Peanut. Twelve chemists participated, and first place was won by T. C. Law, Law and Company, Atlanta, Ga., with 100; second place by Steven Prevost, Law and Company, Wilmington, N. C.; and honorable mention by P. C. Whittier, Law and Company, Montgomery, Ala., with 99.20.

Tallow and Grease. Of the 90 collaborators, first place went to E. R. Dube, Swift and Company, Jersey City, N. J., with 99.77; second place to R. L. Goode, Colgate-Palmolive Company, Jeffersonville, Ind., with 99.73; and honorable mention to Harold Beard, Armour and Company, Spokane, Wash., with 99.50.

Vegetable Oils. With 96 collaborators, first place went to F. M. Tindall, HumKo Company, Memphis, Tenn., with 99.3; second place to T. S. McDonald, Procter and Gamble, Dallas, Tex., with 98.7; honorable mention to W. F. Beedle, George W. Gooch Laboratory, Los Angeles, and to J. J. Ganucheau, Wesson Oil and Snowdrift Company Inc., Gretna, La., with grades of 98.3.

Edible Fats. Out of 56 collaborators in the edible fats series, first place was given to F. A. Adams, Procter and Gamble, Long Beach, Calif., with 99.03; second to R. A. Marmor, Pillsbury Mills Inc., Minneapolis, with 98.03; and honorable mention to William Stewart, Swift and Company, Atlanta, with 96.78.

Glycerine. First place among 23 collaborators was given to J. H. Dietz, Harshaw Chemical Company, Gloucester City, N. J., with a point score of 305; second to R. O. Fosmire, Procter and Gamble, Kansas City, Kans., with 291.5 points; and honorable mention to C. P. Morrison, Procter and Gamble, Staten Island, with 267.

Drying Oils. Seventeen chemists participated; first place went to K. E. Holt, Archer-Daniels-Midland Company, Minneapolis, with a grade of 96.00; second to J. E. Schlupp, National Lead Company, Philadelphia, with 93.75.

Meal. This, the largest and the original Smalley series, had 134 chemists participating. On the determination of moisture two were tied for first place: Mr. Whittier, Law and Company; and J. K. Sikes, Plains Cooperative Oil Mill, Lubbock, Tex., with a score of 100 each.

On the determination of oil first place was attained by Biffle Owen, Planters Manufacturing Company, Clarksdale, Miss., with 99.60. Two were tied for second place with grades of 99.40. A recalculation, using no tolerance, broke the tie, and the second place certificate was given to M. P. Etheredge, state chemist, Mississippi State College, State College; Honorable mention was given to A. G. Thompson Jr., Wesson Oil and Snowdrift Company Inc., Columbia, S. C.

On the determination of nitrogen first place was given to George Dickinson, Texas Testing Laboratory, El Paso, Tex., with 100; second to Mr. Hutton, with 99.60.

Smalley Cup. The winner this year is Mr. Thompson, with a grade of 99.40. This is the third time Mr. Thompson has won the cup: 1939-40, 1948-49, and 1957-58. He thus acquires permanent possession of the cup, which was donated to the Society several years ago by Mr. Cretien. Second place was given to Mr. Hutton, with a grade of 99.32; honorable mention to Mr. Hahn with a grade of 99.24.

R. T. DOUGHTIE JR. D. L. HENRY
LLOYD ANDERSON R. J. HOULE
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Composition and Control of Potato Chip Frying Oils in Continuing Commercial Use[1]

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A RECENT PAPER (1) included a critical review of the literature on the safety of frying oils. The change in iodine value was proposed as a simple method for determining whether thermal polymers may have formed in the heated oils used in a given industry. Results of such a survey were reported (1) for oils used in the potato chip industry. There was an average decrease of 1% in the iodine value of the oils in commercial use. Based upon the reports by Crampton and associates (2, 3), it was concluded that absence of linolenic acid in frying oils precluded the presence of toxic cyclized monomeric acids (1). Cyclized monomers from linoleate are produced with great difficulty (4), requiring temperatures of 554°F. and above (more than 100°F. above the smoke point of frying oils). Under such drastic conditions, disproportionation or even rupture of carbon to carbon bonds may occur (4).

Thus the only polymers which could be formed in the frying oils were of the nonabsorbable type and at most could only interfere with the digestibility of the oil. It was also noted that a drop of about 5% in iodine value (5, 6) is required before there is a measurable decrease in the Coefficient of Digestibility. Growth, reproduction, lactation, and longevity are not impaired when cottonseed oil is heat-polymerized to effect a drop of 5% in iodine value (6). Hence it was concluded that any change in digestibility attributable to an iodine value drop of about 1% found in the survey (1) is insignificant. This conclusion is conservative since it presupposes that the very small drop noted in the survey of frying oils in commercial use may have actually been due to polymer formation. Such is not the case, as will be demonstrated by the data presented in this report.

