Effect of Metallic Salts On the Stability of Palm and Hydrogenated Cottonseed Oils[1]

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In the course of an investigation (1) of the applicability of hydrogenated cottonseed oil as a substitute for palm oil in the hot-dip tinning process for producing tin plate, a number of factors were investigated with respect to their effect on the viscosity and free fatty acid content of these oils when they were maintained at high temperature in the presence of molten tin. It was observed that the addition of small amounts of zinc chloride flux to palm and hydrogenated cottonseed oil resulted in a marked decrease in viscosity of the oils during heating.

The suitability of palm oil for use in the manufacture of tin plate is judged almost entirely on the basis of its viscosity, and the useful range of the oil is generally considered to lie between viscosities of 85 and 102 Saybolt seconds or 15.8 and 21 centistokes at 210° F. It is general practice in the tin plate industry to control the viscosity of the palm oil bath by adding fresh oil before the viscosity reaches 105 Saybolt seconds in an amount sufficient to bring the contents of the bath within the prescribed viscosity range.

The increase in viscosity of the palm oil results primarily from polymerization of the oil when maintained for long intervals at temperatures in the vicinity of 460° F. The rate and degree of polymerization are obviously affected by various metallic products which are necessarily present in the tin bath. These include zinc chloride, tin, tin oxide, iron, and iron oxide, and various reaction products of these metals.

A search of the literature revealed little information relative to the effects of these metals, their oxides, or their salts, on the increase in viscosity of palm oil or hydrogenated cottonseed oil when heated to high temperatures.

It has been reported by Rossi (2) that the addition of small amounts of sulfur monochloride to olive, cottonseed, sesame, peanut, and linseed oils produced large increases in their viscosities (cottonseed from 68.02 to 549.6; olive from 78.9 to 3,422.06; and linseed from 77.7 to 1,651.17 centipoises at 20° C.). No explanation of the probable mechanism or factors inducing this change is given by the author, but it is apparent that various impurities would have marked and different effects upon the different oils. Rossi pointed out that while the oils which were treated with sulfur monochloride gelatinized, this phenomenon was not observed when pure oleic acid was used.

Bradley (3) reported that various investigators had noted in connection with the heat bodying of drying oils, that a sharp drop in iodine value is accompanied by relatively little increase in viscosity during the early stages of the bodying reaction, and that the reverse effect occurs during the later stages of this reaction.

Morrell, Egloff and Faragher (4) found that when Sumatran palm oil was heated to cracking temperatures there were produced 62 percent of motor-grade, and 11.6 percent of diesel-grade, fuel oils. In addition to liquid hydrocarbons, gas, and coke, there were formed water, aldehydes, fatty acids, and glycerides of lower molecular weight than those present in the original oil.

No work appeared to have been reported on the nature of the products formed by thermal breakdown of palm oil during the tinning operation; consequently, an investigation was undertaken to determine what effects the various constituents of the tin bath have on the serviceability of palm oil and its substitutes, especially with a view to increasing the useful life of these oils and thus conserving present supplies.

The common assumption, that when palm oil goes into use in the tin stack its free fatty acid content increases rather rapidly to about 50 percent, was shown to be erroneous in a previous publication (1) which showed that the free fatty acids present or formed in the oil are readily removed by volatilization at the temperature of the tin bath. It was observed that oils of widely different free fatty acid content tended to approach a common value on prolonged heating. In the investigation reported here it was found that the presence of metallic salts exerts a pronounced effect on the formation of free fatty acids, especially at the point where the rate of formation of these acids tends to become constant.

Experimental

Effect of tin on palm and hydrogenated cottonseed oils: Extended heating tests were carried out on hydrogenated cottonseed oil (I. V. 49.1) and Sumatran palm oil (I. V. 50.9) to ascertain the effect of tin upon the rate of formation of free fatty acids and on the increase in viscosity under conditions approximating those which obtain in the production of tin and terne plates.

Samples of oil, of 800 grams each, were heated alone and in the presence of tin at 230° C. for 32 hours in 1,000-ml. Pyrex glass beakers wound with resistance wire and set in well insulated metal containers. The current supply was controlled through manually adjustable voltage regulators and the temperature was measured with thermometers suspended in the oil with the mercury bulbs ½ inch from the bottom. Twenty-five-gram portions of oil were withdrawn at two-hour intervals for analysis. The variations in free fatty acid content which were observed in the oils during these tests are given in Table 1, and the corresponding variations in viscosity and iodine value are recorded in Tables 2 and 3. The viscosity measurements were made in modified Ostwald-Cannon-Fenske viscometers which were maintained in a constant-temperature, oil-viscometer bath at 98.9° C. (210° F.).

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TABLE 1

Effect of Tin on the Free Fatty Acid Content of Hydrogenated Cottonseed and Sumatran Palm Oils Heated at 230° C.

