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CONTENTS

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CORROSION OF METALS BY MILK AND ITS RELATION TO THE OXIDIZED FLAVORS OF MILK

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INTRODUCTION

An oxidized flavor frequently occurs in milk and in practically all of its products. It is often designated as 'metallic' because its origin can usually be traced to the exposure of the milk to metal. This flavor varies in intensity in the different stages of its development, but usually the sequence of flavors is as follows: astringent, papery, metallic, metallic and oily, and, finally, tallowy. Some students of this subject have termed it 'oxidized flavor.' Inasmuch as it is produced through oxidation it would seem desirable to adopt the latter term, and employ the other descriptive terms to indicate the degree of oxidation.

The dairy industry is much concerned about these flavors, for complaints are being made regarding them in many countries. The following illustration of difficulty in a commercial plant as cited by Rogers (p. 38)[(25)] characterizes many observations made by the

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authors: "In the spring of 1928 this bureau was called upon to help solve the problem of off-flavor in bottled milk in one of the plants in Washington, D. C. The milk developed a cappy or cardboard flavor after pasteurization and storage over night. An intensive investigation was started. Samples were taken of all off-flavored raw milk coming to the plant. Laboratory pasteurization of these samples showed that the peculiar flavor noted was not present in the raw milk. Samples were also taken in the plant of all milk after it had passed through each piece of apparatus, and the trouble was finally attributed to one section of the milk cooler. This was a two-way cooler, the top portion of which was a water regenerative coil, while the bottom section was cooled by direct expansion. The water section was made of nickel, whereas the direct expansion section was made of German silver. Numerous samples failed to show any off-flavor after the milk had passed over the nickel section, but the characteristic objectionable flavor was found after the milk had passed over the German silver portion of the cooler. The flavor was not uniformly distributed throughout the milk, and it was found that the procedure of the plant had a good deal to do with this. When the milk was at a relatively high temperature on reaching the lower section of the cooler, the flavor was much more pronounced; but when the milk was around 60° F or lower on reaching the lower section of the cooler, the flavor did not develop. Laboratory experiments with copper, zinc, monel metal, and nickel, separately and in combinations, in milk showed that the characteristic objectionable flavor developed whenever copper was present as one of the metals either in the pure state or as an alloy. As German silver is an alloy containing a high percentage of copper, it was very apparent that this was the cause of the trouble." McKay, Fraser, and Searle(18) corroborate this experience with an illustration of off-flavors coming from monel metal milker pails.

According to the observations made by the authors in many dairy plants, most of the milk equipment is made of copper, tin-plated copper, or copper alloys. It is generally recognized that tin-plated copper soon becomes so badly worn that the copper is exposed. Most of the dairy plants having difficulty with the 'metallic' flavor and its related flavors, experience some variation in the intensity of these flavors from day to day. Under the controlled conditions of the experiments, however, the variations were small.

REVIEW OF LITERATURE

A definite relationship exists between the oxidation of the milk fat and the development of the series of oxidized flavors. Emery and Henley[7] have shown not only that light is necessary for the development of rancidity (oxidative) in fats exposed to air but not in contact with metals, but also that fats stored in contact with metals develop oxidative rancidity even when protected from light. Frazier[10] concluded that the 'catalytic' action of sunlight in the oxidation of milk fat will produce the 'cardboard' taste and the 'linseed oil' odor in a few hours.

Palmer and Combs,[20] the Associates of Rogers (p. 85),[26] Hunziker and Hosman,[15] and others attribute the development of tallowiness in dairy products to the oxidation catalyzed by the presence of certain metallic salts, notably those of copper and iron. The distinction between 'papery,' 'metallic,' and 'tallowy' is no doubt one of degree only.

The metallic and related flavors of milk are usually considered to be the direct result of the solution of metals in milk and the consequent chemical reactions. Guthrie,[12] however, has shown that certain bacteria, in the absence of metal, produce the metallic flavor when propagated in sour milk and when growing under certain other conditions. The results of the study were recently confirmed by Baker and Hammer.[1] Hunziker[13] also attributed the acceleration in certain types of spoilage of dairy products to bacterial activity, and believed that the presence of metals, their salts, and their oxides exerts a selective action on certain species of bacteria. Likewise Donauer,[5] as a result of his study in connection with butter, concluded that whether deterioration results from biological or from chemical agencies, metallic compounds play an important part. It is obvious, therefore, that in comparing metals with respect to their flavor-imparting properties the exposure to sunlight and the bacterial flora should be considered.

That the taste of small quantities of metallic salts can produce marked changes in the flavor of milk or milk products in which they are present has not been substantiated. Seligman[28] has pointed out that the salts of copper, nickel, tin, and zinc all give a metallic, inky taste to liquids containing them, whereas the salts of aluminum are merely astringent. The salts of chromium may be sweet or astringent, according to the form in which they are present. Hunziker[13] has also stated that the lactates of the metals used in dairy equipment all have a bitter, puckery, astringent, metallic taste.

A recent report[14] shows that there is a close correlation between the tendency of a metal to corrode in milk or milk products and the development of abnormal flavors therein. These workers were able to group the metals commonly used in the dairy industry according to their corroding and flavor-imparting tendencies.

The literature relative to corrosion is extensive. McKay[17] has recently summarized the opinions of many in the following words: "Whereas in the past the progress of galvanic corrosion has been conceived to depend largely on some inherent property in the metals involved, the newer view appreciates the importance of the corroding solution and the products of corrosion as modifiers." This view recognizes the importance of such factors as the supply of free oxygen at the corroding surfaces,[4] temperature,[5] motion or agitation,[6] hydrogen-ion concentration,[31] effective potential,[3] polarization and protective films,[7] and other variables. This view likewise reconciles the electrolytic theory of corrosion so generally accepted[4, 29] with the chemical aspect of corrosion emphasized by Bancroft.[2] Corrosion is truly electro-chemical.

Many of the studies concerning corrosion in relation to dairy products have been largely empirical in nature. In a recent review, the associates of Rogers[26] state that copper, because of the ease with which it passes from one state of oxidation to another, has long been known as an excellent catalyst for the oxidation of organic compounds. They add that the presence of small amounts of various metals, especially copper and iron, rapidly produces tallowiness in dairy products. This conforms to the views of others.[27, 13, 19, 11]

Supplee and Bellis[32] reported that the average copper content of fresh cow's milk was 0.52 milligrams per liter, as shown by the xanthate method of analysis. This is somewhat higher than has subsequently been reported[6] when a different method of analysis was employed. Supplee and Bellis showed that the average amount of copper taken up by milk when held in contact with copper pipe for 12 hours at a low temperature was 1.21 milligrams per liter. When the milk was heated in contact with the copper pipe for 2 hours at 150° F, 4 milligrams of copper per liter were taken up. Rice and Miscall[24] report that copper once dissolved in milk may plate out on

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[4] See reference numbers 31, 33, 34, 23, 24, 2, 8.
[5] See reference numbers 31, 3, 9, 21, 30.
[6] See reference numbers 31, 3, 23, 9, 33.
[7] See reference numbers 2, 3, 21, 24, 31.

any tin surface with which it may come in contact, and that where milk is exposed to surfaces of tin and copper together, less copper is dissolved than when there is the same exposure of copper without tin.

