Fatty Acid Morpholides as Plasticizers for Vinyl Chloride Resins. III. Ternary Compatibility-Composition Diagrams for the Oleic-Linoleic-Stearic and Oleic-Linoleic-Palmitic Systems

FRANK C. MAGNE, ROBERT R. MOD, and EVALD L. SKAU, Southern Regional Research Laboratory, New Orleans, Louisiana

A systematic investigation has been made of the effect of fatty acid composition on the compatibility of the corresponding mixed morpholides as plasticizers for vinyl chloride-vinyl acetate copolymer resins. Plasticizer evaluation data were obtained for the morpholides of lauric, palmitic, elaidic, and epoxyoleic acids and compared with the literature values for other fatty acid morpholides and morpholide mixtures.

Ternary compatibility-composition diagrams have been constructed for the oleic-linoleic-stearic and the oleic-linoleic-palmitic morpholide systems. These diagrams make it possible to predict what adjustment, if any, must be made in the composition of any mixture of these fatty acids so that the corresponding morpholide mixture will be compatible. The diagrams will be useful in selecting the most appropriate and economical fatty acid sources from which to make compatible morpholide mixtures.

The morpholide of oleic acid is a good primary plasticizer for vinyl chloride-vinyl acetate copolymer resins (1). The morpholides of stearic and palmitic acids and of the mixed fatty acids from cottonseed oil, though otherwise satisfactory, proved to be incompatible. Preliminary tests with binary and ternary mixtures of oleylmorpholine (OM), with linoleylmorpholine (LM), and stearoylmorpholine (SM), and with LM and palmitoleylmorpholine (PM) revealed that much larger proportions of PM than of SM can be present in such mixtures without causing incompatibility. The present communication deals with the construction of the ternary compatibility-composition diagrams for the systems OM-LM-SM and OM-LM-PM, and with the plasticizer evaluation of a number of long-chain fatty acid morpholides and morpholide mixtures.

Materials and Procedures

Commercial fatty acids of known purity and composition were used. The lauric, palmitic, and stearic acids, 93 to 96% purity, were Armour Neofats Nos. 12, 16, and 18, respectively. The oleic and linoleic acids were obtained from Emery Industries; the former, 233 LL Elaine, was 93% pure, and the latter, Emersol 305, contained 41% of oleic and 6% of stearic acid. The approximate composition of "animal-type acids," Armour Neofat No. 47, was 10% myristic, 43% palmitic, 9% stearic, 30% oleic, and 8% linoleic acids, and that of the "animal acids," Neofat No. 65, was 2% myristic, 26% palmitic, 16% stearic, 48% oleic, and 8% linoleic acids. Elaidic acid was prepared by elaidinization of the oleic acid, followed by two solvent crystallizations.

The procedure for preparing the acid-free morpholides is described elsewhere (2). The "morpholide of epoxyoleic acid" (exirane oxygen, 4.71%) was prepared by epoxidation of the morpholide of a 93%-pure linoleic acid. The epoxidation of the morpholide of cottonseed fatty acids was approximately sufficient to convert all of the linoleic to epoxyoleic acyls.

The various morpholides and morpholide mixtures were screened as plasticizers for 95% poly(vinyl chloride)-5% poly(vinyl acetate) copolymer (Vinylite VYDR) in the following compounding formulation: Vinylite VYDR, 63.5%; plasticizer, 35.0%; stearic acid, 0.5%; basic lead carbonate, 1.0%. This formulation was milled, molded, and tested as previously described (1, 3). Compositions which showed evidence of exudation or smearing during a shelf-life of 90 days were rated as incompatible. The mixtures used for constructing the ternary diagram were tested only for compatibility since the other plasticizing characteristics can be roughly predicted from the complete evaluation data for the individual components and specific mixtures.

Thermal stabilities were established in terms of the relative reflectances of the compositions (10-12 mil sheets) after subjection to increasing exposure periods in a forced draft oven maintained at 176°C. These
values were determined by means of a "Hunter
Multipurpose Reflectometer," using the amber 45°,
6° directional reflectance.

**Results**

Ternary compatibility-composition diagrams were
constructed for the systems OM-LM-SM and OM-LM-
PM. Various binary and ternary compositions were
prepared by mixing stock samples of OM, LM, SM,
and PM, taking into account the known proportion
of saturated, monounsaturated, and diunsaturated
morpholides present as impurities in each stock sam-
ple. The small amounts of saturated morpholides in
the OM and LM were considered to be wholly SM
or PM, depending upon the ternary system involved.
Molded vinyl panels plasticized with the various bi-
ary and ternary mixtures were prepared and observed
at regular intervals to detect the first signs of incompatibility.

The results of these tests are shown in Figures 1
and 2. The compositions represented by open circles
were compatible, and those represented by the black
circles showed signs of incompatibility within 30 days
or less. The dotted curved line indicates the approxi-
mate boundary between the compatible and incom-
patible compositions.

Table I summarizes the more complete plasticizer
evaluation results obtained for the morpholides of
various fatty acids and fatty acid mixtures.

**Discussion**

Though SM and PM are both incompatible (Table
I, Samples 2 and 3), much larger proportions of
PM than of SM can be present in binary mixtures
with OM or in ternary mixtures with OM and LM
without causing incompatibility (Figures 1 and 2).
For example, binary mixtures of OM and SM are
incompatible when SM exceeds about 18% while
almost 70% of PM can be tolerated in an OM-PM
mixture. The presence of more than 10–12% of LM
in either a binary OM-LM mixture or a ternary OM-
LM-SM mixture results in incompatibility. In the
OM-LM-PM system, on the other hand, larger per-
centages of LM can be tolerated, depending upon the
proportion of PM present. For example, as shown by
the dotted curve in Figure 2, a 40% OM-25% LM-
35% PM mixture would be compatible.

