Color Development in C\textsubscript{18} Unsaturated Hydroxyamides\textsuperscript{1}

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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 polysaturated \(N,N\)-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 rosly 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).

\textsuperscript{1}Presented at the AOCS meeting, Dallas, April 1975.

EXPERIMENTAL PROCEDURES

Stearic, oleic, linoleic, linolenic, and \(\text{trans,trans-9,11-octadecadienoic}\) \(N,N\)-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 CuCl\(_2\cdot2H_2O\) or Cu(NO\(_3\))\(_2\cdot3H_2O\)], iron (as FeCl\(_3\cdot6H_2O\)), aluminum (as AlCl\(_3\)), sodium (as NaCl), zinc (as ZnCl\(_2\)), chromium (as CrO\(_3\)), and manganese or cobalt (as napthenates) 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-

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|c|}
\hline
\textbf{Alkyl group} & \textbf{C\textsubscript{14}} & \textbf{C\textsubscript{16}} & \textbf{C\textsubscript{18\textsuperscript{0}}} & \textbf{C\textsubscript{18\textsuperscript{1}}} & \textbf{C\textsubscript{18\textsuperscript{2}}} & \textbf{C\textsubscript{18\textsuperscript{3}}} \\
\hline
\textit{Stearate} & 2.6 & 1.8 & 95.5 & - & - & - \\
\textit{Oleate} & Trace & Trace & 99.9 & - & - & - \\
\textit{Linoleate} & Trace & - & 99+ & - & - & - \\
\textit{Linolenate} & - & - & 99+ & - & - & - \\
\textit{t,\textit{\textit{\textsuperscript{9,11-Octadecadienoate}}} } & - & - & 99+ & - & - & - \\
\hline
\textit{Castor\textsuperscript{a}} & 1.0 & 1.0 & 89.5 & 4.2 & 0.3 & - \\
\textit{Soy} & 1.0 & 4.2 & 24.3 & 52.6 & 8.9 & - \\
\textit{Hydrogenated linseed} & 6.0 & 4.8 & 55.6 & 33.2 & 0.4 & - \\
\textit{Linseed} & 5.6 & 2.8 & 19.8 & 13.8 & 58.0 & - \\
\textit{Tung\textsuperscript{b}} & 5.6 & 6.9 & 8.10 & 76.82 & - & - \\
\hline
\end{tabular}
\caption{Gas-Liquid Chromatographic Composition of Methyl Esters}
\end{table}

\textsuperscript{a}See ref. 10.

\textsuperscript{b}See ref. 11.
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 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 (Gardner color >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 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 II

<table>
<thead>
<tr>
<th>Example</th>
<th>Oil color</th>
<th>Reaction temperature (C)</th>
<th>Wash (1% HCl)</th>
<th>Gardner color</th>
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<tbody>
<tr>
<td>A</td>
<td>6</td>
<td>110</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>RT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+</td>
<td>9</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>110</td>
<td>+</td>
<td>10</td>
</tr>
<tr>
<td>D</td>
<td>6</td>
<td>130</td>
<td>+</td>
<td>15</td>
</tr>
<tr>
<td>E</td>
<td>6</td>
<td>165</td>
<td>+</td>
<td>11</td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>110</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>G</td>
<td>1</td>
<td>110</td>
<td>+</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup>Room temperature.

### Table III

<table>
<thead>
<tr>
<th>Antioxidant and level&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Reaction temperature (C)</th>
<th>Gardner color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>8 Months</td>
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<tr>
<td>None</td>
<td>RT&lt;sup&gt;a&lt;/sup&gt;</td>
<td>9</td>
</tr>
<tr>
<td>1% BHA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>RT</td>
<td>11</td>
</tr>
<tr>
<td>1% BHT&lt;sup&gt;b&lt;/sup&gt;</td>
<td>RT</td>
<td>8</td>
</tr>
<tr>
<td>1% BHA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>130</td>
<td>9</td>
</tr>
<tr>
<td>0.5% BHA&lt;sup&gt;c&lt;/sup&gt;</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>0.5% BHT&lt;sup&gt;c&lt;/sup&gt;</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>0.5% Propyl gallate&lt;sup&gt;c&lt;/sup&gt;</td>
<td>110</td>
<td>15</td>
</tr>
<tr>
<td>0.5% Hydroquinone&lt;sup&gt;c&lt;/sup&gt;</td>
<td>110</td>
<td>15</td>
</tr>
</tbody>
</table>

<sup>a</sup>% by wt. BHA = butylated hydroxyanisole, BHT = butylated hydroxytoluene, RT = room temperature.

<sup>b</sup>Prepared in presence of antioxidant.

<sup>c</sup>Stored with antioxidant at 25 C.