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Disturbances in the Natural Oxidation-Reduction Equilibrium of Milk with Special Reference to the Use of the Dehydrated Milks in the Manufacture of Cottage Cheese

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ABSTRACT

It is very probable that Eh measurements of milk and milk products will find a very significant place in both the theoretical and the practical field. Although the natural oxidation-reduction equilibrium of fresh raw milk appears well poised, it may be altered to a sensitive condition. The Eh of fluid skim milk is less stable than whole milk. The character of the Eh in reconstructed dry milk appears to be altered to a more sensitive state than that of fluid raw or pasteurized milk and is reflected in the resultant cottage cheese. There appears to be a relationship between the Eh and the chemical and physical properties of milk and cottage cheese. The addition of electrolytes affects the Eh depending upon their concentrations.

ACKNOWLEDGMENT

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W. H. E. REID AND R. L. BROCK *

INTRODUCTION

The increased demand of the public for cottage cheese has made it one of the most important of all dairy products.

The improvement in the quality of the product is responsible for this increased consumer demand. Therefore, it is essential that the manufacturer maintain a high standard of quality in the product.

The dehydrated milks are the most valuable reserves available to the manufacturer and since it is very essential that he shall maintain that high level of quality, it is then necessary to not only know how to make a high quality product from the valuable reserve, but how to safeguard the quality as in all other dairy products.

The purpose of this investigation was to study the conditions of manufacture and storage of cottage cheese made from the dehydrated milks, determine those factors which are detrimental to that quality level, and develop possible corrections for application in the plant.

REVIEW OF LITERATURE

Rice and Miscall (1923) working with milk, concluded that open tanks and pasteurizers were more favorable to the solution of copper than those which were closed.

Duncombe (1924) working on the hydrogen ion concentration of milk, concluded that an increase in temperature caused a decrease in pH values.

Chapin (1926) states, "Sunlight increases the speed of certain reactions, notably organic. This may be due to the ionizing power of light".

Whittier and Benton (1927) found an increase in acid when milk was heated and analysis showed that the decrease in lactose was more than the molecular equivalent of the acid produced. The addition of lactose made a corresponding increase in acid with the heating of the

*The data presented in this bulletin were taken from a paper submitted by the junior author in partial fulfillment of the requirements for the degree of Master Arts in the Graduate School of the University of Missouri, 1934.

milk. They concluded that lactose is the source of acid when milk is heated.

Associates of Rogers (1928) state that, " . . . the Eh of fresh unheated milk is of the order of plus 0.2 to 0.3 volts referred to the normal hydrogen electrode . . . " As to the influence of ultra-violet light, the same range of wave length (2400Å to 2800Å) which are most lethal to organisms is absorbed by the amino acids, phenolalanine and tyrosine, the aromatic amino acid radicals of the protein being the agent of absorption.

Frasier (1928) states, "The light apparently acts as a catalyst in the oxidation of the milk fat. The defect develops more rapidly in the pasteurized than in the raw milk . . . the presence of neither enzymes nor bacteria is necessary for the reaction".

Derpher, Webb, and Holm (1929) found that variation in the heat treatment of a milk effect greatly the heat stability of the evaporated product.

Hunziker, Cordes, and Nissen (1929) concluded that two or more metals in the same piece of dairy equipment is fundamentally undesirable. Most metals used may differ in their electrical potentials and invite corrosion by electrolysis.

Miscall, Cavanaugh, and Carodemos (1929) working on the solution of copper in milk, found " . . . either the removal of the milk gasses or the addition of carbon dioxide decreases the copper dissolving power of milk. Oxygen increases the amount of copper which goes into solution but does not change the general type of the solubility curve. Pasteurized milk is shown to dissolve more copper than raw milk at the same temperature. They further concluded that when milk was heated above pasteurizing temperature in contact with bright copper, there was a reaction which took place in the milk serum to decrease the copper dissolving power of milk.

Michaelis (1930) in his publication, *Oxidation-Reduction Potentials,* does not think the gas reduction theory can be applied to "methylene blue-leuco methylene blue, which stands approximately midway between the H_2- and O_2- electrodes.

Colbentz (1930) in the study of ultra-violet transmitting glasses, found that ordinary window glass does not transmit the ultra-violet waves of shorter lengths than 313A, but it does transmit waves of lengths above this point.

Thornton and Hastings (1930) in studying methylene blue reduction tests in milk conclude that the mechanism of reduction takes place in two steps: 1. "Removal of the dissolved oxygen by bacteria"; 2. "The reduction of the dye by constituents of the milk".

Prucha, Brannon, and Ruehe (1931) found that cheddar cheese did not develop mold when stored in carbon dioxide. Unsweetened condensed milk, when super-heated, kept two to four weeks longer when carbonated.

Gebhardt and Sommer (1931) conclude, " . . . the observations on the oxidation-reduction potential may explain the mechanism through which acidity, dissolved gasses, temperature and preheating effects copper solubility." These same authors, (1932) working on the submerged corrosion of various metals in milk, gave a classification of these metals according to their corrosiveness in milk.

Aikens and Fay (1932) found that fat had a stabilizing effect on potential changes to either positive or negative and that the addition of methylene blue to skim milk or cream accentuated the potential changes induced by sun light. They concluded that the action of light is different from bacteria.

Tracy and Ramsey (1932) found that light developed an off flavor in cottage cheese made from fluid skim milk, the flavor being more intense from direct sunlight than from indirect light, artificial light not being effective.

Reid and Fleshman (1932) working with dry skim milk in the manufacture of cottage cheese found that it was necessary to add calcium chloride to obtain a more natural firmness of curd.

Tracy, Ramsey, and Ruehe (1933) found that skim milk or low fat milks developed more pronounced burnt flavors than whole milk or cream dependent upon the amount of oxygen present, heat, light, and the presence of metals such as iron and copper.

Thurston and Gould (1933) found that when using the holding method of thirty minutes, milk pasteurized higher than 145 degrees Fahrenheit gave a curd which did not firm so readily and was prone to shatter.

Henderson and Roadhouse (1934) using photo-electric cell determinations to study the initial induction period in the oxidation of milk fat (by the fading of methylene blue), found in working with pasteurized milk, that direct sunlight, indirect or diffused light, copper and nickel shortened the induction period. Chrome-nickel-iron alloy had no influence on the induction period.

PROCEDURE

The Measurement of Oxidation-Reduction Potentials in Terms of Eh, as compared to the normal hydrogen electrode, were made in the conventional way with a gold wire electrode, connected by a liquid junction and a saturated potassium chloride agar bridge. A Leeds and Northrup's type potentiometer was used for the measurements and a weston cell as standard. The potential which develops in a balanced system by the addition of hydroquinone was taken as the more negative potential.

The measurements on milk were made at seventy degrees Fahrenheit on samples taken at the respective temperatures. Glass was used in each instance unless otherwise indicated.

It was deemed advisable to use concentrations of dehydrated milk, which by previous investigations (Reid and Fleshmen, 1933) have been found to be the practical maximum. Fifty pound batches of fluid skim milk were used for each sample. The control was made from the natural fluid skim milk, the second batch was made from fluid skim reinforced with five per cent of dry skim milk, while the third batch was made from fluid skim reinforced with ten per cent of dry whole milk. The ratio of starter and rennet was such as would give a definite amount of acid development in each batch and a curd which set up at the same time. The addition of rennet and starter did not effect the character of the curd in the batches, since the added quantities served to balance the added solids. The acid developed was determined in the curd by electrometric pH, allowing .01 for the increased solids in the five per cent dry skim and an additional .02 for the solids in the ten per cent dry whole. The batches were set up almost simultaneously, thus permitting the cutting, heating, washing and draining of the curd to be carried out on the three batches under identical conditions.