Time of heating	Free fatty acid content (as oleic)			
	Hyd. Cottonseed Oil		Sumatran Palm Oil	
	With tin	Without tin	With tin	Without tin
hours	*percent*	*percent*	*percent*	*percent*
0	0.08	0.08	5.04	5.04
2	0.18	0.28	4.04	4.06
4	0.27	0.47	3.36	3.35
6	0.41	0.31	2.81	2.98
8	0.59	0.35	2.42	2.44
10	0.79	0.44	1.92	2.14
12	0.96	0.45	1.64	1.76
14	1.11	0.56	1.52	1.55
16	1.21	0.61	1.44	1.36
18	1.30	0.70	1.33	1.24
20	1.24	0.72	1.18	1.14
22	1.18	0.68	1.18	1.12
24	1.10	0.70	1.20	1.00
26	1.09	0.77	1.06	0.90
28	1.07	0.77	1.16	0.87
30	1.04	0.76	1.17	0.86
32	1.02	0.75	1.17	0.87

Examination of the data in Tables 1 and 2 indicates that tin slightly accelerates the increase in viscosity in the case of hydrogenated cottonseed oil but has little or no effect upon palm oil under the same conditions. The viscosity of the palm oil is slightly lower initially than that of the hydrogenated cottonseed oil, but tends to approach that of the cottonseed oil when heated at the temperature of the tin pot. Tin appears to exert a positive effect upon the formation of free fatty acids in both palm oil and hydrogenated cottonseed oil. When the hydrogenated cottonseed oil with a low initial free acid content was heated in the absence of tin the free fatty acid content, calculated as oleic, increased gradually to a value of about 0.75 percent, and remained at that value during the remainder of the experiment. When the same oil was heated similarly in the presence of tin, the free fatty acids increased to a maximum of 1.3 percent and then decreased very slowly to about 1.0 percent.

TABLE 2

Effect of Tin on the Viscosity in Centistokes at 210° F. for Hydrogenated Cottonseed and Sumatran Palm Oils Heated at 230° C.

Time of heating	Hyd. Cottonseed Oil		Sumatran Palm Oil	
	With tin	Without tin	With tin	Without tin
hours				
0	10.00	10.00	8.49	8.49
2	10.18	10.16	8.78	8.95
4	10.49	10.37	9.04	9.02
6	10.71	10.59	9.29	9.27
8	11.03	10.85	9.62	9.53
10	11.51	11.12	9.94	9.86
12	12.16	11.41	10.11	10.11
14	12.24	11.77	10.45	10.46
16	12.61	12.19	10.93	10.88
18	13.17	12.44	11.23	11.31
20	13.63	12.93	11.61	11.72
22	14.10	13.20	12.13	12.15
24	14.68	13.65	12.51	12.65
26	15.15	14.12	13.05	13.32
28	15.76	14.54	13.53	13.77
30	16.38	15.05	14.12	14.41
32	17.09	15.61	14.73	14.97

Palm oil with a high initial free fatty acid content rapidly lost acids by volatilization during the first part of the heating period, both in the presence and absence of tin. In both cases, however, the free acid value leveled off during the latter part of the heating period. In the test made in the absence of tin, this leveling off occurred at a free-acid content of about 0.9 percent, whereas in the presence of tin it occurred at a value of about 1.2 percent.

TABLE 3

Effect of Tin on the Iodine Value of Hydrogenated Cottonseed and Sumatran Palm Oils Heated at 230° C.

Time of heating	Hyd. Cottonseed Oil		Sumatran Palm Oil	
	With tin	Without tin	With tin	Without tin
hours				
0	49.1	49.1	50.9	50.9
2	47.8	48.5	48.4	46.4
8	46.4	46.6	......	44.8
16	44.6	45.0	44.5	42.7
24	......	43.4	44.2	42.6
32	43.5	42.1	42.5	40.3

Comparison of the iodine values of samples of these oils (Table 3) after various heating periods shows a gradual decrease in unsaturation. This decrease is less pronounced where the oils have been heated in the presence of tin. It is difficult to correlate the decrease in iodine values with the increase in viscosity values, since it was observed that tin accelerated the increase in viscosity. If the increase in viscosity is attributed solely to polymerization, it must be assumed that heat polymerization does not occur solely at the expense of loss in unsaturation. This anomaly has also been observed in a similar test (Table 4) when a hydrogenated cottonseed oil was used which had an initial iodine value of 12.6 and an initial viscosity of 10.67 centistokes. After 24 hours of heating at 230° C. in the presence of tin, the iodine value decreased to 10.0 and the viscosity increased to 13.8 centistokes, while

TABLE 4

Effect of Heating at 230° C. on the Iodine Value and the Viscosity of Hydrogenated Cottonseed Oil in the Presence of Tin

Time of heating	Iodine value	Viscosity at 210° F.
hours		*centistokes*
0	12.6	10.67
2	11.0	10.77
4	......	10.94
6	......	11.26
8	10.4	11.39
10	......	11.81
12	......	12.06
14	......	12.33
16	9.7	12.60
18	......	13.02
20	......	13.24
22	......	13.54
24	10.0	13.79
26	......	14.04
28	......	14.37
30	......	14.73
32	10.0	15.17

