

# Heated Fats. IV. Chemical Changes in Fats Subjected to Deep Fat Frying Processes: Cottonseed Oil

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## Abstract

The effects of deep fat frying processes on the formation of polymeric and oxidized materials were determined under practical conditions. Experiments which determined the effect of continuous heating, turnover rate, intermittent heating, steam, and deep frying were carried out. The amounts of polymeric material and other parameters of fat deterioration were determined. The results obtained indicated that the amount of polymeric material formed increased regularly as heating time increased. A high overall turnover of used oil may not increase the useful life of a frying fat when the specific daily turnover of fat is small. Intermittent heating of a fat alternated with cooling cycles increased the deterioration of cottonseed oil. The act of frying a food product (potatoes) or simple addition of water to hot fat exerts a strong deteriorative effect on heated cottonseed oil.

## Introduction

GREAT MASSES OF EVIDENCE have accumulated which indicate that the heating of edible fats and oils at high temperatures results in the formation of nutritionally harmful substances. This material has been recently reviewed (1-4). It is also apparent that much of the published data cannot be directly applied to the problem concerning the effect of heat on fats under practical conditions. Much of this work has been carried out on carefully controlled and laboratory treated samples. The conditions employed are usually more severe than those encountered in practice. Several publications (5-9) have appeared which represent attempts to report work of a more practical nature in an approach to the heated fat problem. Rice (10), Poling (11,12) and Keane (13) have reported that fats obtained from restaurants and those prepared during frying experiments are not significantly damaged by heating during normal use unless they are abused. When abused fats were fed to young weanling rats using a caloric energy restriction feeding technique developed by Rice et al. (14), harmful effects were observed. Poling (11) has reported the effects of various treatments upon the nutritional characteristics of edible fats using this method.

It has been generally accepted that growth depressing materials and other nutritionally harmful materials are present in the oxidized or polymeric portions of heated fats. The deterioration of an oil during frying has been followed by conventional means, usually by measurement of unsaturation and free fatty acid content. Little interest has been shown in the actual amounts of polymeric or polar materials produced in oils heated under practical deep frying conditions, as a true parameter of the deterioration of an oil.

The series of experiments reported in this paper represent part of our general program to determine the chemical changes which take place during deep

fat frying processes. The effects of several variables on the stability of cottonseed oil toward polymer formation and general breakdown were investigated. The nutritional value of the resulting heated fats was also determined and will be reported elsewhere.

## Methods

A representative oil, cottonseed oil, was used in the present study. The cottonseed oil employed was winterized and commercially available. (Armour Star salad oil; analysis by GLC indicated the following fatty acid composition (%): 14:0, 1.07; 16:0, 26.63; 16:1, 0.82; 18:0, 2.33; 18:1, 20.91; 18:2, 48.25.) All experiments were carried out using the same lot of sample.

A standard method of heating was used in all of the experiments to be described unless otherwise specified. Eleven liters of fat were heated with a minimum amount of stirring to maintain even heat distribution in a commercial type electrically heated, 15 lb, stainless steel deep fat fryer, with a surface area of 182 sq in. In order to prevent localized overheating, the oil temperature was raised to 175°C in a stepwise manner; this required about 30 min for final temperature equilibration. Samples of the oil were taken at various time intervals, blanketed with nitrogen gas and stored in the cold (-20°C) until required.

Determinations of the saponification number (15), iodine value (15), peroxide value (15), percentage of free fatty acids (15), percentage of hydroxyls (16), and carbonyl values (17) were carried out on all samples.

In order to determine the concentration of oxidized, polymerized materials in the samples of heated fat obtained during the experiments, three different methods were used. These methods were: *a*) distillation of the fatty acids of the hydrolyzed heated fat samples at reduced pressure (less than 0.5 mm Hg in order to separate unreacted, monomeric and higher polymeric materials); *b*) a batchwise countercurrent distribution process similar to that reported by Zilch, Dutton and Cowan (18) employing redistilled skellysolve F and ethanol (80%) for separating oxidized from non-oxidized products based on polarity differences; and *c*) determination of the percentage of non-urea adduct forming fatty acids in the heated fats according to the method of Johnson et al. (19). The urea complex method was used initially and then dropped in favor of the previously discussed methods.

