The uniform incorporation and distribution of settlings and suspended matter are very significant in determining the accuracy of the result of the analysis. If the results are to be expressed on the basis of oil only, *i.e.*, exclusive of water and foreign material, these should be removed from the portion to be analyzed by filtration through a clean, dry filter paper before weighing.

D. Preparation of the Column

Attach a short piece of rubber tubing equipped with a pinch clamp to the bottom of the chromatographic tube. Fill the tube about one-third full with the ether-methanol solution. Open until about 5 ml. drain from the tube and no air is trapped in the bottom of the tube; then close. Weigh 20 ± 1 g. of activated alumina and transfer into the tube with the aid of a powder funnel. Wash down any alumina remaining on the wall of the tube with a few ml. of solvent.

E. Procedure

Weigh a sample of appropriate size, depending upon the anticipated neutral oil content, into a clean and dry 100-ml. beaker.

Approximate neutral oil	Weight of sample
100–90	2–3 ± 0.001 g.
90–75	1–2 ± 0.001 g.
75–50	0.7–1 ± 0.001 g.
50–0	0.45–0.55 ± 0.001 g.

Add 25 ml. of the ether-methanol solution and swirl to dissolve the sample. Just before pouring the sample solution on the column, remove the rubber tubing at the bottom and allow the excess solvent to drain until the level of the solution is 5 mm. above the level of the activated alumina. Immediately add the sample-solution by pouring the contents on the column, being careful not to disturb the surface of the alumina.

Collect the percolate in a previously dried and tared 250-ml. beaker or Soxhlet flask. Use a total of 25 ml. of ether-methanol solution, divided into four equal portions, to effect the transfer of the sample to the column, adding each washing after the preceding one is only 5 mm. above the top of the alumina.

When the last wash has gone into the alumina except for the 5 mm. remaining above the column, add 100 ml. of ether-methanol solution. Continue collecting the percolate until all the ether-methanol has passed through the column. Wash the drawn end of the tube with a small portion of ether-methanol solution and add to the 250-ml. beaker.

Evaporate the ether-methanol solution on a water bath with the aid of a gentle stream of air. After the solvent fumes have disappeared, remove from the steam bath and place in 105°C. oven for one hour. Remove from the oven, cool in a desiccator, and weigh the beaker and contents.

F. Calculations

$$\text{Neutral oil content, \%} = \frac{100\ (\text{weight of residue})}{\text{weight of sample}}$$

G. Reproducibility

Collaborative studies have shown that the following reproducibility can be expected:

Duplicate determinations made on the same day by an analyst should not differ by more than approximately 0.14.

Averages of duplicate determinations made in two different laboratories should not differ by more than approximately 0.37.

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Absence of Thermal Polymers in Potato-Chip Frying Oils[1]

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DURING the past year there have been articles and statements published in both the lay and scientific press on the disadvantages of fat in the diet. These published statements have neglected the many scientific reports dealing with the noncaloric, essential functions of fats in the diet (1) and particularly the importance therein of certain polyunsaturated essential fatty acids (2). In these general attacks on all types of fats in the diet there is one type of fat regarded by many to be at the bottom of the scale of foods acceptable for human consumption; this is the fat absorbed in fried foods. Toxic polymers have been alleged to be formed during commercial frying operations, and questions have been raised about the possibility of fatty acid isomers developing in these operations.

Publications on the harmlessness of the fats absorbed by fried foods are unfortunately scanty in number. It is the purpose of the present report to review critically what has been published on this subject and to describe the rationale in support and the results of a nation-wide survey of the potato chip industry to determine the extent of polymer formation in the frying oils and the nutritional significance of the findings.

Potential Thermal Polymers in Frying Oils Employed by the Potato Chip Industry. Ease of polymer formation is directly related to the degree of unsaturation of the fatty acids (3). Likewise during hydrogenation of an oil there is a preferential uptake of hydrogen by the more highly unsaturated fatty acids. From the practical standpoint the present study need be concerned only with the possibility of dimers and higher polymers being formed from the linoleic acid in the frying oils. None of the oils employed by the potato chip industry contains linolenic acid. Unhydrogenated soybean oil contains about 8% of this fatty acid, but no potato chip manufacturer in this country uses in his operations such soybean oil because of flavor instability. Soybean oil shortenings contain no linolenic acid.