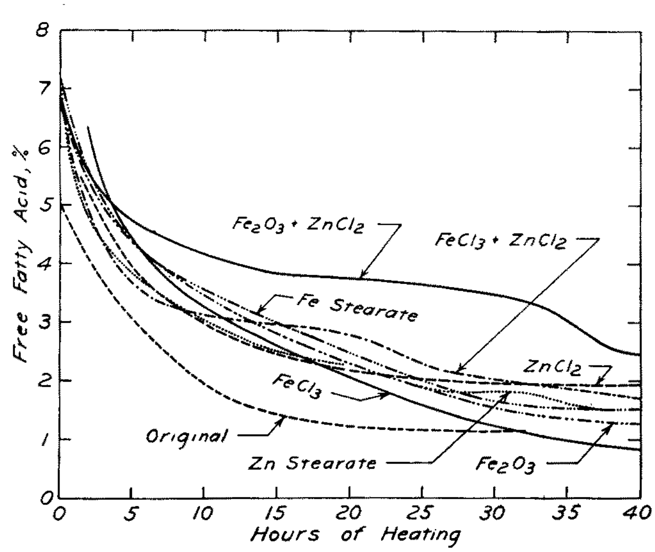

FIG. 1. Effects of metallic salts on the free fatty acid content of palm oil heated at 230°C. in the presence of tin.

in the next 8 hours of heating (total time, 32 hours) the iodine value remained constant at 10.0, whereas the viscosity increased to 15.17 centistokes.

Effect of metallic salts on palm oil: Experiments were carried out in which a palm oil and a hydrogenated cottonseed oil (previously found to be a suitable substitute for palm oil in the production of tin and terne plate) were heated with a number of metallic products which ordinarily are found as contaminants of the oil in the tin pot. These materials, namely zinc chloride, ferric chloride, ferric oxide, and the soaps of zinc and iron, were assumed to be the substances most likely to influence the rate and degree of breakdown of the tinning oils.

An 800-gram sample of palm oil was heated for 32 or more hours at 230° C. with each of the following metallic compounds:

Ferric chloride, 0.1 percent.
Zinc chloride, 0.1 percent.
Ferric oxide, 0.1 percent.
Zinc chloride, 0.1 percent + ferric chloride, 0.1 percent.
Zinc chloride, 0.1 percent + ferric oxide, 0.1 percent.
Ferric stearate (iron equivalent to ferric ion in 0.1 percent ferric oxide).
Zinc stearate (zinc equivalent to zinc ion in 0.1 percent zinc chloride).

Portions of the samples were removed periodically for analyses. The results of this series of heating tests are presented in Tables 5, 6 and 7, and graphically in Figures 1 and 2.

Examination of the data in Table 5 and Figure 1 indicates that the rate of volatilization of free fatty acids in all cases is relatively uniform during the first 8 hours of heating. However, following the initial 8-hour period, the content of free fatty acids of the oils is then apparently affected by the type of impurity present. In the case of the original sample which was heated in the presence of tin only, the content of free fatty acids leveled off at 1.2 percent after 20 hours and remained constant during the remainder of the period of heating.

The curves for palm oil (Figure 1) containing metallic salts leveled off at different fatty acid values. The sample of palm oil heated with the mixture of ferric oxide and zinc chloride had the highest content (2.50 percent after 38 hours of heating) of free fatty acids, while the corresponding value for the oil heated

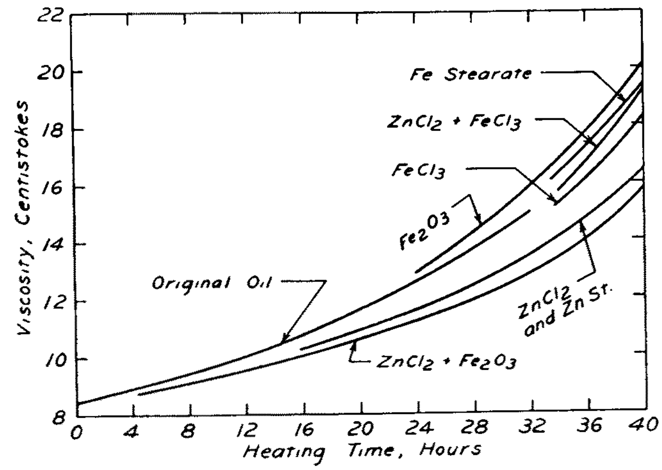

FIG. 2. Effects of metallic salts on the viscosity of palm oil heated at 230°C. in the presence of tin.

with ferric oxide alone was only 0.85 percent after 38 hours of heating.

