

A Study of the Color Stability of Commercial Oleic Acid¹

SHERMAN S. LIN, A.L. HSIEH, DAVID B.S. MIN, and STEPHEN S. CHANG, Department of Food Science, Cook College, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903

ABSTRACT

Commercial oleic acid has a tendency to develop a dark color during heating. It has been found that this discoloration is partially due to oxidation and partially due to the presence of minor constituents. Their characterization as oxidized and polymerized fatty acids will be reported in a separate paper. The effects of the two factors are synergistic to each other and thus accentuate the darkening of the commercial oleic acid when it is heated under air. Removal of the minor constituents from commercial oleic acid by silicic acid treatment drastically improved its color stability. The generally acknowledged concept that the higher the polyunsaturated fatty acid content in the commercial oleic acid, the lower its color stability, is not correct. The color stability of commercial oleic acid is more predominantly dependent upon the content of minor constituents than that of polyunsaturated fatty acid.

INTRODUCTION

Commercial oleic acid manufactured from beef tallow, lard, and sometimes vegetable oils is a major utilization of agricultural products. One of the objectionable qualities of commercial oleic acid is the development of a dark red color when it is heated under air or when it is reacted with

other chemicals to prepare derivatives. Recently, synthetic fatty acids were made available on the market to compete with the natural products. Although a synthetic substitute for oleic acid is not available on the market at the present time, it might be produced in the future. In order to maintain and to increase the market for natural fatty acids, the color stability of commercial oleic acid should be improved.

A literature search revealed no reference directly relevant to the color stability of commercial oleic acid except a report by Chang (1) concerning the minor constituents. That study and the present study investigated the causes of the darkening of commercial oleic acid and resulted in a treatment which can dramatically improve its color stability.

EXPERIMENTAL PROCEDURES

Materials Used

Commercial oleic acid of various grades manufactured from beef tallow by different companies was used.

Test for Thermal Stability of Oleic Acid

The method as described previously (2) was adopted.

Analytical Methods

The Photometric Index of oleic acid was measured according to AOCS Official Method Td 2a-64 (3) with the use of a Beckman DB-G Spectrophotometer. Spectra grade carbon tetrachloride was used as the reference.

Fatty acid composition was analyzed as methyl esters with an Aerograph 202 gas chromatograph equipped with dual stainless steel columns of 10 ft x 1/8 in. packed with 10% diethyleneglycol succinate on Anakrom ABS.

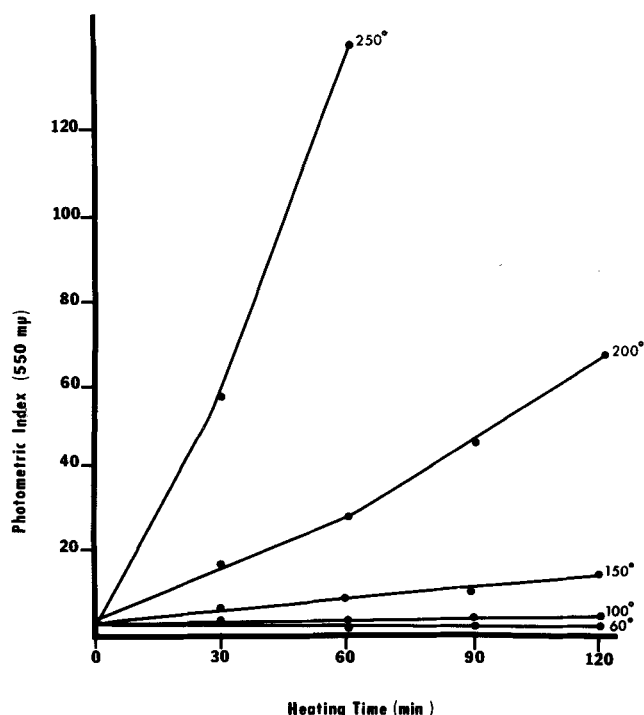


FIG. 1. Darkening of commercial oleic acid during heating under air at different temperatures for different periods of time.