The batches of cheese were manufactured in cooper vats which had been newly tinned with a heavy coat of block tin. The batches of cheese and the curd from each respective batch was allowed to firm over night in ice water, then allowed to drain for one hour. They were weighed for yield, and samples taken for analysis and exposure determination. Creamed samples were prepared by adding twelve per cent cream, containing four ounces of salt for each eight and one-fourth pounds of cream. Ten pounds of the creamed curd contained three pounds of the above cream and seven pounds of curd.

The effect of hydrolysis on the flavor of cottage cheese and the added effect of natural diffused light was determined by placing a definite amount of cheese in a glass battery jar and covering the curd with four liters of water. One jar of each kind of cheese was thus prepared. It was exposed to natural diffused light at seventy degrees Fahrenheit, while a second was held in the dark. Both sets of jars had air in equilibrium with the surface of the liquid.

Fifty cubic centimeter samples of clear supernated liquid were removed (at night), placed in twenty five cubic centimeters of sulfuric acid (sp. g. 1.86) and analyzed in the usual manner for total nitrogen by the Kjeldahl method. Three series were made and checked by Van Slyke amino acid determinations.

The influence of bacteria and enzymes on the flavor of creamed and uncreamed cheese was studied only to the extent of selecting specimens of supernated liquid from each sample of cheese exposed for hydrolysis. A comparison was made between the samples held in the light and those held in the dark.

The part played by lactose in affecting the flavor of the cheese was determined by adding two per cent of pure lactose to the storage water and comparing the resultant flavor with a control sample stored under the same conditions except the lactose was omitted.

The effect of lactic acid upon the flavor was determined by the addition of one per cent of lactic acid to the storage water and by comparing the resultant flavor with a control sample held under the same conditions, except that the lactic acid was omitted.

The pH measurements were made with a gold wire electrode by use of quinhydrone. The temperature corrections were taken at one-fourth degree intervals and the electrode was checked by the conventional acid phthaliate buffer solution.

Samples were taken from the manufactured curd, one portion creamed and the other portion uncreamed. The creamed and uncreamed portions were each divided uniformly and placed on a watch glass. A sufficient number of portions were used to allow one of uncreamed curd and one of creamed curd taken from each of the three kinds of cheese, to be placed in each of twelve desiccators. The desiccators were then divided into four groups of three each. One desiccator of each group was placed in a pure atmosphere of nitrogen, carbon dioxide, and oxygen respectively. Two groups of the desiccators were exposed to natural diffused light of approximately the same intensity, one at a temperature of forty degrees Fahrenheit, the other at a temperature of seventy degrees Fahrenheit, while the other two groups were held at the respective temperatures in the absence of light.

After an exposure of three days and five days respectively, the flavor of the various samples was observed. The Eh potentials of each sample were measured after an exposure of five days to light and darkness.

Tables 1 and 2 show the procedure of manufacture of different batches of cottage cheese and the physical properties of the original curd.

TABLE 1.—THE PROCEDURE USED FOR THE MANUFACTURE OF THE COTTAGE CHEESE

	Control Normal Skim Milk	Five Per Cent Dry Skim Milk in Normal Skim	Ten Per Cent Dry Whole Milk in Normal Skim
Dry Milk, per cent	Control (none)	5	10
Milk, lbs. (skim)	50	50	50
Starter, per cent	5	6	7
Rennet, cc. per 100 lbs.	14	16	18
Temp. set, degrees F.	87	87	87
Temp. cut, degrees F.	85	85	85
Temp. drained, degrees F.	125	125	125
Time-set to cut, hours	5	5	5
Time-cut to drain, hours	2	2	2
Time-set to drain, hours	7	7	7
Acidity set, per cent	0.21	0.21	0.21
pH at cutting	4.65	4.66	4.68
Acidity whey, per cent	0.54	0.74	0.83
Drainage water, per cent	78	70	62
Moisture of curd, per cent	85	84.9	81
Yield, pounds	11	15	19

TABLE 2.—DESCRIPTION OF PHYSICAL PROPERTIES OF ORIGINAL COTTAGE CHEESE MANUFACTURED FROM NORMAL SKIM MILK AND REINFORCED MILKS

Physical Properties	Control (Normal Skim)	Reinforced Milk	
		Five Per Cent Dry Skim Milk in Normal Skim	Ten Per Cent Dry Whole Milk in Normal Skim
Flavor	Neutral, creamy	Smooth, creamy	Creamy
Body	Firm, smooth	Firm, smooth	Firm. smooth
Texture	Pop corn	Pop corn	Pop corn
Color	White	Light cream	Cream
Whey	Acid	Sweet acid	Sweet acid

DISCUSSION OF DATA

The Effect of Heat on the Eh of Milk

The change in the potential of raw milk heated in a vat followed through the normal pasteurization period is shown in Figure 1. The Eh of the milk below 110 degrees Fahrenheit was not easily disturbed, whereas the potential of milk heated above 110 degrees Fahrenheit became less positive when heated slowly in a vat, the Eh decreasing during the holding period, and returning almost to the original potential when cooled to forty five degrees Fahrenheit.

When the pasteurized milk was reheated, the Eh of milk below 142 degrees Fahrenheit was not stable in contrast to the original raw milk, Figures 1 and 2, and was more sensitive to oxygen and movement of the electrode. The Eh of the reheated pasteurized milk at tempera-

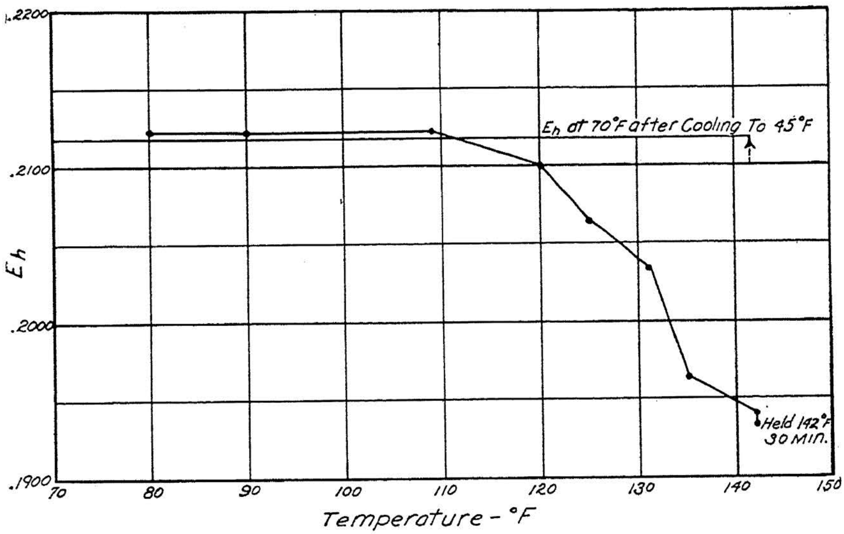


Fig. 1.—Eh changes during normal pasteurization period of milk. Determinations were made at 70 degrees Fahrenheit.