The addition of metallic salts to the palm oil had pronounced and varied effects upon the rate of increase in viscosity during the heating. It is evident from Table 6 that the addition of zinc chloride alone to the oil inhibited the rate of increase in viscosity during the heating period compared to the original palm oil heated without the addition of metallic compounds. While ferric oxide accelerated the rate of increase in viscosity, the addition of a mixture of zinc chloride and ferric oxide markedly inhibited the rate of increase in viscosity of the oil during heating. The viscosity was found to be even lower than that observed with the addition of zinc chloride alone. The addition of zinc stearate to the oils caused a lowering of the viscosity rate comparable to that observed with the addition of zinc chloride or of zinc chloride-ferric oxide mixture. The presence of ferric stearate in the oil also resulted in a pronounced acceleration in the rate of viscosity increase which was comparable to that observed with ferric oxide.

These results would seem to indicate that the increase in viscosity observed with the addition of inorganic salts was due to the presence of zinc and ferric soaps which are formed from the acids produced in the thermal splitting of the glycerides. This assump-

TABLE 5

Effects of Added Metallic Salts on the Free Fatty Acid Value of Palm Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Ferric chloride (0.1 percent)	Zinc chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric oxide (0.1 percent ea.)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Ferric stearate	Zinc stearate
hours								
0	5.04*	......	......	6.57	6.87	7.03	7.33	7.28
2	4.04	6.35	5.29	5.47	5.54	4.77	5.50	4.76
4	3.36	......	......	......	......	......	......	......
6	2.81	3.90	3.69	4.18	4.63	3.47	4.19	3.79
8	2.42	3.55	3.30	3.77	4.39	3.27	3.80	3.07
10	1.92	......	......	......	......	......	......	......
12	1.64	3.20	2.76	3.18	4.03	2.93	3.35	2.82
14	1.52	2.90	2.45	2.95	4.09	3.26	3.23	2.57
16	1.44	2.42	2.45	2.71	3.70	2.92	2.91	2.43
18	1.33	2.11	2.42	2.52	3.69	3.02	2.74	2.39
20	1.18	1.95	2.40	2.29	3.72	2.86	2.64	2.32
22	1.18	2.09	2.11	2.16	3.69	2.64	2.29	1.97
24	1.20	1.52	2.37	1.63	3.57	2.46	2.03	1.96
26	1.06	1.50	2.11	1.61	3.69	2.25	1.93	1.81
28	1.16	1.43	2.21	1.52	3.45	2.16	1.83	1.79
30	1.17	1.38	1.95	1.53	3.50	2.13	1.72	1.82
32	1.17	1.27	1.87	1.47	3.34	2.03	1.52	1.80
34	......	1.08	1.75	1.34	3.20	2.02	......	1.62
36	......	0.95	1.76	1.38	2.78	1.75	1.67	1.53
38	......	0.85	1.75	1.30	2.50	1.85	......	1.49
40	......	0.85	1.86	1.30	2.48	1.78	1.50	1.52

* The fatty acid content of the palm oil increased over the period required to complete the experimental work.

tion is substantiated by the experiments in which ferric chloride, or a mixture of ferric chloride or ferric oxide with zinc chloride, was heated with the oil. Heating the oil in the presence of ferric chloride alone resulted in no more rapid increase in viscosity than was obtained when the oil was heated without the addition of metallic compounds. The addition of the mixture of zinc chloride and ferric chloride caused a negligible decrease in the rate of viscosity increase. The marked inhibition of viscosity increase noted when the oil was heated with a mixture of ferric oxide and zinc chloride may have been due to the suppression of the formation of metallic soaps during heating.

Comparison of the iodine values (Table 7) indicates that the addition of metallic compounds did not affect the degree of unsaturation of the oil during the earlier stages of heating; but the iodine values obtained after 24 hours of heating indicate that the presence of zinc salt retards the breakdown of palm oil. The oil containing zinc chloride or a mixture of zinc chloride with ferric oxide showed a slight decrease in iodine value during heating.

Palm oil containing ferric chloride, ferric oxide, or ferric stearate (whose effects on rate of viscosity increase curves in Figure 2 were practically identical) had essentially the same iodine value as the original unadulterated oil after heating for 24 hours. The curves for changes in viscosity of the oil (Figure 2) exhibit considerable deviation, depending on the nature of the added metallic compound, following the end of the first 24 hours of heating. A similar effect was observed in the case of the iodine numbers (Table 7).

The type of metallic contaminant appears to have a specific effect on the content of free fatty acids of the palm oil. The results of the determinations shown in Table 5 indicate that the palm oil, which had a high initial free fatty acid content, lost free acids by volatilization during the first part of the heating period. The added salts apparently had little effect upon the rate or degree of breakdown of the oil during this initial period of heating, but did affect the value at which the content of free acid leveled off during the latter stages of heating as is indicated in Figure 1. The addition of zinc chloride caused a leveling off at a free acid content of 1.75 to 1.85 percent. The values for free acids obtained with oil that was heated with ferric salts were very erratic, especially the value of 0.85 percent which was observed with ferric chloride. The addition of zinc chloride to the oil containing ferric salts resulted in an increase in the free acid content during heating over that observed with ferric salts alone. While the addition of the zinc chloride and ferric oxide to the same oil had a pronounced effect upon the free acid content, it was noted that the addition of this mixture caused a decided lowering of the rate of viscosity increase of the palm oil during heating. Although the addition of zinc chloride and zinc stearate to the oil had the effect of increasing the fatty acid content and retarding the rate of viscosity increase, the addition of the mixture of zinc chloride and ferric chloride resulted in high fatty acid values and in viscosities almost identical with those obtained on heating the palm oil without addition of metallic compounds.