Polymerized Oils Prepared in the Laboratory

In order to delineate the question of polymer development in frying oils the data shown in Table I are presented. Cottonseed oil was heated at 600°F. with carbon dioxide bubbling through the oil until there was a drop of about 5 in iodine value. Crampton and associates (2, 3) employed comparable conditions in producing oils containing thermal polymers of the nonoxidative type. The same oil was also air blown at the same temperature to effect a comparable drop. The following method was employed to obtain the polymerization changes.

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[1] Much of the material in this paper and in one recently published (1) was presented at the 48th Annual Meeting of the American Oil Chemists' Society in the Symposium on "Fats in Nutrition and Health," New Orleans, La., April 30, 1957.

TABLE I
Composition and Evaluation of Oils Heat-Abused in the Laboratory

Test	Control CS salad oil (A)	CO_2 blown at 600°F. for 16 hours (B)	Air blown at 600°F. for 1.5 hours (C)
Iodine value (Wijs)	114.0	109.4	107.7
Drop in iodine value	—	4.6	6.3
Refractive index at 40°C	1.4645	1.4661	1.4671
Viscosity, cp. at 40°C	29.5	42.7	45.4
Free tocopherol, %	0.040	0.003	0.008
Peroxide value, m.e./kg	0.4	2.7	3.9
Free fatty acids, %	0.05	0.80	0.60
Conjugated dienoic acids, %	0.00	2.76	0.00
Conjugated trienoic acids, %	0.03	0.00	0.07
Linoleic acid, %	52.3	44.1	47.6
Oleic acid, %	21.5	27.8	23.9
Saturated acids, %	21.8	20.9	24.1
Flavor (100%)	good	fairly good	very poor
Flavor 10% in (A)	—	good	very poor
Flavor 1% in (A)	—	good	poor

The 150 g. of deodorized, winterized cottonseed oil were placed in a stainless steel cylindrical chamber measuring approximately 150 mm. in length and 50 mm. in diameter. The chamber was equipped with a gas inlet tube and a gas exit tube. This assembly was placed in a muffle furnace maintained at 610°F., the tubes of which projected through openings in the muffle furnace. After the dried gas was passed through the oil for the period of time required, the assembly was removed from the muffle furnace. The inlet and exit tubes were replaced with stainless steel plugs and the oil in the vessel, under a head of dry carbon dioxide or dry air, was cooled by directing a blast of air at the exterior of the vessel. The cooling period was from 2 to 3 hrs.

Standard test methods (7) were employed for the analyses of the control and heat-abused oils. In the spectrophotometric analyses for fatty acid composition a solution of 11% potassium hydroxide in glycerine was employed as the isomerization medium. The isomerization under air extended over a period of 45 min. (8). Viscosity was determined by using the falling ball method in a Hoeppler Viscosimeter. Tocopherol analyses were conducted according to the Rawlings (9, 10) modification of the Emmerie-Engel (11) colorimetric method. This experiment was conducted on nine different occasions. A period of time ranging from 16 to 20 hrs. was required to obtain a drop in iodine value of about 5 when the heating of the oil was conducted in the presence of carbon dioxide while a period of only one-tenth as long was required when air was bubbled through the heated oil.

The data in Table I present the results of one typical experiment. In both polymerized oils there are increases in viscosity; the concentration of free tocopherol (the effective antioxidant) is reduced to practically zero during the heating operations; residual peroxide values are low and small increases in the free fatty acid concentration are obtained. The flavor picture of these oils is worthy of emphasis. The oil thermally polymerized under carbon dioxide is fairly good in flavor and, when diluted with fresh oil, scores good in flavor. On the other hand, the air-blown is repulsive in flavor, and its objectionable characteristics are detected even when diluted to 1% concentration with fresh control oil. In other words, oils containing thermal polymers of the nonoxidative type lack the safeguard of unacceptable flavor to cause a consumer to reject such oils. Whereas the oxidative polymers *per se* are also free of objectionable flavor (note in Table II the good flavor of freshly steam-deodorized, thermally oxidized oil), oils containing such polymers are definitely unpalatable.

Only in the thermally polymerized oil are there found conjugated dienoic acids. Conjugation is known to be a precursor of polymer formation (12). The absence of conjugated dienoic acids in the thermally oxidized oil is attributed to their disappearance because of ease of oxidation (13). In both oils there is a measurable decrease in linoleic acid content of the order of about 10 to 15% of the initial concentration. Part of this decrease may be caused by the development of linoleic isomers with *trans* configuration or isomers with double bonds so far apart that they cannot be brought into conjugated position by alkali isomerization. Only in the thermally oxidized oil was there a suggestion that conjugated trienoic acids were present.

