor quality of fresh or stored samples.

CHEMISTS engaged in research pertaining to flavor stability of stored foods have often been frustrated by the vagaries of data obtained from taste panels. Long sought has been a simple chemical test or tests whose results could be correlated directly with flavor variations.

In studies of some high fat foods, it has been reported that the extent of oxidative change and the subsequent flavor deterioration in the food could be evaluated by a quantitative determination of the peroxide content of its fat phase (*2, 8, 10*). These peroxides supposedly decomposed to form the carbonyl compounds thought to be responsible for the development of the oxidized flavors detected in stored products (*4, 5, 8, 13*).

During the course of a research program directed toward improving storage stability of foam-dried whole milk, peroxide content and flavor scores of all experimental samples of vacuum foam-dried whole milk were determined in routine fashion. Noting a poorer correlation between these values than was anticipated, the authors made a specific study to determine the extent to which the peroxide content of whole milk powder produced by foam-drying under high vacuum could be related to flavor quality of the product.

This article reports results obtained by studying eight replicate whole milk powder samples held in storage with both unlimited and restricted access to oxygen. Also reported are initial peroxide contents and flavor scores of 43 experimental samples of foam-dried whole milk powders, 15 of which were exact replicates from a production standpoint.

Materials and Methods

All milk powders were made from fresh morning milk obtained from a herd maintained by the Animal Husbandry Research Division, Beltsville, Md. Milk was delivered to the laboratory in full, slosh-proof cans and standardized to a 2.75:1 solids-not-fat to fat ratio before processing.

The standardized milk was pasteurized at 145° F. for 30 minutes, concentrated to 50% total solids, homogenized at 4500 p.s.i. and cooled to 110° F. Nitrogen gas was then incorporated into the concentrate, and the material was foam-dried in a vacuum oven (Stokes Model 900-1384) according to the method of Sinnamon and coworkers. (*14*).

The dried foam was broken through a 20-mesh screen and the resultant powder was split into two lots. One lot was packaged in cans. A special technique was developed to fill the cans with nitrogen containing less than 0.1% of oxygen (*16*). This was done by placing the powder in cans equipped with vents in their covers. The cans were placed in a vacuum oven and evacuated overnight. The oven was then filled with oxygen-free nitrogen, and the vents in the can were closed before the oven was opened to remove the cans. Cans were checked for leakage, and oxygen content of random samples was determined using standard Haldane apparatus.

The remaining lot of powder was held in open stainless steel trays. At least twice a day, the thin layers of powder were stirred to equalize their exposure to air. All powders were stored at 55° F.

Samples for peroxide determination and flavor evaluation were taken every other day for the first 2 weeks and then at weekly intervals during the following 10-week period.

The lipide material used for the peroxide determination was obtained from the reconstituted powder by using the method of Pont (*11*). In this method, the milk emulsion is broken by using a mixture of butanol, sodium salicylate, and sodium citrate. A 0.5-ml. aliquot of the fat released from a 30-ml. sample of reconstituted milk was used for the peroxide determinations.

The peroxide content of the fat was determined by using Pont's modification (*12*) of the Hills and Thiel method (*3, 11, 15*), in which is observed the extent of oxidation of ferrous ions to the ferric form by the peroxides present. The peroxide value (P.V.) determined by this procedure is expressed in terms of milliequivalents of oxygen per kilogram of fat.

The characteristic flavor type and intensity of the samples were determined by an expert taste panel. Ten experienced judges tasted each sample presented to them in random fashion. The judges independently evaluated flavor type and intensity of each sample and assigned it a numerical score in accordance with a score card based on one recommended by the American Dairy Science Association (*16*).

Results

A study of P.V. and flavor scores of freshly prepared powder samples showed no correlation as demonstrated in Figure 1. Even though many of these samples were obtained by minor variations in drying technique, 15 of the samples were exact replicates from a production standpoint.