## Experimental Results

### Experiment 1

The more highly unsaturated fats, cottonseed oil, for example, are widely used in deep fat frying. It is therefore of interest to investigate the effects of heating on the deterioration of cottonseed oil. A commercial deep fat fryer was employed as previously illustrated. Cottonseed oil was heated continuously for a total of 382 hours; potatoes fried in this oil at

TABLE I  
Effect of Continuous Heating on Cottonseed Oil

Hours heating	Iodine value	Free fatty acid (%)	Peroxide value (mEq/kg)	Saponification value	Hydroxyl (%)	Carbonyl value (mEq/kg)	Index of refraction n <sub>D</sub> <sup>20</sup>	Polymeric material	
								Hexane insoluble	NDFA <sup>a</sup>
0	112.8	0.03	11.2	195.0	0.09	182	1.4628	1.4	0.75
22	109.1	0.08	7.8	196.3	0.19	269	1.4635	4.1	6.7
70	103.7	0.16	5.1	198.2	0.22	317	1.4652	8.0	14.8
123	97.6	0.27	—	200.3	—	563	1.4674	13.3	19.5
166	91.9	0.38	3.1	201.0	0.43	239	1.4681	16.7	24.6
190	88.1	0.44	2.1	201.5	0.48	191	—	20.0	26.0
238	87.6	0.55	2.3	203.0	0.51	179	1.4701	22.3	33.9
262	84.9	0.60	1.7	204.4	0.50	195	1.4705	23.7 (35.4) <sup>b</sup>	32.8
334	82.2	0.93	2.1	205.3	0.65	213	1.4714	25.8	39.8
382	79.9	1.04	1.5	207.9	0.66	206	1.4727	30.0	45.6

<sup>a</sup> NDFA, Nondistillable fatty acids.  
<sup>b</sup> NUFA, Nonurea adduct forming fatty acids.

the termination of the experiment were acceptable when sampled fresh and hot; after cooling, however, they became soggy and were not acceptable. Samples of the oil were removed at intervals for analysis. The data obtained are shown in Table I. Iodine values decreased to about 80 during heating with the formation of a dark colored viscous oil. The free fatty acid content increased to about 1%. While the hydroxyl group content increased to 0.66%, the carbonyl value increased markedly indicating the formation of non-volatile carbonyl compounds. Increasing concentrations of polymeric material developed during heating; from an initial value of 1.4% to 30.0% as determined by the solvent partition method and from 0.75% to a maximum of 45.6% as determined by the distillation method. In one case, the percentage of nonurea adduct forming acids was determined. The value obtained (35.4%) was in agreement with that obtained by the distillation method.

**Experiment 2**

The rate of exchange of fresh oil with used oil or the turnover rate may be an important factor in determining the nutritional quality of a used oil. The following experiment was designed to determine the effect of a small turnover rate on the stability of cottonseed oil. Cottonseed oil was heated continuously for 334 hr as in experiment 1, but when samples were removed for analysis (250 cc) an identical amount of fresh oil was added to the fryer. The result was a small but constant turnover of fat (2.5% per day) and a large total turnover during the experimental period (45%). Marked effects on the stability of the oil were observed. The data obtained are shown in Table II. The iodine values of the oil at the termination of the experiment remained about equal to those obtained when the oil was continuously heated without the addition of fresh oil, as did the other constants which were determined. The percentage of hexane insoluble material was about the same as that obtained for continuously heated oil, but the amount of nondistillable acids obtained was quite different. Much less nondistillable material appeared to be formed when small amounts of fresh oil were added constantly to the oil during the heating period. The carbonyl

value of the replenished oil also increased tremendously and may be due to the formation of carbonyl compounds by decomposition of precursors during storage. While a high total turnover of fat may suggest that the original fat has been diluted and thereby protected from deterioration, such an assumption may be misleading since a high total turnover does not correctly express the length of time that some part of the fat has been heated. If the turnover rate of an oil per day is fairly small, the addition of fresh oil has little effect on the oil's stability.