In Table II are the results of a study of flavor stability of and peroxide development in the oils heat-abused in the laboratory. The rapid increase in peroxide value for the heated oils before and after subsequent deodorization in the laboratory was expected because of the absence of protective tocopherols in these oils. However when these same oils are diluted to 10% concentration with the fresh oil to make up for the deficiency in free tocopherols, there is still a more rapid development of peroxides. Apparently the heat abuse has contributed catalysts for further peroxide development which counteract in large part the effect of tocopherol in these test oil

TABLE II
Flavor Stability of and Peroxide Development in Oils Heat-Abused in the Laboratory

Test sample under air at room temperature[a]		Control CS salad oil (A)	CO_2 blown at 600°F. for 16 hours (B)	Air blown at 600°F. for 1.5 hours (C)	90% of (A) + 10% of (B)	90% of (A) + 10% of (C)
Hours	Test	Oils following heat-abuse in laboratory				
	Flavor[b]	G	FG	VP	G	VP
0	Peroxide, m.e./kg.	0.4	2.7	3.9	0.8	1.2
	Flavor	G	F	VP	FG	VP
48	Peroxide, m.e./kg.	1.4	9.8	19.0	6.0	8.4
	Flavor	G	F	VP	FG	VP
96	Peroxide, m.e./kg.	3.9	18.5	36.5	17.1	16.8
	Flavor	G	F	VP	FG	VP
192	Peroxide, m.e./kg.	7.2	27.5	41.0	24.5	24.3
		Above oils deodorized[c] in laboratory				
	Flavor	G	G	G	G	G
0	Peroxide, m.e./kg.	0.0	0.0	0.0	0.0	0.0
	Flavor	G	FG	P	G	G
48	Peroxide, m.e./kg.	1.0	3.7	3.8	2.1	2.8
	Flavor	G	FG	VP	G	G
96	Peroxide, m.e./kg.	1.4	6.4	6.8	3.1	4.2
	Flavor	G	F	VP	FG	FG
192	Peroxide, m.e./kg.	6.2	16.4	19.3	7.5	14.6

[a] The samples were stored in the dark in half-filled, loosely capped jars.
[b] Code: G = good, FG = fairly good, F = fair, P = poor, and VP = very poor.
[c] Steam deodorized under vacuum in all-glass assembly.

TABLE III

Changes in Fatty Acid Composition of Typical Limpid Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Oil tested			Fatty acid composition, %						
	Type	State	Iodine value	Free	*Trans*	Conjugated		Linoleic	Oleic	Saturated
						Dienoic	Trienoic			
24	Corn	Fresh	124.8	0.03	2.3	0.00	0.06	54.7	28.4	12.4
		Heated	122.4	0.20	3.6	0.95	0.08	51.8	29.8	13.0
62	Cottonseed—cooking	Fresh	111.6	0.06	2.0	0.00	0.11	50.3	22.6	22.6
		Heated	109.4	0.18	2.5	0.85	0.11	47.3	24.5	22.8
23	Cottonseed—winterized	Fresh	114.7	0.04	2.4	0.00	0.00	52.3	22.2	21.1
		Heated	112.5	0.20	2.3	1.00	0.04	50.0	22.4	22.2

blends. The organoleptic evaluation of flavor quality of the test oils shows little correlation with peroxide concentration. In general, the thermally polymerized oil exhibits acceptable flavor under all conditions of test whereas the thermally oxidized oil is definitely unpalatable and, when held at room temperature, continues to deteriorate at an accelerated rate, even following deodorization prior to the holding test.

Results such as those described above have justified the conclusion that the problem of concern in frying oils (if one exists) is that related to the possible development of thermal polymers of the nonoxidative type. No commercial fryer could stay in business distributing products that contained absorbed oils with measurable amounts of thermal polymers of the oxidative type since such products would be rejected by the consumer because of unpalatability.