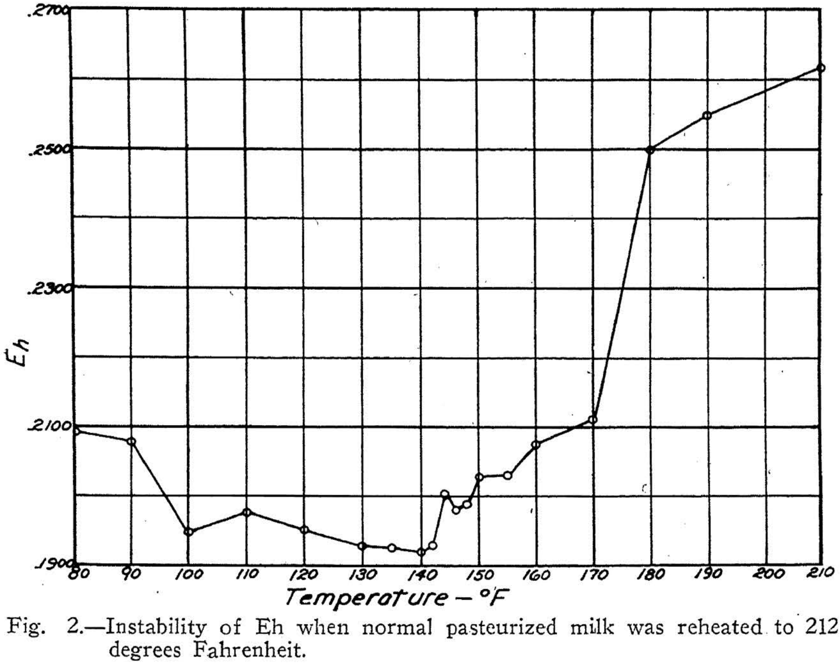


Fig. 2.—Instability of Eh when normal pasteurized milk was reheated to 212 degrees Fahrenheit.

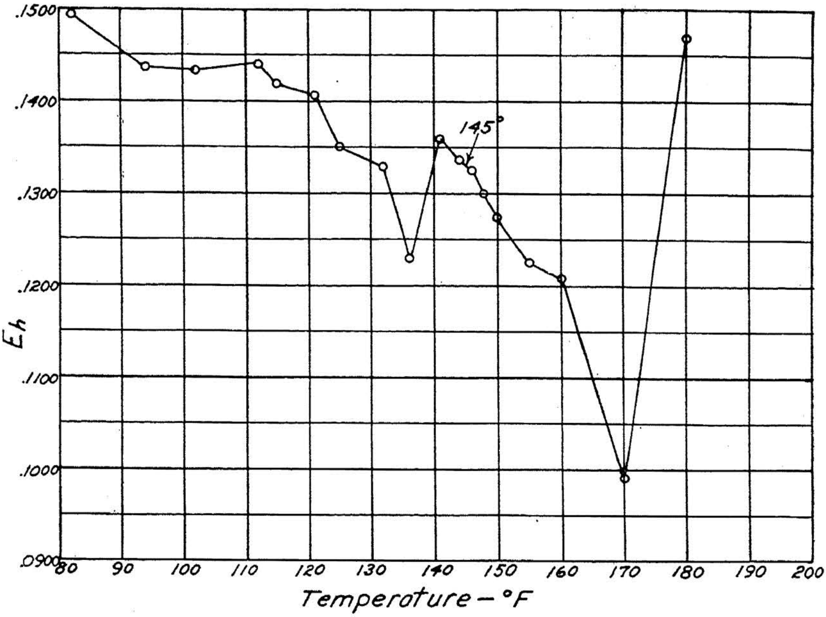


Fig. 3.—Instability of Eh when unaerated raw milk was heated to 180 degrees Fahrenheit.

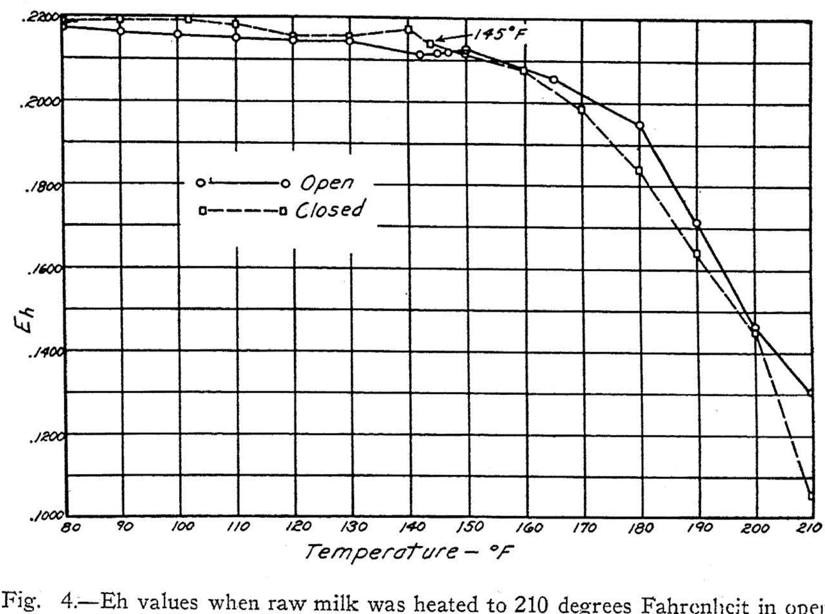


Fig. 4.—Eh values when raw milk was heated to 210 degrees Fahrenheit in open and closed containers.

tures exceeding 142 degrees Fahrenheit was very unstable, seemingly due to the additive effect of heat.

Figure 3 shows the Eh changes in the heating of fresh milk which had been placed in a tight stoppered glass container and cooled without aeration. The Eh was unstable and irregular during the entire heating period and was very sensitive to disturbances such as stirring of the milk and the addition of pure oxygen.

Figure 4 shows the change in potential when raw milk was heated in open and closed top glass containers. The Eh was quite stable until the pasteurization temperature was reached when a decrease to a less

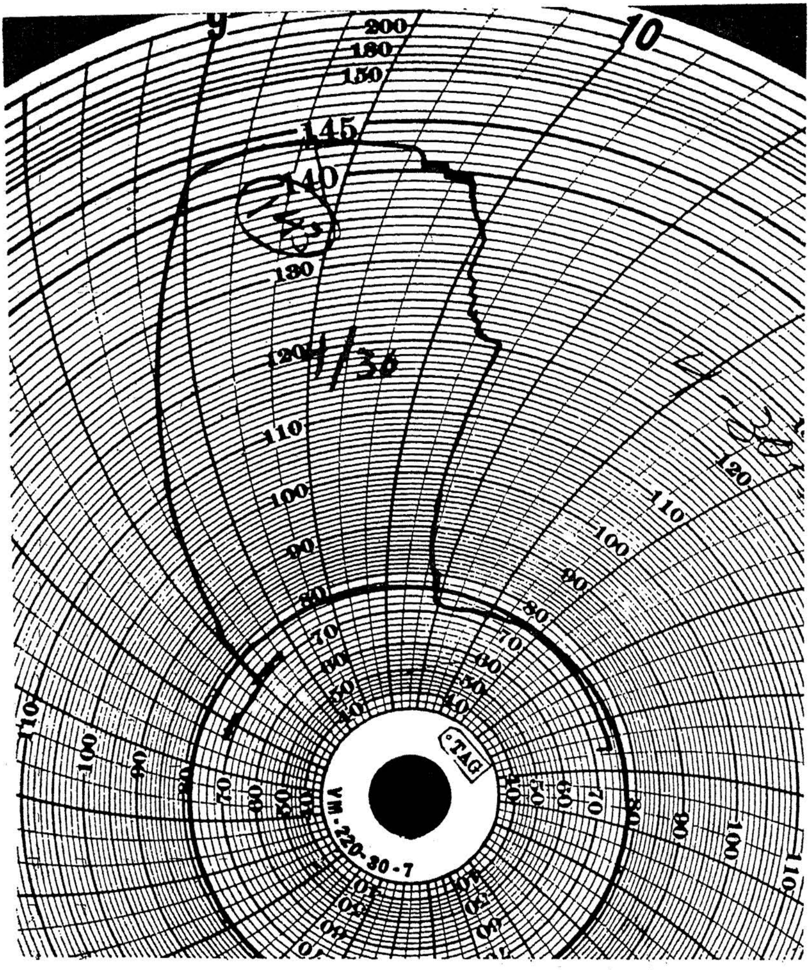


Fig. 5.—Chart of normally pasteurized milk used in observing Eh changes influenced by metals, alloys, and coated metals in Series 1.

positive value occurred. The Eh of the milk was increasingly more easily disturbed, according to the amount of variation from the original potential.