The whole milk powder samples exposed to air quickly developed off-flavors and high peroxide values. Figure 2 shows the relationships between flavor score and P.V. encountered during storage of a typical powder in air. Here a good reciprocal relationship seems to exist between the two factors. Although the same type of plot was obtained from the study of other powder samples (Figure 3), close inspection shows that the P.V. does not establish the flavor score. Powder K2 has a reasonably high score (36.4) with a P.V. of 0.20; whereas, powder K1 scored slightly above 31 with a P.V. of 0.17. This same lack of agreement, between P.V. and flavor scores obtained from powders stored in air, was noted in all samples. In fact, after a relatively few days in air, off-flavors became so intense and disagreeable that the response of the taste panel became ex-

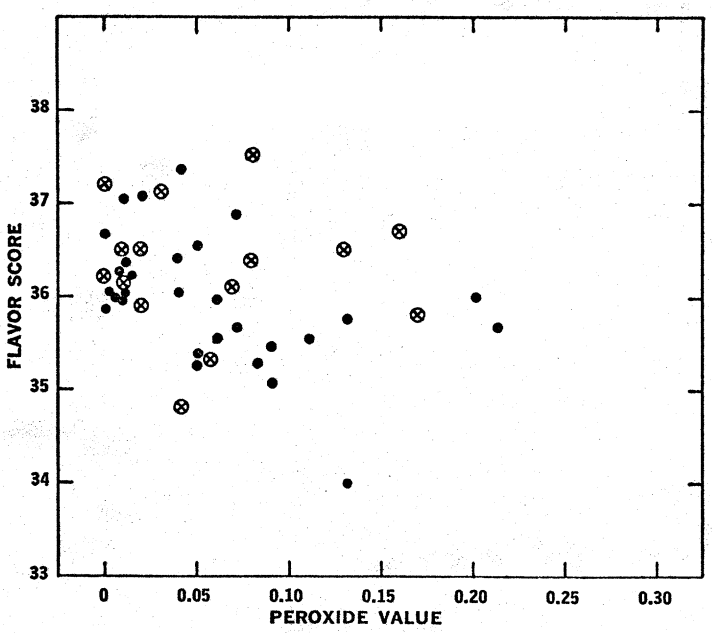

Figure 1. Peroxide value–flavor score relationships in fresh whole milk powders

Crossed points are exact replicates from a production standpoint. All points represent samples obtained by using minor variations of the standard drying procedure

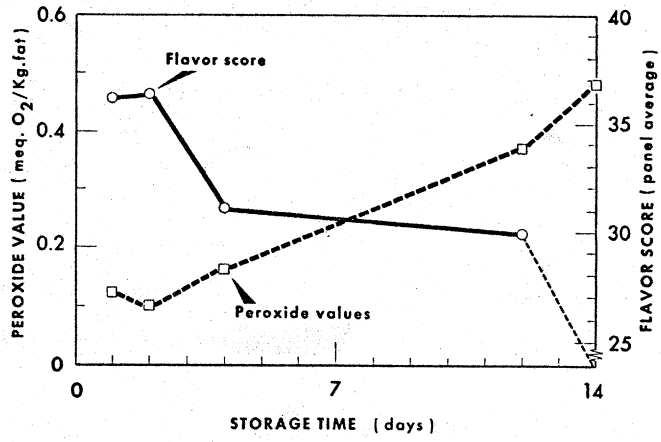

Figure 2. Peroxide value–flavor score relationships during storage of foam-dried whole milk sample K1

Air pack, storage temperature 55° F.

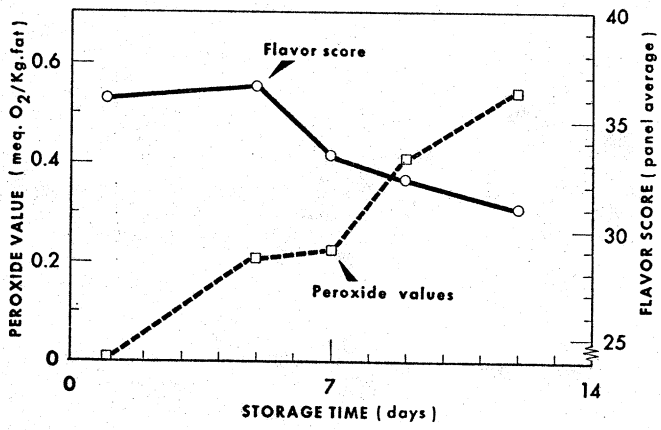

Figure 3. Peroxide value–flavor score relationships during storage of foam-dried whole milk sample K2

Air pack, storage temperature 55° F.

