The Accelerating Effect of Metals on the Development of Peroxides in Oils and Fats

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THE effect of metals on the flavor and keeping qualities of dairy products has been studied for many years. As early as 1905 Golding and Feilman[1] studied the effects of iron and copper on dairy products. Unpublished work by W. H. Irwin of Swift and Company Laboratories in 1913 traced the cause of tallowy, metallic and fishy flavored butter to the presence of copper dissolved from vats in which the tin coating had worn off. In 1918 Hunziker and Hosman[2] published a paper giving the results of experiments with copper, iron, brass, German silver, nickel and tin. Their conclusions were that the first three are active in producing tallowy odor and flavor in butter. Copper and brass were found to be more active than iron. Since 1918 a large volume of literature on the effect of metals on dairy products, and the solubility of metals in milk, cream, lactic acid, etc., has appeared. Some of the more important published articles are listed ([3] to [8] incl.). However, this list is by no means complete. A fairly complete bibliography of articles on the effect of metals on dairy products can be obtained from the references given in these papers.

The effect of metals on food products in general has been discussed by Donauer.[9] The behavior of transformer oils containing copper has also been studied.[10] In the soap industry the effect of metals in promoting rancidity in soaps has been recognized.[17]

The work of the dairy industry has shown that copper is the outstanding offender in promoting oxidative decomposition of dairy products. Hunziker, Cordes & Nissen[8] list the metals used in creamery equipment in order of their desirability based on their solubility in weak organic and mineral acids and the effect of the metals on the flavor of milk products.

- 1
  - allegheny metal
  - tin
  - heavily tinned copper
- 2
  - nickel
  - aluminum
  - manganese aluminum alloy
- 3
  - Monel metal
  - Enduro
  - Ascoloy
  - Nickel silver
- 4
  - tinned iron
  - copper
  - galvanized iron
  - iron
  - zinc

The oil and fat industry has lagged far behind the dairy industry in recognizing the importance of metals used in equipment for handling fats and oils.

In 1909 Emery[12] published a report on the use of metallic containers for edible fats and oils in which some recognition was given the deleterious effects of contact with metals. In 1922 Emery & Henley[18] made a study of the effect of metals on the keeping qualities of oils and fats. The length of time required for fats and oils to become rancid in the presence of various metals and in glass was determined. The tests were judged by the time required to develop a rancid odor and a positive Kreis reaction. The authors concluded the following from their experiments:

1. Air, oxygen or carbon dioxide is necessary for development of rancidity even when metals are present.
2. Carbon dioxide containing no air or oxygen was apparently able to promote rancidity with or without the presence of metals.
3. Oxygen is more effective than air in promoting rancidity.
4. The development of rancidity was accelerated when fats and oils were in contact with metals and air or oxygen was present. Some metals act more energetically than others. Some metals hastened the production of rancidity without being attacked themselves.
5. Light in the absence of metals produced rancidity in about the same time as metals in the absence of light.
6. The direct part taken by moisture in the development of oxidative rancidity as compared with air, light and metals is negligible as indicated by one test.

Emery and Henley draw no conclusions regarding the relative activity of metals in promoting rancidity except to state that copper was the most effective and tin and aluminum the least effective. Copper, lead, tin, aluminum, iron and zinc were the metals studied.

King, Roschen and Irwin[14] comment upon the accelerating effect on rancidity development of copper, brass and Monel metal and performed experiments indicating that copper stearate in solution in fats in as low an amount as 1 part per million has a marked accelerating effect on rancidity development.

Royce[15] used copper in small amounts to shorten the induction period in stability tests. The same author[16] studied the effect of copper, iron, tin and nickel on the fading time of methylene blue incorporated in oils.

The work reported in this paper was undertaken to obtain additional information on the effect of metals when dissolved in fats and also when present in solid undissolved form in contact with fats. In the previous work on metals in fats by Emery & Henley, decomposition was gauged by odor and by the use of the Kreis test. Both methods are open to criticism and the accelerated test devised by the present authors was used to measure the effect of added metals. This test has been described in detail in a recent paper.[14] Essentially the test consists of aerating a measured quantity of melted fat held at 208° F. at a uniform rate until rancidity is developed. The rancid point is established by determining the peroxide value and the test is reported as the number of hours required to produce a peroxide concentration which has been previously found to coincide with the rancid point of the kind of fat being tested as determined organoleptically.

