2.1 INTRODUCTION

Ricinoleic acid [R-(2) -12, hydroxy-9-octadecinoic acid, “d-12 hydroxy oleic acid] C_{18}H_{34}O_3” molecular weight 298.45 with an elemental, analysis carbon 72.43%, hydrogen 11.48%, oxygen 16.08% \( CH_3(CH_2)_5.CH(OH)(CH_2) \rightarrow CH = CH \quad (CH_2)_7 \rightarrow COOH \) found primarily in oils from the seeds of ricinus, Euphorbiaceae, accounts for about 90% of the triglycerides fatty acid of castor oil and up to about 40% of the glyceride fatty acid of the oil. Ricinoleic acid a major constituent of castor oil fatty acid, due to its multifunctional nature offers many possibilities for its conversion into various compounds having ample potential for use as plasticizers for polymeric materials. Modern plasticizers technology, although, rooted in the art of primitive people in their search for materials based on natural products, is now based on a broad spectrum of scientific principle utilizing a vast array or synthetic and natural occurring compound\(^1\). Castor oil was patented for commercial significant plasticizer used in 1856. In 1870 camphor became the plasticizer of choice for cellulose nitrate.
The conversion of castor oil into the proposed ricinoleate plasticizers involves three major steps.

(i) Preparation of alkyl ester of ricinoleic acid from castor oil.

(ii) Introduction of another ester group in the molecular structure of alkyl ester by esterification of the (–OH group) at 12\textsuperscript{th} C-position with halo acetic acid to prepare alkyl halo acetyl ricinoleates.

(iii) Elimination of unsaturation from alkyl halo acetyl ricinoleates subjecting to epoxidation of the double bond present between 9\textsuperscript{th}-10\textsuperscript{th} C-position in their molecular structure.

It was proposed to prepare both methyl and ethyl esters of ricinoleic acid, carrying out their esterification with choroacetic acid, bromoacetic acid and evaluate them as plasticizers for poly (vinyl chloride). It was also proposed to epoxidise the above prepared double ester of ricinoleic acid and to evaluate their performance as plasticizer for PVC, their effect on compatibility instability and heat stability of vinyl composition.

The authors, to achieve the goal of the present studied carried out the preparation of ricinoleate plasticizers for the sake of simplicity and easy reference in the further discussions, they are divided into chloro and bromo series.
1. Chloro series:

   (i) Methyl chloroacetyl ricinoleate.
   (ii) Ethyl chloroacetyl ricinoleate.
   (iv) Methyl chloroacetyl epoxy ricinoleate.
   (v) Ethyl chloroacetyl epoxy ricinoleate.

2. Bromo series:

   (i) Methyl bromoacetyl ricinoleate.
   (ii) Ethyl bromoacetyl ricinoleate.
   (iii) Methyl bromoacetyl epoxy ricinoleate.
   (iv) Ethyl bromoacetyl epoxy ricinoleate.

2.2 ALKYL RICINOLEATES FROM CASTOR OIL

From the survey of the literature; it is revealed that the most economical viable technique of alkyl ricinoleates is through inter-esterification, referred to alcoholysis of castor oil. Alcoholysis is very important commercially as it offers a convenient route to alkyl esters of alcohols other than glycerole and completely eliminates splitting of the fat and re-esterifying with the particular alcohol.

Alcoholysis of the fats with alcohols of low molecular weight such as methanol or ethanol can be catalyzed by acid or alkaline but it is
observed that the alkyl catalyzed reaction is generally superior in speed and completeness and can be effected at relatively low temperatures. Methanolation or ethanolation can be readily accomplished at large scale by the method described by Bradshaw and Meuly\(^2\). Considering castor oil to be a triglyceride of ricinoleic acid, its methanolation in general can be described as:

\[
\begin{align*}
\text{CH}_2\text{OCOR} & \quad \text{CH}_2\text{OH} \\
\text{CHOCOR} + 3\text{CH}_3\text{O}_4 & \xrightarrow{\text{Catalyst}} \text{CHOH} + 3\text{RCOOCCH}_3 \\
\text{CH}_2\text{OCOR} & \quad \text{CH}_2\text{OH} \quad \text{methyl}
\end{align*}
\]

Ricinoleic acid triglyceride    glycerol    ricinoleates

where \( R = \text{CH}_3.(\text{CH}_2)_5 \) \( \text{CH} \) \( \text{CH}_2\text{CH} = \text{CH}_3.(\text{CH}_2)_7 \) \( \text{OH} \)

The fat is heated to about 80\(^{\circ}\)C and to it is added commercial anhydrous methanol (99.5%). In which is dissolved 0.1-0.5% sodium or potassium hydroxide. The recommended quantity of alcohol is about 1.2 to 1.6 times of the theoretically required for the reaction. Use of more than 1.75 times the theoretical amount does not accelerate the reaction and interferes with the subsequent gravity separation of glycerol. After the addition of alcohol, the mixture is stirred for few minutes and allowed to stand, glycerol being virtually dry and heavier immediately settles to the
bottom of the separator. Conversion is usually 98% complete after half an hour. The upper layer contains the alkyl esters, most of the unreacted alcohol, alkali, some glycerole and small amount of soaps. The estes are freed from impurities following successive washing with small amounts of warm water.

Wright et. al.\textsuperscript{3} have strictly recommended using almost neutral fat and an hydrous reaction medium failing which may lead to loss of alkanity and retards glycerole separation due to gel formation.