On heating linoleic acid for a period of time at a sufficiently high temperature, there occurs first a migration of the double bonds to a conjugated position. Such a linoleic acid isomer reacts with natural linoleic acid to form a dimer (4). As a result of this reaction there occurs a reduction in unsaturation from four double bonds to two double bonds. The

[1] Presented at the 20th Annual Conference, National Potato Chip Institute, Dallas, Tex., January 21, 1957.

dimer can react still further with another dienoic acid to form a trimer (4). In this way there occurs a decrease in the iodine value of an oil as polymer formation proceeds (4). Thus there is available for survey purposes a simple and highly precise method for determining whether thermal polymers may have formed in oils used in the frying of foods. Whereas a significant drop in iodine value would justify further work to determine whether reactions other than polymerization may have been responsible, the lack of change in iodine value is proof that no polymerization changes could have occurred.

Flavor of Polymers. It must be emphasized that thermal palymerization changes in an oil cannot be readily detected by flavor. This is in sharp contrast to the situation when oxidative polymers are formed. Whereas the oxidative polymers also may be free of objectionable flavor when isolated as the residues following molecular distillation from the oil heated in the presence of oxygen (5), the oils containing such polymers are definitely unpalatable. Such oils exhibit high peroxide values, *viz.*, at one point in excess of 300 m.e. per kilogram of fat. There have, of course, been reports in the literature on the toxicity of rancid fats, particularly on their deleterious effects on vitamins and other dietary essentials (6). However potato chips or other foods containing such fats would be rejected by the consumer because of exceedingly poor flavor. The oxidized fats *per se* are not highly injurious. Authorities state that peroxidation will not interfere with the nutritional well-being of test animals until the peroxide value of the oil is in the order of 1,000 m.e. per kilogram of oil (7) or well above 100 m.e., using even more delicate indices than growth (8).

On the other hand, subjecting an oil to thermal polymerization changes not only yields an oil that is highly acceptable in flavor but also actually enhances the flavor stability of the oil. The reduction in concentration of the polyunsaturated fatty acids accounts for the increased resistance of these oils to oxidative deterioration. Indeed thermal polymerization has been used in some foreign countries to reduce the degree of unsaturation in fish oils employed in canning operations in order to produce an oil of improved flavor stability. Thus oils containing thermal polymers lack the safeguard of unacceptable flavor to cause a consumer to reject such an oil.

Biological Studies with Heated Fats. In 1951 Deuel and associates (9) published the results of growth tests with rats subsisting for 10 weeks on diets containing heated and unheated fats. The fat employed in this study was a margarine type of fat and contained 4.9% linoleic acid. In this respect it is comparable to the shortenings currently employed by the potato chip industry. The heated oil had been used in consecutive deep-fat-fryings at 205°C. (401° F.) of potato chips for a period of 8 hrs. with oil replenishment keeping pace with that absorbed by the chips. The residual oil and the last batch of potato chips were the items fed to the rats at 11.5 and 23% of the diet, respectively. The "IC," referred to in Table I, covers additional tests conducted with monoisopropyl citrate, a fat-soluble metal-sequestering agent (10) added to the oil. No adverse effects on growth were noted in either the male or female rats when the heated fats or the potato chips containing such absorbed fats were fed to the test animals. The gain in weight in grams per 100 calories consumed, or the so-called Efficiency of the Diet, likewise showed that there was nothing harmful in in either the frying oil or in the potato chips fried in this oil.

Just about the same time that Deuel's work was published, there appeared papers by Crampton and associates (11–13) describing the development of thermal polymers in vegetable oils heated at 275°C. (527°F.) in the absence of air. There is no reason to question the validity of Crampton's studies, which incidentally are still in progress (7, 14); thermal polymers were formed and, as shown in Table II, they suppressed growth. Crampton however never extended conclusions beyond the scope of his findings. A temperature of 527°F. is about 100°F. above the smoke point of frying oils and so is never encountered in the potato-chip-frying industry. Nevertheless these considerations have not prevented others from drawing broad generalizations. One authoritative review journal (15), in introducing Crampton's findings, states that "tremendous quantities of vegetable oils are currently manufactured into such edible products as margarine, salad oils, and cooking oils. Since many of these products are, through routine usage, subjected to varying amounts of heat, it is of importance to determine whether or not heat treat-

TABLE I

Performance of Rats Over 10 Weeks on Diets Containing Unheated Fat, Fat Heated at 205°C. for 8 Hours, and Potatoes Fried in Such Fats [a]