**Experiment 3**

In many instances where deep fat frying is employed, the oil utilized is not heated continuously; the effect of intermittent heating on the stability of cottonseed oil was therefore investigated. Cottonseed oil was heated for a period of 7-8 hr during single time intervals; allowed to cool to room temperature and to remain thus for 12 to 16 hr. The heating cycle was then repeated and alternated with the cooling cycle. The oil was subjected to a total of 62 hr of actual heating; but the experiment was continued for a total of 223 hr to achieve this. Samples were taken at three intervals during each cycle: (a) when the sample had been heating for several hours prior to cooling, (b) after standing at room temperature for 12 to 16 hr, prior to reheating, and (c) one-half hour after reaching the final frying temperature. The data obtained are shown in Table III. When heated cottonseed oil is allowed to cool at room temperature, an expected buildup of fatty acyl peroxides takes place. When the oil is again heated, these peroxides decompose and cause increased damage to the oil as shown by the hydroxyl value and carbonyl value which increase during this period. Other constants showed predictable increases or decreases. When compared to an oil heated continuously, this oil, heated for only 62 hr (223 hr elapsed time) contained as much hexane insoluble or polar material as was present in cottonseed oil which had been heated continuously for 166 hours.

**Experiment 4**

In order to simulate the effect of frying a wet prod-

TABLE II  
Effect of Turnover Rate on Cottonseed Oil

Hours heating	Iodine value	Free fatty acid (%)	Peroxide value (mEq/kg)	Saponification value	Hydroxyl (%)	Carbonyl value (mEq/kg)	Index of refraction n <sub>D</sub> <sup>20</sup>	Polymeric material	
								Hexane insoluble	NDFA <sup>a</sup>
0	110.6	0.02	2.1	195.0	0.17	190	1.4629	5.4	1.3
25	104.6	0.14	2.6	197.0	0.40	561	1.4641	9.7	8.9
73	98.1	0.30	2.7	198.8	0.57	1185	1.4659	12.3	11.6
145	93.1	0.55	2.5	200.3	0.61	1324	1.4676	18.0	16.9
241	88.5	0.72	1.4	202.7	0.65	1251	1.4691	20.6	20.5
334	85.5	0.80	1.2	203.2	0.66	1427	1.4704	23.0	21.9

<sup>a</sup> NDFA, Nondistillable fatty acids.

TABLE III  
 Effect of Intermittent Heating on Cottonseed Oil

Hours heating	Iodine value	Free fatty acid (%)	Peroxide value (mEq/kg)	Saponification value	Hydroxyl (%)	Carbonyl value (mEq/kg)	Index of refraction $n_D^{50}$	Polymeric material	
								Hexane insoluble	NDFA <sup>d</sup>
0	110.5	0.01	2.4	195.2	.14	35.3	1.4630	2.4	1.4
30 E <sup>a</sup>	104.8	0.14	5.6	197.4	.27	135	1.4646	8.7	5.4
46	101.1	0.23	7.1	198.3	0.34	202	1.4658	11.7	9.3
54	100.1	0.25	4.8	199.2	.38	191	1.4662	13.1	11.9
54 M <sup>b</sup>	99.9	—	7.0	—	.41	241	1.4662	13.0	11.5
54 MH <sup>c</sup>	99.8	—	5.0	—	.38	267	1.4662	13.3	12.9
62	98.7	0.31	3.3	199.5	.39	297	1.4668	16.9	13.5
62 M	98.3	0.31	7.3	199.6	.41	307	1.4668	15.6	13.8

<sup>a</sup> E, sampled before heat off.

<sup>b</sup> M, sampled when cold before heating.

<sup>c</sup> MH, sampled when temp. of 175°C is reached.

<sup>d</sup> NDFA, Nondistillable fatty acids.

uct such as fresh potatoes without the added variable of the food product itself, water was discharged into the oil in the form of small droplets at an average rate of 28.8 cc per hour for 188 hr. A total of 54.14 liters of water was added to 9 liters of oil during the total heating period. The data obtained are shown in Table IV. The addition of water to the oil resulted in a decreased iodine value, increased the free fatty acid content by a factor of seven, doubled the hydroxyl content and increased the polymer content by almost 30% when compared to cottonseed oil heated continuously for the same amount of time. It is apparent that water (steam) exerts a considerable influence on the stability of a fat. The formation of free fatty acids indicates an increased degree of hydrolytic cleavage. The decrease in unsaturation and an increase in the percentage of hydroxylated compounds and polymeric material indicates that the presence of water (as such or from a food product) strongly accelerates the deterioration of a frying fat.