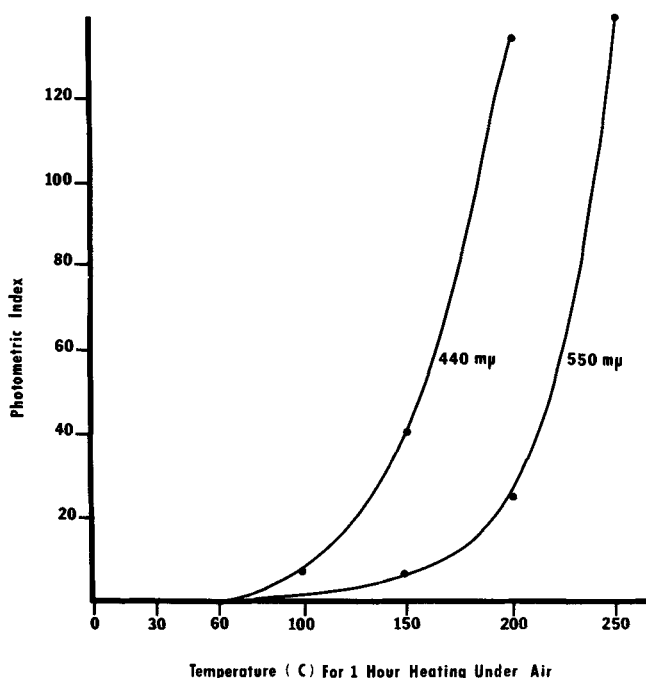


FIG. 2. Darkening of commercial oleic acid by heating under air for 1 hr at different temperatures.

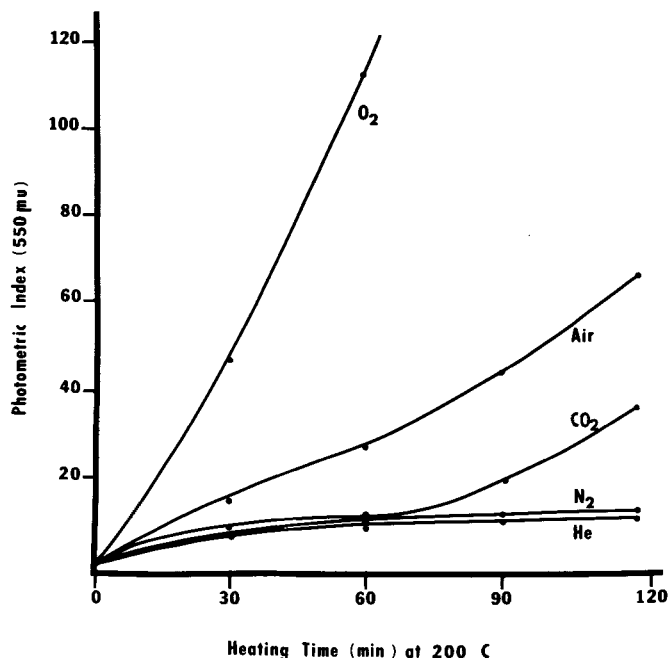


FIG. 3. Darkening of commercial oleic acid by heating at 200 C under different atmospheres.

TABLE I

Effect of Antioxidant upon the Color Stability of Commercial Oleic Acid

	Photometric Index (550 mμ) After heating at 200 C for hours	
	0.5	1.0
Control	60.2	125.0
Antioxidant added ^a	60.2	91.6

^a0.4% Tenox IV.

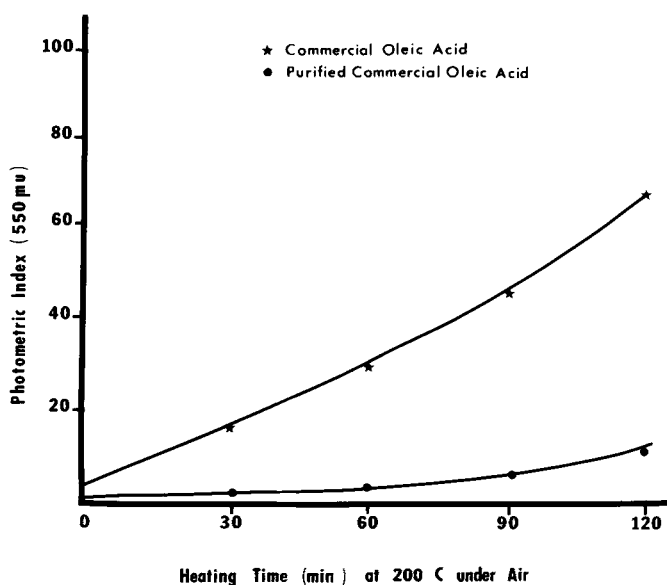


FIG. 4. Improvement in color stability by passing commercial oleic acid through a silicic acid column.