No.	Category	Body weight		Gain in weight	Food eaten	Efficiency of diet [b]
		Start	End			
	Experiments on male rats					
		g.	*g.*	*g.*	*g.*	
I	Unheated fat (control)	35.4	258.2	222.8	819	6.68
II	Heated fat	36.2	265.5	229.3	758	7.08
III	Heated fat plus IC [c]	37.3	262.3	225.0	748	7.04
IV	Potato chips from II	39.9	260.4	221.4	758	7.43
V	Potato chips from III	36.3	263.0	226.4	789	7.04
	Experiments on female rats					
I	Unheated fat (control)	39.7	180.2	140.5	701	4.93
II	Heated fat	38.1	187.0	148.9	670	5.20
III	Heated fat plus IC	38.0	193.7	155.7	680	5.37
IV	Potato chips from II	37.2	182.1	144.9	677	5.42
V	Potato chips from III	39.2	185.7	146.5	689	5.22

[a] From Deuel *et al.*, *Food Research*, *16*, 258 (1951).
[b] Grams gain in weight per 100 calories consumed.
[c] Mono-isopropyl citrate, a fat-soluble, metal-sequestering agent (10).

TABLE II
Development of Thermal Polymers in Vegetable Oils [a] Heated at 275°C.(527°F.) Under CO_2

Oil	Iodine No.	Linolenic acid	Linoleic acid	Heated	Oil in rat diet	Growth per 1,000 calories absorbed
		%	%	*hrs.*	%	*g.*
				0	10	91
				6	10	74
				12	10	72
Linseed	180	47	24			
				0	20	80
				12	20	4
				0	10	92
				6	10	87
Soybean	133	8	51			
				0	20	90
				6	20	80
				9	20	76
Corn	125	0	54	0	10	78
				15	10	71
Peanut	95	0	25	0	10	87
				15	10	80

[a] Data based upon papers by Crampton *et al.*, J. Nutrition (1951–56).

ment has any effects that would influence the nutritional value of such products."

In Table II are listed the results of 28-day growth tests reported by Crampton and co-workers in investigations conducted on heat-abused, limpid vegetable oils, those rich in polyunsaturated fatty acids. With linseed oil, progressive interference with normal growth was noted as the period of heating was extended or as the concentration of the heated oil in the diet was increased. Heating soybean oil likewise showed this effect, but to a lesser degree. Corn and peanut oils had to be heated for a period of 15 hrs. before interference with growth occurred. Incidentally growth has been expressed here in terms of calories absorbed rather than in terms of calories consumed. Since all animals ingesting the heated fats exhibited diarrhea of some degree, the results would have been even more striking had they been expressed in relation to calories consumed.

In the later studies Crampton and associates (7, 14) fractionated the heated oils into a number of components which were then fed separately to the test animals. On the basis of these tests it was concluded that the "cyclized" monomeric acids were highly toxic; death resulted within the first 16 days on the test diet. The harmful effect was measurable even when this fraction comprised as little as 2.5% of the diet. It is to be emphasized that the cyclized monomeric acids were derived from the linolenic acid present in certain of the vegetable oils. On the other hand, the dimers and higher polymers were considered to be nontoxic in the usual sense of the term; they were largely unabsorbed from the gastrointestinal tract and thereby contributed only to the diarrhea noted (7, 14). Thus in the commercial frying of potato chips where oils lacking linolenic acid are used there need be concern only with the possibility of dimers and higher polymers forming in sufficient concentration from the linoleic acid in the oils to be responsible for poor digestibility of the oils. Frying oils free of such dimers and higher polymers obviously will not provoke a diarrhea.

Kummerow and co-workers (16) have sought to extend in a practical way the findings reported by Crampton and associates. These workers have stated in a recent publication that "an attempt was made to evaluate the effect of heat on corn oil, margarine base stock (a hydrogenated vegetable oil), and butter oil in the presence of air when temperatures similar to those found in batch-type, commercial deep-fat-frying processes were followed." The authors admit that "these experimental conditions cannot be compared directly to deep-fat-frying conditions as no fresh oil was added during the heating period nor was any product such as potato chips in contact with the oil." They conclude thus: "however under these experimental conditions it was possible to compare the relative heat stability of corn oil, margarine base stock, and butter fat." We would challenge this last statement since we believe that the only way to obtain such information is to run tests on these oils when subjected to practical conditions of use and not employ an oil simply held at 200°C. (392°F.) for a period of 24 hrs. with air bubbling through the hot oil.

