

Color Development in C₁₈ Unsaturated Hydroxyamides¹

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ABSTRACT

Dark colors both of hydroxyamides produced from unsaturated fatty acids and of alkanolamine compounds in general might possibly limit their industrial applications. While metal salts have long been recognized as probably involved in the problem, little appears in the literature concerning the nature of these colored compounds. When we prepared linseed and soy *N,N*-bis(2-hydroxyethyl)amides as intermediates for protective coatings, we discovered that metals—iron and copper in particular—formed highly colored products with these unsaturated hydroxyamides. On standing at room temperature, these intermediates became deep reddish brown (18 on the Gardner scale) if only 1 ppm of copper was present. Because purified starting materials (i.e., alkanolamines, methyl esters, or oils) do not color or darken in the presence of copper and air, several structural features and conditions must be present if color is to develop. While either chelating agents or antioxidants are somewhat effective over a short time, color formation has been successfully retarded during long-term storage of polyunsaturated *N,N*-bis(2-hydroxyethyl)amides by adding 1% potassium borohydride.

INTRODUCTION

During the preparation of polyesteramides for protective coatings, *N,N*-bis(2-hydroxyethyl) linseed amide (HELA) became rosy to reddish brown on standing at room temperature. After several months, these hydroxyamides had developed Gardner colors of 16-18. The dark color of HELA, the hydroxy intermediate, carried through to the final polyesteramide or urethane derivative (1,2). As such highly colored products are undesirable for certain commercial applications, we investigated the possible cause. Industry has long pointed to oxidation as the primary reason for discoloration of products containing alkanolamines, but we found no single factor, such as oxidation, to be responsible, but instead we discovered a unique combination of conditions, functional groups, and trace metal contamination. Because we found methods to control or inhibit color, light products can now be prepared (2).

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EXPERIMENTAL PROCEDURES

Stearic, oleic, linoleic, linolenic, and *trans,trans*-9,11-octadecadienoic *N,N*-bis(2-hydroxyethyl)amides were prepared from the respective methyl esters, whereas the amides of linseed, hydrogenated linseed, soy, castor, and tung were prepared from the oils (3). Compositions based on gas-liquid chromatography of methyl esters on an EGSS-X column are shown in Table I.

HELA was prepared in the presence of antioxidants, chelating agents, or potassium borohydride by adding the respective agent to diethanolamine (DEA) before adding oil. Linseed oil was heated under a nitrogen atmosphere at 150 C for 1.5 hr with 0.5% citric acid for metal deactivation. Alkali-refined linseed oil (LSO) was decolorized by chromatography on a 450 mm x 50 mm column packed with silicic acid: Celite: carbon (9:1:1). The oil (600 g, Gardner color 6) was eluted with distilled petroleum ether, and 545 g decolorized oil (color 1) was recovered after solvent was removed.

Room temperature oxidations in the presence of metals were conducted by slowly bubbling air through the samples, whereas oxidations at 100 C were heated in air on spot test plates on an aluminum block placed on a hot plate. Copper [as CuCl₂·2H₂O or Cu(NO₃)₂·3H₂O], iron (as FeCl₃·6H₂O), aluminum (as AlCl₃), sodium (as NaCl), zinc (as ZnCl₂), chromium (as CrO₃), and manganese or cobalt (as naphthenates) were added as solutions at the 1- to 3- or 25-ppm level.

Colors were determined by the Gardner color method (4) and spectroscopically on a Beckman DB Spectrophotometer over the visible region from 380 to 780 nm. Trace metal analyses were obtained by emission spectroscopy and atomic absorption. A polymeric dark reddish-brown material from HELA was isolated by chromatography on a column packed with silicic acid: Celite (9:1). Diethyl ether was used to elute and separate the HELA first before the highly colored strongly adsorbed component was eluted with methanol.

