Photoactivation and Color Formation in Antioxidant Treated Lard[1]

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SINCE the introduction for use in lard of the antioxidant composed of butylated hydroxyanisole (BHA), propyl gallate (PG), and citric acid (CA) (1, 2), sporadic cases of bluish discoloration have been observed. Usually a blue-black sludge in settlings of a tank of lard or a bluish discoloration of the lard have been reported. The color has been attributed to the interaction of propyl gallate from the antioxidant and the contaminating iron in the lard.

Efforts have been made to avoid the development of bluish colors in lard by eliminating propyl gallate from the antioxidant mixture[2] or by use of a formulation supposed to result in greater solubility of the antioxidant and more efficient chelation of the contaminating iron.[3]

Recently another factor in the formation of the blue color was discovered. A commercial sample of lard treated with an antioxidant containing BHA, PG, CA, and lecithin, when exposed to daylight for some hours, was found to develop a blue color over the entire surface exposed to light. The surface of the lard protected from light remained white. This suggested that a photochemical activation of the reaction occurred and led to a study of some of the factors involved in the development of the bluish coloration.

Color Effects from Iron Contamination

Three commercial formulations were used in tests designed to indicate their color-forming tendencies with iron in the lard, their relative solubilities, and their tendency to form the colored sludges in systems involving both the presence of water and iron. These three antioxidants will be referred to hereafter as A, B, and C. The composition of each is:

A. Butylated hydroxyanisole, propyl gallate, and citric acid in propylene glycol;

B. Butylated hydroxyanisole, propyl gallate, and citric acid in propylene glycol and monoglycerides made from cottonseed oil;

C. Butylated hydroxyanisole, propyl gallate, lecithin, and citric acid in corn oil.

The color-forming tendencies of the three antioxidants were determined by adding each to lard in the recommended quantities by means of vigorous mechanical stirring for 20 minutes. The recommended quantities are 0.05% A, 0.05% B, and 0.075% C in the lard. The iron was added as ferric chloride in alcohol to provide a concentration of 5 parts per million in the lard. Colors were determined as Lovibond yellow and red immediately after preparation and after heating at 375°F. for one hour to simulate the effect of frying on the system.

The results are shown in Table I. The lards with iron contamination were progressively less colored from antioxidant mixture A through C just after incorporation of the antioxidant. The heating period of one hour at 375°F. produced rather marked color changes. The changes were small in the control lard, but the lards containing iron and antioxidant were noticeably darker. At this point the lard containing B was least colored and that with C was most intensely colored. This indicates that while C may afford the least color production in freshly prepared lard when iron contamination is present, it does not maintain its effectiveness under simulated conditions of usage.

TABLE I

Color Effects in Antioxidant-Treated Lard in the Presence of Iron Contamination

Antioxidant	Lovibond Color Values			
	Before heating		After heating at 375°F.	
	Y	R	Y	R
A	14	2.5	35	6.8
B	4.5	1.4	23	4.5
C	2.5	0.8	53	8.5
No antioxidant	1.5	0.2	4.5	0.8

Most of the dark-colored sludges reported have been found in the bottom of storage tanks where they are intimately associated with moisture. All of these sludges gave positive iron tests and were soluble in mineral acids but insoluble in organic solvents. It has been suggested frequently that the appearance of these sludges is connected with the solubility of the antioxidant in the lard and that incomplete mixing will result in settling out and a greater tendency for sludge formation to appear.

Attempts were made to duplicate sludge formation and at the same time to compare solubilities of antioxidants and their relative sludge-forming tendencies. Because agitation was a factor in mixing, antioxidant solubility tests were set up to attain equilibrium conditions with a minimum of agitation.

Solubility tests were made by adding 0.1 g. and 1.0 g. of antioxidant to 20 g. of lard in a large test tube and allowing them to equilibrate in a water bath at 65°C. Antioxidant A was less soluble than B or C. It did not form a distinct 2-phase system however when equilibrated at 65°C. without agitation and tested at a level which was 100 times the recommended use level.