In Kummerow's report (16) it was concluded that the thermally oxidized corn oil was toxic. The corn oil exhibited a drop in iodine value of 16, was reddish in color, "painty" in odor, and had a free fatty acid content of 1.23%. Obviously such an oil would be rejected by the human for lack of palatability. The margarine oil in the Kummerow study showed a drop in iodine value of 9 while the butter oil showed a drop of 5 in iodine value. The latter two heated fats were well tolerated, with no difference noted between the heated and the fresh butter oil.

Just as irrelevant as Kummerow's investigations to practical operations are the studies by Kaunitz and associates (17), wherein it was reported that cottonseed oil heated and aerated at 90 to 95°C. for periods of 50 to 300 hrs. became toxic. We know that cottonseed oil under these conditions (essentially the A.O.M. stability test) will have a peroxide value of 100 m.e. per kilogram of fat within 15 hrs. The more recent and related studies (5, 18) by these investigators, with lard as well as cottonseed oil as the test fats, are just as unrealistic from the practical viewpoint. In order to assist the reader to draw conclusions on the pertinency of the findings, these authors should have emphasized the lack of palatability of the thermally oxidized fats even though the residues following molecular distillation may have been free of objectionable flavor.

Survey of Fresh and Heated Oils in the Potato Chip Industry. In the last few years more and more attention has been directed toward the possible toxicity of oils used in continuous frying operations, prompted undoubtedly by the reports of the latter university investigators just reviewed. It was decided at the meeting of the Production and Technical Committee at the time of the 1956 Conference of the National Potato Chip Institute that a survey should be conducted to determine the extent of thermal polymer formation in the oils absorbed by the potato chips manufactured in this country. Ora Smith, research director of the Institute, wrote to chip manufacturers for cooperation in a survey of the quality of fats and oils used by the industry. Sample bottles were sent to each "Chipper," two to be filled with the fresh oil, and two with the same oil after it had been in constant commercial use for four days or more, *i.e.*, in its equilibrium state of use. One set of bottles containing the fresh and heated oils was sent by Dr. Smith to the laboratory of The Best Foods Inc., and another set was sent to a second outside laboratory. Neither of the two testing laboratories knew the identity of the Chipper supplying these oils since he was identified only by a number assigned to him.

The objective of the present study was to determine whether or not there was a decrease in the iodine values (Wijs) of the frying oils employed on a continuing basis by the potato chip industry. As mentioned earlier, if there were no decrease, then one would have to conclude that there were no thermal polymers in the frying oils employed by the industry. If there were an appreciable decrease in iodine value, its nutritional significance would have to be established. Oxidative polymers were ruled out of the picture since no Chipper could stay in business distributing highly rancid chips to retail outlets.

Results list the iodine values of the fresh and heated oils categorized according to the type of oil used. In Table III are shown the results with corn oils. The agreement in values reported independently by the two laboratories is very good. For the most part there are small decreases in iodine value, averaging —1.22 according to Laboratory A, and —1.29 according to Laboratory B. It is theoretically impossible to obtain an increase in iodine value as a result of frying operations. In the last column of Table III are averaged the results reported by the two laboratories. The significance of these figures will be discussed later in this report.

Data of the same type, this time contributed by another type of unhydrogenated oil—cottonseed cooking oil, are shown in Table IV. The same general picture is obtained, namely, a small decrease in iodine value with good agreement in the results reported by both laboratories.

In Table V are listed the results obtained in analyzing the winterized cottonseed oils used in potato chip fryings. Again a small but consistent reduction in iodine value is noted. The increase in iodine value of 3 obtained by both laboratories in testing the oils submitted by Chipper No. 4 is beyond the precision of the method of analysis and undoubtedly reflects an error in sampling the test oils. Possibly the heated oil was not from the same lot as the fresh oil.