Quam, Soloman, and Hellwig[22] found that the solubility of copper in milk increased with a rise in temperature to a maximum at 85° to 90° C. They state that the break in the temperature curve probably resulted from the decreasing solubility of oxygen. Rice and Miscall[24] obtained somewhat different results. Less copper went into solution in milk at the boiling temperature than at room temperature, and about three times as much copper went into solution at the pasteurization temperature (145° F) as at the boiling point. The removal of copper from copper strips immersed in milk at 140° F was found to be much greater when air or oxygen was added to the milk than when either was omitted. Rice and Miscall suggest that the increase is related to the fact that copper dissolves from a surface coated with oxide more readily than from a polished surface. That the temperature effects result from something beyond the mere presence of oxygen in the milk is illustrated by the fact that the replacing of the air in boiled and cooled milk does not re-establish the same solvent power exhibited at 145° F in unboiled milk. Miscall, Cavanaugh, and Carodemos[16] have recently reported that the copper-dissolving power of milk is dependent not only upon the temperature of exposure but also upon the previous heat treatment to which milk has been subjected.

EXPERIMENTAL PROCEDURE

Throughout this study the corroding liquid was sweet milk, the metals investigated were those used in the manufacture of dairy equipment, and the experimental conditions conformed closely to those prevailing in the dairy industry.

Treatment of the Metals.—With few exceptions the metals were obtained from the manufacturers in the form of strips 2 inches in length, 1 inch in width and from 1/16 to 1/32 inch in thickness. Most of the metals employed had already been polished, but before treatment the strips were again polished with carborundum flour, and washed with distilled water, alcohol, and finally ether. They were thoroughly dried at 100° C for 30 minutes and cooled in a desiccator at room temperature for 1½ hours. They were then weighed on a sensitive balance. All were free of corrosion when the tests began. After exposure to the milk they were again washed in warm distilled water, alcohol, and ether, and then dried and weighed as before. In order that the strips of metal might be kept separate during both the drying and cooling periods they were placed on end in narrow slots made in blocks of wood which were placed in beakers. For weighing they were transferred by means of wooden forceps to small beakers. The approximate compositions of the metals selected are shown in table 1.

TABLE 1

COMPOSITION OF THE IMPORTANT METALS STUDIED

Name of metal	Percentage composition*										
	Copper	Nickel	Zinc	Tin	Lead	Iron	Chromium	Silicon	Manganese	Carbon	Misc.
Copper	100	—	—	—	—	—	—	—	—	—	—
Nickel silver (German silver)	72	18	10	—	—	—	—	—	—	—	—
Monel metal	28	67	—	—	—	+	—	—	+	—	—
Ambrac	75	20	5	—	—	—	—	—	—	—	—
Bronze	85	—	2	9	4	—	—	—	—	—	—
Waukesha metal	55	—	28	+	—	+	—	—	+	—	—
Nickel bronze	65	20	5	5	5	—	—	—	—	—	—
Nickel	—	99	—	—	—	—	—	—	—	—	—
Solder	—	—	—	50	50	—	—	—	—	—	—
Ascoloy	—	—	—	—	—	83–87	12–16	0.5	0.5	0.1	+
Enduro A	—	0.25	—	—	—	81.5–83.5	16–18	0.5+	0.5	0.1	+
Allegheny metal	—	8–10	—	—	—	69–74	17–20	0.5—	0.5—	0.1	+
Enduro Nirosta KA2	—	7–10	—	—	—	68–75	16.5–20	Under 0.75	Under 0.5	Under 0.16	+

* The percentage composition is approximate in most cases.

Selection of Milk and Method of Scoring.—Inasmuch as one feature of the study was an observation of the effect of the corrosion of the various metals in the milk on its flavor, the experimental milk obviously had to be as free as possible from abnormal flavors. The milk used in the regular trials was obtained from a selected cow which produced milk with a pleasing taste. It was drawn into a new, clean, sterile tinned pail. In order that feed flavor in the milk might be avoided, the cow was not allowed to eat any roughage during the five-hour period before milking. The milk always came from the early morning milking, and the experiments were started within a few hours after the milk left the cow.

At the conclusion of the test period the samples of milk were stored in a darkened room at 34° F and were examined at different stages of the holding period. These stages varied from immediately after exposure to metal to seven days after treatment. Inasmuch as oxidation flavors in milk are never apparent immediately after exposure to metal, the examination was made usually from 2 to 5 days after treatment.

In scoring the milks the judges first examined the check samples, one of which was agitated during the process, the other of which received no agitation. The checks were exposed to no metal except the tin bucket. When pasteurization was one of the variants, an additional check sample of raw milk was retained. Having thus established the standard, and also having increased the acuteness of the senses of smell and taste by a short period of practice on these check samples, the judges, individually, examined the treated samples. These had been renumbered as an additional precaution to prevent their identity being known at the time of the examination. An additional check sample was also placed with the other bottles to insure extra care in scrutiny. At the outset it was decided to assign an arbitrary flavor score of 13.5 to the milk from the cow which was used throughout the experiment to indicate that the milk was free from criticism as far as the usual defects are concerned.

In recording the scores of the individual samples of milk it was recognized that the assigning of numerical scores would give relative values. Inasmuch as the judges were experienced in scoring and all samples of milk were obtained from an individual cow yielding a good flavored product, and the milking was done under uniform and ideal conditions, numerical values were considered to indicate slight differences in flavor much more satisfactorily than any other system employed for indicating such relative differences.

The Agitator.—When investigating the corrosion of metals, it is necessary to control such major factors as temperature, agitation, and aeration. In order that these important features might be closely maintained or varied as planned, a mechanical agitator, which is shown in figure 1, was constructed.

The milk was put into one-pint glass milk bottles which were placed in water in tank (T), and the metal strips were placed in a glass carriage (C) which was inserted in the bottle. Figure 2 shows the carriage, which is constricted at the bottom sufficiently to hold the metal, but which affords an opening wide enough to permit the easy passage of the milk through it and around the metal. There was sufficient room on the two arms of the agitator to attach 12 carriages. Provision was made for the control of the temperatures of the cooling or of the pasteurizing water in the tank.