Ethanolysis is a bit difficult a free acid content of oil exceed about 0.5% and the presence of as little as 0.3% moisture in the reaction mixture appreciably lowers the yield of glycerole. It is observed that water tolerance can be increased to about 0.7% if amount of catalyst is doubled and that is made 40 times.

The time required for glycerole separation controls the rate of the overall reaction. This was evident from the observation of Wright et. al.\textsuperscript{3} that centrifugation of the reaction products at 65\textdegree C which took only 5 minutes, gave a fairly good yield about 85% of the theoretical calculation. Bradshaw and Meuly\textsuperscript{2} claim less alcohol is required if addition of alcohol and glycerole separation are incremental. This is not true for ethanolysis where this technique caused gel formation.
2.3 ESTERIFICATION OF HYDROXY FATTY ACID ESTER

Esters are usually prepared by the method described by Morrison and Boyd that is by the reaction of alcohols with carboxylic acids, acid chlorides and acid anhydrides. Alcohols are directly converted into esters when heated with carboxylic acid in presence of little mineral acid such as sulphuric acid or dryhydrogen chloride.

\[ 
\begin{align*}
\text{ROH} + R_1\text{COOH} \rightleftharpoons & R_1\text{COOR} + \text{H}_2\text{O} \\
\text{Alcohol} & \quad \text{acid} \quad \text{ester} \\
\end{align*} 
\]

The reaction is reversible and often reaches in equilibrium at uneconomical level of conversion.

High yields of ester can be attained by acylation of alcohols with carboxylic acid halides.

\[ 
\begin{align*}
R_1\text{-COCl} + \text{ROH} \xrightarrow{\text{Pyridine}} & R_1\text{COOR} + \text{HCl} \\
\text{acid chloride} & \quad \text{alcohol} \quad \text{ester} \quad \text{hydrogen chloride} \\
\end{align*} 
\]

The reaction is irreversible and ensures high yields. The method is particularly suitable for esterification of tertiary alcohols and phenols. All types of alcohols or phenols can be acylated with acid anhydride.

\[ 
\begin{align*}
(R\text{CO})_2 + R_1\text{OH} \xrightarrow{\text{Catalyst}} & R\text{COOR}_1 + \text{ROOH} \\
\text{acid anhydride} & \quad \text{alcohol} \quad \text{ester} \quad \text{acid} \\
\end{align*} 
\]
The advantage of anhydride esterification is that no water of reaction is formed and the reaction can be catalyzed by para toluene sulphonic acid, dry HCl, lewis acid i.e., zinc chloride. The beauty of the catalyst system is that ester produced have almost no colour and do not need purification by distillation. These are especially suitable for production of plasticizers.

2.4 EPOXIDATION OF UNSATURATED FATTY ACID ESTERS

Epoxy plasticizers are produced by adding oxygen across the double bond linkage present in unsaturated fat or unsaturated fatty acid esters. In synthetic chemistry the process is commonly referred to as epoxidation and is generally affected by oxidation of double bond by hydrogen peroxide. In presence of formic acid and acetic acid the per acid form during the reaction infect function as oxidizing agent. The scheme may be represented as follows:

\[
\text{CH}_3\text{COOH} + H_2O_2 \xrightarrow{\text{acid catalyst}} \text{CH}_3\text{C}^=\text{OOH} + H_2O
\]

\[
-\text{CH} \equiv \text{CH} + \text{CH}_3\text{C}^=\text{OOH} \rightarrow \text{CH} - \text{CH} - + \text{CH}_3\text{COOH}
\]
It is observe that the epoxidation of unsaturated ester takes place in the oil phase while in contact with the aqueous phase.

From the survey of the existency literature it is revel that several methods\(^5\) are used commercially for the manufacture of epoxidised oils. Preformed per acetic acid process\(^6\) is although useful for laboratory preparations, has never been a commercially significant process. In the in-situ process, hydrogen per oxide, acetic acid and sulphuric acid as catalyst are added to the oil/fatty acid ester in a stirred reactor. When formic acid is used, addition of mineral acid is not required\(^7\).

The epoxidation of high molecular weight olefins (C\(_8\) to C\(_{18}\)) with per acetic acid solution is accompanied by appreciable quantities of hydroxy-acetoxy compound arising from the reaction of the solvent with the epoxide ring\(^8\). Similar treatment with high molecular weight unsaturated acid esters has been more successful\(^9\). Ricinoleic acid is reported difficult to be epoxidised in high yield. Use of solid polystyrene sulphonic acid ion exchange resin catalysts has been reported to effect less ring cleavage and higher conversion\(^{10-11}\).

**Bhatnagar and Jain\(^{12}\)** disclosed that epoxidation of acetylated castor oil or acetylated ricinoleates could be satisfactorily carried out at relatively milder temperature condition by using 32-35% hydrogen
peroxide instead of prevalent 50% concentration. The workers also reported that conventional epoxidation catalyst like Zeocarb-225 and Dowex-50X (trade names) had limited efficiency in the presence of 30% hydrogen peroxide. They evaluated 10 different chemicals for their catalytic efficiency and observe that sodium hydrogen phosphate to be the more efficient catalyst. Optimum reaction condition has been reported\textsuperscript{13}.

**2.5 EXPERIMENTAL**

The authors, in order to achieve the required goal to synthesis the desired plasticizers, experimental process has been divided in four parts:

(i) Proper selection of castor oil.