The next three series of oils comprise the hydrogenated oils, those containing reduced concentrations of the polyunsaturated fatty acids and thereby exhibiting a marked increase in resistance to oxidation. In Table VI are the results obtained in analyzing the lightly hydrogenated cottonseed oils. Cottonseed oil, selectively hydrogenated to about 85 iodine value, contains 35 to 40% as much linoleic acid as the original cottonseed oil. Nevertheless, when such lightly hydrogenated oils are employed in the preparation of potato chips, there is again the small decrease in iodine value noted in frying with the unhydrogenated oils. The rather large decrease noted in iodine value of one oil is attributed to a sampling error and not to thermal polymer formation; there was no increase in the concentration of conjugated fatty acids in the heated oil as compared to the fresh oil (3). Of course, in this particular series of oils, containing small amounts of stearine in suspension in limpid oil at room temperature, there is much more opportunity for sampling errors (*i.e.*, of obtaining a non-representative sample) than in sampling an all-liquid oil or the much firmer all-hydrogenated shortenings.

In Table VII are presented the results obtained in testing the fresh and heated shortenings employed in the commercial manufacture of potato chips. Here also there is a definite tendency for the iodine value to decrease, although to a small degree. Considering that these shortenings contain only about one-tenth as much linoleic acid as found in the original unhydrogenated oils, no measurable drop in iodine value had been expected.

The most erratic results in the present survey, shown in Table VIII, were obtained in testing the oil-and-shortening blends employed in the manufacture of potato chips. The apparent changes in iodine

TABLE III

Iodine Values of Fresh and Heated Corn Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
1	125.8	124.9	−0.9	124.9	123.5	−1.4	−1.15
7	124.9	124.2	−0.7	123.9	122.7	−1.2	−0.95
12	125.2	122.8	−2.4	124.1	123.3	−0.8	−1.60
17	126.7	124.3	−2.4	125.8	124.9	−0.9	−1.65
24	125.3	122.9	−2.4	124.3	121.8	−2.5	−2.45
41	125.5	126.9	+1.4	125.4	123.8	−1.6	−0.10
44	124.3	121.3	−3.0	122.7	120.9	−1.8	−2.40
45	124.9	123.0	−1.9	123.7	122.3	−1.4	−1.65
85	122.0	123.3	+1.3	122.0	122.0	0.0	+0.65
Average	125.00	123.73	−1.22	124.09	122.80	−1.29	−1.26

TABLE IV

Iodine Values of Fresh and Heated Cottonseed Cooking Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
9	112.1	112.2	+0.1	112.0	111.3	−0.7	−0.30
19	111.6	109.7	−1.9	109.6	109.2	−0.4	−1.15
46	107.0	107.4	+0.4	106.1	105.9	−0.2	+0.10
58	114.5	112.4	−2.1	114.1	112.5	−1.6	−1.85
62	111.2	109.2	−2.0	112.0	109.6	−2.4	−2.20
70	107.2	105.2	−2.0	106.8	105.0	−1.8	−1.90
75	115.2	112.7	−2.5	114.4	111.9	−2.5	−2.50
77	108.4	104.1	−4.3	107.5	105.2	−2.3	−3.30
86	105.5	104.1	−1.4	105.5[a]	103.8	−1.7	−1.55
Average	110.30	108.56	−1.74	109.78	108.27	−1.51	−1.63

[a] Sample bottle broken in transit; value listed is that obtained by Laboratory A.

TABLE V

Iodine Values of Fresh and Heated Winterized Cottonseed Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
4	111.5	115.0	+3.5	111.0	114.1	+3.1	+3.30
5	111.7	112.0	+0.3	111.4	111.9	+0.5	+0.40
10	114.3	112.0	−2.3	113.6	113.0	−0.6	−1.45
22	112.6	111.1	−1.5	111.2	109.3	−1.9	−1.70
23	115.2	113.1	−2.1	114.1	111.8	−2.3	−2.20
26	112.8	111.8	−1.0	111.3	110.5	−0.8	−0.90
27	115.8	114.0	−1.8	113.5	113.1	−0.4	−1.10
32	114.2	114.2	0.0	113.6	113.1	−0.5	−0.25
37	116.2	115.3	−0.9	115.9	115.2	−0.7	−0.80
39	109.0	107.7	−1.3	107.8	107.6	−0.2	−0.75
43	112.9	112.9	0.0	111.8	110.8	−1.0	−0.50
47	111.9	109.2	−2.7	111.7	110.5	−1.2	−1.95
50	111.3	110.5	−0.8	110.3	109.7	−0.6	−0.70
61	112.1	112.1	0.0	112.7	112.4	−0.3	−0.15
68	113.1	110.3	−2.8	113.2	111.1	−2.1	−2.45
76	109.8	109.2	−0.6	108.9	108.0	−0.9	−0.75
79	112.5	112.3	−0.2	113.2	111.5	−1.7	−0.95
89	114.4	112.8	−1.6	113.6	112.0	−1.6	−1.60
Average	112.85	111.97	−0.88	112.16	111.42	−0.74	−0.81