Removal of Minor Constituents by Silicic Acid Column

Commercial oleic acid was continuously passed through a chromatographic column (4.4 x 55 cm) which was packed with 300 g of activated silicic acid (100 mesh, Mallinkrodt

TABLE II

Comparison of the Color Stability of COA and POA Heating at 200 C for 1 hr: Under Air and Helium^a

		Photometric Index	
		550 mμ	440 mμ
Air	POA	20.7	166.0
	COA	125.0	too large to read
Helium	POA	2.2	12.7
	COA	9.6	57.5

^aCOA = commercial oleic acid, POA = purified oleic acid.

2847) purified and activated according to the procedure of Sahasrabudhe and Chapman (4). The oleic acid was applied to the column from a separatory funnel whose tip was extended to the level of the oleic acid above the silicic acid column. The separatory funnel was closed with a glass stopper. The end of the chromatographic column was connected to a suction flask with vacuum applied to control the flow rate. Two bands, one yellow and one dark reddish brown, were formed on top of the silicic acid column. The application of oleic acid was stopped when the colored bands reached near the bottom of the column.

To increase the flow rate, the silicic acid column was wrapped with a layer of aluminum foil and then a heating tape. The temperature was then controlled by a variable transformer.

To determine the amount of minor constituents, the commercial oleic acid was sucked out of the column as completely as possible. The column was then thoroughly eluted with hexane to remove the residual fatty acids. The minor constituents were then eluted out of the column with methanol. The crude minor constituents thus obtained were dissolved in hexane:ethyl ether (9:1) and applied to a column (4.4 x 55 cm) packed with silicic acid suspended in hexane. The column was eluted with the solvent mixture until the colored band reached the bottom of the column. The minor constituents were then recovered by elution with methanol and weighed.

Batch Process Treatment of Commercial Oleic Acid with Silicic Acid

Commercial oleic acid (200 g) was stirred with varying amounts of activated silicic acid from 1 to 10% by wt for 1 hr. The commercial oleic acid was also stirred with 20% by wt of silicic acid for 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 hr. The slurry was then filtered with a Buchner funnel.

RESULTS AND DISCUSSION

Effect of Temperature and Time of Heating Upon the Darkening in Color of Commercial Oleic Acid

A sample of commercial oleic acid (COA) of the highest quality was heated under air at different temperatures for different lengths of time. The color of the heated samples indicated that the rate of discoloration was increased with the increase of temperature at which the sample was heated (Fig. 1 and 2). The rate of discoloration was slow at temperatures below 100 C, but increased rapidly at higher temperatures. The color of COA heated at 200 C for 30 min was darker than that heated at 150 C for 2 hr.

It was also shown that, during heating, both the yellow color (absorbance at 440 mμ) and the red color (absorbance at 550 mμ) were increased, thus causing the highly objectionable dark red appearance of the heated sample (Fig. 2).

Effect of Oxygen

Commercial oleic acid was heated at 200 C under

TABLE III
Color Stability of Commercial Oleic Acids (COA)

	Octadecadienoic acid (%)	Photometric Index (440 mμ)	
		Original	Heated ^a
COA, Sample 1	6.1	16.9	186.9
Purified Sample 1	6.1	0.2	14.7
COA, Sample 2	2.3	7.6	82.3
COA, Sample 3	4.2	1.9	43.0
COA, Sample 4	7.1	1.8	36.5
COA, Sample 5	6.3	2.7	62.6
COA, Sample 6	6.1	8.6	118.7
COA, Sample 7	12.2	32.3	317.9
Purified Sample 7	12.2	2.1	21.1

^a200 C 1 hr.

TABLE IV
Effect of Minor Constituents upon the Color Stability of Commercial Oleic Acids (COA)

Sample	Minor constituents (%)	Linoleic acid (%)	Photometric Index			
			550 mμ		440 mμ	
			Original	Heated ^a	Original	Heated ^a
COA, Sample 1	2.67	6.1	1.4	57.5	16.8	342.3
COA, Sample 4	0.83	7.1	0.1	7.0	4.0	51.6

^a200 C 1 hr.

oxygen, air, carbon dioxide, nitrogen, and helium for different periods of time. The inert gases decreased the degree of darkening while oxygen greatly accelerated the discoloration. The darkening of the heated sample thus indicated that it was caused by oxidation (Fig. 3). This obvious conclusion was further evidenced by the retardation of the darkening through the use of an antioxidant (Table I).