(ii) Inter esterification, alcoholysis of castor oil with alcohols to produce alkyl ricinoleates.

(iii) Esterification of alkyl ricinoleates with halo acetic acid to produce alkyl halo acetyl ricinoleate.

(iv) Epoxidation of alkyl halo acetyl ricinoleates to produce alkyl halo acetyl epoxy ricinoleates.

**2.6 SELECTION OF THE CASTOR OIL**

Castor oil is the main raw material for the production of proposed plasticizer. Its ricinoleic acid content is found to vary with the place of its origin. Since the present investigation is related to the production of the
plasticizers so the content of ricinoleic acid has a great significance. Besides, the acid value and moisture content of the fat also form important criteria for the selection of the right quality of castor oil. The colour of the raw materials is also reflected in the products, care is to be taken to use the raw material of a fade colour.

Considering, all the aspect of the selection of castor oil the authors have procured four sample of refined grade castor oil from different sources and analyzed for their ricinoleic acid content, acid value, moisture content and colour index. The samples were procured from Delhi and Bombay market. Verse

(i) M/s Pioneer Chemicals, Tilak Bazar, Delhi.
(ii) M/s Ganga Ram and Son’s (whole-sale delars of Non-edibles Oil), New Delhi.
(iii) M/s Jayant Oil Miles,, Bombay.
(iv) M/s Tata Oil Miles Co., Bombay.

27. DETERMINATION OF RICINOLEIC ACID CONTENT

Gas chromatography method is most reliable and widely used for the determination of amount present in the fats and oils. Due to their low volatility and high polarity, “[α]D 26 + 7.15”, free fatty acid are usually not analyzed directly but first converted to their methyl ester. It is not
necessary to hydrolyse the fat-1, because the fatty acid methyl ester can be directly prepared from the glycerides by alcoholsysis\textsuperscript{2-3}.

2.8 PREPARATION OF METHYL ESTER

Castor oil was converted to the methyl ester of its constituent fatty acid by using standard analytical procedure\textsuperscript{14}. This method employs alkaline catalyst and ensures almost complete conversion and is suitable for glycerides containing fatty acids with hydroxyl groups. 40 gms of sodium metal were cut to small pieces and carefully dissolved in one liter anhydrous methanol. 50 ml of this sodium methoxide solution was then taken in 250 ml round bottom flask containing about 2 gms of the oil sample. The contents of the flask were then refluxed for 2-hours, cooled and made slightly acidic by drop wise addition of glacial acetic acid. The contents were diluted with 100 ml water and extracted thrice with 30 ml portions of ethyl ether in a separating funnel. The ether extract was dried over anhydrous sodium sulphate. Methyl esters were recovered by evaporating the ether extract over a steam bath under a moderate steam of nitrogen.

9. GLC OF METHYL ESTER

The mixture of methyl ester of castors oil fatty acid was subject to GLC under the following condition:
**Gas chromatography:** Varian model 3700

**Coloumn:** 1, 4-butane diol succinate (liquid phase)

**Detector:** Flame ionization detector (FID)

**Carrier gas:** Nitrogen.

**Flow rate of Carrier gas:** 30 – 40 mL/min.

**Temperature:** 210°C (Isothermal)

**Chart Speed:** 0.5 cm/min.

**Attention:** 1

**Sample size:** 1 μL

**Solution medium:** CS₂

### 2.10 INTERPETATION OF CHROMATOGRAM

The authors have interpreted the gas chromatogram obtained by plotting a curve between retention time in minutes on the axis of X and detector response on the axis of Y at a isothermal temperature maintained at about 210°C. The peak corresponding to methyl ricinoleates was identified by simultaneously running a standard solution of methyl ricinoleate under identical condition. **Fig. – 1** shows the chromatogram obtained with the standard methyl ricinoleate solution. As the condition reported here for the analysis, methyl ricinoleate was found to emerge at a retention time of 30.4 minutes. The area counts under this peak for all the
sample of castor oil was read from the chromatogram and used for the
determination of ricinoleic acid content of the castor oil fatty acid.

2.11 CALCULATION OF RICINOLEIC ACID CONTENT

The ricinoleic acid contents were calculated by gas chromatography
of various castor oil samples under evaluation. The percent of methyl
ricinoleate was calculated using the standard equation viz.

\[
\% \text{ methyl ricinoleate} = \frac{A_{CO}}{A_{MR}} \times \frac{C_{MR}}{C_{CO}} \times P_{MR}
\]

via \( A_{CO} \) = Area counts under methyl ricinoleates peak in
chromatogram of castor oil fatty acid methyl ester
mixture.

\( A_{MR} \) = Area counts under methyl ricinoleate peak in
chromatogram of standard methyl ricinoleate solution.

\( C_{CO} \) = Solution concentration of castor oil fatty acid methyl ester
mixture.

\( C_{MR} \) = Solution concentration of standard methyl ricinoleate.