Changes in the Fatty Acid Composition of Frying Oils in Commercial Use

In the survey of the frying oils employed and furnished by the potato chip industry (1) both fresh and equilibrium oils were analyzed. The latter oils were those which had been in continuous use for a period of at least four days. In Table III are shown the changes in fatty acid content of typical limpid oils selected at random and employed in the commercial manufacture of potato chips. Small increases in the free fatty acid value are noted in the heated oils. There are no significant increases in the concentration of *trans*-fatty acids according to infrared absorption (14). The small decreases in linoleic acid content of the heated oils based upon the results of ultraviolet spectrophotometry (7, 8) reflect the small decreases in iodine value. Of major interest is the finding that there are small but definite increases in the conjugated dienoic acid content without increase in conjugated trienoic acid content. There is nothing objectionable in the conjugated dienoic acids from the nutritional standpoint, as is shown in studies conducted in Deuel's laboratory (13). Such acids are not anti-metabolites for linoleic acid but are readily and completely metabolized to carbon dioxide and water.

However the presence of these dienoic acids, without conjugated trienoic acid development, is very good proof that we are not concerned here with thermal oxidative polymers since, under the conditions leading to the formation of the latter, no conjugated dienoic acids survive (Table I). In the oxidation of vegetable oils containing linoleic acid (and no linolenic acid), as the most labile of the unsaturated fatty acids, formation of triene conjugation in oxidized linoleate by enolization of the conjugated ketone precursor or after alkali isomerization might have been expected (4). No increase in conjugated trienes before or after alkali isomerization is found in the commercially heated oils.

The same analyses (Table IV) were conducted on typical hydrogenated fats employed in the commercial manufacture of potato chips. The free fatty acid contents are slightly greater in the heated oils, and again there are no significant increases in the *trans*-fatty acid content. The decreases in linoleic acid concentration are very small, and these parallel the small decreases in iodine value. Although the reliability of the ultraviolet spectrophotometric method for the determination of linoleic acid in hydrogenated fats may be questioned, the relative picture of linoleic acid content in comparing a fresh with a heated fat of almost identical *trans*-acid content is valid.

In these hydrogenated fats there are present some conjugated dienoic acids at the very start, particularly in the lightly hydrogenated cottonseed oils. These accumulate during the early stages of hydrogenation and then disappear as the hydrogenation continues (13). Here again, the finding of conjugated dienoic acids, without increased concentration of conjugated trienoic acids before and after alkali isomerization, in all the heated fats is evidence that one is not concerned with thermal oxidative polymers in the commercial frying oils.

In Table V are summarized values obtained in analyzing the same test fats according to other indices to determine whether measurable changes in the fatty acid composition of the fats occur during the frying operations. The constancy in values for

TABLE IV

Changes in Fatty Acid Composition of Typical Hydrogenated Fats Employed in the Commercial Manufacture of Potato Chips

Chipper No.	Fat tested			Fatty acid composition, %						
	Type	State	Iodine value	Free	*Trans*	Conjugated		Linoleic	Oleic	Saturated
						Dienoic	Trienoic			
28	Lightly hydrogenated cottonseed	Fresh	85.6	0.04	26.1	3.04	0.04	20.2	47.6	24.3
		Heated	85.1	0.33	27.4	3.12	0.06	19.4	49.5	23.5
72	Lightly hydrogenated cottonseed	Fresh	88.3	0.06	21.1	1.48	0.02	25.0	44.8	24.3
		Heated	88.6	0.15	19.5	1.44	0.03	25.1	44.9	24.1
74	Shortening	Fresh	69.1	0.03	37.1	0.57	0.02	7.8	60.0	27.2
		Heated	67.6	0.20	34.3	0.43	0.02	7.1	60.0	28.0
51	Oil-and-shortening blend	Fresh	88.4	0.03	22.1	0.38	0.00	26.3	44.7	24.2
		Heated	87.0	0.11	22.8	0.57	0.02	25.3	44.6	25.1

TABLE V

Changes in the Solids Content Index of Typical Fats Employed in the Commercial Manufacturing of Potato Chips

Chipper No.	Fat tested		Analytical constants			Solids Content Index at			
	Type	State	M.P., °F.	S.P., °C.	I No.	50°F.	70°F.	80°F.	92°F.
28	Lightly hydrogenated cottonseed oil	Fresh	87.1	14.8	85.6	17.3	7.8	4.3	0.0
		Heated	87.5	15.0	85.1	16.1	7.5	4.0	0.0
72	Lightly hydrogenated cottonseed oil	Fresh	86.0	13.9	88.3	14.3	6.5	3.7	0.1
		Heated	86.2	13.8	88.6	13.6	6.3	3.6	0.0
74	Shortening	Fresh	104.2	29.6	69.1	36.5	24.0	20.4	11.6
		Heated	104.5	29.4	67.6	34.9	23.5	20.1	11.7
51	Oil-and-shortening blend	Fresh	94.3	23.2	88.4	22.0	12.8	8.5	2.4
		Heated	94.5	23.5	87.0	21.0	13.2	8.9	2.7
						20°F.	50°F.	70°F.	80°F.
62	Cottonseed cooking oil	Fresh	51.0	—	111.6	3.3	0.0	0.0	0.0
		Heated	52.0	—	109.4	3.0	0.2	0.0	0.0