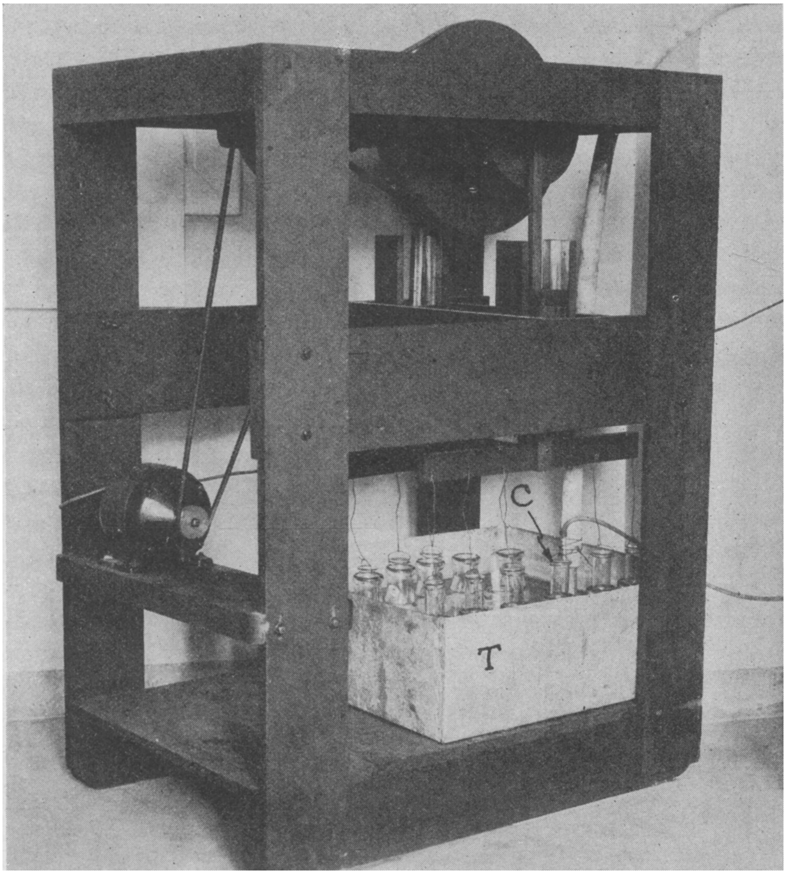

Fig. 1. The agitator. This mechanical device assured uniform agitation. The temperature was controlled in tank T; provision was made for 12 glass carriages (*C*) to be suspended in the bottles containing milk by wires attached to the arms of the stirrer.

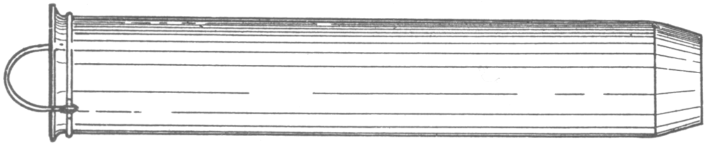

Fig. 2. The glass carriage in which the strip of metal was placed for agitation. The constriction at the bottom retained the metal strip within the tube.

By varying the amount of milk in the bottle it was possible to control the type of agitation undergone by each sample. Because the stroke of the agitator was only 2½ inches, it was possible to run some samples through the process and keep them completely submerged in milk. In other instances, only a sufficient amount of milk was put into the bottle to submerge the metal at the lower end of the stroke, the metal being completely exposed to the air at the upper end of the stroke.

Besides providing for the control of temperature and of agitation, the agitator permitted such variation of manipulation as the forcing of additional air through the milk or the passing of an electric current through the milk, without disturbing the type of agitation.

RESULTS OF EXPERIMENTS

Changes Produced When Metals Were Exposed to Warm Milk.—Two types of agitation were studied. In one type, the metal strips were completely immersed in the milk throughout the agitation period; in the other the strips were alternately completely submerged in the milk and fully exposed to air. The milk was maintained at 80° F during the agitation, the agitation period for the most part being of 2½ hours duration. The results of the examination of the metal for corrosion and loss of weight, and of the milks for flavor are shown in tables 2 and 3. It is clearly evident that copper and copper-bearing alloys not only exhibit weight losses but also induce in the milk chemical reactions which result in oxidation flavors. On the other hand, nickel, although showing large weight losses, and dense tarnishing, may or may not induce undesirable flavors. The remaining metals proved very satisfactory especially when it is considered that the holding of milk at 80° F for 2½ hours imposes a severe test on the milk from the standpoint of flavor. A comparison of tables 2 and 3 shows that in those trials where corrosion occurs it is usually greater when the metal is exposed alternately to air and milk. This is further evident when one examines the flavor scores.

TABLE 2

EFFECT OF CORROSION OF METALS IN SWEET MILK

The strips of metal were completely submerged in fresh milk at 80° F for 21½ hours.

Metal	Lot No.	Loss in weight, mg./dm.²/day*	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk†	Flavor—score and criticism: Treated milk
Copper	1	8.96	Slightly clouded	3	13.2 old	13.2 astringent
	1	1.79		3	13.2 old	13.2 astringent
	2	35.86		3	13.5	13.2 astringent
	2	28.69		3	13.5	13.2 astringent
Nickel silver (German silver)	1	53.79	Brassy	3	13.2 old	13.0 oxidized
	1	0.00		3	13.2 old	13.0 oxidized
	2	7.17		3	13.5	13.0 oxidized
	2	7.17		3	13.5	13.0 oxidized
Monel metal	1	21.52	Cloudy	3	13.2 old	13.2 astringent
	1	16.14		3	13.2 old	13.2 astringent
	2	75.31		3	13.5	13.1 oxidized
	2	39.45		3	13.5	13.1 oxidized
Pure nickel	1	116.54	Densely clouded	3	13.2 old	13.2 old
	1	62.75		3	13.2 old	13.2 old
	2	190.06		3	13.5	13.3 Slightly astringent
	2	179.30		3	13.5	13.3 Slightly astringent
Copper, tinplated, edges bare	1	0.00	Clear	3	13.2 old	13.2 old
	1	0.00		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.4 Slightly oxidized
	2	0.00		3	13.5	13.4 Slightly oxidized
Tinned copper	1	0.00	Clear	3	13.2 old	13.2 old
	1	0.00		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5
Steel, tin-plated, edges poorly tinned	1	0.00	Clear	3	13.2 old	13.2 old
	1	3.57		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5
Pure aluminum	1	0.00	Clear	3	13.2 old	13.2 old
	1	0.00		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5
Enduro A	1	3.57	Clear	3	13.2 old	13.2 old
	1	3.57		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5
	29	——		3	No criticism	Slightly oxidized
Enduro Nirosta KA2	29	——	Clear	3	No criticism	Very slightly astringent
Allegheny metal	1	0.00	Clear	3	13.2 old	13.2 old
	1	0.00		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5

* Milligrams per square decimeter per day.

† In these studies a flavor score of 13.5 indicates that the milk is free from criticism.

TABLE 3

EFFECT OF CORROSION OF METALS IN SWEET MILK

The strips of metal were alternately completely exposed to air and completely submerged in milk at 80° F for 21½ hours.