There was an apparent relation between the degree of change of Eh and the sensitivity of the milk system to foreign elements such as oxygen. Metals, alloys and coated metals were introduced into pasteurized milk to determine their effect on its Eh. Periods of exposure varying from twenty four hours to one hour were used. It was learned that when using periods exceeding one hour the Eh was not

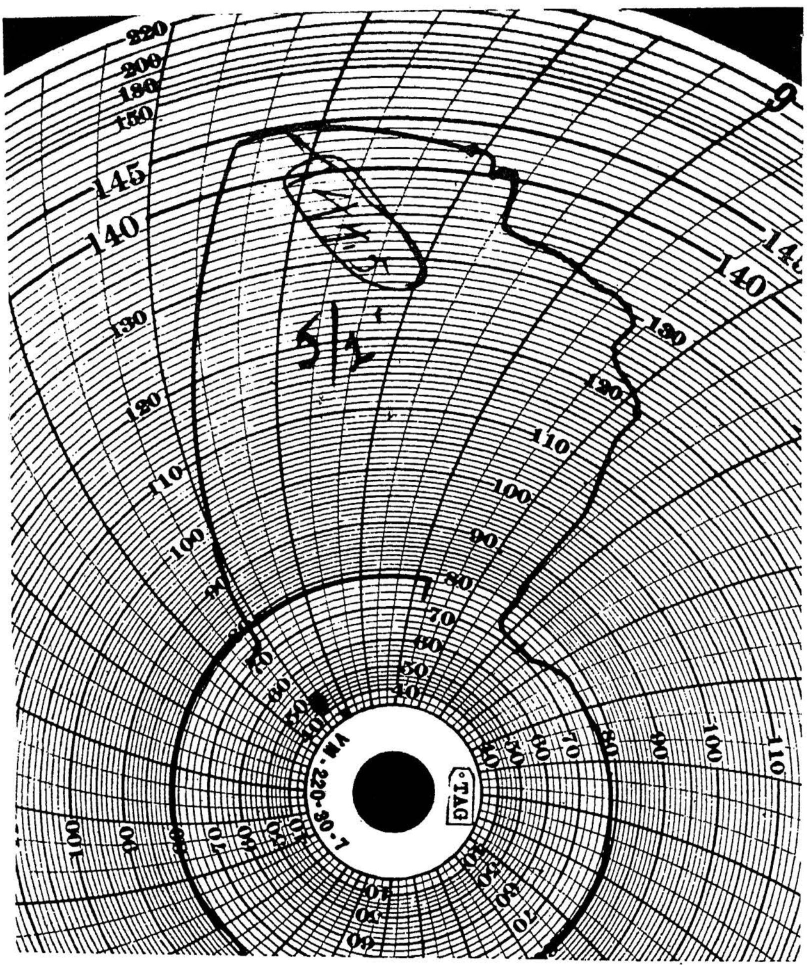


Fig. 6.—Chart of Milk pasteurized at excessive temperature and holding period used in observing Eh changes as influenced by metals, alloys, and coated metals in Series 2.

definite because of its instability, whereas the Eh of the original sample of milk was very stable.

TABLE 3.—METALS AS AFFECTING THE OXIDATION-REDUCTION POTENTIAL OF PASTEURIZED MILK

Metals Exposed	E_h After 1 Hour Exposure to Metals		Variation of E_h From That of Control Sample	
	Series 1	Series 2	Series 1	Series 2
Control Sample	.2240	.2208	.0000	.0000
Aluminum	.2240	.2208	.0000	.0000
Aluminum (2S)	.2240	.2208	.0000	.0000
Inconel	.2253	.2225	.0013	.0017
Stainless Steel	.2296	.2269	.0056	.0061
Stainless Steel	.2296	.2269	.0056	.0061
Tinned Copper	.2295	.2264	.0055	.0056
Electro-Tinned Copper	.2295	.2261	.0051	.0053
Hot Tin Copper	.2289	.2253	.0049	.0045
Tinned Iron	.2284	.2250	.0046	.0042
Block Tin	.2285	.2248	.0045	.0040
Commercial Nickel Silver	.2462	.2487	.0222	.0279
Nickel	.2329	.2284	.0089	.0076
Zinc	.2335	.2286	.0095	.0078
Copper	.2554	.2715	.0314	.0507
Copper	.2559	.2719	.0319	.0511
Galvanized Iron	.2334	.2286	.0094	.0078
Solder Coated Copper	.2322	.2280	.0082	.0072

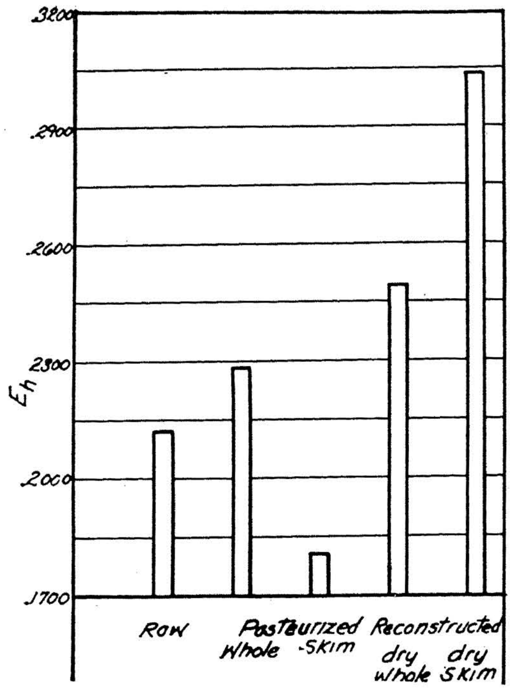


Fig. 7.—Comparison of the Eh of raw and pasteurized fluid milk and reconstructed milks.

When the metal strips were exposed for one hour the character of the Eh was not affected by the usual changes in the milk for that period, and it seems that the Eh readings, Table 3, were significant of the effect of the respective metals. Apparently, an increase in temperature and holding period as shown in Figure 6, as compared with Figure 5, has an effect of causing the milk to be more active with the particular metals involved. The variations were more noticeable with those metals which are considered most corrosive.

A comparison of the Eh of raw and pasteurized fluid milk with that of the reconstructed milks, Figure 7, shows that the reconstructed milks have a high Eh. It was also found that the reconstructed milks proved to be more sensitive to Eh changes by foreign elements such as oxygen. When oxygen was bubbled through the samples of milk in Figure 7, it was found that the Eh of the pasteurized whole milk was more sensitive than the raw milk, followed with relative increased sensitivity in the pasteurized skim, reconstructed whole and skim respectively.