RESULTS AND DISCUSSION

HELA prepared via the sodium methoxide-catalyzed aminolysis of alkali-refined LSO or methyl ester with DEA at 110 C darkens and becomes reddish brown on standing. Typically, a 100% molar excess of DEA was used to drive the reaction to completion, and then high purity HELA was isolated by washing an ether solution of the reaction mix-

TABLE I

Gas-Liquid Chromatographic Composition of Methyl Esters						
Alkyl group	C ₁₄	C ₁₆	C ₁₈ ⁰	C ₁₈ ¹	C ₁₈ ²	C ₁₈ ³
Stearate	2.6	1.8	95.5	---	---	---
Oleate		Trace	Trace	99.9	---	---
Linoleate				Trace	99+	
Linolenate					Trace	99+
<i>r,r</i> -9,11-Octadecadienoate					98+	
Castor ^a		1.0	1.0	89.5	4.2	0.3
Soy		1.0	4.2	24.3	52.6	8.9
Hydrogenated linseed		6.0	4.8	55.6	33.2	0.4
Linseed		5.6	2.8	19.8	13.8	58.0
Tung ^b			5-6	6-9	8-10	76-82

^aSee ref. 10.

^bSee ref. 11.

TABLE II
Influence of Preparative Procedures on Color of *N,N*-bis(2-hydroxyethyl) Linseed Amide

Example	Oil color	Reaction temperature (C)	Wash (1% HCl)	Gardner color	
				Initial	After 2 weeks
A	6	110	-	9	15
B	6	RT ^a	+	9	16
C	6	110	+	10	15
D	6	130	+	9	15
E	6	165	+	11	15-16
F	1	110	-	8	12
G	1	110	+	5	10-11

^aRoom temperature.

TABLE III
Effect of Antioxidants on Coloration of *N,N*-bis(2-hydroxyethyl) Linseed Amide

Antioxidant and level ^a	Reaction temperature (C)	Gardner color		
		Initial	8 Months	>2 Years
None	RT ^a	9	15	>18
1% BHA ^b	RT	11	15	18
1% BHT ^b	RT	8	9	12
1% BHT ^b	130	9	15	16
0.5% BHA ^c	110	15	-	13
0.5% BHT ^c	110	15	-	14
0.5% Propyl gallate ^c	110	15	-	14
0.5% Hydroquinone ^c	110	15	-	>18

^a% by wt. BHA = butylated hydroxyanisole, BHT = butylated hydroxytoluene, RT = room temperature.

^bPrepared in presence of antioxidant.

^cStored with antioxidant at 25 C.

ture with 15% aqueous sodium chloride to remove the catalyst and excess DEA. Initial Gardner colors ranged from 9 to 11 depending on the ease with which the products could be washed and isolated. On standing, noticeable color changes occurred; first rosy tinges developed which turned orange to orange-brown and finally deep reddish-brown (Gardner color >18).

No significant differences in either initial colors or those after standing were observed (Table II) for products prepared at room temperature, 110 C, 130 C, or 165 C (B-E). Washing with 1% hydrochloric acid to remove traces of DEA did not reduce the color (A and C). Removal of colored components from alkali-refined LSO (Gardner color 6 reduced to 1) gave slightly lighter initial colors (A vs. F and C vs. G), and after storage the products from decolorized oil were better.

A polymeric dark-brown component (0.71 g) isolated by column chromatography from a representative preparation of HELA (20 g) was similar to HELA; both contained peroxides and ketones by IR analysis. Microanalysis indicated 0.76% ash by wt and an empirical formula of $C_{18.6}H_{35.7}NO_{6.3}$ derived from carbon, hydrogen, and nitrogen analyses. This formula suggests a highly oxidized fraction. Thin layer chromatography showed HELA and presumably unidentified oxidation products.

Highly oxidized products suggested that antioxidants would minimize color formation (Table III). HELA was prepared or stored at 25 C with commonly used antioxidants for fats and oils, i.e., butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and propyl gallate. Although these samples did darken somewhat after ca. 1 month, long-term storage (2 years or more) shows them to be much lighter than those without antioxidants (>18); BHT appeared to be the most effective with a color increase from 8 to only 12. HELA, color 15, when stored with 0.5% by wt of BHA, BHT, or propyl gallate, showed no increase in color and actually lightened to 13 or 14. However, the sample that contained hydroquinone

darkened like untreated HELA to >18.