melting point, setting point, and iodine value of each fat in its fresh and heated state shows that no significant changes in composition have occurred as a result of the frying operations. For example, an increase in *trans*-fatty acid content would be expected to cause an increase in the melting point values since the iso-acids have much higher melting points than the natural isomers. The Solids Content Index (S.C.I.) of each of these fats obtained by the highly precise dilatometric procedure (15) shows no difference between fresh and heated product; the distribution of solids to liquid in each paired grouping over a wide range of temperature remains remarkably constant. Confirmation has thus been obtained of the nondevelopment of *trans*-fatty acids in the heated oils as previously shown by the unrelated infrared test procedure (Tables III and IV).

Physical Properties of the Frying Oils in Commerical Use

Flavor considerations and the retention of conjugated dienoic acids in the heated oils have eliminated from consideration thermal oxidative polymers but not the thermal nonoxidative polymers. A sensitive tool was then sought to measure with precision the formation even in trace quantities of the thermal polymers of the nonoxidative type. An adaptation of the dilatometric method proved to be highly satisfactory for this purpose.

When the control cottonseed salad oil is held at 32°F. for a sufficient period of time, some solid fat slowly crystallizes from solution (Table VI). When the same oil, thermally polymerized under carbon dioxide to effect an iodine value drop of about 5, is similarly stored in the cold, there is an immediate precipitation of a large amount of solid fat with a slow and progressive increase thereafter. When as little as 10% of the thermally polymerized oil is added to the fresh oil so that the over-all change in iodine value amounts to 0.5, there is an immediate deposition of solid fat in quantity greatly in excess of that expected from the 10% addition alone of the thermally polymerized oil. Apparently coprecipitation occurs in this system. Measurements of the Solids Content Index in this range of values are reproducible to within 0.2 S.C.I. units so that with this tool the signifiance of less than a 0.1 drop in iodine value can be evaluated.

TABLE VI

Dilatometric Studies of an Oil Heat-Abused in the Laboratory and Then Held in the Cold

Hours at 32°F.	*Solids Content Index at 32°F.*		
	Control CS salad oil (A)	CO_2 blown at 600°F. for 16 hours (B)	90% (A) + 10% (B)
16	0.0	11.6	3.9
20	0.9	11.8	4.0
24	1.2	12.0	4.3
28	2.1	12.5	4.4
32	2.3	13.0	4.6
40	3.0	13.5	4.8
48	3.7	14.4	4.9
60	3.9	14.4	5.1
72	4.7	14.4	5.2
96	5.5	14.4	5.8

Using this highly sensitive dilatometric approach, evidence was sought for the presence of thermal polymers in six of the more labile oils employed in the commercial manufacture of potato chips. These oils are characterized as more labile since they contain about 50% linoleic acid. They are listed in Table VII in a decreasing order of change in iodine value. One would expect at an earlier time an increase in the Solids Content Index of the heated oils if thermal polymers were present. Such does not occur. Indeed the reverse is generally noted. In every paired grouping of oils held at 32°F. there is found with the heated oil a delay or no change in the precipitation of solid fat.

This then is evidence that the small decrease in iodine value of about 1% noted in the survey of potato chip frying oils (1) is not caused by the presence of thermal polymers. Undoubtedly, slight oxidation of linoleic acid occurs, and the volatile degradation products escape through the stack; this is believed to be responsible for the slight lowering of iodine value noted.

Further tests on these heated oils and on a number of control systems (Table VIII) have shown that the heated samples, with one exception, have lower interfacial tension values. Measurements were made by using a Cenco-du Nouy Interfacial Tensiometer (16). Readings taken with oil layered over water were off the scale, making it necessary to use a solvent (carbon tetrachloride) immiscible with water. A 10-minute contact time between layers was found to be optimum since longer periods of 30 to 60 min. caused film development and haze in the solvent layer and erratic readings. In the case of the oils supplied by Chipper No. 32, there was no difference between heated and fresh oil in either crystallizing properties (Table VII) or in the interfacial tension values (Table VIII). The data obtained with these frying oils point to the presence of emulsifiers developed during the frying operations which delay crystallization of solid components in the heated oils.