#### Experiment 5

In this experiment the effects of deep frying potatoes in continuously heated cottonseed oil was investigated. During a period of 100 hr, approximately 43 lb of cut potatoes were fried in 1 lb batches at regular intervals (1 batch/1 hour) during 8 hr time periods. Fresh unheated oil (approximately 200 cc) was added each day to replace that absorbed by the fried product. After frying had been carried out for approximately 30 hr, foaming of the oil when the potatoes were introduced became a serious problem, and the frying time was increased from 6 to 10 min in order to obtain a good quality product. The potatoes which were used were commercially prepared, precut, French fries. They were washed, and drained for 2 hr prior to frying and had been sodium sulfite treated (before being washed with water) for increased storage life. The data obtained are given in Table V.

A comparison of these data with that obtained from the heating of cottonseed oil alone for identical time periods indicated that the process of frying contributed substantially to the deterioration of an oil; a decrease in iodine value; and increase in free fatty acid values, hydroxyl value and polymeric materials was observed. The deteriorative effect of frying may result

from a combination of at least four effects: 1) the effect caused by the composition of the food product; 2) the extra agitation and subsequent increased incorporation of air into the hot fat resulting from the introduction of the food product; 3) the effect of that portion of water displaced from the food product into the hot oil as steam; and 4) the amount of oil absorbed by the food product would ultimately reflect itself in the useful life of an oil. It is difficult to separate the effects of water in such a system but it would seem that its presence would be one of the predominant factors involved in fat deterioration. When the data resulting from this experiment was compared with that obtained when water alone was added to heated cottonseed oil, it was evident that frying drained potatoes in cottonseed oil resulted in less overall damage to the oil. It is apparent that the larger amounts of water added to the heated oil in the previous experiment caused a considerable increase in both the rate and extent of deterioration of cottonseed oil.

It has been reported previously (20) that foaming becomes a serious problem during deep fat frying. During the course of this study it was observed that a fine dense foam formed in cottonseed oil used to fry potatoes when the oil contained about 8% of polymeric materials. The polymer content of cottonseed oil which had been heated in the presence of water was adjusted to 8% by the addition of fresh oil. Potatoes were fried in the resulting oil. No fine dense foam was formed. When the same procedure was applied to an oil which had been used to fry potatoes, the foam was produced. Some foam was observed when this method was applied to an oil which had been heated continuously. An increase in frying temperature from 175°C to 195°C had no effect on foam formation. These results indicate that the formation of foam during frying may be dependent upon the types of oxidized and polymeric products present in a heated oil.

#### Discussion

The effects of practical frying conditions upon the deterioration of an oil are many and varied. When cottonseed oil is heated (Table I), the iodine value decreases as expected; the free fatty acid content, saponification values, and hydroxyl values increase as

 TABLE IV  
 Effect of Water on Cottonseed Oil

Hours heating	Iodine value	Free fatty acid (%)	Peroxide value (mEq/kg)	Saponification value	Hydroxyl (%)	Index of refraction $n_D^{50}$	Polymeric material	
							Hexane insoluble	NDFA <sup>a</sup>
0	112.2	0.03	11.1	194.8	0.11	1.4627	2.1	2.3
44	104.0	0.19	4.2	197.7	0.35	1.4653	7.5	12.7
123	91.8	1.48	2.6	203.7	0.68	1.4686	18.7	28.6
164	87.7	1.70	2.1	205.7	0.76	1.4701	21.9	32.0
188	84.4	3.12	3.0	207.1	0.89	1.4709	26.0	38.0

<sup>a</sup> NDFA, Nondistillable fatty acids.

TABLE V  
 Effect of Frying Potatoes in Cottonseed Oil

Hours heating	Iodine value	Free fatty acid (%)	Peroxide value (mEq/kg)	Saponification value	Hydroxyl (%)	Carbonyl value (mEq/kg)	Index of refraction $n_D^{60}$	Polymeric material	
								Hexane insoluble	NDFA <sup>a</sup>
0	110.9	0.03	1.7	195.0	0.14	0	1.4612	4.0	2.3
31	104.9	0.22	2.7	196.9	0.36	184	1.4630	7.0	5.9
70	100.4	0.55	2.4	199.7	0.48	1187	1.4641	11.5	8.4
100	98.1	0.87	2.1	200.3	0.49	1195	1.4653	12.5	10.7

<sup>a</sup> NDFA, Nondistillable fatty acids.

well. The data obtained in the present study indicates that an appreciable amount of carbonyl containing material is also formed. The amount of polymeric material formed in such an oil increased regularly as it was heated for longer time periods. The amount of polar or highly oxidized material increased more rapidly than did the amount of high molecular weight nonpolar material as evidenced by larger percentages of material insoluble in hexane.

