APPENDIX - II

Experimental Conditions for Preparing Partial Hydroxy Ester of Linseed Oil and Calculations of Hydroxy Number:

Experimental conditions:

Saponification value of linseed oil = 195

Molecular weight of linseed oil = \( \frac{56100}{195} \times 3 = 863 \)

Molar ratio of linseed oil to glycerol used for alcoholysis = 1:3

Actual weight of oil taken = 46.74 g.

Glycerol taken = 15.00 g.

Catalyst (NaOH) taken = 0.185 g.

Reaction temperature = 220 - 230°C

Reaction period = 6 hours.

Experimentally determined hydroxy number of the product = 365.2 and acid number = 2.2

Corrected hydroxy number (exptl.) = 367.4

Calculations of hydroxy number:

Molecular weight of linseed oil = 863

Av. mol. wt. for each ester group in the oil molecule = \( \frac{863-41}{3} = 27 \)

Therefore, the characteristic values of the different components of the mixed ester can be calculated as:

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular weight</th>
<th>Hydroxy number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglyceride (TGL)</td>
<td>863</td>
<td>-</td>
</tr>
<tr>
<td>Diglyceride (DGL) (863-27x17)</td>
<td>606 (( \frac{12}{606} \times 56100 \times 17 ))</td>
<td>92.57</td>
</tr>
<tr>
<td>Monoglyceride (MGL)</td>
<td>349</td>
<td>321.49</td>
</tr>
<tr>
<td>Glycerol (GL)</td>
<td>92</td>
<td>1829.35</td>
</tr>
</tbody>
</table>
Reaction started with:

- Linseed oil = 46.74 g. = 0.0542 mole
- Glycerol = 15.06 g. = 0.1635 mole
- Total weight = 61.78 g.

According to Bianchini's method of statistical distributions (187), the mole fraction of any component in the mixed ester is given by the expression,

\[ Y_{a_1} = f_p \left( \frac{a}{a_1} \right)^{a_1} \left( 1 - \frac{a}{a_1} \right)^{f_p - a_1} \]

where

- \( Y_{a_1} \) = Molar fraction of the individual components in the product.
- \( f_p \) = Number of possible combinations.
- \( \bar{a} \) = Average number of ester groups for each polyol molecule.
- \( a_1 \) = Number of ester groups in the actual product.

Thus,

\[ \bar{a} = \frac{3 \times 0.0542}{0.0542 + 0.1635} = 0.7469 \]
\[ f_p = 3 \]

The mole fractions of different components are then calculated as,

- \( Y_0 \) (for TGL) = \( \frac{3}{3} \) \( \left( \frac{0.7462}{3} \right)^3 \left( 1 - \frac{0.7462}{3} \right)^{(3-3)} \) = 0.0154
- \( Y_1 \) (for DGL) = \( \frac{3}{3} \) \( \left( \frac{0.7462}{3} \right)^2 \left( 1 - \frac{0.7462}{3} \right)^{(3-2)} \) = 0.1397
- \( Y_2 \) (for MGL) = \( \frac{3}{3} \) \( \left( \frac{0.7462}{3} \right)^1 \left( 1 - \frac{0.7462}{3} \right)^{(3-1)} \) = 0.4213
and, 

$$J_3(\text{for GL}) = 3c_o \left( \frac{0.7462}{3} \right)^0 \cdot (1 - \frac{0.7462}{3})(3 - 0) = 0.4236$$

Preliminary mass calculations on the basis of different mole fractions have been shown in table II-1.

<table>
<thead>
<tr>
<th>Component</th>
<th>Mole fraction</th>
<th>Mol.wt.</th>
<th>Wt.,g.</th>
<th>Wt. fraction based on 61.78 g of product mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGL</td>
<td>0.0154</td>
<td>863</td>
<td>13.290</td>
<td>$\frac{(13.29 \times 61.78)}{283.953} = 2.892$</td>
</tr>
<tr>
<td>DGL</td>
<td>0.1397</td>
<td>606</td>
<td>84.658</td>
<td>18.419</td>
</tr>
<tr>
<td>MGL</td>
<td>0.4213</td>
<td>92</td>
<td>38.971</td>
<td>31.99</td>
</tr>
<tr>
<td>GL</td>
<td>0.4236</td>
<td>92</td>
<td>38.971</td>
<td>31.99</td>
</tr>
</tbody>
</table>

Weight of glycerol removed after settling $= 3.55$g.
Wt. of mixture left $= 61.78 - 3.55 = 58.23$g. and
wt. of glycerol left behind $= 8.479 - 3.55 = 4.929$g.
The corrected composition of the mixed ester (Wt. %) can then be calculated as in table II-2.

<table>
<thead>
<tr>
<th>Component</th>
<th>Corrected Wt.,g.</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGL</td>
<td>2.892</td>
<td>4.967</td>
</tr>
<tr>
<td>DGL</td>
<td>18.419</td>
<td>31.631</td>
</tr>
<tr>
<td>MGL</td>
<td>31.99</td>
<td>54.940</td>
</tr>
<tr>
<td>GL</td>
<td>4.929</td>
<td>8.465</td>
</tr>
</tbody>
</table>

The theoretical hydroxyl number of the mixed esters is thus given by:

$$(0 \times 0.0496) + (92.57 \times 0.3163) + (321.49 \times 0.5494) + (1829.35 \times 0.08465)$$

$= 29.28 + 29.57 + 154.85 = 360.76$$