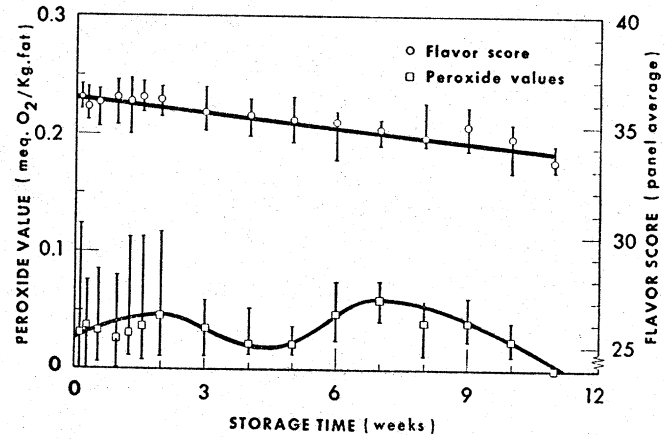

Figure 4. Average peroxide value–flavor score relationships during storage of eight foam-dried whole milk samples

Nitrogen pack, storage temperature 55° F.

tremely erratic and internal agreement was lost.

Figure 4 summarizes data obtained from the study of eight different samples of nitrogen-packed powder prepared over a 6-month period. In this case, the average values as well as the extent of deviation are shown. The powders undergo a relatively linear deterioration in flavor score, while peroxide values remain low and approach zero after 10 weeks of storage. The plot of the average peroxide values describes a doubly peaked curve. This general pattern was exhibited by all powders studied, although the location of maxima and minima varied somewhat. During storage under nitrogen, the flavor of the powder became increasingly stale.

Table I presents typical experimental results in which the pertinent criticism of the judges, flavor score, and peroxide values of the powders are shown.

Discussion

The validity of various methods of determining peroxides has been extensively studied with conflicting results (*6*, *7*). In this study, the recommendations of Glavind and Hartmann (*1*) were taken and a method of high sensitivity was used. It is known from the authors' investigation, and that of others, that this method does not give absolute peroxide concentration according to the laws of stoichiometry. Since relative values were all that was needed, it was felt that the sensitivity and relative simplicity of the method would justify its use. Variations observed in P.V. values of replicate samples was ±0.015.

Equal in importance to the method of peroxide determination used is the method employed in obtaining the lipide sample used in the analysis. In preliminary investigations, it was found that P.V.'s determined would depend to a large extent on the extraction method used. Chlorinated organic solvents and detergents gave rise to high values. Pont's method gives relatively low values. Since this problem was investigated by Pont, his recommendations were followed. No evidence was obtained showing that de-emulsification by use of butanol and sodium salicylate gave rise to peroxides other than those initially present in the fat.

The data obtained by the use of the described methods, in spite of its limitations, show that the determination of peroxides provides information of little value

Table I. Storage Behavior of Nitrogen-Packed Foam-Dried Milks

Storage Time, Days	Flavor Score[a]		Pertinent Criticism[b]		Peroxide Value[c]	
	Sample K7N	Sample K8N	Sample K7N	Sample K8N	Sample K7N	Sample K8N
Initial	36.5	36.6	1 stale 2 oxid.	2 stale	0.012	0.010
3	35.6	..	7 stale	....	...	...
5	..	36.4	....	5 stale	...	0.047
7	36.3	..	5 stale	....	0.019	0.038
9	..	35.3	....	3 stale 1 oxid.	0.026	0.026
11	36.1	..	3 stale 1 oxid.	....	0.026	...
12	..	35.8	....	1 stale 1 oxid.	...	0.033
14	36.1	36.2	4 stale	3 stale 2 oxid.	0.033	0.033
21	35.3	35.2	6 stale 2 oxid.	8 stale	0.028	0.016
28	34.9	35.4	....	....	0.014	0.014
35	35.0	34.3	4 stale 4 oxid.	5 stale 4 oxid.	...	0.024
42	35.2	34.8	8 stale 1 oxid.	7 stale 1 oxid.	0.038	0.066
49	35.3	35.0	6 stale 1 oxid.	6 stale 1 oxid.	0.054	0.058
56	34.7	34.6	8 stale	8 stale 1 oxid.	0.040	0.046
63	35.6	33.9	7 stale	8 stale 2 oxid.	0.026	0.036
70	34.6	34.4	6 stale 3 oxid.	5 stale 3 oxid.	0.012	0.024

[a] Average score from 10 judges. [b] Number of judges. [c] Meq. O_2 kg. fat.

in establishing the flavor quality of foam-dried whole milk. This is particularly true in those instances where the powder has access to relatively low levels of oxygen. Even in the extreme case where less than 0.1% oxygen is present in the inert gas in the powder package, flavor deterioration occurs. This deterioration in flavor can in no way be related to the peroxide value of the fat removed from the stored powder.