TABLE VI

Iodine Values of Fresh and Heated Lightly Hydrogenated Cottonseed Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
6	93.2	91.9	−1.3	92.0	90.2	−1.8	−1.55
18	91.0	89.6	−1.4	90.4	88.5	−1.9	−1.65
28	85.7	85.4	−0.3	85.4	84.7	−0.7	−0.50
40	95.4	94.3	−1.1	94.0	93.9	−0.1	−0.60
59	78.5	78.2	−0.3	78.8	77.8	−1.0	−0.65
64	91.6	91.7	+0.1	91.0	90.4	−0.6	−0.25
69	82.3	77.2	−5.1	81.0	77.1	−3.9	−4.50
71	93.1	90.0	−3.1	93.1	91.2	−1.9	−2.50
72	88.8	88.3	−0.5	87.7	88.8	+1.1	+0.30
87	77.0	77.9	+0.9	76.2	77.0	+0.8	+0.85
Average	87.66	86.45	−1.21	86.96	85.96	−1.00	−1.11

TABLE VII
Iodine Values of Fresh and Heated Shortenings Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
2	70.6	69.0	−1.6	70.2	69.4	−0.8	−1.20
8	61.6	61.9	+0.3	61.3	62.3	+1.0	+0.65
13	65.8	65.9	+0.1	65.8	65.4	−0.4	−0.15
15	66.6	65.5	−1.1	65.8	65.8	0.0	−0.55
20	66.6	65.3	−1.1	64.4	64.8	+0.4	+0.55
21	64.5	63.6	−0.9	63.2	63.0	−0.2	−0.55
29	65.4	65.1	−0.3	64.9	64.3	−0.6	−0.45
30	66.4	65.6	−0.8	65.4	65.0	−0.4	−0.60
31	69.1	67.8	−1.3	68.6	67.9	−0.7	−1.00
35	68.6	66.8	−1.8	68.0	66.7	−1.3	−1.55
38	70.0	69.4	−0.6	70.5	69.4	−1.1	−0.85
42	70.4	70.6	+0.2	69.5	69.7	+0.2	+0.20
52	67.5	66.2	−1.3	67.0	66.7	−0.3	−0.80
53	72.5	71.6	−0.9	71.8	70.9	−0.9	−0.90
55	72.5	71.7	−0.8	73.1	72.0	−1.1	−0.95
56	69.5	70.1	+0.6	69.4	69.6	+0.2	+0.40
63	67.1[a]	67.3	+0.2	67.1	67.2	+0.1	+0.15
65	64.4	65.0	+0.6	64.5	65.2	+0.7	+0.65
66	55.9	56.1	+0.2	55.8	55.5	−0.3	−0.05
73	66.0	66.7	+0.7	66.5	66.5	0.0	+0.35
74	69.1	67.8	−1.3	69.1	67.3	−1.8	−1.55
78	65.1	64.2	−0.9	64.5	63.7	−0.9	−0.90
80	69.4	69.3	−0.1	69.1	68.8	−0.3	−0.20
83	73.1	70.6	−2.5	73.3	72.0	−1.3	−1.90
84	68.7	68.7	0.0	68.4	68.4	0.0	0.00
88	69.5	68.5	−1.0	69.5	68.3	−1.2	−1.10
90	61.8	60.1	−1.7	61.3	59.5	−1.8	−1.75
Average	67.25	66.68	−0.57	66.96	66.49	−0.47	−0.52

[a] Sample bottle broken in transit; value listed is that obtained by Laboratory B.

value obtained by both laboratories in testing the blends sent in by come Chippers are extraordinary, increases of 11 and 14 in iodine value and a drop in one case of 8.5. Additional tests have shown that these large differences are caused entirely by errors in sampling the blends. Such blends tend to fractionate on cooling to yield liquid oil as well as high-melting components, and this complicates sampling to obtain representative aliquots.