The Characteristic Eh of Dehydrated Milk Apparent in Cottage Cheese Involving the Use of Dehydrated Milk

In the manufacture of cottage cheese involving the use of dry milk it was found as shown in Figure 8, that as the milk solids increase

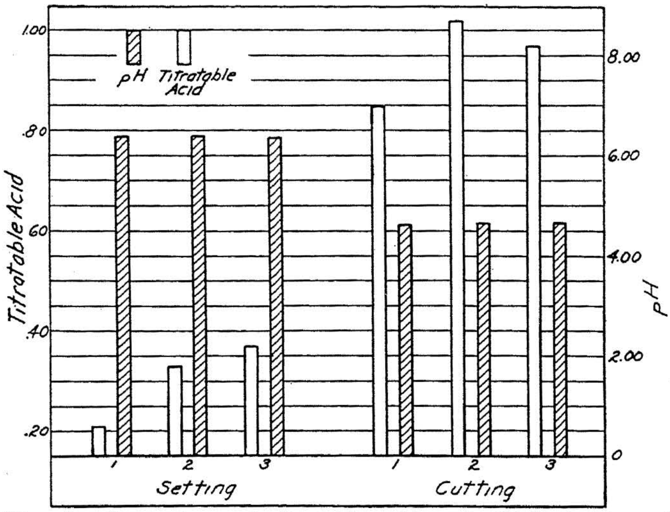


Fig. 8.—Comparison of titratable acid and pH in batches of cottage cheese when (1) fluid skim; (2) dry skim; and (3) dry whole milk are involved.

the titratable acidity also increases in such a manner as to make it impractiable for use in determining a uniform cutting point when the milk solids are varied. The pH, in contrast, was found to be quite reliable in determining a desirable cutting point when there was a large variation in the milk solids content. For instance pH of 4.7 was found to be satisfactory for determining the coagulation point irrespective of milk solids content.

The changes in the Eh were followed through the manufacturing process of cottage cheese. Figure 9 shows a comparison of the Eh of cottage cheese made from fluid milk and cottage cheese in which dehydrated milk is involved. In the batches in which dry milk was involved, it will be noted that the Eh was higher in this milk at time of setting and that the same batches had not become so negative in potential at cutting as had the fluid skim batch. In the samples of cheese in which dry milk was involved the Eh was slower to adjust

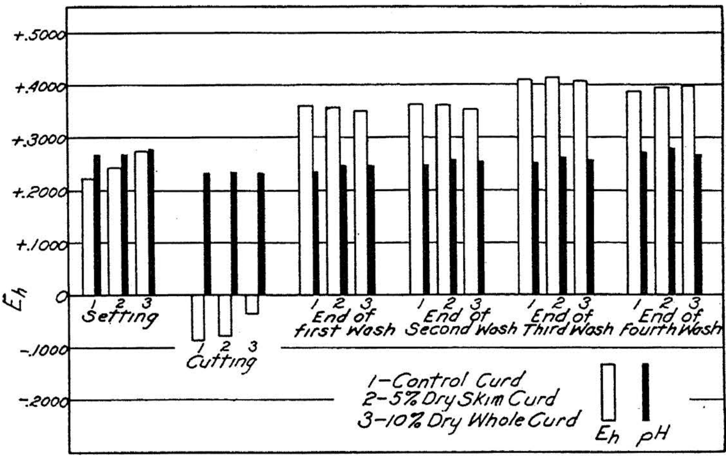


Fig. 9.—Comparison of Eh during the process of manufacture of cottage cheese involving the use of fluid skim milk and dehydrated milks.

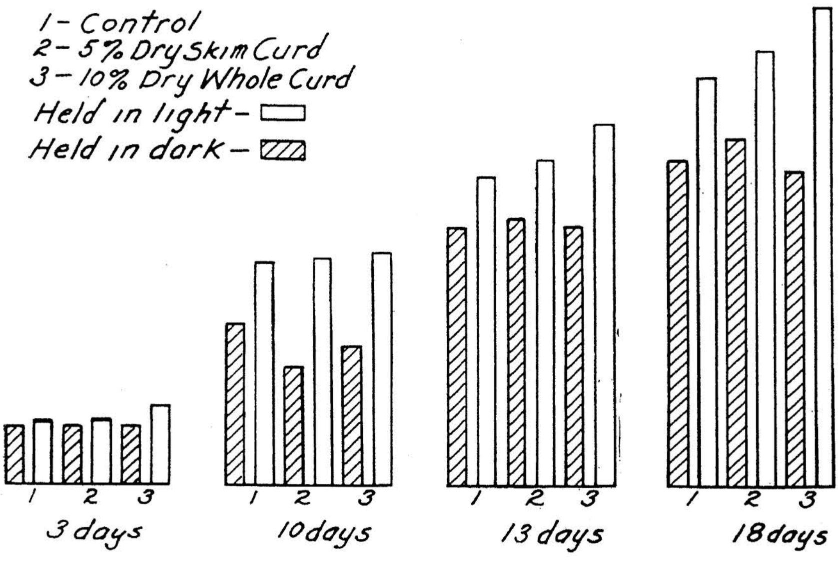


Fig. 10—Comparative influence of light on the hydrolysis of cottage cheeses involving the use of fluid skim milk and dehydrated milks.

itself in the washing of the curd, which may be due to a change in the character of Eh inasmuch as it becomes extremely sensitive.

The dry milk apparently influenced the cheese by its characteristic high Eh, and since there appeared to be a previous relation of the Eh and the activity of the given system, it was decided to determine if the cheese in which dry milk was involved supported this observation. Samples of the cheese, in which dry milk had been involved in its manufacture, were held under water, in the presence of natural diffused light and in the absence of light. It was found, as shown in Figure 10, that cheeses involving dry milk were more sensitive to the effect of light than the fluid skim curd, as measured by the increasing amounts of water soluble proteins.

Figure 11 shows also that the samples containing the 5 per cent of dry skim and the 10 per cent of dry whole were more sensitive to changes in Eh by light. A direct microscopic examination of the water soluble protein samples tended to indicate the effect of light on the Eh and hydrolyses was independent of the bacteria count.

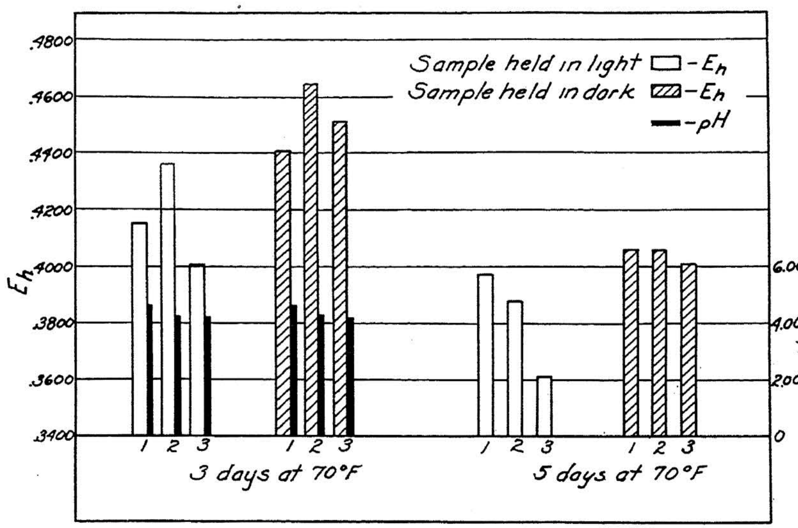


Fig. 11.—Sensitivity of Eh of cottage cheese to light when (1) fluid skim; (2) dry skim; and (3) dry whole milks are involved.

Figure 12 shows that the curd containing the dehydrated milk was more susceptible to substances commonly used in the manufacturing process of cottage cheese, such as sodium chloride, lactose and lactic acid. The changes in flavor seemed to correspond to the findings in the Eh readings since the addition of lactic acid and lactose were counteractive in potential but resulted in the occurrence of an undesirable flavor in the cheeses.