The useful life of an oil employed in deep fat frying may be strongly dependent upon the turnover rate, or the rate of addition of fresh oil to the used oil. Melnick et al. (6,21) have indicated that fats used in large volume potato chip fryers are not appreciably damaged. It has also been argued that fats resulting from small deep frying operations, where fat turnover is very small, may be considerably damaged. The results obtained from the present experiments confirm the suggestion of these authors. The rate of turnover is one of the factors which determine the degree to which a heated fat has been abused. The overall turnover rate of a fat may be quite large, but even though such a high overall turnover rate may indicate great dilution of the fat, it does not indicate the true length of time that a fat may have been heated. The detailed study of Poling et al. (11) concerning the effects of aeration on the nutritive value of fats has shown that the degree of exposure of a fat to oxygen is proportional to its nutritional effect. It is reasonable to expect that a fat which is continuously heated in the presence of air may actually be harmed to a lesser extent than an oil which has been heated intermittently. Such intermittent heating may be frequently employed by smaller establishments in attempts to prolong the useful life of a frying fat. It is possible that such intermittent heating, cooling, and heating cycles would encourage the destruction of the oil through an increased build-up of peroxides and carbonyl compounds which may then be destroyed by subsequent heating. Our results indicate that an oil which had been heated for 62 hr intermittently (or a total of 223 hr total time elapsed) contained 16.9% oxidized material; an oil heated continuously for 166 hr contained 16.7% oxidized material. The constants such as iodine value, percentage of free fatty acids, index of refraction, etc., remained comparable. These preliminary results indicate that such an oil had a shorter useful life when compared to an oil heated continuously as measured by the time required to reach a given polymer content as determined by the amount of hexane insoluble fatty acids present in the heated fat.

It would be desirable to know the effects of water upon deep frying and oil stability, since most products which may be cooked by deep frying contain an appreciable water content. The presence of steam in a deep fryer may aid in protecting an oil because of a deodorization effect causing the removal of some free fatty acids and decomposition products. Our results (Table IV) indicate that steam exerts a strong deteriorative effect on cottonseed oil. Reaction of hot cottonseed oil in a deep fryer with water injected into

the oil quickly results in an oil of very inferior quality when compared to continuously heated oil. The addition of water to the hot fat caused greatly increased free fatty acid content, presumably due to hydrolytic cleavage of the triglycerides. A sizable increase in the amount of polymeric material was also observed when compared to the amounts formed during continuous heating. For example, after 23 hr heating time, the amount of high molecular weight and polar material were 18.7 and 28.6% compared to 13.3 and 14.5% for continuously heated oil.

The act of frying a food product, French fries, in the present study contributed substantially to the breakdown of cottonseed oil, but it appeared to be less damaging than the addition of water to hot fat. Although the amount of water added to the fat was probably the determining factor in the effect of water on a hot fat, the greater surface area of moisture contained upon a food product and that trapped within the product may be of greater significance than the actual percentage of water added to fat during frying. It is of interest to note that even though potatoes fried in such oil are completely acceptable, the fat remaining in the fryer after only 31 hr of use contained about 7% of oxidized high molecular weight material, and foamed extensively during the frying process. The study of Robinson et al. (20) indicated a correlation between the time that an oil has been used for frying and the frying temperature with foaming tendencies. This was also correlated with the development of viscosity in a fat and the formation of free fatty acids. These authors found that the addition of 25% of highly polymerized blown cottonseed oil to a sample of shortening caused it to foam immediately while the addition of 2.5% of the same blown oil cause foaming within 24 hr. Our results confirm this and indicate that foaming is related to the formation of oxidation products of high molecular weight.