It is apparent from the data in Table 6, as well as from the smoothness (i.e. lack of points of inflection) of the various viscosity curves (Figure 2), that the viscosity of an oil increases on heating, irrespective of its content of free fatty acids. Therefore, in this respect it can be assumed that an oil having a content of free acid equivalent to 0.2 percent will function, after a short initial period of heating in the tin pot, as well as or better than a palm oil with an initial free acid content of 5 to 10 percent.

Effect of metallic salts on hydrogenated cottonseed oil: Experiments similar to those described above were carried out with hydrogenated cottonseed oil in place of palm oil. The data thus obtained with respect to the changes in the free fatty acid content of the oil are given in Table 8 and in Figure 3, while the changes in the iodine values are presented in Table 10 and changes in viscosities are given in Table 9 and Figure 4.

TABLE 6

Effects of Added Metallic Salts on the Viscosity in Centistokes at 210° F. of Sumatran Palm Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Zinc chloride (0.1 percent)	Ferric chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric oxide (0.1 percent ea.)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Ferric stearate	Zinc stearate
hours								
0	8.49	......	...	......	......	......	......	......
2	8.78	8.81	8.86	8.97	8.63	8.59	8.92	8.88
6	9.27	9.17	9.41	9.34	8.98	9.26	9.35	9.30
8	9.53	9.32	9.31	9.56	9.12	9.37	......	......
12	10.11	9.80	10.10	10.05	9.93	9.87	10.13	9.98
16	10.88	10.35	10.04	10.75	10.21	10.70	10.74	10.43
20	11.72	10.95	11.75	11.53	10.59	11.50	11.54	10.96
24	12.65	11.57	12.71	12.92	11.23	12.41	12.57	11.65
28	13.77	12.48	13.61	14.20	11.95	13.45	13.78	12.48
32	14.97	13.37	14.82	15.86	12.92	14.83	15.30	13.30
36	......	14.75	16.06	17.73	13.85	16.62	17.34	14.63
40	......	16.34	16.45	20.12	15.94	19.34	19.19	15.91

TABLE 7

Effects of Added Metallic Salts on the Iodine Value of Sumatran Palm Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Zinc chloride (0.1 percent)	Ferric chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric oxide (0.1 percent ea.)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Ferric stearate	Zinc stearate
hours								
0	50.9	......	......	......	......	......	......	......
2	48.4	49.6	50.2	49.2	49.5	49.8	49.4	49.4
8	......	48.8	49.4	......	......	......	......	......
16	44.5	47.3	47.0	......	......	......	46.4	......
24	44.2	45.8	44.4	44.1	46.0	46.4	44.9	45.0
32	42.5	44.0	42.6	......	......	......	42.5	43.3
40	41.9	41.6	39.0	40.1	42.7	42.4	41.1	40.9

It was found that although the viscosity of the palm oil (8.49 centistokes) was originally slightly lower than that of the hydrogenated cottonseed oil (10.0 centistokes), it tended to approach the viscosity of the cottonseed oil when it was heated at the temperature of the tin pot. It is also apparent from the results of these heating tests, that the hydrogenated cottonseed oil is much more stable than palm oil in the presence of metallic salts.

It is apparent from the viscosity curves (Figure 4) for hydrogenated cottonseed oil alone and hydrogenated cottonseed oil containing 0.1 percent ferric oxide that the rate of viscosity increase is unaffected by the presence of this metallic oxide.

The addition of zinc chloride or zinc stearate to the oil produced a decided lowering in the rate of viscosity increase throughout the entire heating period, whereas the addition of ferric chloride caused little change during the first twenty hours, but resulted in a lowering of the rate of increase in viscosity during the latter part (20 to 40 hours) of the heating period. The addition of zinc chloride or ferric chloride, which had no effect on the rate of viscosity increase in the case of palm oil caused a marked decrease in the case of hydrogenated cottonseed oil during the first 32 hours of heating.

The addition of metallic salts had a pronounced effect upon the free acid content of the hydrogenated cottonseed oil during heating. It was observed that although palm oil lost free fatty acids by volatilization when heated with these substances, the reverse was true with hydrogenated cottonseed oil. In the cottonseed oil with a low initial free acid content, there was an accumulation of acids during the early stages of the heating followed by a decrease and leveling off at about 1.0 percent (Table 8). The addition of zinc chloride to the hydrogenated oil resulted in a decided increase in free fatty acid during the first 12 hours of heating. It was observed that the addition of zinc stearate to the hydrogenated cottonseed oil resulted in decidedly lower free fatty acid values than were observed with the same oil containing ferric stearate.