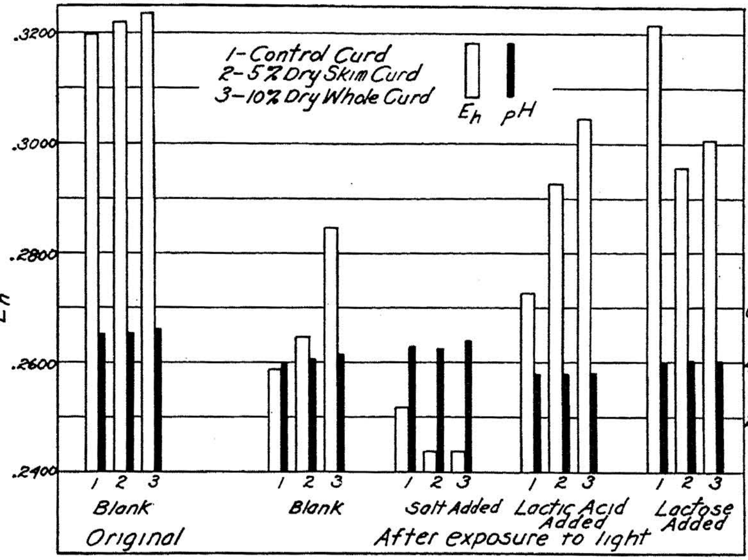


Fig. 12.—The effect of sodium chloride, lactose and lactic acid in the presence of light upon the Eh of cottage cheese.

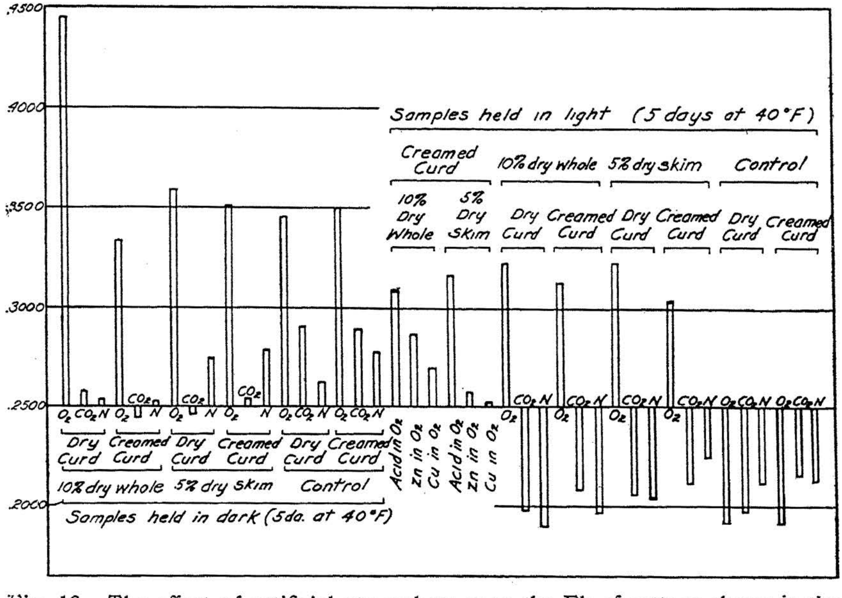


Fig. 13.—The effect of artificial atmosphere upon the Eh of cottage cheese in the presence and absence of light.

TABLE 4.—THE EFFECT OF ARTIFICIAL ATMOSPHERES UPON THE PHYSICAL PROPERTIES OF COTTAGE CHEESE HELD IN STORAGE IN THE PRESENCE OR ABSENCE OF LIGHT

FLAVOR PRODUCED IN ARTIFICIAL ATMOSPHERES (40°F.)

	Held in Light (3 days)						Held in Dark (3 days)					
Atmosphere	Control (normal skim)		5% dry skim in normal skim		10% dry whole in normal skim		Control (normal skim)		5% dry skim in normal skim		10% dry whole in normal skim	
Type of Curd	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed
Nitrogen	rough woody bitter	bitter hang-over	card-board bitter	strong sickening bitter	bitter acid	slight bitter acid	watery flat	creamy mild acid	slight watery	creamy mild acid	slight watery	creamy mellow mild acid
Carbon Dioxide	rough (body) card-board bitter	tallowy acid slight card-board	rough (body) card-board bitter	creamy carbonic	puckery bitter carbonic acid	tallowy decided dry milk	very very slight card-board	creamy carbonic	very slight card-board	slight cured flavor	very slight card-board	creamy slight cured flavor
Oxygen	sickening peptone bitter or very strong dry milk	rough chalky tallowy bitter	very very chalky and watery bitter	very chalky tallowy and card-board	rough chalky strong bitter	rough chalky tallowy card-board	peptone bitter or dry milk	smooth slight tallowy	rough watery bitter	slight tallowy flavor	rough (body) bitter dry milk	rough (body) dry milk

	Held in Light (5 days)						Held in Dark (5 days)					
Atmosphere	Control (normal skim)		5% dry skim in normal skim		10% dry whole in normal skim		Control (normal skim)		5 dry skim in normal skim		10% dry whole in normal skim	
Type of Curd	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed	Dry	Creamed
Nitrogen	sharp bitter	sickening bitter	bitter puckery	slight puckery bitter	tallowy sickening bitter	sharp sickening bitter	very very slight watery bitter	mild acid cured cheese flavor	slight watery cured cheese flavor	slight bitter cured cheese flavor	slight dry milk bitter	cured cheese flavor
Carbon Dioxide	sickening bitter	tallowy acid slight card-board	carbonic puckery bitter card-board	slight bitter	very rough (body) and strong cardboard bitter	slight puckery carbonic	strong acid slight bitter	pleasant very mild acid	acid slight bitter	cured flavor	bitter acid	creamy cured flavor
Oxygen	very very strong copper flavor	tallowy acid slight card-board	very strong copper flavor	copper bitter	copper bitter	copper bitter	very very bitter card-board or peptone dry milk flavor	acid tallowy card-board	very bitter card-board	very acid and card-board	slight card-board tallowy bitter	tallowy acid

When subjecting the different types of curd to artificial atmospheres it was found, as shown in Table 4 that the cheese containing the dry milk was more susceptible to oxygen than nitrogen or carbon dioxide.

When the oxygen was reduced to a minimum as in the nitrogen atmosphere there was a corresponding improvement in the flavor of the cheese, however the light remained effective and the uncreamed or dry curd samples had a tendency to acquire a hydrolized flavor even in the absence of light. Carbon dioxide apparently acted as an excellent preservative, but could not counteract the effect of the light. When oxygen was not a strong factor as in the nitrogen atmosphere in the absence of light and in dark storage, the cheeses involving dry milk seemed to possess better keeping qualities in each instance.

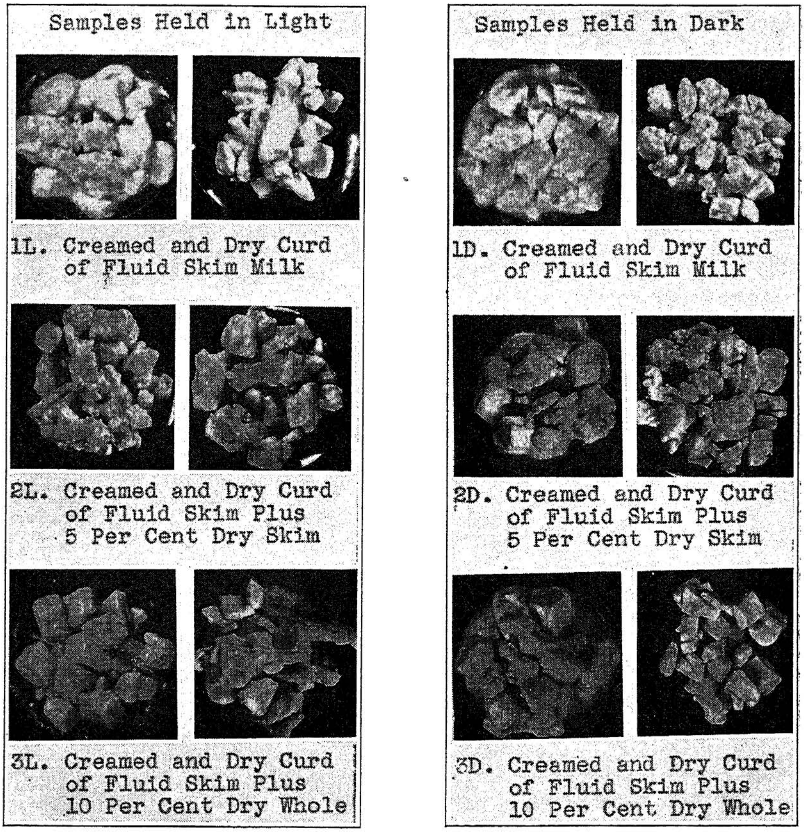


Fig. 14.—Samples of cottage cheese held in an atmosphere of oxygen for five days at 40 degrees Fahrenheit.