In order to try to develop a sludge these same tubes of antioxidant treated lard were used. A suspension of iron rust in 5 ml. of water was transferred to each tube. The tubes were placed in a constant temperature room at 37°C. and observed at the end of one-week and two-week periods. The results are shown in Table II. The color-forming effects were variable but always were associated with the aqueous phase or the fat water interface. The relative solubilities of the antioxidants in the fat had no apparent relation to their tendency to form the colored products when both iron rust and moisture were present in the system. It appears probable then that under

[1]Journal paper No. 73, American Meat Institute Foundation.
[2]Nordihydroguaiaretic acid replaced propyl gallate in one commercial formulation.
[3]Interaction of lecithin and citric acid has provided a more fat-soluble synergist in one commercial formulation.

TABLE II

Miscibility and Sludge-Forming Characteristics of Antioxidants in Lard

Antioxidant	Miscibility at 65°C.		Iron rust effect	
	1 hr.	2 hr.	1 week	2 weeks
A 0.1 g./20 g. lard	Clear	Clear	Blue-green flecks at bottom	Same as 1 week
A 1.0 g./20 g. lard	Cloudy 2 phases	Cloudy 1 phase	Blue-black	Blue-black at lard-water interface and water
B 0.1 g./20 g. lard	Clear	Clear	Sl. green soln. at bottom	Sl. green soln.
B 1.0 g./20 g. lard	Cloudy 1 phase	Cloudy 1 phase	Blue-green soln. at bottom	Blue-green Soln. at bottom
C 0.1 g./20 g. lard	Clear Foamy Dark	Clear Foamy Dark	Lt. blue band at fat-water interface	Lt. blue band at fat-water interface
C 1.0 g./20 g. lard	Clear Foamy Dark	Clear Foamy Dark	Lt. blue band at fat-water interface	Blue-black sludge at bottom

the proper conditions a colored sludge may be obtained regardless of the characteristics of solubility and chelating activity of the antioxidants tested.[4]

Photoactivated Blue Color in Lard

Since the color observed in lard treated with antioxidant C and exposed to light was similar to the blue color in lard resulting from reaction of propyl gallate with iron, it was assumed that this may be the cause of the color. Tests were set up to determine whether there was a requirement for iron in the system and to determine the antioxidant or antioxidant combination responsible. The effect of the state of oxidation of the lard also was tested since photoactivation could be a factor in the autoxidation of fats. All colors were measured in Lovibond units.

A suitable lard was treated with propyl gallate (PG) at 0.003%, with antioxidant A at 0.05%, and with antioxidant C at 0.075%. Portions of each lard and of the control were treated with ferric chloride in alcohol to provide 5 parts per million of ferric ion contamination. These samples were irradiated in beakers at room temperature for 17 hours with two 15-watt daylight fluorescent lamps placed about 4 inches above the top of the lard samples. The colors developed are shown in Table III.

This test revealed the importance of iron contamination for blue color formation since the blue colors measured in all samples without iron were equivalent. The iron effect on red and yellow color values is comparable to that observed previously. A small increase in blue values was measured with A in the lard and marked increase in blue occurred with C in the lard. PG was virtually without effect.

Lard at three stages of oxidation was treated with each of these antioxidant systems and then subjected to fluorescent lamp irradiation for 41 hours at 35°F. The lards were, respectively, a fresh lard with a peroxide value (PV) of 3, the same lard with a PV of 5 after 9 hours' aeration on the A.O.M. apparatus, and the same lard with a PV of 20 after 13 hours' aeration. The colors were measured, and the samples were irradiated for an additional 17 hours at 70°F. Results are shown in Table IV.

[4] At the suggestion of the reviewer tests for sludge formation were repeated, using antioxidants at the recommended use levels in iron contaminated lard. An additional antioxidant mixture was tested in which NDGA was substituted for PG. When the antioxidants were stirred into the lard, sludge formation was not apparent with any of the mixtures. When lard was added to the antioxidant without stirring, sludge was formed in the aqueous layer at the bottom of each vessel with all the antioxidants. The sludge formed with the mixture containing NDGA was dark brown whereas all other sludges were blue-black in color. As noted in earlier tests, solubility of the antioxidant in fat was not a factor in sludge formation.