Metal	Lot No.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk	Flavor—score and criticism: Treated milk
Copper	3	10.76	Slightly clouded	4	13.3 slightly old	12.0 oxidized, papery
	3	0.00		4	13.3	12.0
	4	50.20		2	13.5	12.9
	4	14.34		2	13.5	12.9
Nickel silver (German silver)	3	28.69	Brassy	4	13.3 slightly old	12.0 oxidized, green pea taste
	3	28.69		4	13.3	12.0
	4	25.10		2	13.5	13.3 slightly oxidized
	4	14.34		2	13.5	13.3
	8*	215.14		7	13.0 old	11.5 oxidized
	9*	44.82		6	13.0 old	11.5
Monel metal	3	43.03	Clouded	4	13.3 slightly old	12.0 astringent, sweet pea taste
	3	68.13		4	13.3	12.0
	4	64.55		2	13.5	13.1 Slightly oxidized
	4	39.45		2	13.5	13.1
	8*	17.93	Slightly clouded	7	13.0 old	12.5 Oxidized, papery
	9*	53.78		6	13.0 old	12.5
Brass strainer cloth	8*	35.86	Difficult to determine	7	13.0 old	12.9 Slightly oxidized
	9*	17.93		6	13.0 old	11.5 Oxidized, papery
Bronze union	8*	107.37	Partly clouded	7	13.0 old	12.8 Slightly oxidized
	9*	81.82		6	13.0 old	12.8
Pure nickel	3	301.22	Densely clouded	4	13.3	13.3
	3	143.5		4	13.3	13.3
	4	315.57		2	13.5	13.3
	4	129.10		2	13.5	13.3
	8*	116.53	Clouded	7	13.0 old	12.8 Slightly astringent
	9*	295.81	Clouded	6	13.0 old	12.8 Slightly oxidized
Copper, tin-plated, edges bare	3	0.00	Clear	4	13.3 slightly old	13.3 Slightly old
	3	0.00		4	13.3	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5
Copper, tin-plated, edges trimmed	3	0.00	Clear	4	13.3 slightly old	13.3 Slightly old
	3	0.00		4	13.3	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5

* Exposed for 1 hour at 80° F.

TABLE 3 (*Concluded*)

Metal	Lot No.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism	
					Check milk	Treated milk
Copper, tin-plated, edges soldered	1	0.00	Clear	3	13.2 old	13.2 old
	1	0.00		3	13.2 old	13.2 old
	2	0.00		3	13.5	13.5
	2	0.00		3	13.5	13.5
	3	0.00		4	13.3 slightly old	13.3 Slightly old
	3	0.00		4	13.3 slightly old	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5
Steel, tin-plated, edges poorly tinned	3	0.00	Clear	4	13.3 slightly old	13.3 Slightly old
	3	0.00		4	13.3 slightly old	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5
Pure aluminum	3	0.00	Clear	4	13.3 slightly old	13.3 Slightly old
	3	0.00		4	13.3 slightly old	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5
	8*	0.00		7	13.0 old	13.0 old
	9*	0.00		6	13.0 old	13.0 old
Enduro A	3	0.00	Clear	4	13.3 slightly old	13.3
	3	0.00		4	13.3 slightly old	13.3
	4	0.00		2	13.5	13.3 slight odor
	4	0.00		2	13.5	13.3 slight odor
Ascoloy	8*	35.86	Clear	7	13.0 old	13.0 old
	9*	....	Clear	6	13.0 old	13.0 old
Allegheny metal	3	0.00	Clear	4	13.3 slightly old	13.3 slightly old
	3	0.00		4	13.3 slightly old	13.3 Slightly old
	4	0.00		2	13.5	13.5
	4	0.00		2	13.5	13.5
	8*	62.75	spot on surafce	7	13.0 old	12.9 "off"
	9*	0.00	Clear	6	13.0 old	13.0 old

Changes Produced When Metals Were Exposed to Milk During the Pasteurization Process.—In the series of experiments the strips of metal were exposed to the milk for 1½ hours, which included 30 minutes required to raise the temperature to 144° F, 30 minutes holding at 144° F, and 30 minutes for cooling the milk to approximately 68° F.

Many of the metals went through the corrosion test without being discolored. Those which were most discolored were nickel and copper and their alloys. Figure 3 shows the appearance of several metals before and after exposure to milk during the pasteurization process.

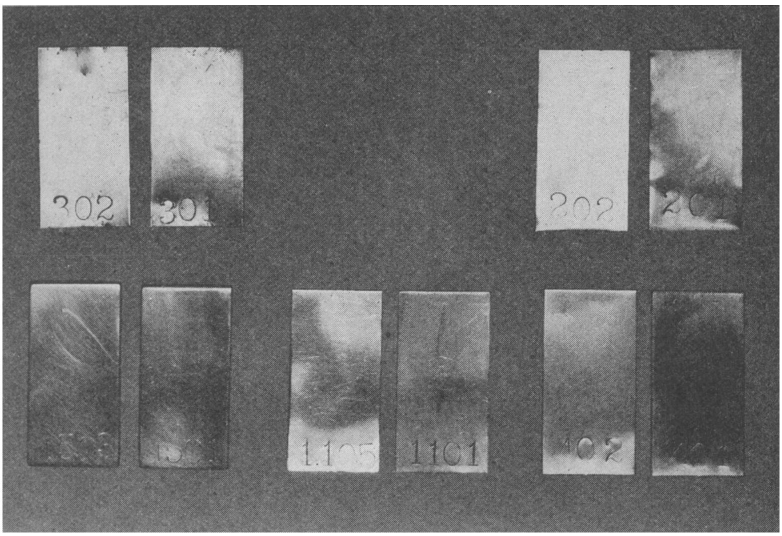

Fig. 3. The effect of corrosion in sweet milk on the appearance of some of the metals. The strip on the left of each pair was not exposed to milk, while its duplicate on the right was agitated in milk during the pasteurization period. In pairs, left to right: upper row, copper, monel metal; lower row, nickel silver, nickel, nickel.

Numbers 302 and 301 are the copper exhibits. Ordinarily the copper is free from stain or cloudiness immediately after treatment, but it soon becomes tarnished in the air as shown in figure 3. Number 202 is monel metal which has not been exposed to milk and 201 is the same metal after pasteurization. Numbers 1503 and 1501 are nickel silver (German silver) samples. The one on the left, which represents the original appearance of the metal, is uniformly bright in color; whereas, the one on the right, having been exposed to milk during the pasteurization period, is cloudy in appearance particularly in the central area and along the right side. Number 1105 is a sample of untreated nickel, whereas its duplicate, 1101, is fairly uniformly clouded. Number 402 is also a clear nickel; but its duplicate, 401, which was in the milk during pasteurization, is very densely clouded throughout a large central zone.

The results shown in table 4 were secured from trials in which the strips of metal were completely submerged in the milk throughout the entire period. In the trials recorded in table 5 the strips were alternately completely exposed to air and completely submerged in the milk. A comparison of tables 4 and 5 with tables 2 and 3 indicates that in the case of those metals which lose weight and impart flavors to milk the pasteurization procedure induces greater changes than does the raw milk treatment.