A comparison of the Eh values of the cheeses in Figure 13 and the flavors in Table 4 shows that the cheese which had a potential varying decidedly from .2500 developed a correspondingly greater off flavor.

It was coincidental to find that in the cheese held in carbon dioxide that there was a good preservation of the flavor and the potential did not deviate to any marked extent from .2500. There appeared again to be an agreement between the Eh and the actual flavor or the changes that had apparently taken place in the cheese. Comparing Figures 14, 15, and 16 with Table 4 and Figure 13 it will be observed that there appears to be a direct relationship between the Eh and the physical and chemical properties of the cheese. The effect of light can

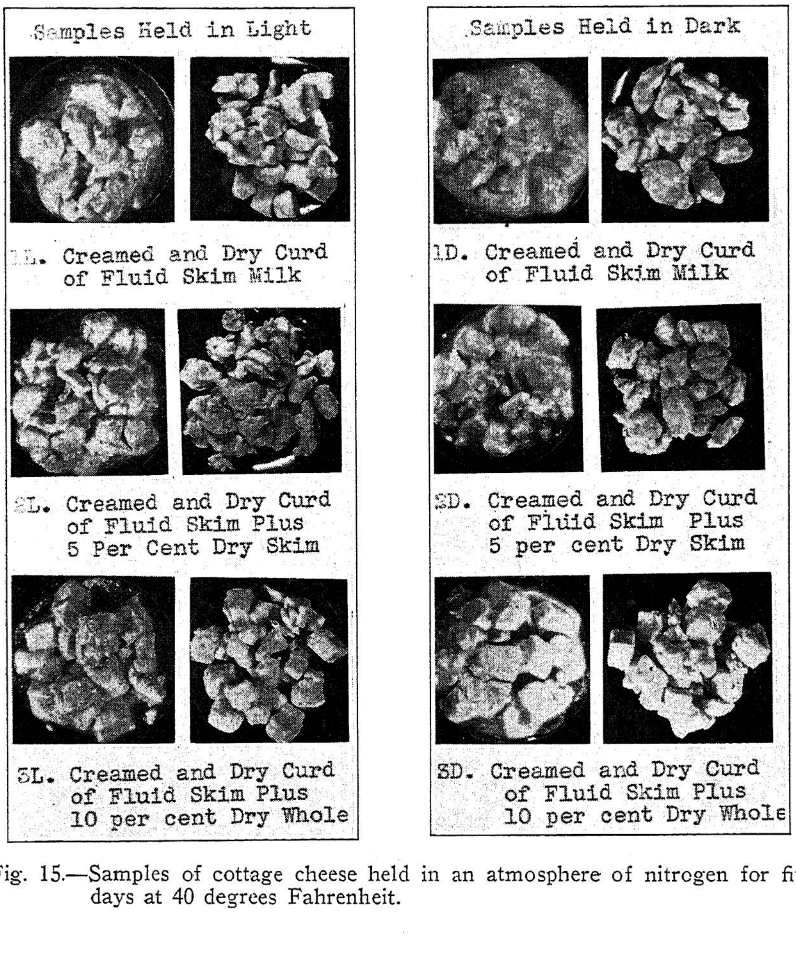


Fig. 15.—Samples of cottage cheese held in an atmosphere of nitrogen for five days at 40 degrees Fahrenheit.

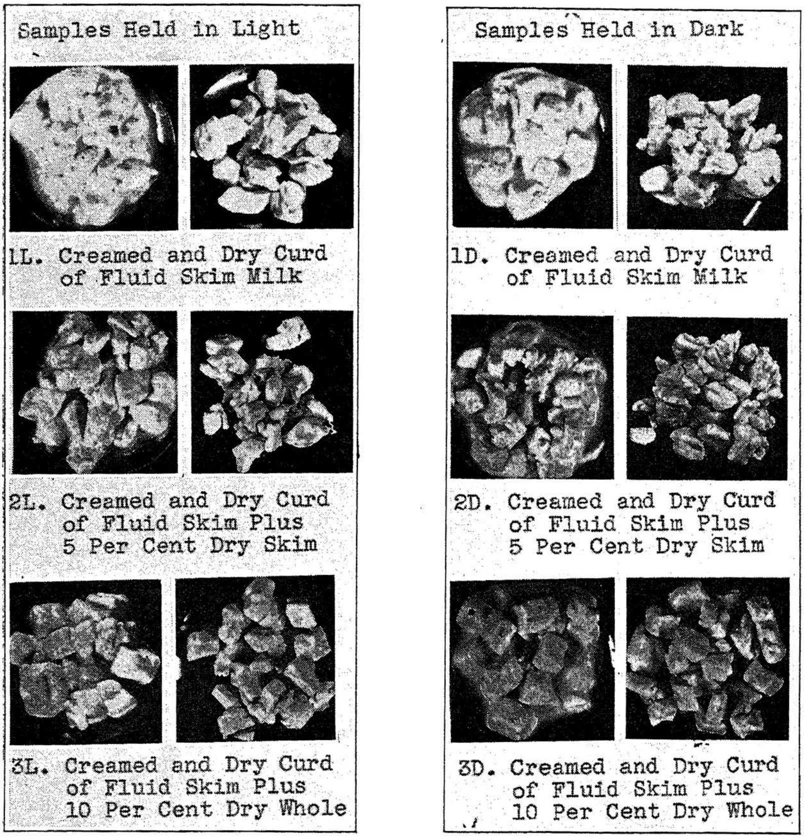


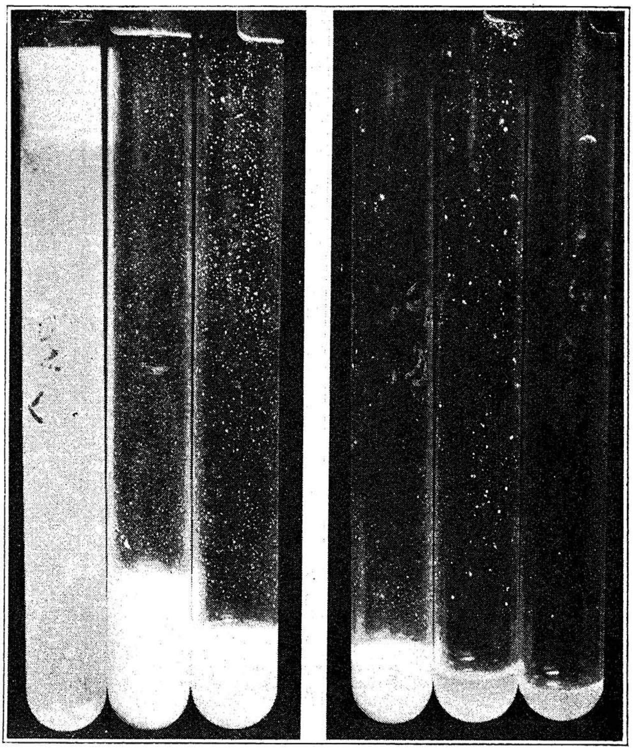
Fig. 16.—Samples of cottage cheese held in an atmosphere of carbon dioxide for five days at 40 degrees Fahrenheit.

be particularly observed in the photographs of the samples. The physical changes in samples of cheese held in an oxygen atmosphere were very marked. The cream had become very watery and separated from the curd where in the instance of the cheese held in the dark the cream was plainly visible around the curd.