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# Precision and Accuracy in Gas Liquid Chromatography of C<sub>14</sub>-C<sub>18</sub> Fatty Methyl Esters<sup>1</sup>

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## Abstract

Repetitive analyses of four primary standards for fatty methyl esters by gas liquid chromatography (GLC) with polyester columns and thermal conductivity detection established standard deviations ranging from  $\pm 0.3$ – $0.5\%$  corresponding to coefficients of variation of 1.0–2.0%. These data, representing a relative error of measurement of 1.5–3.0% at a 99% confidence level, suggest a precision approaching that of conventional spectrophotometric measurements.

Proportionality factors, calculated from known mass or molar concentration divided by area % from GLC analysis, were found to be reproducible correction factors which may be generally applicable to GLC analysis of fatty methyl esters with polyester columns and thermal conductivity detectors.

Mass response to a thermal conductivity detector was found to decrease with either increasing molecular weight for saturated C<sub>14</sub>–C<sub>18</sub> fatty methyl esters or with unsaturation among the C<sub>18</sub> unsaturated esters, while molar response increases with molecular weight and decreases with degree of unsaturation.

The use of uncorrected area % data can introduce significant absolute mass errors ranging from about +11% for myristic acid to -17% for linolenic acid.

THE EXPANDING USE of gas liquid chromatography (GLC) in routine fatty acid analysis lends importance to the precision and accuracy of this technique. Very little information is available on the precision of GLC analysis of fatty methyl esters, particularly the commonly encountered C<sub>14</sub>–C<sub>18</sub> acids. More attention has been given to the relative thermal conductivity detector response of the individual methyl esters. From the work of several investigators (1–3) it is apparent that the response of a thermal conductivity detector is not a simple function of either weight or molar concentration. The need for suitable correction factors has prompted study of the response of individual fatty methyl esters, relative to the response of various arbitrary internal standards. These relative response factors have been proposed as suitable constants of general applicability to GLC analysis with thermal conductivity detectors (2,3), although the factors vary with the internal standard chosen.

The current work was undertaken to obtain information both on the precision of GLC analysis for the C<sub>14</sub>–C<sub>18</sub> fatty methyl esters, and to determine the proportionality factors for correction of GLC data.

## Materials and Methods

Four primary standards (Table I) were used. Standards A, B, and C were prepared, with a weight accuracy of at least one part per thousand, from highest purity methyl esters (ca. 99%+), each of which was independently analyzed by GLC to insure the absence of impurities. Standard D was a calibration standard furnished by the Hormel Foundation. All standards were stored at 0F prior to analysis. A Beckman GC-2A chromatograph equipped with a thermal conductivity detector was used for all analyses. The flash chamber was modified for controlled operation at 325C, and equipped with a syringe guide to insure reproducible sample injection.

Two 6 ft copper columns 0.25 in. O.D., each packed with Gas Chrom A, 80–100 mesh, and coated with 20% diethylene glycol succinate polyester were used for the analyses reported here. Both column and detector were operated at 190C, with 250 ma detector current, and helium at 25 lb pressure as carrier gas. Samples of approximately 0.10  $\mu$ l were injected by use of a 1  $\mu$ l syringe.

Relative concentrations of components in each standard were estimated from peak areas, by triangulation, and are reported as area percent (Table I).

Relative mass response factors for the individual fatty methyl esters were calculated by dividing the average area response per unit weight, from repetitive analysis of each standard, by the corresponding response of methyl palmitate as an internal standard. Average values for the four standards are reported in Table II.

Absolute proportionality factors (PF) were calculated from the average data from replicate analysis of each standard from the relationships:

$$\text{PF (Mass)} = \text{Known, wt. \%} / \text{Found, area \%}$$

$$\text{PF (Molar)} = \text{Known, Mole \%} / \text{Found, area \%}$$

These proportionality factors obtained over a period of several months were found to be reproducible, and the factors reported (Table III) are average data from the same number of replicates as reported for the relative response factors (Table II).

## Results and Discussion

### Precision

Standard deviations, coefficients of variation and the 99% confidence limits of the means, from repetitive analysis of four standards are listed in Table I. These analyses were conducted over a period of several days and reflect variations associated with day-to-day changes in operating parameters. Average values for the standard deviations and coefficient of variation indicate no significant differences in the pre-

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