\( P_{MR} \) = Purity of standard methyl ricinoleate.
### Table – 1

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Detail</th>
<th>Tata Oil Miles, Co., Bombay</th>
<th>Pioneer Chem., Delhi</th>
<th>Jayant Oil Miles, Bombay</th>
<th>Ganga Ram &amp; Sons, Delhi</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Solution conc. mg/5ml</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Standard*</td>
<td>62.5</td>
<td>62.4</td>
<td>62.4</td>
<td>62.4</td>
</tr>
<tr>
<td></td>
<td>(b) Sample**</td>
<td>83.7</td>
<td>91.7</td>
<td>87.2</td>
<td>75.6</td>
</tr>
<tr>
<td>2</td>
<td>Area counts under methyl ricinoleate peak</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Standard*</td>
<td>1848930</td>
<td>1848930</td>
<td>1848930</td>
<td>1848930</td>
</tr>
<tr>
<td></td>
<td>(b) Sample**</td>
<td>212511</td>
<td>1933839</td>
<td>2256150</td>
<td>1792652</td>
</tr>
<tr>
<td>3</td>
<td>Ricinoleic acid in castor oil fatty acid (%)</td>
<td>85.2</td>
<td>70.8</td>
<td>86.4</td>
<td>79.3</td>
</tr>
</tbody>
</table>

* Standard solution of methyl ricinoleate, purity 99%.

** Solution of methyl ester of castor oil fatty acid.
Fig. – 2. shows the GLC chromatogram of the fatty acid methyl ester mixture from the castor oil sample showing the maximum ricinoleic acid content. For other samples the data derived from the chromatogram is represented in Table – 1.

2.12 SELECTION OF THE CASTOR OIL

The criteria for the final selection of the castor oil out of the above food sample obtained from different companies is, “lower acid value, low moisture content and higher ricinoleic acid content”. The authors thought it worthwhile to select finally the castor oil procured from M/s Jayant Oil Miles, Bombay, based on these considerations, for synthetic work.

2.13 INTERESTERIFICATION OF CASTOR OIL WITH ALKYL ALCOHOL

Interesterification which is also termed as alcoholysis is an economical single step route to alkyl ricinoleates from oils and fats. A systematic work on alcoholysis of oils and fats is reported by Bradshaw\(^2\), Wright\(^3\) and others. All of them have emphasized the need for bone drying of the reagent. For the present work, the procedure reported by Pathak and Bhatnagar was employed for alcoholysing the castor oil to alkyl ricinoleates precaution has been taken to use sufficiently anhydrous alcohol to obtained maximum yields. Alcoholysis with both methyl and
ethyl alcohols was carried out to prepare methyl and ethyl esters of ricinoleic acid respectively.

2.14 RAW MATERIALS

In order to carry out the desired reaction the following raw material were used:

1. **Castor Oil:** Refined grade from M/s Jayant Oil Miles.

2. **Methyl alcohol:** Commercial grade-purified and dehydrated as per procured given below.

3. **Ethyl alcohol:** Commercial grade-purified and dehydrated as per procured given below.

4. **Catalyst:** Prepared by dissolving analytical grade sodium hydroxide pellets in alcohol.

2.15 PURIFICATION OF ALCOHOL

In order to achieve the good result and maximum yield of the products, the authors were very careful to use the materials/chemicals in a maximum purified form. Commercial grade alcohols were procured from the market and purified as below:

1. **Methyl alcohol:** Commercial methanol was distilled twice and stored over molecular sieves type 4 A.
2. **Ethyl alcohol:** Many methods for the recovery and dehydration of ethanol are reported in the literature. They include supercritical carbon di-oxide extraction\(^{15}\), per evaporation technique\(^{16}\), solvent extraction\(^{17}\) and molecular sieve dehydration method\(^{18}\).

Procedure given by Vogal\(^{19}\) is the most adequate and satisfactory method for laboratory synthetic work. The authors have used this method for the present under investigation. All these method through ensure alcohol of excellent purity ranging 99.85 to 99.9% by volume, are of commercial significance only.

Commercial ethanol was distilled to get rectified sprit. Two liters of rectified spirit was placed over 500 gms of freshly ignited and cooled calcium oxide in a three liters round bottom flask fitted with a reflux condenser carrying a calcium chloride guard tube. The mixture was refluxed for eight hours and allowed to stand overnight. The alcohol was then distilled discarding the first 20-25 ml of the distillate to obtained absolute alcohol with 99.5% purity.

Super dry alcohol was prepared from absolute alcohol by treatment with iodine activated magnesium. The last traces of water are removed through the step following the reaction.
\[
\text{Mg} + 2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{iodine}} \text{Mg} (\text{OC}_2\text{H}_5)_2 + \text{H}_2
\]
magnesium ethanol \hspace{1cm} \text{magnesium ethanolate} \hspace{1cm} \text{Hydrogen}

\[
\text{Mg}(\text{OC}_2\text{H}_5) + \text{H}_2\text{O} \rightarrow \text{Mg} (\text{OH})_2 + 2\text{C}_2\text{H}_5\text{OH}
\]
magnesium ethanolate \hspace{1cm} \text{magnesium hydroxide} \hspace{1cm} \text{ethanol}

5 gms of clean dry magnesium turnings and 0.5 gm iodine were taken in a 2 liter round bottom flask fitted with a reflux condenser carrying a CaCl\textsubscript{2} guard tube followed by addition of 50 to 75 ml of absolute ethyl alcohol as prepared above. The reaction mixture was warmed till whole of the iodine got disappeared. Heating was continued further until whole of the magnesium converted into magnesium ethanolate. 900 ml of absolute alcohol was then added to the ethanolate and refluxed for half an hour. Ethanol was then distilled and stored over type 4A molecular sieves in air tight container.