Significance of the Change in Iodine Values of the Frying Oils. A summary of the changes in iodine values of the oils, analyzed in this survey of the potato chip industry, is presented in Table IX. Not only is there shown the average change in the value for each type of oil as reported by each laboratory, but there is also listed the statistical significance of this change; for this purpose Student's t-test for paired differences (19, 20) was used. When $p = 0.05$, it is concluded that there are 95 chances out of 100 that the observed change is a real one. Statisticians hold that this probability must be satisfied or no significance can be assigned to the change noted. There is no question that the changes in iodine value obtained in analyzing the three types of unhydrogenated oils and the shortenings are all highly significant from the statistical standpoint. The fact that the lightly hydrogenated cottonseed oils and the oil-and-shortening blends fail to exhibit statistical significance for the observed change in iodine values is attributed to inadequate sampling of these oils. The fact that these oils contain more linoleic acid that the shortenings supports this interpretation (21).

TABLE VIII
Iodine Values of Fresh and Heated Oil-and-Shortening Blends Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Laboratory A			Laboratory B			Average change
	Fresh	Heated	Change	Fresh	Heated	Change	
3	120.1	120.3	+0.2	120.6	120.2	−0.4	−0.10
11	66.0	76.7	+10.7	65.6	76.4	+10.8	+10.75
14	78.1	77.9	−0.2	78.3	78.4	+0.1	−0.05
16	116.0	107.4	−8.6	116.1	107.7	−8.4	−8.50
25	72.1	86.0	+13.9	71.3	85.7	+14.4	+14.15
33	95.5	95.4	−0.1	90.1	94.9	+4.8	+2.35
34	76.9	79.9	+3.0	76.7	78.8	+2.1	+2.55
36	92.6	96.1	+3.5	91.7	94.4	+2.7	+3.10
48	83.7	84.6	+0.9	82.7	84.2	+1.5	+1.20
49	117.0	117.7	+0.7	117.8	116.3	−1.5	−0.40
51	88.5	87.0	−1.5	88.2	87.0	−1.2	−1.35
54	87.8	89.5	+1.7	89.0	88.7	−0.3	+0.70
57	86.5	86.1	−0.4	87.0	85.4	−1.6	−1.00
60	119.0	120.0	+1.0	118.9	121.8	+2.9	+1.95
67	94.2	94.0	−0.2	95.9	93.9	−2.0	−1.10
82	.....	.....	.....	72.2	67.9	−4.3	.....
Average	92.93	94.57	+1.64	91.38	92.61	+1.23	+1.62

TABLE IX
Summary of Changes in Iodine Values of Fats Employed in Commercial Manufacture of Potato Chips

No. of chippers	Type of fat	Iodine value observations	Laboratory		
			A	B	Avg.
9	Corn oil	Change on use	−1.22	−1.29	−1.26
		Significance[a]	p=0.10	p=0.001	p=0.01
9	Cottonseed cooking oil	Change on use	−1.74	−1.51	−1.63
		Significance	p=0.01	p=0.001	p=0.01
18	Winterized cottonseed oil	Change on use	−0.88	−0.74	−0.81
		Significance	p=0.02	p=0.02	p=0.02
36	Above unhydrogenated oils	Change on use	−1.18	−1.07	−1.12
		Significance	p=0.01	p=0.001	p=0.001
10	Lightly hydrogenated cottonseed oil	Change on use	−1.21	−1.00	−1.11
		Significance	p=0.05	p=0.10	p=0.10
27	Shortenings	Change on use	−0.57	−0.47	−0.52
		Significance	p=0.01	p=0.01	p=0.001
16	Oil-and-shortening blends	Change on use	+1.64	+1.23	+1.62
		Significance	None	None	None

[a] For the observed change to be a real one and not due to chance, the value for "p" must be 0.05 or less.

The conclusion therefore is justified that there is about a 1% decrease in the iodine value of oils in frying potato chips on a continuing commercial basis and that this change is statistically significant. However this should not be confused with nutritional significance. As mentioned earlier, none of the oils employed in this study contained linolenic acid so there is no possibility of the toxic, cyclized monomeric acids, discussed by Crampton (7, 14), having been formed. The dimers and higher polymers, capable of being formed from the linoleic acid present in these frying oils, can interfere only with the digestibility of the oil (7, 14) if present in sufficiently high concentrations.