TABLE VII
Dilatometric Studies on Winterized Cottonseed Oils Employed in the Commercial Manufacture of Potato Chips

Chipper No.	State of the oil	Iodine value	Oils held at 32°F. for period of					
			16 hours	20 hours	28 hours	40 hours	60 hours	96 hours
			Solids Content Index at 32°F.					
68	Fresh	113.2	0.0	0.0	0.6	4.8	5.7	6.9
	Heated	110.7	0.0	0.0	0.0	2.5	5.1	5.7
22	Fresh	111.9	3.2	3.8	4.5	6.5	7.1	7.5
	Heated	110.2	1.8	2.5	4.0	6.5	7.2	7.7
10	Fresh	114.0	0.5	2.7	4.2	5.9	6.9	7.1
	Heated	112.5	0.0	0.6	1.5	3.3	6.6	6.8
27	Fresh	114.7	0.0	0.0	0.0	0.0	2.5	2.8
	Heated	113.6	0.0	0.0	0.0	0.0	1.5	3.2
26	Fresh	112.1	0.0	0.0	0.1	0.9	4.5	4.9
	Heated	111.2	0.0	0.0	0.0	0.5	4.0	4.6
32	Fresh	113.9	0.0	0.0	0.0	0.3	1.8	3.5
	Heated	113.6	0.0	0.0	0.0	0.3	2.3	3.4

Discussion

The findings presented in this paper and in the earlier report (1) cover only operations in the potato chip industry. Studies similar to these 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 oils is concerned, is a relatively mild treatment. Temperatures of frying oils in the potato industry are not significantly different from those in other frying operations; these temperatures vary from about 350° to about 385°F. Oil temperature is at the lower range in the fryer where the raw chips are being added and at the higher range where chips are being discharged. All fryings are conducted continuously under a blanket of an inert gas: the steam generated by the potatoes being fried. In conventional potato chip frying operations there is volatilized as steam one pound of water per three pounds of heated oil per hour. There is also 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. Finally 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. The ratio of water volatilized to oil heated in this frying operation is much greater than that employed in the steam-deodorization process in making vegetable oils palatable for human consumption.

The change in Wijs iodine value has been recommended (1) as a simple and highly precise method for determining whether thermal polymers may have formed in frying oils. 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 means that no polymerization changes could have occurred. These other reactions include a) a very high peroxide value, b) development of conjugation in the double-bond positions, and c) oxidation of linoleic acid during the fryings and volatilization of the degradation products up the stack. On the other hand, carbonyl compounds in exceedingly high concentrations may raise the iodine value but even then only after correction is made for the dilution of the substrate frying oil with the added carbonyl.

As would be expected from the high ratio of water volatilized from the oil, the latter at a temperature of 350° to 385°F., there is no significant increase in the concentrations of peroxides or of carbonyl compounds in potato chip frying oils. Calculations indicate that it would require a peroxide value of about 80 m.e. per kg. of oil before there would be a decrease of 1.0 in iodine value. Actually the peroxide values of the heated oils in our study were only 1.04 m.e. per kg. greater than those of the fresh oils. Only 11 of the 89 samples showed an increase in excess of 5 m.e., and none were in excess of 10 m.e. per kg. of oil.

The increase in carbonyls according to the dinitrophenyl hydrazine procedure (17) amounted to only 4 micromoles per gram of oil expressed as hexaldehyde. Redistilled hexaldehyde gives an apparent iodine value

TABLE VIII
Interfacial Tension Measurements [a] Conducted on Cottonseed Salad Oils Employed in the Commercial Manufacture of Potato Chips and on Reference Control Systems

Chipper No.	State of the oil	Change in iodine value	Interfacial tension	Control systems		Change in iodine value	Interfacial tension
				Code	Identity		
			dynes/cm.				*dynes/cm.*
68	Fresh	......	31.7	(A)	Fresh winterized cottonseed salad oil, 114.3 I#	......	34.6
	Heated	—2.5	23.3				
22	Fresh	......	31.2	(B)	A above, CO_2 blown at 600°F. for 16 hours	—5.3	32.3
	Heated	—1.7	25.1				
10	Fresh	......	33.2	(C)	90% A + 10% B	—0.5	34.4
	Heated	—1.5	24.5				
27	Fresh	......	31.4	(D)	99%A + 1% (MG + DG) [b]	—0.1	26.9
	Heated	—1.1	27.0	(E)	97.5% A + 2.5% (MG + DG)	—0.2	19.0
26	Fresh	......	28.7	(F)	99.5% A + 0.5% Lecithin [c]	—0.1	27.4
	Heated	—0.9	22.3				
32	Fresh	......	25.1	(G)	99.5% A + 0.5% Span 60 [d]	—0.6	8.6
	Heated	—0.3	25.5				

[a] Readings made at 27°C. at the interface of distilled water over a 10% solution of the oil in carbon tetrachloride after 10 min. of contact time.
[b] Mixed mono- and diglycerides of corn oil; the monoglyceride was present in 40% concentration and the diglyceride in 55% concentration.
[c] Commercial product containing about 50% phospholipids in soybean oil.
[d] Sorbitan monostearate.