A sample of prime steam lard of excellent keeping qualities was obtained for use in this work. This sample was kept under refrigeration during the period of experimentation. Tests made at regular intervals showed that this lard suffered no measurable decomposition dur-

Fig. I

STABILITY OF LARD OVER PERIOD OF TEST

Hrs. of Aeration 208° F.	Lard as received 8/25	Lard Held at 32° F. to 8/29	Lard Held at 32° F. to 9/11	Lard 9/11 with 2.0 cc. chloroform added to each portion	Lard Held at 32° F. to 9/21
	Peroxide Value in Milli-equivalents Per Kilo				
14..........		8.4		8.0	
15..........		12.0	9.8	11.0	
16..........	16.2	25.6	18.2	29.2	29.4
17..........	94.0	150.0	56.0	57.0	74.0
18..........		204.0	98.0	127.0	
Induction period. (Hrs.	17	16	17	16	16

ing this period. Keeping tests on the lard alone are shown in Figure I.

Solutions of the stearates of copper, iron, manganese, vanadium, nickel, aluminum, lead, zinc, tin and chromium were made using chloroform as a solvent. The soaps were dissolved in such proportions that the amount required in every case was contained in 2 cc. of solution. An exception is the case of manganese stearate, the low solubility of which made it necessary to use 2.5 cc. of chloroform to dissolve an amount equivalent to 10 parts per million. In the tests using less than 10 parts per million of manganese as manganese stearate, 2 cc. of chloroform solution was used. In the table showing the results of the keeping tests on lard containing metallic soaps, the concentration in parts per million is that of the metal itself and not of its stearic acid soap.

The procedure used was to treat several 20 cc. portions of lard with 2 cc. portions of the metal soap solutions containing known amounts of the metal. The lard was then aerated at 208° F. and its keeping test compared with that of the original untreated lard. This original lard had a keeping test of 16 hours under the standardized conditions of the test.

The results obtained are tabulated in Figure II and show a great variation in the effectiveness of the dissolved metals as catalysts. For instance, copper in a concentration of .15 parts per million lowered the keeping test of lard more than ferric iron in a concentration of 10 parts per million.

The keeping test method results are reported in one hour units. For this reason the one hour induction periods shown for copper in lard in concentrations of .312 parts per million up does not indicate that all tests were alike, but merely that the smallest test unit is too large to show the variation.

The results from Figure II have been produced in graphical form in Figure III.

These results indicate that dissolved tin in as high a concentration as 40 parts per million has little effect on the keeping quality of this lard. This was rather sur-