A comparison of table 4 with table 5 indicates that during the pasteurization process the continuous alternate exposure of the metal to milk and air is responsible for only slight increases in corrosion and flavor defects over those induced by continuous total submersion. Nickel appears to be the chief exception to this result. Under all conditions nickel showed large losses in weight and became densely clouded, but only under certain conditions did this result in the production of oxidized flavors in the milk. Copper and its alloys in every trial lost in weight, changed in appearance, and induced rapid and extensive oxidation in the milk. Pure aluminum, glass enamel, well-tinned metals, and the chromium-nickel irons all yielded favorable results. Enduro A, representing the chromium steels, gave variable results. In every instance the loss in weight was practically negligible and no change in appearance was observed, but in certain instances definite oxidized flavors were induced. This latter was observed only after repeated trials in which the milk from certain cows was used. Thus lot numbers 28 and 29 in table 4 and 28 in table 5 became distinctly oxidized by the third day. Samples of these milks when similarly exposed to Enduro Nirosta KA 2, a chromium-nickel iron, were judged as equal in flavor to the check sample, with the exception of lot 28, table 4, in which a defective strip of the metal had been used. Use of this particular strip was discontinued.

TABLE 4

EFFECT OF CORROSION OF METALS IN SWEET MILK

The strips of metal were completely submerged in the milk during pasteurization at 144° F for 30 minutes and during the additional time of 60 minutes required for raising and lowering the temperature.

Metal	Lot No.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk	Flavor—score and criticism: Treated milk
Copper	5	95.62	Slightly clouded	7	13.3 slightly old	11.0 oxidized (papery)
	6	95.62		6	13.2 slightly old	11.0
	7	77.41		3	13.1	11.0
Nickel silver (German silver)	5	101.59	Brassy	7	13.3 slightly old	11.0 oxidized (papery)
	6	131.47		6	13.2 old	11.0
	7	89.64		3	13.1 old	11.0
Monel metal	5	185.45	Densely clouded	7	13.3 slightly old	11.5 oxidized (papery)
	6	197.20		6	13.2 old	11.0
	7	179.25		3	13.1 old	12.0
Pure nickel	5	364.45	Densely clouded	7	13.3 slightly old	12.9 slightly oxidized
	6	316.73		6	13.2 old	13.1 old
	7	256.97		3	13.1 old	12.5 oxidized
	26	329.34		3	13.1 old	13.1 old
Copper, tin-plated, edges bare	5	23.90	Clear	7	13.3 slightly old	12.0 oxidized
	6	29.88		6	13.2 old	13.0 slightly oxidized
	7	0.00		3	13.1 old	12.8
Copper, tin-plated, tin worn thin	5	0.00	Clear	7	13.3 slightly old	13.2 very slightly oxidized
	6	17.86		6	13.2 old	13.2
	7	0.00		3	13.1 old	13.0
Copper, tin-plated, edges soldered	5	11.95	Clear	7	13.3 slightly old	13.2 old
	6	11.95		6	13.2 old	13.2
	7	0.00		3	13.1 old	13.0
Steel, tin-plated, edges poorly tinned	5	11.95	Clear	7	13.3 slightly old	13.2 slightly astringent
	6	11.95		6	13.2 old	13.2 old
	7	0.00		3	13.1 old	13.0 slightly astringent
Pure aluminum	5	0.00	Clear	7	13.3 slightly old	13.3 slightly old
	6	17.92		6	13.2 old	13.2 old
	7	0.00		3	13.1 old	13.1

TABLE 4 (*Concluded*)

Metal	Lot No.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk	Flavor—score and criticism: Treated milk
Enduro A	5	11.95	Clear	7	13.3 slightly old	13.2 old
	6	17.93	Clear	6	13.2 old	13.2 old
	7	0.00	Clear	3	13.1 old	13.1 old
	28	2.25	Clear	3	13.1 very slightly astringent	13.0 slightly oxidized
	29	——	Clear	3	No criticism	Oxidized odor and taste
Enduro Nirosta KA2	28	17.98	Spot in center	3	13.1 very slightly astringent	12.9 slightly oxidized, astringent
	29	——	Clear	3	No criticism	No criticism
Allegheny metal	5	0.00	Clear	7	13.3 slightly old	13.3 slightly old
	6	5.98	Clear	6	13.2 old	13.2 old
	7	5.98	Clear	3	13.1 old	13.1 old

TABLE 5

EFFECT OF CORROSION OF METALS IN SWEET MILK

The strips of metal were alternately completely submerged in milk and completely exposed to air during pasteurization at 144° F for 30 minutes and during the additional time of 60 minutes required for raising and lowering the temperature.

Metal	Lot No.	Loss in weight, mg./dm.^{2}/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism	
					Check milk	Treated milk
Nickel silver (German silver)	10	101.59	Brassy	4	13.2 old	11.5 oxidized
	11	125.50		3	13.2 old	11.5
Monel metal	10	250.99	Densely clouded	4	13.2 old	11.0 oxidized (papery)
	11	191.23		3	13.2 old	11.0
Brass strainer cloth	10	268.92	Difficult to determine	4	13.2 old	11.0 oxidized
	11	....		3	13.2 old	11.0
Bronze union	10	104.63	Partly clouded	4	13.2 old	11.5 oxidized
	11	77.11		3	13.2 old	11.9
Ambrac	23	157.37	Brassy	4	13.2 old	12.2 oxidized (papery)
	24	161.77		4	13.2 old	12.2
Waukesha metal	23	114.21	Brassy	4	13.2 old	12.2 oxidized (papery)
	24	155.04		4	13.2 old	12.3
Nickel bronze	23	56.90	Brassy	4	13.2 old	12.4 oxidized (papery)
	24	125.54		4	13.2 old	12.5
Brass pipe, tin-plated, ends bare	10	0.00	Clear	4	13.2 old	13.2 old
	11	0.00		3	13.2 old	13.0 astringent
Steel, one side tin-plated	23	0.00	Densely clouded	4	13.2 old	13.2 old
	24	38.84		4	13.2 old	13.2 old
	25	17.80		3	13.2 old	13.2 old
	26	11.87		3	13.1 old	13.1 old
Copper and Enduro A soldered together	13	35.86	Copper, tarnished	5	13.0 old	12.0 oxidized
	14	47.81	Enduro A, clear	6	13.1 old	11.9
Nickel and Allegheny metal soldered together	12	11.95	Both metals clear	4	13.2 old	13.2 old
	13	0.00		5	13.0 old	13.0 old
Solder: Lead 50% Tin 50%	12	Slight	Clear	4	13.2 old	13.2 old
	13	0.00		4	13.0 old	13.0 old
Pure nickel thinly tin-plated	12	17.93	Clear	4	13.2 old	13.2 old
	13	0.00		4	13.0 old	13.0 old