TABLE 8

Effects of Added Metallic Salts on the Free Fatty Acid Value of Hydrogenated Cottonseed Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Zinc chloride (0.1 percent)	Ferric chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Zinc stearate	Ferric stearate
hours							
0	0.08*	......	0.57	0.69	0.52	0.14	0.95
2	0.18	2.23	1.58	0.48	2.89	1.00	1.82
4	0.27	......	......	......	......	......	......
6	0.41	2.49	2.01	1.09	2.99	1.20	2.28
8	0.59	2.47	2.10	1.54	2.94	1.62	2.39
10	0.79	......	......	......	......	......	......
12	0.96	2.43	2.09	1.52	2.71	1.77	2.25
14	1.11	2.28	2.19	1.53	3.14	1.51	2.24
16	1.21	2.19	2.18	1.46	2.80	1.64	2.35
18	1.30	2.18	2.10	1.43	2.75	1.64	2.18
20	1.24	2.14	1.57	1.21	2.69	1.33	2.06
22	1.18	2.19	1.78	1.21	2.49	1.48	1.85
24	1.10	2.01	1.67	1.09	2.38	1.47	1.87
26	1.09	2.06	1.74	1.28	2.41	1.43	1.86
28	1.07	1.89	1.68	1.27	2.20	1.23	1.81
30	1.04	1.98	1.82	1.37	2.37	1.43	1.92
32	1.02	1.85	1.47	1.56	1.93	1.49	1.86
34	......	2.04	1.60	1.32	1.95	1.47	1.78
36	......	1.82	1.59	1.28	2.05	1.35	1.76
38	......	1.66	1.56	1.35	1.93	1.37	1.75
40	......	1.64	1.35	1.21	1.76	1.40	1.68

* The fatty acid content of the palm oil increased over the period required to complete the experimental work.

TABLE 9

Effects of Added Metallic Salts on the Viscosity in Centistokes at 210° F. of Hydrogenated Cottonseed Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Zinc chloride (0.1 percent)	Ferric chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Zinc stearate	Ferric stearate
hours							
0	10.00	....	....	....	......	....	....
2	10.18	10.00	10.21	10.19	9.99	10.37	10.07
6	10.71	10.41	10.73	10.92	10.22	11.02	10.53
8	11.03	10.82	10.96	11.27	10.70	....	....
12	12.16	11.42	11.95	12.06	11.47	11.96	11.44
16	12.61	11.92	12.58	12.82	11.98	12.67	11.96
20	13.63	12.73	13.62	13.74	12.80	13.68	12.94
24	14.68	13.36	14.23	14.66	13.85	14.88	13.75
28	15.76	13.71	15.41	15.76	15.23	16.13	14.48
32	17.09	15.05	16.88	17.00	17.02	17.67	15.42
36	....	16.18	18.29	18.54	18.93	19.60	16.65
40	....	17.42	20.17	20.35	22.66	22.02	17.75

TABLE 10

Effects of Added Metallic Salts on the Iodine Value of Hydrogenated Cottonseed Oil Heated at 230° C. in the Presence of Tin

Time of heating	Original oil only	Zinc chloride (0.1 percent)	Ferric chloride (0.1 percent)	Ferric oxide (0.1 percent)	Zinc chloride + Ferric chloride (0.1 percent ea.)	Ferric stearate	Zinc stearate
hours							
0	49.1	......	......	......	......	......	......
2	47.8	47.9	47.6	44.8	48.0	47.8	49.2
8	46.4	48.0	......	......	......	......	......
16	44.6	47.4	......	......	......	......	......
24	......	46.6	45.5	43.8	46.2	44.6	45.5
32	43.5	45.5	......	......	......	43.7	43.8
40	......	42.6	43.5	41.6	44.8	42.5	42.3

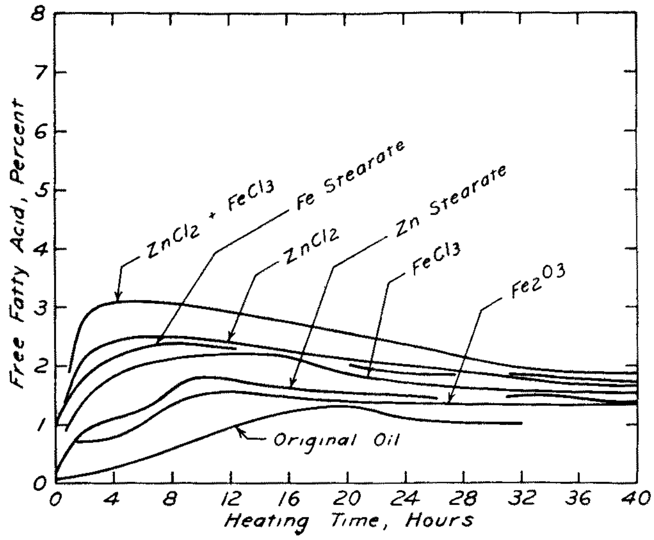

FIG. 3. Effects of metallic salts on the free fatty acid content of hydrogenated cottonseed oil heated at 230°C. in the presence of tin.