TABLE III

Lovibond Color Values in Antioxidant-Treated Lard After 17 Hr. Irradiation

Antioxidant	Lovibond color values 5.25" column		
	Yellow	Red	Blue
Lard (control)	10	1.7	0.9
Lard + Fe[a]	14	3.6	0.9
Propyl gallate	10	1.5	0.9
Propyl gallate + Fe[a]	16	4.5	1.0
A	10	1.7	0.9
A + Fe[a]	16	4.0	1.3
C	11	1.8	0.9
C + Fe[a]	18	5.0	3.5

[a] Fe added at 5 parts per million of lard.

TABLE IV

Effect of Oxidation State of Lard on Photoactivated Color Production in Lard

Antioxidant	Lard sample[a]	41 hr. irradiation at 35°F.			Additional 17 hr. irradiation at 70°F.		
		Lovibond color			Lovibond color		
		Y	R	B	Y	R	B
Propyl Gallate + Fe[b]	1	16	3.9	1.2	17	4.4	1.1
	2	16	4.4	0.8	17	5.0	1.1
	3	16	4.4	0.5	17	5.1	1.0
A + Fe[b]	1	16	3.8	0.9	16	3.9	1.1
	2	16	3.5	0.8	16	3.7	0.9
	3	16	3.3	0.8	16	3.5	0.9
C + Fe[b]	1	14	3.4	1.9	15	4.4	2.5
	2	14	2.7	1.1	15	4.0	2.6
	3	14	2.8	1.1	15	3.6	2.2

[a] Lard sample: 1—Fresh lard, PV = 3; 2—aerated 9 hrs., PV = 5; 3—aerated 13 hrs., PV = 20.
[b] Fe added = 5 p.p.m. lard.

The state of oxidation of lard had no enhancing effect on color values. There was an apparent bleaching effect of red and blue as the state of oxidation was increased. As noted before, irradiation developed the most blue in the lard treated with antioxidant C.

At this point the chief factor which seemed to be different in any of the systems studied was the presence or absence of lecithin, which is used in the preparation of antioxidant C. Accordingly, lard was contaminated with ferric iron at 5 parts per million. Portions of the lard were treated with A, B, and PG both with and without lecithin and with C which contains lecithin as one of its ingredients. The sam-

TABLE V

Effect of Lecithin on Photoactivated Color in Lard

Antioxidant	Iron added, p.p.m.	Lecithin added, %	Lovibond color value 5.25" column					
			Original			Irradiated		
			Y	R	B	Y	R	B
Control lard	0	0	10	1.5	1.2	10	2.0	1.3
Control lard	5	0	11	2.3	1.3	11	3.7	1.2
Control lard	5	0.01	13	2.0	1.2	14	3.3	1.3
A	5	0	14	2.7	1.4	14	3.7	1.6
A	5	0.01	11	2.0	1.4	14	5.0	4.2
B	5	0	12	2.4	1.4	14	3.8	2.5
B	5	0.01	11	2.1	1.4	14	5.3	4.8
C	5	0	12	2.4	1.6	16	5.9	4.8
Propyl gallate	5	0	20	4.4	2.0	20	5.1	2.2
Propyl gallate	5	0.01	14	3.4	2.6	15	4.7	2.5

TABLE VI

Antioxidant	Lecithin added, %	Lovibond color value 5.25" column					
		Original			Irradiated		
		Y	R	B	Y	R	B
Control lard	0	13	2.2	2.2	12	2.2	1.8
Control lard + Fe[a]	0	16	4.5	2.0	16	4.7	2.1
BHA .01% + Fe[a]	0	18	4.6	2.4	20	5.5	2.1
BHA .01% + Fe[a]	0.01	14	2.8	1.5	14	3.6	1.0
PG .003% + Fe[a]	0	16	5.3	3.5	16	5.0	2.2
PG .003% + Fe[a]	0.01	18	5.5	3.4	16	5.0	2.5
CA .002% + Fe[a]	0	16	4.5	4.1	15	4.4	2.0
CA .002% + Fe[a]	0.01	16	3.6	3.0	16	4.2	2.0
BHA .01% + Fe[a] PG .003% +	0	24	5.5	3.2	26	6.0	2.5
BHA .01% + Fe[a] PG .003% +	0.01	20	5.0	3.6	20	6.2	3.6
BHA .01% + PG .003% + Fe[a] CA .002% +	0	20	5.1	3.4	20	5.3	3.3
BHA .01% + PG .003% + Fe[a] CA .002% +	0.01	13	2.8	1.5	20	7.0	6.0

[a] Fe—5 p.p.m.

ples were irradiated for 66 hours at room temperature as described previously. The colors before and after irradiation are shown in Table V.