**2.16 APPARATUS USED**

The most suitable assembled apparatus used for alcoholysis process is shown in **Fig. – 3**. It consist of a three necked round bottomed reaction flask fitted with a reflux condenser carrying a calcium chloride guard tube, a thermometer and a mechanical stirrer. The assembly was kept into a water bath fitted with a thermostat to maintain the desired temperature condition.
2.17 PROCEDURE OF INTERESTERIFICATION

The procedure described here is the standard procedure\(^{19}\) which was adopted for methanolysis as well as ethanolysis of castor oil. 1\% castic soda on weight of the oil was dissolved in the alcohol and added to castor oil kept under moderate agitation in the reaction flask. **Fig. – 3.** The temperature of the reaction mixture was maintained at 35°C while keeping the system under constant agitation for 2.5 hours. At this stage the catalyst was neutralized by adding a calculated amount of glacial acetic acid. At this stage the excess alcohol was recovered by distillation under reduced pressure and the ester left in the flask was poured into a pear shaped separating funnel to effect glycerol separation. A major portion of the glycerole got separated immediately while the remaining glycerole required 6 to 8 hours for its separation. The upper layer rich in the ester, residual acid or alkali, some glycerole, soaps and the unreacted alcohol was washed with small portions of warm water. The reaction condition for methanolysis and ethanolysis are summarised in **Table – 2.**
Table – 2

Reaction conditions for alcoholysis of castor oil.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Particulars</th>
<th>Methanolysis</th>
<th>Ethanolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mole ratio, alcohol : Oil</td>
<td>12:1</td>
<td>6:1</td>
</tr>
<tr>
<td>2</td>
<td>Reaction time (hrs)</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>Reaction temp. (°C)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst, Based on Oil weight (%) (NaOH)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The products of alcoholysis, when analyzed were found to have high acid values (5.5 and 6.0 for methyl and ethyl ricinoleate respectively). Since high acid values are determinate to plasticizers, they were subjected to an alkali treatment for effecting reduction in their acid values. A suitable quantity of the ricinoleate was treated with small quantities of brine saturated 5% of NaOH solution. Soaps formed were removed by decantation and the neutralized products were washed with cold brine solution to remove the dissolved soap. The acid values before and after alkali treatment are given in Table – 3.

The methyl ricinoleate and ethyl ricinoleates prepared above were examined by thin layer chromatography following a 6 : 4 : 0.1 : : hexane :
diethyl ether: acetic acid mixture for the development of plates. Both of them showed two spots, the major spots matching with the spots obtained with the standard ricinoleate sample their by indicating good conversion.

**Table 3**

**Various characteristics of alkyl ricinoleates prepared by alcoholsysis of castor oil**

<table>
<thead>
<tr>
<th>Alkyl ricinoleate</th>
<th>Characteristic</th>
<th>Specific gravity 20(^\circ)C/20(^\circ)C</th>
<th>Refractive Index</th>
<th>Acid Value 1</th>
<th>Acid Value 2</th>
<th>Iodine value</th>
<th>Hydroxyl value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl ricinoleate</td>
<td></td>
<td>0.9238 (\text{(0.9236)*})</td>
<td>1.4632 (\text{(1.4628)*})</td>
<td>5.5 - 2.2</td>
<td></td>
<td>83</td>
<td>(171)**</td>
</tr>
<tr>
<td>Ethyl ricinoleate</td>
<td></td>
<td>0.9148 (\text{(0.9145)*})</td>
<td>1.4617 (\text{(1.4618)*})</td>
<td>6.0 - 2.3</td>
<td></td>
<td>77</td>
<td>163.5</td>
</tr>
</tbody>
</table>

**Acid value:** 1: Before alkali neutralization.

2: After alkali neutralization.

*: Literature values.

**: Literature value (data sheets from Baker castor oil co., USA, Page 33).

**Analysis and Evaluation of Efficiency of Inter-esterification process**

In order to analyze and to evaluate the efficiency the process was subjected to GLC under the specified conditions. **Fig. 4** shows the gas
chromatograms obtained by plots methyl ester of castor oil fatty acid product verses detector response. Similarly the gas chromatogram obtained with standard ethyl ricinoleate and mixtures of castor oil fatty acid ethyl ester obtained in a representative batch of ethanolysis are shown in Fig. – 5 and 6 respectively. The data obtained from the chromatogram are shown in Table – 4.

**Table – 4**

**Gas chromatographic analysis of methanolysis and ethanolysis products of castor oil.**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Particulars</th>
<th>Fatty acid alkyl ester mixture obtained from</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Methanolysis of Castor oil</td>
</tr>
<tr>
<td>1</td>
<td>Solution conc. mg/5ml</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Standard</td>
<td>62.7</td>
</tr>
<tr>
<td></td>
<td>(b) Sample</td>
<td>83.1</td>
</tr>
<tr>
<td>2</td>
<td>Area counts under the alkyl ricinoleate peak</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) Standard</td>
<td>1848930</td>
</tr>
<tr>
<td></td>
<td>(b) Sample</td>
<td>2154020</td>
</tr>
<tr>
<td>3</td>
<td>Alkyl ricinoleate content (%)</td>
<td>83.10</td>
</tr>
<tr>
<td>4</td>
<td>% conversion</td>
<td>95.62</td>
</tr>
</tbody>
</table>
2.18 CHARACTERIZATION OF ALKYL RICINOLEATES

The products of methanolysis and ethanolation of castor oil and the synthesis of the proposed plasticizers were characterized by IR spectroscopy and determination of various physicochemical characteristics like specific gravity, refractive index, acid value, iodine value and hydroxyl value.