In Figure 1 are data plotted by Lassen and associates (22), showing the decrease in the digestibility of a highly unsaturated oil as the degree of polymerization increases; polymerization has been plotted as the percentage of drop in the iodine value. It will

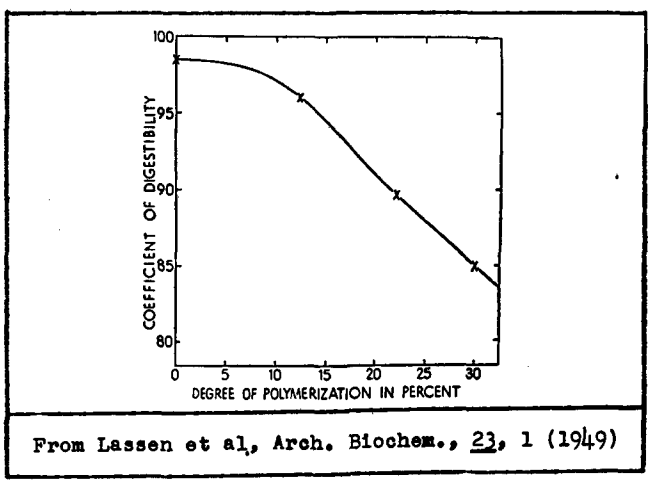

FIG. 1. Decrease in digestibility of a highly unsaturated oil as the degree of polymerization increases, the latter plotted as the percentage of drop in iodine value.

be noted that an iodine value drop of about 5% is required before there is a measurable decrease in the Coefficient of Digestibility of the oil. Hence it must be concluded that any change in digestibility attributable to the iodine value drop of about 1% found in the present study is beyond the realm of measurement and therefore is of no nutritional significance. This conclusion presupposes that the very small drop in iodine value, noted in the present survey of frying oils in commercial use, may have actually been due to polymer formation. Such however is not the case; in an extension of the present studies (21) the constancy in composition of the frying oils—heated as compared to fresh—and the results of physico-chemical studies have confirmed the absence of thermal polymers in the commercial oils.

The findings presented in this report cover only operations in the potato chip industry. Studies similar to this one should be conducted on oils employed in other frying operations, especially when limpid unhydrogenated oils are used. The frying of potato chips, insofar as heat abuse of the frying oil is concerned, is a relatively mild treatment. There is such a rapid turnover in oil, *i.e.*, constant replenishment with fresh oil to compensate for the oil absorbed by the potato chips, that undesirable by-products do not accumulate in the frying oils (21). The free fatty acid value seldom exceeds 0.5% and there is very seldom, if ever, the need to discard the frying oil. It is also worth remembering that the rapid and almost complete volatilization of the water from potato chips during frying is, in essence, continuous steam-deodorization and refining of the frying oil throughout its use.

Summary

The problem of thermal polymers of acceptable flavor in potato-chip-frying oils has been discussed from the standpoint of potentiality of such polymers forming during commercial frying operations. Publications on heat-abused oils have been critically reviewed, and many of these have been shown to yield findings irrelevant to practical operations. Conclusions based upon such studies should not be extended beyond the scope of the findings reported. The change in iodine value has been shown to constitute a simple and highly precise method to determine for survey purposes whether thermal polymers may have formed in the oils used in a given industry. Such a survey has now been completed covering the operations of 89 different potato chip manufacturers, using all types of frying oils. A 1% decrease in the iodine value of the oils in commercial use has been noted. Whereas this change in iodine value is statistically significant, it is shown to have no nutritional significance. The constancy in composition of the frying oils—heated as compared to fresh—and the results of physico-chemical studies, noted in a related study (21), support the present conclusion that thermal polymers are absent from the oils employed in the commercial manufacture of potato chips.

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Paper Chromatographic Separation of Aliphatic Lactones[1]

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GAMMA AND DELTA LACTONES, particularly those aliphatic lactones containing 8 to 12 carbon atoms, have strong persistent odors most often described as reminiscent either of peach or coconut. Gamma hendecalactone (so-called aldehyde C_{14}) is a common constituent of synthetic peach essence, and gamma nonalactone (aldehyde C_{18}) is often added to synthetic coconut flavor preparations. In addition to these two lactones, other lactones of both the gamma and delta series have been suggested for use in a variety of synthetic fruit, berry, and nut flavors. A recent patent application (1) covering both the synthesis and use of certain lactones in synthetic butter flavor indicates that these flavor compounds might eventually find wide use in margarine and shortenings.

Lactones have been implicated in the flavor deterioration of dry whole milk (6), and delta decalactone (the lactone of 5-hydroxy decanoic acid) subsequently was found to be present in butteroil (anhydrous milk fat), dry whole milk, dry cream, and evaporated milk

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