The effects of the presence of lecithin with the other antioxidant ingredients and the effects of irradiation are demonstrated clearly. Propyl gallate apparently did not contribute to the blue color formation when used alone. Antioxidants A and B with lecithin added to the lard contributed blue colors after irradiation which were quite comparable to those provided by C.

These results then required one further test to learn the ingredients contributing to the photoactivated blue color in lard. Lard was contaminated with iron as described before. The lard was treated with BHA, PG, and CA and with the combinations of these ingredients both with and without added lecithin. The Lovibond color values are shown in Table VI.

This test showed that no one ingredient or combination of antioxidant ingredients was responsible for the photoactivated blue color in lard. It revealed that lecithin and iron are necessary components for the production of the photoactivated blue color in a lard system containing BHA, PG, and CA.

Summary

1. A study has been made of factors causing blue colors in antioxidant treated lards.

2. The formation of blue-colored lards or of blue-black sludges in lard storage tanks is due to reaction of propyl gallate in the antioxidant with iron contamination in the lard.

3. The solubility of the antioxidant mixture in lard is not a factor in the formation of blue-colored lard.

4. A new cause of blue-colored lard has been discovered. This is a photoactivated blue color resulting from irradiation of antioxidant treated lard. The blue color was developed in lard treated with BHA, propyl gallate, and citric acid only when lecithin was present and the lard was contaminated with iron. The state of oxidation of the lard did not contribute to these colors.

REFERENCES

1. Kraybill, H. R., Dugan, L. R. Jr., Vibrans, F. C., Swartz, VeNona, and Bondi, Vera, American Meat Institute Foundation *Bull. No. 4*, (1949).

2. Kraybill, H. R., Dugan, L. R. Jr., Beadle, B. W., Vibrans, F. C., Swartz, VeNona, and Rezabek, Helen, J. Am. Oil Chemists' Soc., *26*, 449-453 (1949).

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Modification of Vegetable Oils. XV. Formation of Isomers During Hydrogenation of Methyl Linoleate[1]

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IN the hydrogenation of normal linoleic acid (cis-9, cis-12-octadecadienoic acid) or its esters, linoleic acid tends to be hydrogenated to an oleic acid before hydrogenation to the saturated or stearic acid commences;[3] that is, the reaction tends to be selective. Moore, Richter, and Van Arsdel (13) first discovered this fact on determining the composition of hydrogenated cottonseed oils. Later investigators (7, 17) confirmed the discovery. Since then numerous investigations of the hydrogenation of linoleic acid and its esters have been made. Hilditch and Vidyarthi (8) concluded that on hydrogenation of methyl linoleate no methyl stearate is produced until 90% of the methyl linoleate has been transformed into methyl oleate. Bailey (3), in an analysis of hydrogenation data on cottonseed oil, found that under very nonselective operating conditions the ratio of hydrogenation rates for linoleic acid and oleic acid (combined as glycerides) is about 4:1. For very selective operating conditions this ratio is about 50:1.

It is generally believed that in the hydrogenation of linoleic acid esters the bond farthest removed from the ester linkage tends to be reduced first. Suzuki and and Inoue (19) found that hydrogenating 1 mole of normal methyl linoleate with 1 mole of hydrogen produced oleates having the double bond in the 9:10 position. Similar experiments with isolinoleic acid (10) also showed that the bond farthest removed from the ester linkage was hydrogenated first. In another investigation (15) it was found that in the hydrogenation of isomeric oleic acids the highest rate was observed when the single bond was farthest removed from the carboxyl group.

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[3] The terms linoleic acid, methyl linoleate, etc., will be used in the general sense and will refer to any octadecadienoic acid and its esters unless indicated otherwise. In a similar manner the terms oleic acid, methyl oleate, etc., will refer to any octadecenoic acid and its esters. The term normal will be used in referring to naturally-occurring cis-9, cis-12-octadecadienoic acid, and cis-9-octadecenoic acid and their esters.