2.19 I. R. SPECTROSCOPY

The infra red spectroscopy studies were conducted on Pye-Unicam, PU 9514 infra red spectrophotometer. The spectra were taken with neat substances between sodium chloride plates. In this method the liquid sample is pressed between two flat salt plates to produce a thin film of about 0.01 nm. thickness. The plates remain held together by capillary action. The IR spectra for methyl ricinoleate and ethyl ricinoleate are shown in Fig. – 7 and 8 respectively.

2.20 PHYSICOCHEMICAL CHARACTERIZATION

Alkyl ricinoleate were analyzed for various physicochemical characteristics like specific gravity, refractive index, acid value, iodine value and hydroxyl value following the standard procedure.
# 2.21 Esterification of Alkyl Ricinoleates with Halo-Fatty Acid

**Mechanism:** Methyl ricinoleate and ethyl ricinoleate prepared by the alcoholysis process still contain a hydroxyl group at 12th C-position in their structure.

![Diagram of esterification](image)

\[
CH_3 - (CH_2)_5 - CH - CH_2 - CH = CH - (CH_2)_7 - COOR
\]

R = CH₃ (or) C₂H₅, alkyl ricinoleate

The hydroxyl group in their structure is of little value except as a means of attaching additional group. To improve compatibility with the vinlys, both these products were esterified with halo acetic acid, both with mono chloroacetic acid and mono bromoacetic acid to produced double ester of ricinoleic acid.

![Diagram of esterification](image)

\[
CH_3(CH_2)_5 - CH - CH_2 - CH = CH - (CH_2)_7 - COOR + X- CH₂COOH \xrightarrow{PTS \text{ catalyst}} \]

Alkyl ricinoleate  Halo acetic acid

\[
CH_3 - (CH_2)_5 \quad CH - CH_2 - CH = CH - (CH_2)_7 - COOR + H₂O
\]

R = CH₃ (or) C₂H₅
X = Cl (or) Br  Alkyl halo acetyl ricinoleate
The esterification was carried out according to the procedure\textsuperscript{20} by refluxing the alkyl ester with the halo acids in presence of a catalyst and an organic entrainer benzene to facilitate azeotropic removal of water esterification.

**Raw Material:**

- **Alkyl ricinoleate**: Prepared by a Alcoholysis of Castor oil
- **Mono Chloroacetic acid**: L. R. Grade
- **Mono Bromoacetic acid**: L. R. Grade
- **Benzene**: L. R. Grade (Dehydrated by distillation)
- **Catalyst (PTS)**: L. R. Grade

**Apparatus used:**

The assembled suitable apparatus for the esterification of alkyl ricinoleates is shown in Fig. – 9. It consisted of a three necked round bottom flask with a mechanical stirrer through a mercury seal and a thermometer. One of the necks carried a Dean Stark Apparatus fitted with a water condenser. The reaction flask was placed into a hot liquid bath or heating mantal fitted with a thermostat for maintaining the desired temperature.
2.22 PROCEDURE FOR ESTERIFICATION

The procedure described below is generalized one and was employed for the esterification of methyl and ethyl ricinoleate with both chloro and bromoacetic acid. The ratio of the reaction mixture used was as follows:

- **Alkyl ricinoleate**: 1 mole
- **Halo acetic acid**: 1.5 mole
- **Benzene**: 1:5 (Weight of ester : Volume of benzene)
- **PTS**: 1% by weight of ester
- **Reaction temperature**: 80°C
- **Reaction time required**: 5 hours.

All the reactants were charged to the reaction flask under stirring to effect uniform mixing of the reactants. Some porcelain beads were also added to avoid bumping. Heating was started and adjusted to effect an adequate speed of refluxing. Stirring was stopped at this stage. The benzene-water azeotrop started distilling and collecting in the receiver of Dean-stark apparatus, where in water formed the lower layer while benzene layer over flow back into the reaction flask. Reaction was assumed to be complete when no more water of reaction distilled. Heating was continued for one more over after this stage. During the source of
reaction it was notice that the reaction was almost complete in 3.5 to 4.0 hours. When more than 95% of the theoretical yield of water of esterification got separated. The reaction was however continued for some more kind to complete the reaction. Starting with 250 gm of the respective alkyl ricinoleate. The products obtained are quantitatively given in Table 5.

**Table – 5**

**Details of the esterification of alkyl ricinoleate with halo acetic acid**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Particulars</th>
<th>Quantity of reactants/Products related with the preparation of</th>
<th>MCAR</th>
<th>ECAR</th>
<th>MBAR</th>
<th>EBAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methyl ricinoleate (gm)</td>
<td>250.0 - 250.0 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ethyl ricinoleate (gm)</td>
<td>- 250.0 - 250.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Mono chloro acetic acid (gm)</td>
<td>106.0 101.5 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Mono bromo acetic acid (gm)</td>
<td>- - 156.0 149.25</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Para toluene sulphonic acid (gm)</td>
<td>2.5 2.5 2.5 2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>% Conversion</td>
<td>96.8 96.2 96.4 96.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Yield percentage</td>
<td>88.5 86.8 88.0 84.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| MCAR   | - | Methyl Chloro Acetyl Ricinoleate |
| ECAR   | - | Ethyl Chloro Acetyl Ricinoleate  |
| MBAR   | - | Methyl Bromo Acetyl Ricinoleate  |
| EBAR   | - | Ethyl Bromo Acetyl Ricinoleate  |
2.23 DECOLOURISATION OF PRODUCT

The products of the esterification reaction were found to have a pale yellow to mild brown colour, which is not required for it may impose limitation for the vinyl compounding. Hence the decolourisation of the products was necessary.