Effect of Minor Constituents

The effect of the minor constituents removed by the silicic acid upon the color stability of commercial oleic acid was dramatic (Fig. 4). The purified oleic acid (POA) eluted from the silicic acid darkened only slightly when heated at 200 C as compared with the original COA.

Synergistic Effect Between Oxygen and Minor Constituents

The strong dark red color which developed during the heating of COA under air could be due to oxidation catalyzed by the minor constituents. The POA darkened only slightly when heated at 200 C for 1 hr under helium. Its darkening under air was also minimal. The COA also discolored only slightly when heated under helium. However, in the presence of both air and minor constituents, an intense dark red color developed (Table II).

Effect of Octadecadienoic Acid

It is a generally accepted rule in the trade that the lower the content of octadecadienoic acid, the better the color stability of the COA. Analysis of the seven samples of COA indicated that this is not true (Table III). The minor constituents were more predominant in determining the color stability of the COA than the dienoic acid content. Purification of the COA by the removal of minor constituents with the use of silicic acid could dramatically improve the color stability without changing the content of the octadecadienoic acid (Table III). The predominant effect of minor constituents upon the color stability of COA was further indicated by the analyses of two samples with a slight difference in octadecadienoic acid content but a considerable difference in minor constituents (Table IV).

The POA which was prepared at room temperature and

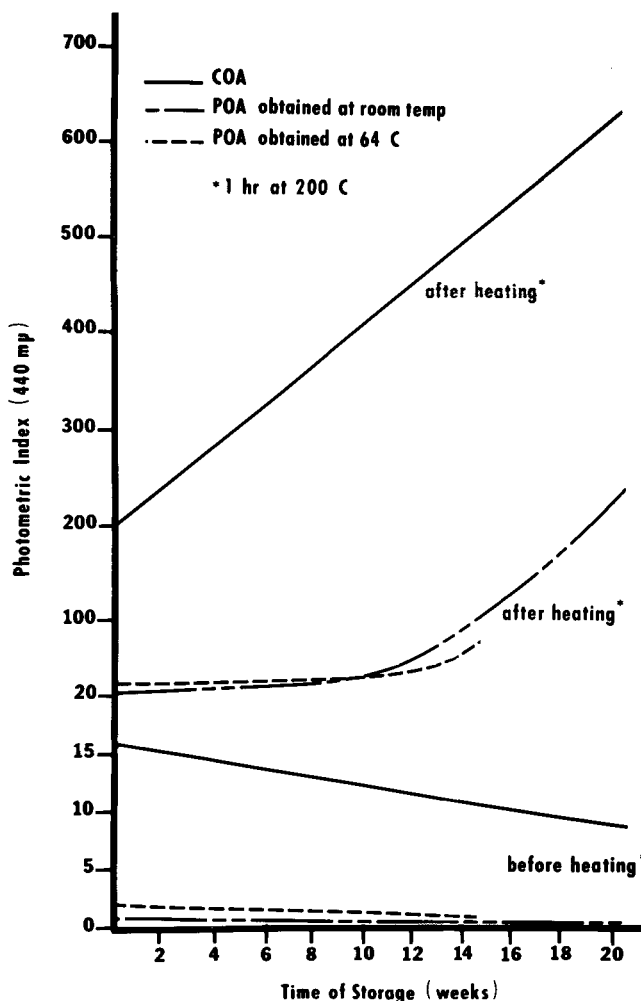


FIG. 5. Color stability of purified oleic acid (POA) after storage. COA = commercial oleic acid.