TABLE 5 (*Concluded*)

Metal	Lot No.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk	Flavor—score and criticism: Treated milk
Pure nickel	10	388.44	Densely clouded	4	13.2 old	13.2 old
	11	233.06		3	13.2 old	13.2 old
	12	370.51		4	13.2 old	13.2 old
	25	372.13		3	13.2 old	13.1 slightly oxidized
	25	438.24		3	13.2 old	12.9 oxidized and astringent
Cadmium	12	81.69	Clear	4	13.2 old	13.2 old
	13	65.74		5	13.0 old	13.0 old
Glass Enamel	13	0.00	Clear	5	13.0 old	13.0 old
	23	——		4	13.2 old	13.2 old
	24	0.00		4	13.2 old	13.1 old
	25	0.00		3	13.2 old	13.2 old
	26	0.00		3	13.1 old	13.1 old
Pure aluminum	10	0.00	Clear	4	13.2 old	13.2 old
	10	0.00		4	13.2 old	13.2 old
	11	0.00		3	13.2 old	13.2 old
	11	0.00		3	13.2 old	13.2 old
	13	0.00		5	13.0 old	13.0 old
Ascoloy	10	0.00	Clear	4	13.2 old	13.2 old
	11	0.00		3	13.2 old	13.1 very slightly astringent
Enduro A	25	0.00	Clear	3	13.2 old	13.2 old
	28	4.49		3	13.1 very slightly astringent	12.95 oxidized
	30	——		4	13.2	13.1 slightly astringent
	31	——		3	13.3	13.3
Enduro Nirosta KA2	28	2.25	Clear	3	13.1 very slightly astringent	13.1 very slightly astringent
	30	——		4	13.2	13.2
Allegheny metal	10	0.00	Clear	4	13.2 old	13.2 old
	11	0.00		3	13.2 old	13.1 old
	12	11.95		5	13.2 old	13.2 old
	13	0.00		5	13.0 old	13.0 old
	30	——		4	13.2 old	13.2 old
	31	——		3	13.3 old	13.3 old
Copper, chromium-plated:						
Polished	30	——	Wearing off	4	13.2	13.0 slightly oxidized
Polished	31	28.09	Wearing off in places	3	13.3	13.2 slightly astringent
Unpolished	31	33.71	Wearing off	3	13.3	13.2 slightly astringent

The results of trials in which chromium-plated copper was used are shown in table 5. Lot numbers 30 and 31 are representative of many trials in which chromium-plated metals from various sources were used. These results do not indicate definitely that chromium itself is responsible for either the loss in weight or the production of the astringent and oxidized flavors. In every sample studied it was clearly evident that the treatment accorded the metal caused a wearing away of the thin layer of chromium plating, with the consequent, slight exposure of the copper base.

Effect of Air on Loss in Weight of Metals in Sweet Milk.—In order to determine more fully the relation of air to the corrosion of metals than was done in the regular trials, a special group of experiments was conducted. The results of these experiments are recorded in table 6. In one trial the metals were completely submerged in the milk at 80° F. In another trial they were alternately subjected to complete submersion in milk at 80° F and complete exposure to air.

TABLE 6

EFFECT OF AIR ON LOSS IN WEIGHT OF METALS AGITATED IN SWEET MILK

Metal	Loss in weight of metal strips, mg./dm.²/day*; averages of several trials				
	Agitated 2½ hours at 80°F		Agitated for 1½ hours during pasteurization procedure (144°F)		
	Complete submersion	Alternately submerged in milk and exposed to air	Complete submersion	Alternately submerged in milk and exposed to air	Air bubbled through from hand rubber bulb
Copper	21.89	18.29	87.12	87.36	101.76
Monel metal	37.44	52.13	181.92	214.58	191.52
Nickel silver	16.42	32.26	102.00	109.68	118.32
Pure nickel	132.52	215.86	314.40	318.24	342.00
Pure aluminum	....	....	0.00	0.00	0.00
Allegheny metal	....	....	0.00	0.00	0.00

* Milligrams per square decimeter per day.

In the remaining trials pasteurization temperatures were maintained, agitation being carried out as in the first two trials with the addition of further modification in which air was continuously bubbled through the milk during the process. As shown in table 6 the experiments with pure aluminum and Allegheny metal produced no loss in weight under the various conditions. In the trials with those metals which do corrode in milk, the results show (1) that greater corrosion occurs in the 1½-hour pasteurization procedure than in the 2½-hour period when the temperature was held at 80° F; and (2) that the type of agitation exerts a greater influence on the extent of corrosion at the 80° F temperature than at the 144° F temperature. The alternate exposing of the metal to air during the pasteurization period, however, did increase the extent of corrosion over that which occurred when the metal was completely submerged, and, with one exception, the bubbling of air through the milk still further increased the amount of corrosion.

Effect of the Passage of an Electric Current Through Milk on the Corrosion of Metals and the Flavor of the Milk.—Both alternating and direct currents were studied, the current being passed through individual samples of milk between the strip of metal and a strip of solder. Solder is known not to affect the flavor of milk, this characteristic being substantiated in table 5. In the case of the direct current the metal was the anode, a platinum wire having been soldered to the metal to complete this electrode; the solder strip was the cathode. These studies were made during the pasteurization procedure, the metal strips being alternately submerged in milk and exposed to air. The flow of current was measured and controlled.

The results of the experiments are shown in table 7. The treatment produced rapid and extensive corrosion in the case of copper, copper alloys, and nickel, as indicated by the loss in weight of these metals and their change in appearance. Allegheny metal lost in weight but remained clear in appearance. In all trials the greatest amount of corrosion occurred in the case of the direct current. Strong oxidized odors and flavors were rapidly produced in those milks exposed to the copper and copper alloys, and to a lesser extent in those exposed to nickel. No oxidized flavors were produced in the case of Allegheny metal, or tin-plated steel.

The Copper Content of Milk as Affected by Exposure to Metals.—In order to determine the amount of copper passing into milk when exposed under various conditions to metals containing copper, analyses for copper were made of these samples of milk before and after exposure. The potassium ethyl xanthate method[32] was used. This method proved sufficiently accurate to give comparative values at least. Considerable difficulty was encountered in getting accurate values in the case of monel metal, presumably because of interfering substances.

Table 8 shows the results of the analyses. They clearly indicate that fresh milk removes copper from such metals as copper, monel metal, nickel silver, and tin-plated copper under certain conditions. The results in the case of lots 21, 22, and 23 show that there is a slight increase of copper in the milk as it passes through certain milk plants.

TABLE 7

Effect of Corrosion of Metals in Sweet Milk

An electric current was passed through the milk between the strip of metal and a solder electrode, during the pasteurization procedure. The metal was alternately submerged in milk and exposed to air.