The watery condition and separation of the cream from the curd held in light and artificial atmosphere, particularly oxygen resulting in different volumes of drainage water is shown in Figure 17.

There appears to be an actual relationship of the Eh with the physical and chemical properties of the liquid milk and this relation seems to be prevalent in the resultant cheese. Should there be any alteration in the colloidal milk system which would change the Eh of

Samples held in light. Samples held in dark.



O_2 N Co_2 O_2 N Co_2

Fig. 17.—Drainage water from samples of cottage cheese held in the artificial atmospheres. (Figures 14, 15, 16).

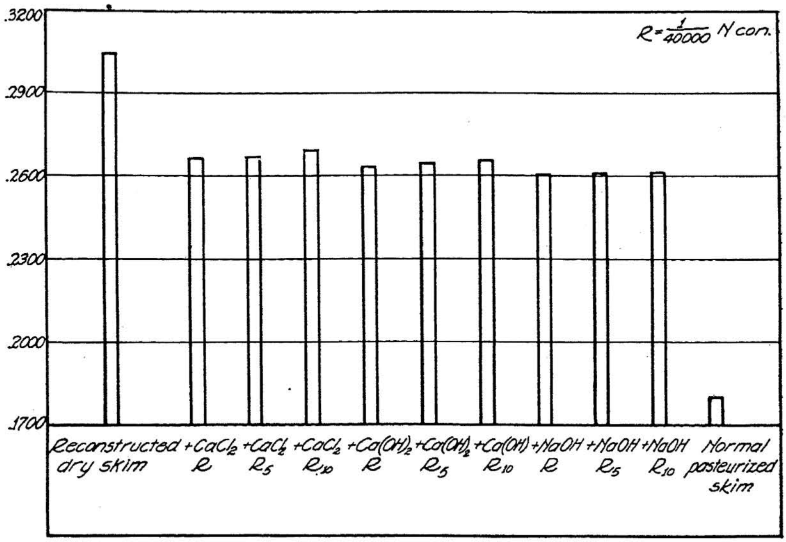
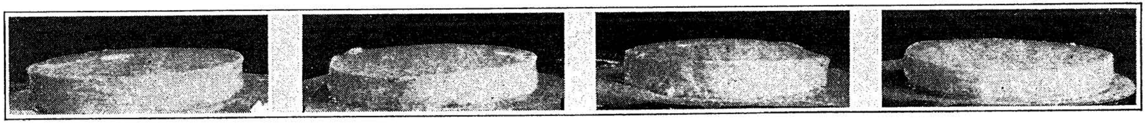


Fig. 18.—The effect of electrolytes upon the Eh of reconstructed dry skim milk.

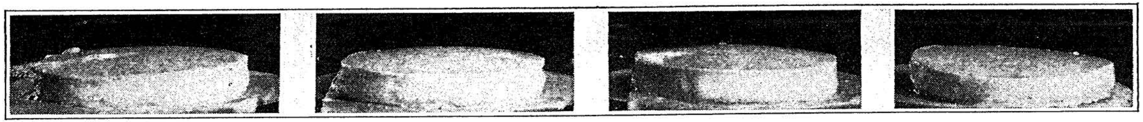
Reconstructed Dry Whole Milk Curd | Reconstructed Dry Skim Milk Curd | Fluid Skim Milk Curd

Original Curds to Which Electrolytes Had Not Been Added



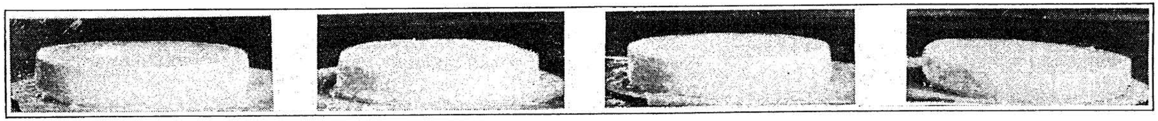
$Ca(OH)_2$ | $CaCl_2$ | NaOH | Fluid Skim Curd

Reconstructed Dry Skim Milk Curd When .000025 Normal Concentration of the Above Electrlytes Were Used.



.000025 N | .000125 N | .000250 N | Fluid Skim Curd

Reconstructed Dry Skim Milk Curd When the Above Concentrations of Sodium Hydroxide Were Used.



$Ca(OH)_2$ | $CaCl_2$ | NaOH | Fluid Skim Curd

Reconstructed Dry Whole Milk Curd When .000025 Normal Concentration of the Above Electrolytes Were Used.

Fig. 19.—The effect of varying the concentrations of different electrolytes on the formation of curd from the reconstructed milk.

the reconstructed milk to more nearly that of the natural fluid skim, it seems that it might affect the physical and chemical properties of the system.

The effect of different electrolytes on the Eh of reconstructed dry skim milk is shown in Figure 18. The addition of the different electrolytes had the effect of changing the Eh to more nearly that of normal pasteurized skim. It is considered that a small concentration of monovalent and divalent electrolytes act as peptizers in the formation of colloids, and we find that their lowering effect of the Eh was slightly greater with the smallest concentrations.

The sodium compound which had the greatest lowering effect on the Eh, correspondingly gave the best flavor which resembled that of the fluid skim milk when set up in a raw curd, Figure 19, whereas the addition of either calcium chloride or calcium hydroxide gave the typical calcium bitter flavor. The desirability of the curd followed very markedly the findings in the Eh measurements, in that those having the greatest change in Eh toward that of normal fluid skim milk, were also the most desirable in body and flavor. The sodium in the lower concentration was the most satisfactory and appeared to show that the changing of the Eh was significant in correcting the physical and chemical properties of the dehydrated milk when used in the manufacture of cottage cheese.

CONCLUSIONS

1. The natural oxidation reduction equilibrium of fresh raw milk appears to be well poised, however it may be altered to a sensitive condition.

2. The character of the Eh in milk may be decidedly changed by its exposure to room temperature for a period of five hours or more.

3. The Eh of the fluid skim milk is less stable than whole milk.

4. Normal pasteurization does not alter the character of the Eh of raw fluid whole milk appreciably, but temperatures exceeding one hundred and forty three degrees Fahrenheit or holding periods exceeding thirty minutes effects the character of the Eh according to the excess time or temperature applied.

5. The character of the Eh in reconstructed dry milk appears to be altered to a more sensitive state than that of fluid raw or pasteurized milk.

6. The character of the Eh of cottage cheese is altered when dry milk is involved in its manufacture.

7. Cottage cheese having an altered Eh such as exists when dry milk is involved, appears to be more sensitive to oxygen, light, lactose, lactic acid and electrolytes, with a corresponding change in its physical and chemical properties.

8. Eh appears to be related to the physical and chemical properties of milk and cottage cheese.

9. Eh adjustment of electrolytes to more nearly that of the fluid milk is accompanied by more normal physical and chemical properties.

10. Sodium hydroxide of .00002 Normal concentration or less in the reconstructed milk is more desirable than calcium compounds or higher concentrations of either sodium or calcium.

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