64 C retained a light color when stored separately at room temperature for up to 20 weeks. As a matter of fact, there

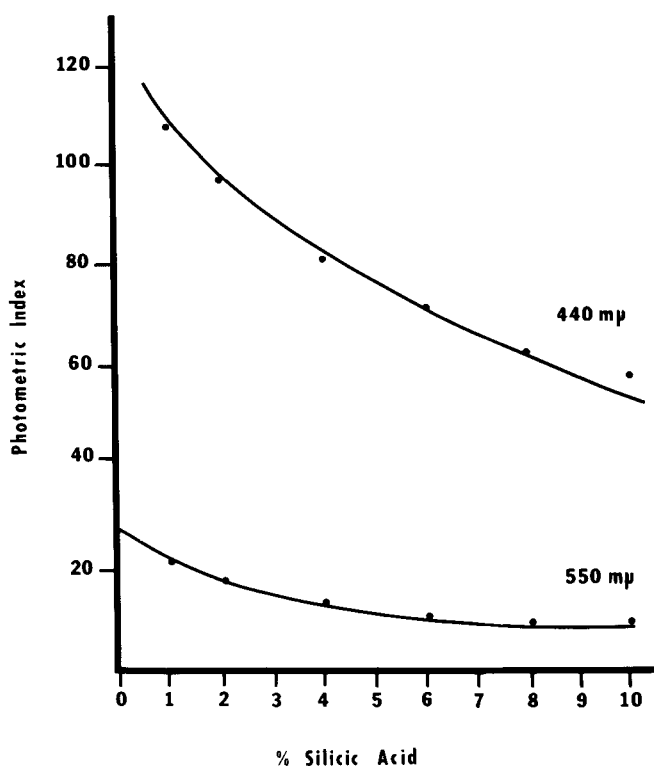


FIG. 6. Color stability of commercial oleic acid after treating with silicic acid by batch process (Photometric Index measured after the sample was heated at 200 C for 1 hr).

was a slight decrease in color intensity during storage (Fig. 5). Heating of the stored POA at 200 C for 1 hr showed an increased darkening in color with the time of storage. However, the color stability of the POA after storage remained consistently better than that of the original COA.

Evaluation of Different Adsorbents

Among the different adsorbents evaluated, the 100 mesh silicic acid was most desirable, both from its capacity and

the color of the eluted POA (Table V). It was found that the silicic acid could be reused for up to 7 times without decreasing in efficiency after the minor constituents had been thoroughly eluted from the column with methanol. Presumably, the silicic acid could be reused much longer if it were reactivated by heat.

The flow rate of the COA from a 4.4 x 55 cm column packed with 300 g of 100 mesh silicic acid was only 11.6 g/hr at 23 C. Increasing the column temperature to 70 C will increase the flow rate to 38.2 g/hr. The color of the eluate obtained at the higher temperature was only slightly higher than that obtained at the lower temperature (Table VI). Furthermore, the color stability of the POA prepared at the higher column temperature remained comparable to that prepared at room temperature (Fig. 5). It therefore appears that, for larger scale production purposes, a higher column temperature should be used to increase the flow rate.

Purification of COA with Silicic Acid

It was found that the silicic acid column method, as described in this paper, can be replaced by a batch process to remove the minor constituents from COA. By stirring with varying amounts of silicic acid (100 mesh) from 1 to 10% by wt at room temperature for 1 hr, the color stability of the COA was improved significantly (Fig. 6). By stirring the COA with 20% by wt of silicic acid, it was found that 30 min of contact was sufficient. Stirring for a longer period of time did not further improve the color of the oleic acid. However, the batch process was not as efficient as the continuous column method. With 7.5% silicic acid, the COA purified by the column method had a color intensity of 3.5 at 550 mμ and 35 at 440 mμ, while that purified by the batch process had a color intensity of 10 at 550 mμ and 65 at 440 mμ.

ACKNOWLEDGMENTS

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TABLE V
Purification of Commercial Oleic Acid by Different Adsorbents

Adsorbent	Capacity ^a	Photometric Index (440 mμ) ^b
Dry silicic acid (100 mesh) (Mallinckrodt)	450	0.0
Silicic acid + 5% water	150	0.7
Silica gel (20-40 mesh, grade 28) (Fisher)	0	14.2
Silica gel (28-200 mesh, grade 12) (Fisher)	70	1.2
Silica gel (30-70 mesh, EM reagent)	200	0.5
Florisil (60-100 mesh, Fisher)	155	0.6
Clay (Tonsil) + silicic acid (1:1)	200	0.0

^aCapacity: g of purified oleic acid per 100 g of adsorbent before photometric index at 440 mμ reached 1.5.

^bFor the first 100 g of purified oleic acid eluted.

TABLE VI
Effect of Temperature upon the Flow Rate of Commercial Oleic Acid on a Silicic Acid Column

Temperature of column	Flow rate (g/hr)	Photometric Index			
		Eluate	550 mμ	440 mμ	
70 C	38.2	First 200 g	0.0	1.3	
		Next 300 g	0.0	3.5	
23 C	11.6	First 200 g	0.0	0.0	
		Next 300 g	0.0	0.2	

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