5 gms of the decolourising mixture consisting of a 80:20 mixture active earth and activated carbon was added to the reaction flask with all its ingredients left after esterification. The mixture was kept under moderate stirring at 60 to 70°C for 2 to 3 hours. At this stage the heating and stirring was discontinued and allowed to cool to room temperature. The crud mixture obtained after decolourising step, contained in addition to the desired product di esters, activated charcoal and activated earth, excess halo acetic acid, catalyst and entrainer benzene. The solid particles were removed by filtration while the filtrate was given repeated washing, first with small portion of warm water and then with brine saturated 5% alkali solution to free it from organic and inorganic impurities.

The washed product was finally distilled to remove benzene. The last traces of benzene, were removed by applying vacuum. The diesters thus recovered were stored over molecular sieve, type-4A. The yields of the final products were determined as percentage of the theoritical yield the values are reported in Table – 5. The theoretical yields were
calculated on the basis of hydroxyl value of the concerned alkyl
ricinoleate Table – 3.

2.24 EPOXIDATION OF ALKYL HALO ACETYL RICINOLEATES

The double esters of ricinoleic acid prepared by esterification of the
products of alcoholysis of castor oil, still carry a double bond at C-9 and
C-10 position in their structure. As per proposed plan, these unsaturated
esters were epoxidised to get rid of the unsaturation with an added
advantage of increased compatibility with the vinyls due to their increased
polarity the chemistry of epoxidation reaction can be represented as
follows:

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_5 - \text{CH} & \quad \text{CH}_2 - \text{CH} = \text{CH} - (\text{CH}_2)_7 \text{ COOR} \\
\text{O} & \quad \text{C} \quad \text{CH}_2 - \text{X} \\
\text{O} & \quad \text{C} \quad \text{CH}_2 - \text{X} \\
\text{H}_2\text{O}_2(\text{CH}_3)\text{ COOH} & \quad \text{Catalyst}
\end{align*}
\]

Alkyl halo acetyl ricinoleate

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_5 & \quad \text{CH} - \text{CH}_2 \\
\text{O} & \quad \text{C} \quad \text{CH} \quad \text{CH} \quad (\text{CH}_2)_7 - \text{COOR} \\
\text{O} & \quad \text{C} \quad \text{CH}_2 - \text{X} \\
\text{O}
\end{align*}
\]

Alkyl halo acetyl epoxy ricinoleate

Here  \( R = \text{Me (or) Et} \)

\( X = \text{Cl (or) Br} \)
Epoxidation was carried out by reacting the unsaturated ricinoleates with 30% hydrogen per oxide in presence of acetic acid oxygen carrier and the suitable catalyst.

**Raw Material:**

- **Alkyl halo acetyl ricinoleate**: Prepared by a esterification of alkyl ricinoleate with halo acetic acid.
- **Hydrogen per oxide**: 30% wt/wt.
- **Acetic anhydride**: L. R. Grade
- **Di sodium hydrogen phosphate**: L. R. Grade

**Apparatus used:**

The laboratory set up for the epoxidation process is shown in **Fig. – 10.** It consisted of a three nacked reaction flask fitted with a mechanical stirrer, a thermometer and a dropping funnel. The reaction flask was placed into a water bath, and thermostatically controlled to maintain the desired temperature.

**Procedure of Epoxidation:**

The procedure described below was employed for the epoxidation of chloroacetyl as well as bromoacetyl derivatives of methyl and ethyl ricinoleates. The conditions used for the reaction were as follows:
**Halo acetyl alkyl ricinoleate** : 1 mole

**Hydrogen per oxide**
*(30% wt/wt)* : 1.2 mole

**Acetic anhydride** : 0.8 mole

**Di-sodium hydrogen phosphate (catalyst)** : 1% on weight of ester

**Reaction temperature** : 35°C

**Reaction time** : 3 hours.

The requisite quantities of ricinoleate ester and acetic anhydride were charged into the reaction flask. Hydrogen per oxide solution was then charged under stirring over a period of 30 minutes. So as not to allow temperature to rise above 125°C.

The catalyst di-sodium hydrogen phosphate was then added, the temperature raised to 55°C and maintained their at for a period of three hours. The product was cooled and washed free of acidity and other residues by washing with small portions of dilute solution of sodium bicarbonates. The products were evaluated for their iodine value and oxirane oxygen content.
Table – 6

Process details of the epoxidation of alkyl halo acetyl ricinoleate

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Particulars</th>
<th>Reaction temperature 55°C/ Reaction time-3 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Quantities/Values related with the preparation of</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MCAER</td>
</tr>
<tr>
<td>1</td>
<td>Alkyl halo acetyl ricinoleate (gm)</td>
<td>250.0</td>
</tr>
<tr>
<td>2</td>
<td>Hydrogen per oxide (30% w/w)</td>
<td>87.5</td>
</tr>
<tr>
<td>3</td>
<td>Acetic anhydride (gm)</td>
<td>52.2</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst (gm), di-sodium hydrogen phosphate (before epoxidation)</td>
<td>66.8</td>
</tr>
<tr>
<td>5</td>
<td>Iodine value (after epoxidation)</td>
<td>10.0</td>
</tr>
<tr>
<td>6</td>
<td>Oxirane oxygen content (%)</td>
<td>2.62</td>
</tr>
<tr>
<td>7</td>
<td>% epoxidation</td>
<td>65.0</td>
</tr>
</tbody>
</table>