These ternary diagrams make it possible to predict
what adjustment, if any, must be made in the compo-
sition of any mixture of these fatty acids so that the
corresponding morpholide mixture will be compatible.

The fatty acid mixture obtained from cottonseed oil
consists almost entirely of oleic, linoleic, and palmitic
acids; therefore the morpholide mixture obtained from
cottonseed acids can be considered as belonging to
the OM-LM-PM system. The composition of a typical
morpholide mixture made from cottonseed fatty acids
can be represented by point a in the incompatible
region of Figure 2.

As previously reported (1,4), a compatible mor-
pholide mixture can be prepared from cottonseed or pean-
ut oil fatty acids by removing the saturated acids
and converting the polyunsaturated to monounsatu-
rated acyls by selective hydrogenation. This is con-
sistent with Figures 1 and 2. Removal of the satu-
rated fraction and subsequent conversion of the LM
to the morpholide of epoxystearic acid by epoxidation
also resulted in a compatible mixture (1). This like-
wise would be expected from the diagrams since the
morpholide of linoleic acid is compatible when epoxi-
dized to this extent (Table I, Sample 7). Either of
these procedures would obviously have been effective
even if the saturated acid involved had been stearic
or a longer-chain acid.

For cottonseed fatty acids the removal of the satu-
rated fatty acids in the above procedures can be
omitted. A completely compatible morpholide mixture
should be obtainable by merely reducing the poly-
unsaturation to less than about 20%, i.e., by chang-
ing the composition along ab (Figure 2). This has
been confirmed (2) by plasticizer evaluation tests on
the morpholide mixture, roughly of composition b,
prepared directly from the fatty acids of selectively
hydrogenated cottonseed oil (Table I, Sample 9) and
on the morpholide of cottonseed fatty acids epoxi-
dized to an oxirane oxygen content corresponding to
the conversion of most of the LM to epoxystearicmor-
pholine (Sample 11). Compatibility could obviously
have been attained with a lesser degree of hydro-
genation or epoxidation.

An incompatible morpholide mixture can be made
compatible by mixing it with a highly compatible
morpholide mixture. For example, the morpholide
of hydrogenated cottonseed acids (Sample 9, represen-
ted by point b, Figure 2) can be effectively employed,
in predictable proportions, with the incompatible mor-
pholide of cottonseed acids (Sample 8, point a) to
produce a compatible blend, as illustrated by Sample
10, point c. Similarly blends of Sample 8 with the

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**TABLE I**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Morpholide of</th>
<th>Tensile strength</th>
<th>100% Modulus</th>
<th>Elongation</th>
<th>Brittle point</th>
<th>Volatility loss</th>
<th>Compatibility</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Linoleic acid</td>
<td>p.s.i.</td>
<td>42.5</td>
<td>19.7</td>
<td>350</td>
<td>45</td>
<td>C</td>
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<td>2</td>
<td>Palmitic acid</td>
<td>2530</td>
<td>12.0</td>
<td>28.0</td>
<td>19.5</td>
<td>45</td>
<td>C</td>
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<tr>
<td>3</td>
<td>Stearic acid</td>
<td>3750</td>
<td>17.8</td>
<td>52.0</td>
<td>21.0</td>
<td>31.0</td>
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</tr>
<tr>
<td>4</td>
<td>Oleic acid</td>
<td>2600</td>
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<td>13.0</td>
<td>13.0</td>
<td>42</td>
<td>C</td>
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<tr>
<td>5</td>
<td>Elaidic acid</td>
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<tr>
<td>6</td>
<td>Linoleic acid</td>
<td>2860</td>
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<td>30.0</td>
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<td>6.8</td>
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</tr>
<tr>
<td>7</td>
<td>Epoxystearic acid</td>
<td>3030</td>
<td>12.0</td>
<td>30.0</td>
<td>16.0</td>
<td>6.8</td>
<td>C</td>
</tr>
<tr>
<td>8</td>
<td>C16:C18 acids</td>
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<td>33.0</td>
<td>45</td>
<td>1.26</td>
<td>C</td>
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<td>9</td>
<td>Hydrogenated cottonseed acids</td>
<td>2940</td>
<td>13.0</td>
<td>36.0</td>
<td>40</td>
<td>1.24</td>
<td>C</td>
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<td>10</td>
<td>30% Sample 8 + 70% Sample 9</td>
<td>2940</td>
<td>13.0</td>
<td>36.0</td>
<td>40</td>
<td>1.23</td>
<td>C</td>
</tr>
<tr>
<td>11</td>
<td>Epoxystearic cottonseed acids</td>
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<td>12.0</td>
<td>40.0</td>
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<td>0.83</td>
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<td>&quot;Animal type&quot; acids</td>
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<td>39.0</td>
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<td>C</td>
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<tr>
<td>13</td>
<td>&quot;Animal&quot; acids</td>
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<td>13.0</td>
<td>39.0</td>
<td>30</td>
<td>0.84</td>
<td>C</td>
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<td>14</td>
<td>DOP (control)</td>
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<td>35.0</td>
<td>45</td>
<td>1.99</td>
<td>C</td>
</tr>
</tbody>
</table>

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* Reference (1).
* Sampleomerized without rupture beyond range of IP-4 tester.
* Selectively hydrogenated to convert all polyunsaturated to monounsaturated acyls (2).
* Epoxidized sufficiently to convert all LM to epoxystearic morpholine (2).
* C = compatible, I = incompatible.