TABLE IX
Summary of Changes in Free Fatty Acid Values of Fats Employed in the Commercial Manufacture of Potato Chips

No. of chippers	Type of fat	Free fatty acid values of the fat, %			
		Fresh	Heated	Change	Standard deviation
9	Corn oil	0.05	0.44	+0.39	±0.34
9	Cottonseed cooking oil	0.04	0.21	+0.17	±0.06
18	Winterized cottonseed oil	0.05	0.24	+0.19	±0.11
10	Lightly hydrogenated cottonseed oil	0.05	0.29	+0.24	±0.23
27	Shortening	0.06	0.24	+0.18	±0.18
16	Oil-and-shortening blend	0.05	0.29	+0.24	±0.15
89	All the above	0.05	0.27	+0.22	±0.17

by the Wijs Method of about 50 or about 0.005 for 100 micromoles. It was impossible to obtain a measurable increase in the iodine value of a cottonseed oil by the Wijs Method even after the addition of 20 micromoles of hexaldehyde per gram of the cottonseed oil. Of course, unsaturated aldehydes will give higher iodine values but, with unsaturation derived from the originating unsaturated fatty acid, this contributing factor to iodine value is not pertinent. Confirmation of the negligible concentrations of peroxide decomposition products in the heated oils was obtained in using the thiobarbituric acid test (18).

The free fatty acid value of the heated oils in the recently completed survey (1) average 0.27% (Table IX), an increase of only 0.22% over that of the fresh oils. The total free fatty acid content seldom exceeds 0.5%, and there is seldom, if ever, the need to discard the frying oil. In the recently completed survey (1) only three oils out of 89 tested had a free fatty acid value in excess of 0.5%.

The data in Table IX have been subjected to statistical analysis in order to define precisely the oils which comprised the test samples in the survey completed. A free fatty acid value of 0.60% for the heated oils encompasses two standard deviations from the average value for these oils. This means that 95% of the potato chip manufacturers had been operating within this upper limit in producing the oils submitted.

In Table X is a statistical analysis of the changes in iodine value of the oils submitted. Only those types of frying oils which have shown a change in iodine value between the fresh and heated sample, which was of statistical significance, have been included in the calculations. Reasons have been presented (1) for the failure to observe a statistically significant difference in the change of iodine value for the other two types of frying oils not included in Table X. Again, the adding of two standard deviations to the average percentage change in iodine value establishes a 3.0% decrease in the iodine value as the limit within which 95% of the industry operated in providing the test samples for the survey completed.

The characterization of the heated oils within statistically defined limits is necessary to support the generalization made on the absence of thermal polymers in commercial potato chip frying oils. This generalization holds as long as operations continue to yield oils with free fatty acid and iodine values within the limits set forth above.

In other frying industries limits of a different order of magnitude may be acceptable, provided it can also be shown with the resulting oils that the wider limits do not jeopardize the nutritive value and safety of these heated frying oils. Rice and associates (20) have recently reported on the wholesomeness and nutritive value of frying oils in a number of different commercial operations. These investigators were also critical of the results of studies of highly unsaturated fats heated under unrealistic, arbitrarily selected laboratory conditions.

Summary

The oils in use on a continuing commercial basis in the production of potato chips on a nation-wide scale are found to be free of thermal polymers. This conclusion is supported by the similarity in physical properties and in chemical composition between the fresh and heated oil in any one operation. In a) degree of unsaturation of oils, b) melting point, c) setting point, d) fatty acid composition, e) free fatty acid content, f) concentration of fatty acid isomers, g) solids content index, and h) in the crystallizing properties of the oils, there are no differences between fresh and heated oil of such magnitude to warrant criticisms of the wholesomeness of the oil being absorbed by the chip.

The constancy in composition between heated and fresh oil, particularly with respect to the essential fatty acid content, which is largely responsible for the noncaloric functions of fats in the diet (19), permits the same conclusions to be made in regard to the nutritive value of the heated oils, *i.e.*, of the triglycerides contained therein, as have been drawn from studies conducted on the corresponding fresh oils.