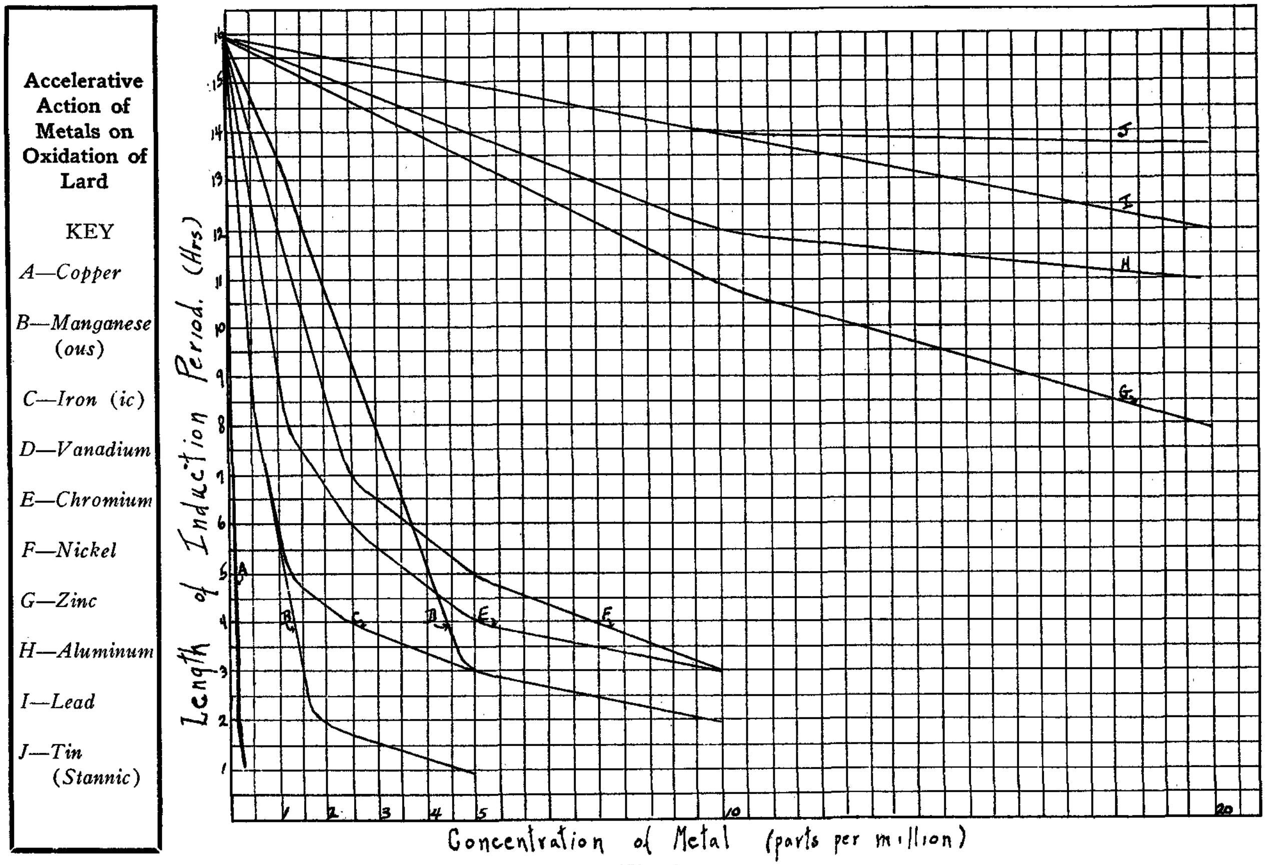

Fig. 3.

Fig. II

INDUCTION PERIOD (Hrs.) OF LARD TREATED WITH METALS

Conc. of Metal (ppm.)	Cu	Mn^{++}	Fe^{+++}	V	Cr	Ni	Zn	Al	Pb	Sn^{++++}
0.000	16	16	16	16	16	16	16	16	16	16
0.156	2	..	..	..	..	..	..	..	..	..
0.312	1	..	..	..	..	..	..	..	..	..
0.625	1	8	8	..	..	..	..	..	..	..
1.25	1	2	5	13	8	..	..	..	..	..
2.50	1	2	4	..	6	7	..	..	..	..
5.00	1	1	3	3	4	5	..	..	..	..
10.0	1	1	2	2	3	3	11	11	14	14
20.0	..	..	..	..	..	..	8	12	12	13
40.0	..	..	..	..	..	..	..	11	..	15

prising in view of results previously obtained in an experiment in which a piece of pure tin was immersed in the melted lard while aerating. Under these conditions the presence of the metal had accelerated the production of rancidity greatly.

Strips of copper, lead, zinc, tin, iron and aluminum were obtained and cut into pieces of approximately identical apparent area. These strips were completely immersed in 20 cc. of lard contained in the test tube and the aeration and incubation carried out as usual. The results obtained are tabulated in Figure IV.

The results classify the metals in a different order than the tests run with known amounts of dissolved metals. To check the amounts of metal dissolved the test pieces were weighed before and after their use in the accelerated test. In the case of copper, iron, zinc, aluminum and tin, the loss in weight could not be detected on an ordinary analytical balance. In the case of lead the loss was appreciable amounting to 10 to 20 mg. per 20 cc. of lard, depending on the conditions of the test. The observation that some metals accelerate the oxidation of fats without being attacked or oxidized themselves, checks that of Emery & Henley previously noted. The free fatty acid figures indicate a slight rise in acidity during the aging of the lard except in the case of the lead where it shows a drop. This is probably due to the formation of lead soaps and is in keeping with the high solubility shown by lead.

Fig.IV

Metal—Listed in order of activity in sheet metal form	Approximate Induction Period (hrs.) of lard containing metal strip	Free Fatty Acids after Treament	Order of Activity of Metals in Dissolved form as taken from Figure II
Cu	1	....	Cu
Pb	1¼	0.21	Fe
Zn	1¾	0.30	Zn
Sn	2½	0.25	Al
Fe	5	0.28	Pb
Al	7½	0.24	Sn

Original Lard had an Induction Period of 16 Hrs. and a Free Fatty Acid Content of 0.24%.

In interpreting the results obtained in the above tests it is apparent that metals have a catalytic effect on the oxidation of fats which is different when the metal is dissolved in the fat than it is when the sheet of metal is merely in contact with the fat. Copper is active whether dissolved or in the form of a sheet. Dissolved iron is very active but in the solid form is relatively inactive. Dissolved tin is very inactive but a tin sheet catalyzes oxidation quite effectively. The mechanism of catalysis which in any event is not clearly understood, is apparently different in the case of dissolved metals than it is in the solid form which allows a metal which is quite inert in solution to be an effective surface catalyst and in other cases causes the reverse to be true.