While oxidation is definitely involved, it is not the only cause of color formation. Many literature references on copper complexes of amines, amino acids, and peptides can be found, and the function of metals and metal-complexes in lipid oxidation has been the subject of a symposium (5). DEA and other amines reportedly form complexes with copper and iron; some copper complexes are known to be powerful pro-oxidants (6). Trace amounts of metals in HELA were confirmed by atomic absorption and spectroscopic emission analyses. A typical highly colored sample (>18) analyzed 0.63 ppm copper and 2.1 ppm iron by emission spectroscopic analyses. Other metals identified were aluminum, barium, strontium, boron, zinc, manganese, chromium, and sodium. Metallic contamination of HELA could occur during the work-up procedure (salt water wash) since ACS grade sodium chloride contains small amounts of metals. Apparently, HELA reacts rapidly with the soluble metal ions to form complexes that may themselves be colored or that may act as pro-oxidants leading to colored condensation products.

A molecularly distilled purified sample of HELA (Gardner color 6, no copper by atomic absorption) after oxidation for 8 days at room temperature showed no additional coloration. However, when only 1 ppm copper as cupric chloride was added and then the mixture was oxidized, a deep reddish-brown product resulted. A Gardner color of 7 resulted after room temperature oxidation for 3 weeks with 2 ppm iron added to the purified HELA. After 3 months, similar air oxidations with aluminum and cobalt showed no appreciable increase in color. Apparently colors develop more slowly with iron, aluminum, and cobalt, and, after storage for more than a year, colors of 18, 14, and 13, respectively, were observed.

HELA free of trace metals (molecularly distilled) was treated with 25 ppm of copper, iron, sodium, aluminum, cobalt, chromium, manganese, or zinc and heated in air at 100 C for 1 hr (Table IV). Treated samples were compared

TABLE IV

Color Formation by Metals in Purified <i>N,N</i> -bis(2-hydroxyethyl) Linseed Amide ^a	
Metal added	Gardner color
Copper	15
Iron	13
Aluminum	10
Sodium	7
Chromium	11
Zinc	12
Cobalt	13
Manganese	9
None	6

^aHeated 1 hr at 100 C in air with 25 ppm metal.

with a control. Almost all metals produce some color, but clearly copper and to a lesser extent iron and cobalt form highly colored products. Similar experiments established that colors were not formed when copper or iron was added to either LSO, the methyl ester, or DEA.

Earlier work with soy dihydroxyamides (DHA) produced colored products, too, but generally color intensity was less and development slower than with HELA, which reaction suggested that the degree of unsaturation was also related to the color problem. We studied the effect of unsaturation in the alkyl group of selected DHA listed in Table V. These samples were heated at 100 C for 3 hr in air with 0.5-1.0 ppm copper introduced during preparation and 25 ppm of added copper (as cupric chloride). Saturated and monoene DHA do not form colors (H-J). DHA from methylene-interrupted or conjugated dienes (L-N) gave moderate colors. The DHA from partially hydrogenated LSO (K) that contained 33.2% nonconjugatable diene (Table I) did not increase in color during heating. The most intense colors resulted from products that contained triene in the alkyl side chain (O-R).

Monoethanolamides of linseed oil undergo similar coloration and darkening when heated at 50 C in air and the presence of 1 ppm copper. A product with Gardner color of >18 resulted. When linseed monoethanolamide (mp 43-45 C) prepared and isolated by the regular procedure was allowed to stand at room temperature for 7 months, only a thin layer of product at the surface has darkened. Apparently, diffusion of oxygen through the solid substrate has not occurred. This observation clearly demonstrates that, although the entire product contains trace amounts of copper, only the more highly oxidized material has colored. It further demonstrates that only one hydroxyethyl group on the amide nitrogen is needed for