Metal	Lot No.	Current, amp.	Loss in weight, mg./dm.²/day	Appearance of metal	Age of milk when examined, days	Flavor—score and criticism: Check milk	Flavor—score and criticism: Treated milk
Copper	17	0.004 D.C.	209.16	clouded	1	13.4	11.0 oxidized (papery)
	20	0.004 A.C.	179.49		3	12.5 rancid	11.0 oxidized (papery)
Nickel silver	15	0.012 D.C.	657.36	brassy	5	13.0 old	11.5 oxidized
	17	0.004 D.C.	615.53		1	13.4	11.0 oxidized
	20	0.004 A.C.	123.80		3	12.5 rancid	11.5 oxidized (papery)
Monel metal	17	0.004 D.C.	400.39	densely clouded	1	13.4 old	11.0 oxidized
	20	0.004 A.C.	198.87		3	12.5 rancid	11.0 oxidized (papery)
Pure nickel	15	0.012 D.C.	896.40	densely clouded	5	13.0 old	12.1 oxidized
	17	0.006 D.C.	657.36		1	13.4	13.3
Allegheny metal	15	0.002 D.C.	119.52	clear	5	13.0 old	12.8 old
	17	0.004 D.C.	507.96		1	13.4	13.4
	20	0.004 A.C.	29.67		3	12.5 rancid	12.9 rancid
Steel, tin-plated, edges poorly tinned	15	0.004 D.C.	1111.54	clear	5	13.0 old	13.0 old
	20	0.005 A.C.	17.80		3	12.5 rancid	12.0 cooked

TABLE 8

THE EFFECT OF CERTAIN TREATMENTS OF MILK UPON ITS COPPER CONTENT

Lot No.	Metals to which milk samples were exposed	Conditions of exposure	Copper, mg. per liter
14*	Copper and Enduro A soldered together	Electrolytic action between two metals	0.62
14*	Cadmium	In milk during pasteurization	0.55
14*	Glass enamel, Cry. Pkg. Mfg. Co.	In milk during pasteurization	0.54
17*	Monel metal	Metal as anode for direct current of 0.004 amperes; solder as cathode	1.00
17*	Copper	Metal as anode for direct current of 0.004 amperes; solder as cathode	2.50
17*	Nickel silver	Metal as anode for direct current of 0.006 amperes; solder as cathode	1.30
18*	Copper	Air bubbled slowly through the milk during the experiment	1.40
18*	Nickel silver	Air bubbled slowly through the milk during the experiment	1.40
18	———	Check sample of milk not pasteurized, agitated	0.62
19*	Copper, tin-plated	In milk during pasteurization	0.60
19*	Copper, tin-plated	In milk during pasteurization	0.65
19*	Copper, tin-plated, edges bare	In milk during pasteurization	0.60
19*	Copper	In milk during pasteurization	1.90
19*	Steel, tin-plated on one side	In milk during pasteurization	0.53
20*	Allegheny metal	Metal as electrode for alternating current of 0.004 amperes; solder as the other electrode	0.60
20*	Steel, tin-plated	Metal as electrode for alternating current of 0.004 amperes; solder as the other electrode	0.58
20*	Nickel silver	Metal as electrode for alternating current of 0.004 amperes; solder as the other electrode	0.90
20*	Monel Metal	Metal as electrode for alternating current of 0.004 amperes; solder as the other electrode	1.00
20*	Copper	Metal as electrode for alternating current of 0.004 amperes; solder as the other electrode	1.70
20	———	Check samples of milk, agitated and pasteurized	0.55
20	———	Check sample of milk, not agitated and not pasteurized	0.54
21	Milk of commercial plant, from weigh tank		0.50
21	Same milk after being passed through the fore-warmer and filter		0.65
21	Same milk after being passed through the fore-warmer and filter the second time		0.65
21*	Same milk after being pasteurized, cooled and bottled		0.62
22	Milk from another commercial plant, milk not pasteurized		0.50
22	Same milk after being heated in the fore-warmer		0.65
22*	Same milk after being pasteurized		0.63
22	Same milk after being bottled		0.66
23	Raw milk		0.30
23*	Same milk after being pasteurized		0.55

* Pasteurized at 144° F for 30 minutes.

DISCUSSION OF RESULTS

The mechanical agitator used throughout these studies afforded a means whereby uniform stirring was secured without undue agitation or foaming. In this way all strips of metal were accorded similar treatment and therefore the results are truly comparable. The appearance of the metal strips gave a qualitative index of the extent to which corrosion took place, the loss in weight gave a fairly accurate measure of the extent of the corrosion, and the resulting flavor of the milk samples was a reasonably definite guide to the effect of corrosion of metals on the quality of the milk. In calculating the loss in weight in milligrams per day per square decimeter from the weight losses in the 1½ and 2½ hour periods, the assumption was made that the rate of loss would remain uniform over the 24 hour period. This assumption would probably be correct provided the milk would remain fresh, and no polarization films would form between the surface of the metal and the surrounding milk.

In these experiments the area of the metal exposed to the milk amounts to slightly over 4 square inches to each pound of milk when the pint bottle was full, or 8 square inches per pound of milk in the case of a pint bottle one-half full of milk. The interior surface of a 300-gallon coil vat-pasteurizer, which is used in commercial practice, has an area of approximately 18,000 square inches. In this vat there is a ratio of 6.98 square inches of metal surface per pound of milk. The ratio of exposed metal surface in the full pint bottle to that in the full vat is 4 to 6.98 or nearly 4 to 7, while in the pint bottle one-half full of milk the ratio is 8 to 6.98 or about 8 to 7. Doubtless a relation exists between the extent of corrosion and the ratio of exposed metal area to the volume of the corroding liquid.

The variation in the amount of corrosion under normal conditions extended from Allegheny metal, Enduro Nirosta KA 2, pure aluminum, tin-plated metals, and glass enamel, all of which showed practically no loss in weight and were free from tarnish, to nickel, which showed the greatest loss in weight and became the most clouded. The strongly corroding effect of agitating milk in the presence of certain metals and air, and of exposing the metal to milk and air successively confirms the principle that oxidation is significant in the corrosion of metals.

The greatest amount of corrosion occurred when a direct electric current was passed through the milk from the metal (anode) to a strip of solder (cathode). In the case of copper and copper-bearing alloys, a much greater amount of copper was found in the milks through which the current passed than in those through which there was no flow of current. This fact was reflected in the more rapid development of oxidized flavor. Electric currents were studied because of the possibility of a current from a poorly grounded motor or other electric equipment passing through the milk. As such a possibility is obviously remote, experiments with this phase of the problem were limited.

The soldering together of two metals, as shown in table 5, is not a satisfactory way of studying the galvanic action between the two metals when immersed in milk, for the losses in weight of each metal could not be ascertained. The combined effect of the two metals on the flavor of the milk, as far as this limited experiment indicates, appears to be determined by the effect which the least satisfactory of the metals has when exposed individually to milk.