The question of the most desirable metal or metals for use in fat and oil handling equipment is a difficult one to answer. The advent of a host of new alloys has made the problem more complex. Some of these alloys have been found useful in the dairy industry. One of the dairy industry's most promising chromium, nickel, iron alloys was tested by the authors, however, and was found to be a surface catalyst for oxidation of fats practically equivalent to iron.

On the basis of our work to date we can draw little in the nature of definite conclusions.

Copper is beyond a doubt an active catalyst for oxidation and its use in fat and oil handling and processing equipment should be avoided. All of the other metals tested had a catalytic effect on the oxidation of lard. The work done has not been sufficient to list even the common metals in order of their desirability. The phenomenon of catalysis depends on a variety of factors including the presence or absence of promoters, presence or absence of catalytic poisons, surface arrangements in the metals, total surface area, contour of surface and the presence of greater or smaller patches of catalytically active surface. It is quite evident that the same metals may fall into different orders in tests made at various times due to variation in the above factors. There is also some possibility of minute quantities of impurities being present in some of the metal strips used. Analysis of the strips indicated that all of them contained small quantities of copper. However, the aluminum contained a great deal more than any of the others and, since the aluminum strips showed the least effect on the keeping qualities of the lard tested, it can probably be assumed that the copper content is too small to be significant, at least in those metals which were insoluble in lard. The metals were the purest readily obtainable, however, and in the case of the softer metals, zinc, lead and tin, the sheets were made in the laboratory from C. P. metals.

It is hoped that eventually sufficient agreeing data may be accumulated to make a complete accurate classification of common construction metals in order of their desirability for holding and processing oils and fats.

References

1. *Golding & Feilman, J. Soc. Chem. Ind.* 24-1285 (1905).
2. *Hunziker & Hosman, J. Dairy Sc. Vol.* 1, *P.* 320 (1918).
3. *Hunziker, Cordes & Nissen, J. Dairy Sc. Vol.* 12, *P.* 179 (1929).

4. *Quam, J. I. E. C.* 21-703 (1929).
5. *Hess, J. I. E. C.* 13-1115 (1921).
6. *Supplee & Bellis, Jour. Dairy Sc. Vol.* 5, *P.* 455 (1922).
7. *Rice & Miscall, Jour. Dairy Sc. Vol.* 6, *P.* 260 (1923).
8. *Gebhardt & Sommer, Jour. Dairy Sc., Vol.* 14, *P.* 416 (1931).
9. *Donauer, Butter, Cheese & Egg Jour.* 13, *P.* 12 (1922).
10. *Donauer, Chem. Age,* 31, 427, 8 (1923).
11. *Von Der Heyden & Typke, Petroleum Zeitung,* 20-320 (1924).
12. *Emery, The Use of Metallic Containers for Edible Fats and Oils, U. S. Dept. of Agri. Bur. An. Ind., 26th Annual Report* 1909.
13. *Emery & Henley, J. I. E. C.* 14, *P.* 937 (1922).
14. *King, Roschen & Irwin, Oil & Soap, Vol. X, No.* 6, *P.* 105-109 (1933).
15. *Royce, Oil & Soap, Vol. X, No. 7, P.* 123-125 (1933).
16. *Royce, J. I. E. C., Anal. Ed. Vol.* 5, *No.* 4, *P.* 244 (1933).
17. *Rayner, Perfumery & Essential Oil Record,* 17-120-123 (1926).

Discussion of Paper

Dr. Lowry asked how the metals were prepared.

Mr. King replied that they were polished with fine emery paper, washed with HCl and distilled water, and dried in vacuum.

Dr. Lowry asked how long after cleaning the metals were put in the fat.

Mr. King replied 15 to 20 minutes.

Dr. Lowry commented that if they had been left an hour, some oxidation would have taken place and the results of the experiments would have been different.

Dr. Roeg inquired if any tests were made at room temperature.

Mr. King replied that in order to accelerate the tests, all experiments were made at a temperature of 208° F.

Dr. Barbour asked if the experimenters determined whether stannic or stannous stearate was formed.

Mr. King replied that due to the highly oxidizing conditions under which the experiments were carried out, it was assumed that only stannic stearate was present.

Dr. Barbour asked how the salts of the various metals were prepared.

Mr. King referred this question to Mr. Roschen who explained that an alcoholic solution of stearic acid was made and NaOH added to neutralization. The solution was diluted with 9 or 10 times its quantity of water and aqueous solutions of the various metals were added in excess. The solution was then filtered, the soap washed with water and dried.

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