While the determination of peroxide concentration in the fat phase of milk powder may be of some value in the study of the mechanisms of oxidative processes, it has no direct bearing on the establishment of flavor quality, except in those instances where the oxidized flavor is so pronounced that it can be established unequivocally by taste.

It is interesting to note the scattering of peroxide values in the initial determinations at the start of the storage study. Although these powders were exact replicates from a production standpoint, they varied widely in the extent to which oxidation had occurred during the drying process. Since the samples were made at intervals over a 6-month period, it is not known if these observed deviations arose from seasonal changes in the milk or slight uncontrolled variances in processing. A study of the oxidative stability of milk taken from individual cows during various seasons has been initiated in this laboratory. The effects of this fluctuation in milk stability on the storage stability of milk powders will be presented in a future article.

Also, some oxidation occurs in nitrogen packs containing approximately 0.1% oxygen. Although the peroxide values in the powder never become high and drop to zero in less than 12 weeks, the powder becomes progressively more stale in flavor. This stale flavor may have resulted from the low level of oxidation that did occur. At present, experiments are being carried out to reduce in-package oxygen to near zero levels, to study the effect of oxidation on the development of stale flavors in milk powders.

Somewhat curious is the shape of the curve describing the change in peroxide values with time in powders packed in nitrogen containing low levels of oxygen (Figure 4). The periodicity shown occurred in all samples studied. This periodicity was verified at the Eastern Utilization Research and Development Division, Wyndmoor, Pa., with similar milk powder samples prepared in the same fashion using a micro iodometric titration to establish the peroxide content of the samples. The data may be taken to indicate a multiplicity of oxidative substrates in the powder. Alternatively, the curve may reflect a chemical reaction proceeding in a periodic manner. According to Lotka (*9*), undamped vibrations occur when a substance A in constant concentration forms a substance B autocatalytically which in turn changes to a substance C autocatalytically. If this occurs, the amplitude is dependent on the initial concentration. The period of vibration should be constant and is given by:

$$T = \frac{2\pi}{\sqrt{ab}}$$

where a and b are velocity constants in the formation of B and C.

At present, sufficient information is not available to ascertain the correct explanation for the observed periodicity in the peroxide value curves obtained from a study of the storage of milk powders in packages containing low levels of oxygen.

Literature Cited

(1) Glavind, J., Hartmann, S., *Acta. Chem. Scand.* **9,** 497 (1955).
(2) Greenbank, G. R., *Intern. Dairy Congr. Proc., 12th, Stockholm* **2,** 2, 284 (1949).
(3) Hills, G. L., Thiel, C. C., *J. Dairy Res.* **14,** 340 (1946).
(4) Keeney, M., Doan, F. J., *J. Dairy Sci.* **34,** 713 (1951).
(5) *Ibid.*, p. 719.
(6) Kolthoff, I. M., Medalia, A. I., *Anal. Chem.* **23,** 595 (1951).
(7) Lea, C. H., *J. Sci. Food Agr.* **3,** 586 (1952).
(8) Lea, C. H., "Rancidity in Edible Fats," 1st Ed., 79–121, Chemical Publ. Co., New York, 1939.
(9) Lotka, A. J., *J. Am. Chem. Soc.* **42,** 1959 (1920).
(10) Malhan, P. R., Kartha, A. R. S., *J. Sci. Ind. Res. (India)* **15B,** 326 (1956).
(11) Pont, E. G., *Australian J. Dairy Technol.* **10,** No. 2, 75 (1955).
(12) Pont, E. G., Rogers, W. P., *Ibid.*, **13,** No. 3, 146 (1958).
(13) Riel, R. R., Sommer, H. H., *J. Dairy Sci.* **38,** 1215 (1955).
(14) Sinnamon, H. I., Aceto, N. C., Eskew, R. K., Schoppet, J. H., *Ibid.*, **40,** 1036 (1957).
(15) Stine, C. M., *Ibid.*, **37,** 202 (1954).
(16) Tamsma, A., Pallansch, M. J., Mucha, T. J., Patterson, W. I., *Ibid.*, **44,** 1644 (1961).