At the end of 12 hours of heating it was found that the free fatty acid content of the hydrogenated oil rose to 2.49 percent when zinc chloride was present and to 2.99 percent when a mixture of zinc and ferric chlorides was present. The values at which the free acid leveled off were 1.60 percent with zinc chloride and 1.90 percent with the mixed chlorides. Each of the metallic compounds or mixtures added produced a specific free-acid value in the leveling-off period. The addition of zinc chloride or zinc chloride-ferric chloride mixture tends to suppress the rate of viscosity increase on the one hand, while on the other hand, it accelerates the formation of free fatty acids in both palm oil and hydrogenated cottonseed oil.

Effects of added acid and inert atmosphere on palm oil: A comparison of the free fatty acid values (Table 11) obtained during heating of samples of palm oil

TABLE 11

Effects of Added Free Fatty Acid on the Formation of Free Acid During the Heating of Palm Oil at 230° C.

Time of heating	Stearic acid (1.0 percent)	Oleic acid (1.0 percent)	Stearic acid (1.0 percent) CO_2 Atmosphere
hours	*percent*	*percent*	*percent*
0	7.47	7.45	7.72
2	4.87	4.75	6.42
4	3.10	3.16	5.67
6	2.01	1.92	4.79
8	1.38	1.17	4.04
10	1.07	1.04	3.36
12	1.12	0.95	2.97
14	1.04	0.95	2.38
16	0.95	0.99	2.39
18	......	......	2.21
20	......	......	1.75
22	......	......	1.80

at 230° C., in the presence of tin, with 1.0 percent of added stearic acid and with 1.0 percent of added oleic acid substantiates the previously reported observation (1)that free acid is lost through volatilization. Both of the palm oil samples lost free acid at the same rate and leveled off at approximately 1.0 percent of free acid after heating for 10 hours.

Higher viscosity values (Table 12 and Figure 5) were obtained on heating the palm oil sample containing the added oleic acid than were obtained when stearic acid was added to the oil. However, the sample

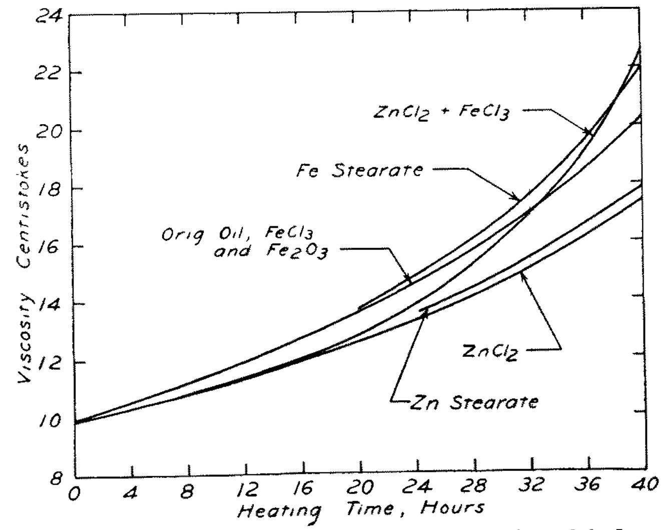

FIG. 4. Effects of metallic salts on the viscosity of hydrogenated cottonseed oil heated at 230°C. in the presence of tin.

containing added oleic acid had a slightly higher iodine value after 16 hours than the sample containing the stearic acid.

When palm oil containing 1.0 percent of added stearic acid was heated at 230° C. in the presence of tin in an atmosphere of carbon dioxide, both the volatilization of free fatty acid and the rate of viscosity increase were noticeably retarded. The free acid content of the palm oil was 2.4 percent after 16 hours

TABLE 12

Effects of Added Fatty Acid and Inert Atmosphere on the Viscosity and Iodine Value of Palm Oil Heated at 230°C. in the Presence of Tin

Time of heating	Stearic acid (1.0 percent)		Oleic acid (1.0 percent)		Stearic acid CO_2 Atm. (1.0 percent)	
hours	*Iodine value*	*Viscosities at 210° F.*	*Iodine value*	*Viscosities at 210° F.*	*Iodine value*	*Viscosities at 210° F.*
2	47.9	9.05	49.4	8.96	49.0	8.80
6	......	10.04	......	10.44	......	9.61
10	......	11.81	......	12.14	......	10.70
12	......	12.70	......	12.79	......	11.21
14	......	13.56	......	13.68	......	11.78
16	40.9	14.97	41.7	15.36	43.5	12.45
18	......	....	......	....	......	13.52
20	......	....	......	....	......	14.26
22	......	....	......	....	41.4	15.07