Based upon statistical quality control considerations, the oils employed in the survey of the potato chip industry have been characterized by having a free fatty acid value of no greater than 0.60% and a decrease in iodine value of no greater than 3.0% in 95% of the operations. These control limits characterize the oils, which, on test, have led to the

TABLE X
Summary of Changes in Iodine Value of Fats Employed in the Commercial Manufacture of Potato Chips

No. of chippers	Type of fat	% Change in iodine value			Standard deviation of change		
		Lab. A	Lab. B	Average	Lab. A	Lab. B	Average
9	Corn oil	−0.97	−1.04	−1.01	±1.31	±0.56	±0.82
9	Cottonseed cooking oil	−1.58	−1.37	−1.48	±1.27	±0.79	±0.97
18	Winterized cottonseed oil	−0.77	−0.65	−0.71	±1.29	±1.07	±1.12
27	Shortening	−0.82	−0.69	−0.75	±1.27	±1.07	±1.10
63	All the above	−0.94	−0.83	−0.88	±1.28	±0.95	±1.05

generalization about the absence of thermal polymers in commercial potato chip frying oils.

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Alcoholic Extraction of Vegetable Oils. V. Pilot Plant Extraction of Cottonseed by Aqueous Ethanol[1]

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IT HAS BEEN POINTED OUT previously (10) by the authors that ethanol, because of its availability and low price relative to imported petroleum solvents, would be an attractive solvent for vegetable oils in Asiatic countries if it could be shown to have proper solvent properties. Data by the authors (8, 9, 10) and others (11, 12) have shown that ethanol is a good solvent at near boiling temperature for commonly used vegetable oils such as corn, cottonseed, peanut, sesame, and soybean.

The studies in this paper deal primarily with the pilot plant extraction of cottonseed meats by ethanol. Preliminary studies of the rate of extraction of cottonseed flakes of three different moisture contents by four concentrations of aqueous ethanol at three different temperatures over extraction periods from 10 to 100 minutes were made. The results of these studies were considered sufficiently favorable to justify pilot plant studies.

Extraction Rate Studies

Apparatus. The extraction rate apparatus (Figure 1) consisted of three major parts: a 3-liter round bottom flask serving as the solvent tank; a 16-in. straight tube condenser as a solvent preheater; and the extractor. The latter was a glass tube 1 in. in diameter, 6 in. in height, with a jacketed section through which water was circulated from a constant temperature bath. Water from the same supply was used to control accurately the temperature of the solvent.

Procedure. Prime cottonseeds were dehulled by passing the seed through a pair of corrugated rolls and separating the loosened hulls by screening. The resulting meats were adjusted to a moisture content of 10% and flaked on a set of laboratory flaking rolls.

A weighed sample of cottonseed flakes (about 15 g.), having a thickness of 0.013 in., was added to the extractor and heated to the desired temperature by circulating water from the heated water bath. At the same time heated solvent was allowed to flow into the extractor at a controlled rate. The starting time was taken as the first drop of miscella flowed from the extraction tube. The miscella was collected in 100-ml. graduated cylinders at the rate of 10 ml. per minute, transferred into tared flasks, and evaporated free of solvent on a water bath. At the end of the extraction experiment the remaining liquid was drained from the extractor, and the flake sample was transferred to a Soxhlet extractor where the residual

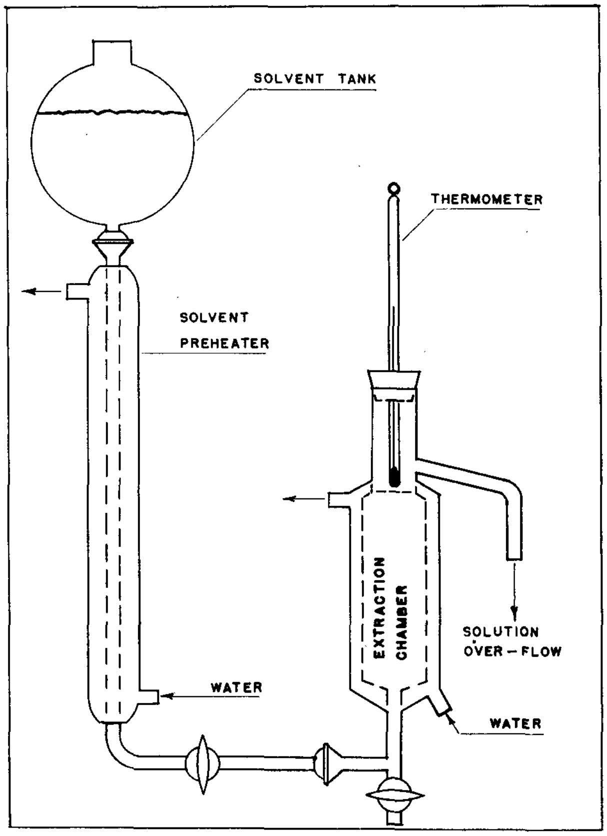

FIG. 1. Extraction rate apparatus.

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