The oxidized and related flavors of milk such as 'astringent,' 'papery,' 'oily' and 'metallic,' are believed to be caused largely by copper, the reaction being greatly accelerated if the milk is subsequently exposed to sunlight. This metal and its alloys are a constant source of trouble in the dairy plant. In about 30 per cent of the experiments nickel gave a 'metallic' flavor, which varied in intensity. Copper and its alloys caused oxidized and related flavors in every sample. In this comparison of copper and nickel it should be noted that, in many cases, the flavor score of the milk which had been exposed to nickel was only slightly less than that of the check sample. On the other hand, the judges invariably gave copper and its alloys markedly lower scores on flavor.

In these studies a distinct 'papery,' 'metallic,' or 'oxidized' flavor was found in milk which was exposed to copper which was tin-plated and on which the plating was worn thin. A strong oxidized flavor was invariably found in those samples exposed to those tin-plated copper strips whose edges were not plated. Chromium-plated copper proved unsatisfactory. The chromium plating is too easily removed by friction, is subject to hairline cracks, and lacks uniformity. It has been suggested[35] that an undercoat of nickel offers possibilities for the successful electro-plating of copper with chromium.

In the handling of milk, the places of greatest opportunity for the harmful effects of metals are in the pump, in the piping, in the pasteurizer, and over the cooler. The pump is likely to be the greatest source of metal contamination to the milk because of the severe agitation and the type of metals necessarily used in the construction of the pump. Next in importance are the sanitary piping and internal tubular coolers which are largely made of tin-plated copper, but from which the tin-plating becomes worn in the cleaning processes. Third is the upper part of the external cooler, where the hot milk comes into contact with a comparatively large area of metal.

Of the metals used in this study, only copper and its alloys are recognized as likely to produce oxidized and related flavors in the sweet milk of the average plant. Under the more or less highly corrosive conditions of handling sweet milk, such as those at pasteurization temperatures and in cases when the metal is alternately exposed to air and milk, the effect of nickel on the flavor should be closely scrutinized.

Special reference should be made to the results obtained with Enduro A, reported in tables 2, 3, 4, and 5. This metal belongs to the class of chromium irons. In all milks studied Enduro A showed little or no loss in weight, and remained clear in appearance. Many of the milk samples were unaffected as regards flavor, but in a fairly large number of trials in which milk samples from different cows were studied, Enduro A was found occasionally to produce slightly oxidized flavors. Well-polished chromium-nickel irons, such as Enduro Nirosta KA 2 and Allegheny metal, on the other hand, produced no unfavorable flavors in these milks. The variation in the oxidizability of different milks is being studied at this station.

The results of the foregoing experiments do not warrant a grouping of the metals in complete agreement with that reported by Hunziker, Cordes and Nissen.[14] In this connection it should be stressed that the results here recorded were obtained with fresh milk as the corroding medium, the time-temperature conditions of exposure closely approximating those existing in market-milk practice. Reference to the tables indicates that the extent of corrosion and the occurrence and the intensity of the oxidized flavors are about the same for copper, nickel silver, and monel metal. In no instance did these metals compare favorably with the chromium irons, Ascoloy, or Enduro A.

CONCLUSIONS

A satisfactory method for determining the suitability of metals to be used in contact with sweet milk has been developed and described.

Copper, and copper alloys, such as ambrac, brass, bronze, monel metal, nickel silver (German silver), and Waukesha metal, showed weight losses when exposed to sweet milk and produced oxidized flavors in such milk.

Tin-plated copper or copper alloys were unsatisfactory on account of mechanical wearing away of the plating. Chromium-plated copper was less satisfactory in this regard than tin-plated copper.

Pure nickel showed high weight losses and became badly clouded when exposed to sweet milk. This metal often induced oxidized flavors in milk.

The chromium alloys, Ascoloy and Enduro A, showed little or no weight losses and remained clear in appearance, but in certain milks induced slight oxidized flavors.

The chromium-nickel alloys—Enduro Nirosta KA 2 and Allegheny metal—when well polished, pure aluminum, glass enamel, and carefully tin-plated metals showed little or no weight losses, remained clear in appearance, and produced no oxidized flavors when exposed to sweet milk.

Aeration of the milk during the pasteurization procedure (144° F for 30 minutes with an additional 60 minutes for raising and lowering the temperature) increased the tendency for the development of oxidized flavors.

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The titles of the Technical Papers of the California Agricultural Experiment Station, Nos. 1 to 20, which HILGARDIA replaces, and copies of which may be had on application to the Publication Secretary, Agricultural Experiment Station, Berkeley, are as follows:

4. Effect of Sodium Chlorid and Calcium Chlorid upon the Growth and Composition of Young Orange Trees, by H. S. Reed and A. R. C. Haas. April, 1923.

5. Citrus Blast and Black Pit, by H. S. Fawcett, W. T. Horne, and A. F. Camp. May, 1923.

6. A Study of Deciduous Fruit Tree Rootstocks with Special Reference to Their Identification, by Myer J. Heppner. June, 1923.

7. A Study of the Darkening of Apple Tissue, by E. L. Overholser and W. V. Cruess. June, 1923.

8. Effect of Salts on the Intake of Inorganic Elements and on the Buffer System of the Plant, by D. R. Hoagland and J. C. Martin. July, 1923.

9. Experiments on the Reclamation of Alkali Soils by Leaching with Water and Gypsum, by P. L. Hibbard. August, 1923.

10. The Seasonal Variation of the Soil Moisture in a Walnut Grove in Relation to Hygroscopic Coefficient, by L. D. Batchelor and H. S. Reed. September, 1923.

11. Studies on the Effects of Sodium, Potassium, and Calcium on Young Orange Trees, by H. S. Reed and A. R. C. Haas. October, 1923.

12. The Effect of the Plant on the Reaction of the Culture Solution, by D. R. Hoagland. November, 1923.

14. The Respiration of Potato Tubers in Relation to the Occurrence of Blackheart, by J. P. Bennett and E. T. Bartholomew. January, 1924.

16. The Moisture Equivalent as Influenced by the Amount of Soil Used in its Determination, by F. J. Veihmeyer, O. W. Israelsen and J. P. Conrad. September, 1924.

17. Nutrient and Toxic Effects of Certain Ions on Citrus and Walnut Trees with Especial Reference to the Concentration and Ph of the Medium, by H. S. Reed and A. R. C. Haas. October, 1924.

18. Factors Influencing the Rate of Germination of Seed of Asparagus Officinalis, by H. A. Borthwick. March, 1925.

19. The Relation of the Subcutaneous Administration of Living Bacterium abortum to the Immunity and Carrier Problem of Bovine Infectious Abortion, by George H. Hart and Jacob Traum. April, 1925.

20. A Study of the Conductive Tissues in Shoots of the Bartlett Pear and the Relationship of Food Movement to Dominance of the Apical Buds, by Frank E. Gardner. April, 1925.