MCAER - Methyl Chloro Acetyl Epoxy Ricinoleate
ECAER - Ethyl Chloro Acetyl Epoxy Ricinoleate
MBAER - Methyl Bromo Acetyl Epoxy Ricinoleate
EBAER - Ethyl Bromo Acetyl Epoxy Ricinoleate
2.25 RESULTS AND DISCUSSION

Preparation of alkyl ricinoleate:

Any conversion process is said to be efficient if it produces the desired product in good yield and adequate quality. The efficiency of the alcoholysis process was evaluated by analyzing the alkyl ricinoleate contents of the alcoholysis products by GLC technique. The methyl ricinoleate content of the methanolysis product was found to be 83.10% by comparing it with the ricinoleic acid content of the raw material castor oil (86.9%) determined by standard analytical technique\textsuperscript{14}, the conversion efficiency was found to be 95.62% similarly the conversion efficiency for the ethanolysis process is found to be 95.16%. No doubt these can be said good conversion efficiency.

Further, the process has resulted in the production of high acid value products (Table – 3). Although these acid values are not different from those given in the literature yet may cause deterioration of the quality of the plasticizers synthesized from them.

The I. R. Spectra of methyl ricinoleate and ethyl ricinoleate (Fig. – 7 and 8) depict the following features:
1. In the region 3200-3600 cm\(^{-1}\) a broad band is visible which may be assigned due to \(-\text{OH}\) stretching vibration of the H-bond hydroxy compounds.

2. Presence of the weak bands at 1640 cm\(^{-1}\) and 3000 cm\(^{-1}\) are indicating of C=C unsaturation.

3. A sharp band at 720 cm\(^{-1}\) is due to methylene rocking absorption and indicates the presence of \((-\text{CH}_2)_n -\) where \(n \geq 4\).

4. A prominent band at 1725 cm\(^{-1}\) is due to \(\text{C} = \text{O}\) stretching and indicate carboxylic acid ester.

5. Medium intensity bands at 1015 cm\(^{-1}\) and 1025 cm\(^{-1}\) respectively, in the spectra of methyl and ethyl ricinoleate, are due to \(\text{C} - \text{O} - \text{O}\)

\[
\text{O} \\
\text{\|} \\
\text{C} - \text{O} - \text{C}
\]

Stretching in \(-\text{C} - \text{O} - \text{C}\) grouping of esters.

6. A strong band at 1170 cm\(^{-1}\) is attributable to \(\text{C} - \text{O} - \text{C}\) vibrations due to the presence of ester group other than acetate group.

Presence of all these absorptions supplemented by the presence C–H stretch absorptions at 2920 cm\(^{-1}\), \(-\text{CH}_3\) bending absorption at 1350 cm\(^{-1}\) and 1450 cm\(^{-1}\) etc. confirms the structure of long chain hydroxyl fatty acid.
Refractive index, specific gravity, iodine values and hydroxyl value observed during the course of experimentation are in good agreement with those are reported in the literature. Summing up all the above factors the authors have concluded that alcoholyis of castor oil has resulted in the production of alkyl ricinoleate of good qualities and adequate conversion rates. The products were directly used for the synthesis of proposed plasticizers.

2.26 ALKYL HALO ACETYL RICINOLEATE

Table – 5 shows the details of the esterification of alkyl ricinoleates with halo acetic acids. The alcoholic group present in the alkyl ricinoleates is secondary in nature and hence a slow rate of esterification was expected. But the higher reactivity of the halo acids gives an impetus to the secondary alcohols regarding a satisfactory reaction rate.

The yields of the pure diesters were found to range from 84.8 to 88.5 of the theoretical values. The region for the low yield according to the authors may be attributed to the losses occurred during neutralization and decolourisation.

2.27 PREPARATION OF ALKYL HALO ACETYL EPOXY RICINOLEATE

The details of the epoxidation of alkyl haloacetyl ricinoleate are given in Table – 6. The extent of epoxidation ranged from the lowest
61.6% for ethyl bromoacetyl epoxy ricinoleates to the highest 65.0% for methyl chloroacetyl epoxy ricinoleate. This small differences in the level of epoxidation are quite insignificant and may be due to the difference in the reactivity of the concert reactant towards epoxidation. The epoxidised compound were also found to possess residual iodine value (I. V.) ranging 10 to 11.6. Though the process used for epoxidation was a standard one and an outcome of extensive research work\textsuperscript{12} extensive research work it cause further work so as to prevent formation of hydroxyl compound.

**Badra Bouchareb, Mohamed Tohar Benoniba**\textsuperscript{21} studied and observed that the epoxide soyabean oil ( – ESBO) is one of the most commonly used epoxidised because of its typical combined role as a plasticizer and heat stabilizer. In this studied a novel plasticizer of poly (vinyl-chloride) (PVC) resin, epoxidised sunflower oil (ESO), was synthesized and it performance was evaluated. All mechanical and dynamical properties of plasticized PVC sheet varied with the oxirane oxygen of the ESO.

*****
REFERENCES


2. Bradshaw, G. B. and Meuly, W. C., U. S. Pats. 2271619 (1942) and 2360844 (1944).