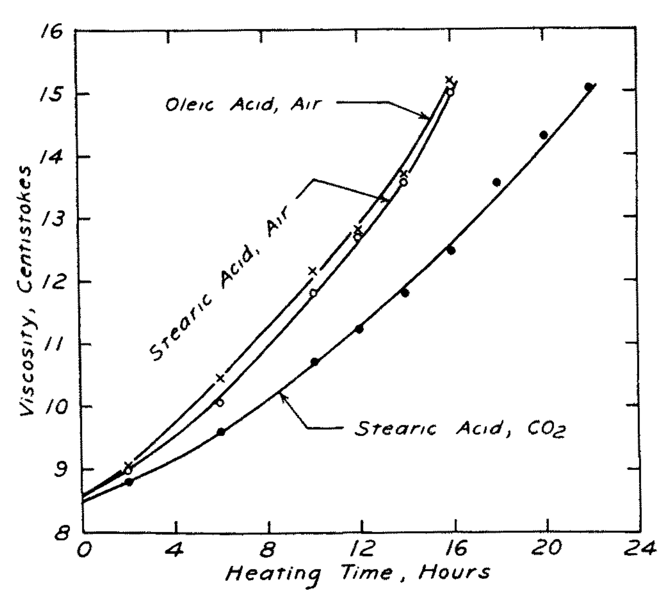

FIG. 5. Effects of inert atmosphere and added fatty acids on the viscosity of palm oil heated at 230°C. in the presence of tin.

heating compared with 1.0 percent for the same oil heated in air. A significant difference was observed in the final iodine values of these two samples and it is evident that, if it were feasible to blanket the oil chamber of the tinning bath with an inert atmosphere, the life and utility of tinning oils would be increased appreciably.

Summary and Conclusions

An investigation has been made of the relative effects of added metallic compounds, normally found as contaminants in the tin bath, upon the formation of free fatty acids and the rate of increase in the viscosity of heated palm and hydrogenated cottonseed oils.

It was found that when palm and hydrogenated cottonseed oils were heated in the presence of tin to temperatures comparable with those obtaining in the tin pot during the hot dipping of tin, palm oil showed a slightly lower rate of increase in viscosity compared to hydrogenated cottonseed oil. On the other hand, when zinc and ferric salts were added to the otherwise similarly treated oils, hydrogenated cottonseed oil was found to be more stable than palm oil.

Metallic contaminants such as ferric oxide, which had a marked effect on the rate of viscosity increase of palm oil, produced no change in the rate of increase in viscosity in the case of hydrogenated cottonseed oil.

The addition of zinc stearate, of zinc chloride alone, or of zinc chloride and ferric salt, had the effect of retarding polymerization of both oils, as measured by the rate of increase in viscosity. The addition of either ferric oxide or ferric stearate resulted in acceleration of the rate of viscosity increase of the heated oils. It may, therefore, be assumed that the inorganic salts are partly converted to ferric and zinc soaps *in situ* by reaction with free fatty acids already present or formed in the heated oils.

It was observed that when palm oil was heated with various metallic compounds, it lost free fatty acids rapidly during the early stages of heating until the concentration attained a definite value, at which it remained during further heating. The concentration at which the free fatty acids in the palm oil became constant was directly affected by the specific nature of the added metallic compound. Also, when hydrogenated cottonseed oil, having a lower initial content of free fatty acids than the palm oil was treated in the same manner, there was an accumulation of free fatty acids during heating until the concentration attained a definite value, after which it remained constant on further heating. The concentration at which the free fatty acids of any sample of oil became constant was found to be dependent on the specific nature of the added metallic compound.

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Unsaturated Synthetic Glycerides*

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The complexity of the glyceride composition of animal and vegetable fats and the inherent difficulties of isolating single components with definite and known configuration are facts well known to investigators in the field of fat chemistry. While considerable progress has been made in the analysis of the fatty acid composition of individual fats, the determination of the glyceride composition has not been nearly so precise.

The isolation of individual glycerides from naturally occurring fats has been reported by many investigators but the assignment of specific configurations to them has been accompanied with some degree of uncertainty. Greater assurance of the structure and configuration of those glycerides isolated from natural sources can be, and in a few instances has been, obtained by comparing their physical and chemical properties with those prepared by reliable synthetic methods. Certainly complete information relative to the properties of synthetic glycerides would be of considerable value in planning methods of isolating and identifying individual glycerides in anticipated mixtures. As a case in point, solubility studies should be of inestimable value when solvent partition and crystallization methods are used for isolation purposes. A fact much more important than the actual isolation of components in glyceride mixtures is the determination of the glyceride composition of a fat without, necessarily, an accompanying isolation. This latter, while seemingly impossible at the moment, may be accomplished through the correlation of properties of glycerides of proved configuration obtained by synthetic methods.

Since methods for the synthesis of glycerides of a high degree of purity containing primarily saturated fatty acids have been discussed recently in other reviews (1, 2, 3), this report will be concerned mainly with the adaptability of those methods to the synthesis of glycerides composed of both saturated and unsaturated fatty acids and to a discussion of some of the physical properties of such unsaturated glycerides. As most naturally occurring fats are composed of glycerides containing some unsaturation, this group of synthetic glycerides assumes increasing importance in the study of glyceride mixtures.

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