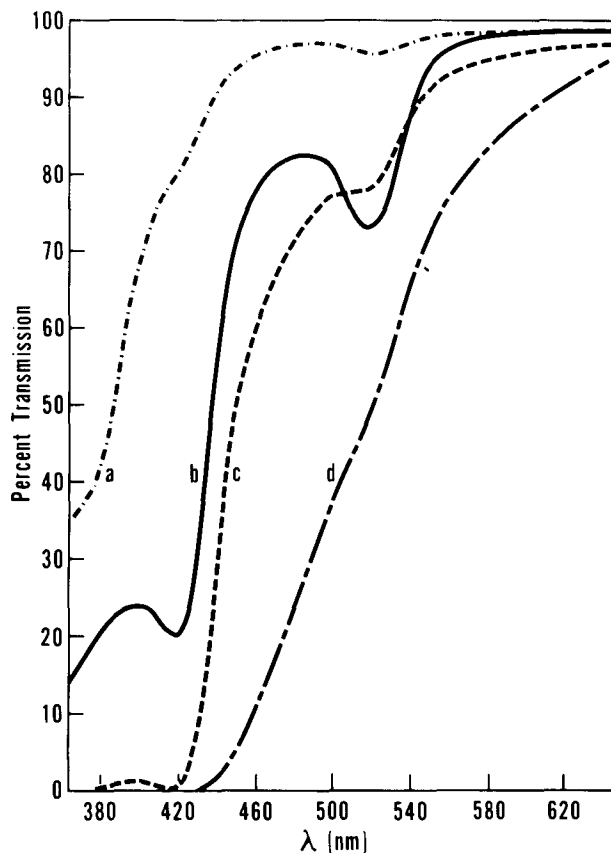


FIG. 1. Visible absorption spectra of colored *N,N*-bis(2-hydroxyethyl) linseed amide. Sample age: curve a—1 week, b—3 months, c—1 year, d—>1 year. Concentration: 25 g/liter in methanol, 1 cm cell.

color formation reactions.

Visible absorption spectra of HELA as it darkens and discolors are shown in Figure 1. Peaks were observed at 419 and 519 nm, and these bands were also characteristic of other copper-containing oxidized colored polyunsaturated fatty diethanolamides, i.e., linolenate and tung. These bands at 419 and 519 nm appear in 1-week old HELA samples (curve a), become very pronounced at 3 months (curve b), on aging and further oxidation appear as shoulders (curve c), and finally disappear as the sample shows a broad general curve, shifted to longer wavelengths (curve d).

Ethylenediamine tetraacetic acid (EDTA), a chelating

TABLE V

Coloration of Alkyl *N,N*-bis(2-hydroxyethyl)amides by Copper

Example	<i>N,N</i> -bis(2-hydroxyethyl) amide RCON(CH ₂ CH ₂ OH) ₂	Gardner color		
		Initial	Heated with copper ^a (ppm)	
			0.5-1.0	25
H	Stearic	White solid	1	1
I	Oleic	1	2	3
J	Castor	6	5	6
K	Hydrogenated linseed	5	6	7
L	Soy	6	7	12
M	<i>z,z</i> -9,11-octadecadienoic	Tan solid	6	13
N	Linoleic	4	7	13
O	Linolenic	5	14	18
P	Tung	8	17	17
Q	Linseed	9	13	15
R	Linseed ^b	6	-	17

^aHeated 3 hr at 100 C in air.

^bPurified by molecular distillation.

agent incorporated either during preparation or before storage, met with limited success in preventing coloration, probably due to its extreme insolubility. EDTA inhibits color formation briefly, but on long-term storage (2 years) Gardner colors were 17. Metal deactivation experiments with citric acid had little or no effect either.

According to the patent literature (7-9), alkali metal borohydrides have been used to stabilize amines and nitrogen-containing compounds or to reduce color. Industrial applications include addition of potassium borohydride directly to the process stream or to storage tanks to remove carbonyl, peroxides, and other reducible impurities. Merck Index states it is a scavenger for traces of aldehydes, ketones, and peroxides in organic chemicals. Color in HELA has been stabilized by adding 1% potassium borohydride to freshly prepared samples (Table VI). In light of the structural requirements needed for color formation, we feel that potassium borohydride acts as a reducing agent for aldehydes, ketones, and peroxides already present in HELA and that it prevents further oxidation of the polyunsaturated fatty acyl group. When these oxidative products are reduced or their formation is retarded as with the antioxidants, no colored compounds can be formed.

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TABLE VI

Color Stabilization of *N,N*-bis(2-hydroxyethyl) Linseed Amide with Potassium Borohydride

Oil color	Borohydride level (% by wt)	Gardner color	
		Initial	Storage 1 month
6	0.1	10	14
6	0.5	10	11-12
6	1.0	10	7
1	0.1	5	14-15
1	0.5	5	8
1	1.0	5	6

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