PURITY OF MATERIALS

(1) **Castor Oil**

Castor oil used in the experiments was Swastik medicinal castor oil supplied by Swastik Oil Mills, Wadala, Bombay and had the following constants:

- Iodine value (Wob) 90.4
- Acid value 1.2
- Hydroxyl value 168.2
- Acetyl value 145.0
- Saponification value 188.2
- Ref. index (40°C) 1.4660
- Colour on Lovibond Tintometer (10 mm. cell) B=0; R=0; Y=0.8

(2) **Catalysts**:

Catalysts used in the present investigation are:

- (a) supplied by reliable firms, or
- (b) prepared in our laboratory from refined sodium salts, which are supplied by reliable firms.

The following sulphonic acids were supplied in pure state:

- (1) Methane sulphonic acid - Indoil Chemical Co., U.S.A.
- (2) Ethane Sulphonic acid - Indoil Chemical Co., U.S.A.
- (3) p-Toluene sulphonic acid, m.p. 124°C. B.D.H.
(4) Naphthalene 2-sulphonic acid, m.p. 124°C. B.D.H.
(5) Benzene sulphonylic acid. 32% W/V Soln. B.D.H.
(6) O-phenol sulphonylic acid 75% W/V Soln. B.D.H.
(7) p-bromobenzene sulphonylic acid, m.p. 103°C. B.D.H.
(8) Potassium phenol sulphonate, m.p. 265°C. B.D.H.
(9) Phosphoric acid, Johnson and Co.
(10) Sulphuric acid sp. gr. 1.84. (98%)
(11) Sodium bisulphate, m.p. 185°C. B.D.H.
(12) Sulphosalicylic acid, m.p. 120° B.D.H.
(13) m-Cresol sulphonylic acid B.D.H.
(14) Phosphotungstic acid Johnson C P.
(15) m-Sulphobenzoic acid, m.p. 98° B.D.H.

(b) The following catalysts were prepared from the corresponding sodium salts.

The general method of preparing free acid from sodium salts consisted of the following two stages:

(i) Preparation of corresponding sulphonylic chloride by the action of phosphorus pentachloride.

(ii) Hydrolysis of the sulphonylic chloride to sulphonic acid.


10 gms. of sodium salts were mixed with 25 gms. of phosphorus pentachloride in a clean dry flask. The contents were heated in an oil bath at 150°C. under reflux condenser,
for thirty minutes. The contents were then cooled and extracted with 100 c.c. of benzene. Filtered benzene
extract was washed thoroughly with water till the washings did not give an acidic test to litmus paper. Benzene was
distilled off and the sulphonyl chloride which remained behind was recrystallized from petrol ether or chloroform.

(2) Hydrolysis of sulphonyl chloride (C.R.Noller; 'Chemistry of Organic Compounds' p. 456; W.B.Saunders

Because of insolubility of sulphonyl chlorides they react slowly with water. The sulphonyl chlorides required from 6 to 6 hours of boiling water for complete hydrolysis. The following equation represents the reaction:

\[ \text{RSCl}_2 + \text{H}_2\text{O} \rightarrow \text{RSO}_2\text{H} + \text{HCl} \]

The completion of hydrolysis was tested by complete elimination of hydrochloric acid (as tested by litmus paper holding a drop of NaOH on it).

The sulphonlic acids so prepared were used in the form of solution, after finding out strength of the acid.

The purity of the sulphonlic acid was tested by determining the M.P. of corresponding sulphonyl chloride. The method of determining the equivalent weight of the acid to ascertain the purity of the acid was of little use since most of the sulphonlic acids are hygroscopic.
Benzene m-di sulphonyl chloride m.p. 63°C.

Anthraquinone 1:3 di " 223°C.

Naphthalene tri sulphonic acid " 1:3:6 191°C.

Phenol trisulphonic acid was prepared in the laboratory by sulphonation of phenol (Beilstein, Vol. 11, System No. 1552 p. 252). Phenol 2-4-6 trisulphonic acid.

(Senhofer: Liebigs Annalen der Chemie. 170, 110, (1875))

Chemicals: used for analytical work were all pure and were supplied by well-known firms.

Some of them are listed below:

1. Iodine (resublimed) B.D.H.
2. Sodium thiosulphate B.D.H. M.P. 48°C.
3. Potassium iodide B.D.H. L.R.
5. Potassium hydroxide B.D.H.
6. Acetic acid glacial B.D.H.
7. Carbon tetrachloride, B.D.H.
8. Ether sulphuric B.D.H.
9. Benzene B.D.H.
   (Extra pure for mol. wt. determination).

* Acetic acid was freezeed in ice salt bath and water removed. Crystals were taken in a separate flask and 1% (acetic anhydride was added and refluxed for some
time distilled and stored in a glass stoppered bottle).

(10) Sulfine Johnson and Co. Ltd.

(11) Acetic anhydride S. Merck Ltd.

(12) Driers Cobalt naphthenate) Imperial Chemical Industries Ltd.

(13) Toluene - Schering Kahlbaum Ltd.
EXPERIMENTAL PROCEDURE

(a) **Dehydration of Castor Oil**

The detailed procedure for the dehydration of castor oil is the same as is described in the previous work (Dole and Keskar, Proc. Ind. Aca. Sciences, Vol. 38, pp. 135-36; 1953).

500 grams of castor oil were dehydrated by using different catalysts. In two cases the dehydration was carried out under reduced pressure (20 mm.) while in the remaining experiments the reaction was carried out at atmospheric pressure in an atmosphere of carbon dioxide. The conditions, such as, temperature, concentration of the catalyst and time of reaction employed for the individual experiments are summarized in Table B. The temperature of reaction was maintained within a range of ± 5°C. of that mentioned in the individual experiments. Time required to attain the temperature was 15-20 minutes. After dehydration the oil was filtered, cooled and stored in bottles in an atmosphere of carbon dioxide.

The following characteristic values of DCO samples were found out :-

(1) Iodine value (Wöburn)
(2) Hydroxyl value
(3) Acid value
(4) Molecular weight
(5) Refractive index
(6) Viscosity

which are summarized in Table B.

(b) Polymerization of Oil

(i) Heat polymerization: - 100 grams of dehydrated castor oil were taken in a 250 c.c. flask, fitted with a cork having three holes in it. A thermometer was inserted in the oil through one of the holes, a glass tubing carrying dry carbon dioxide was inserted through the second hole, while third hole in the cork served the purpose both of an exit passage for vapours and for drawing out samples of the oil at various time intervals. The whole flask was dipped in a metal bath (melting at 185°C.) which was kept at the requisite temperature. The temperature of the oil was maintained within the range of ± 5°C. Samples were drawn out at intervals mentioned in the individual experiments. The oil was rapidly cooled to room temperature and kept closed under the atmosphere of carbon dioxide. The samples, drawn at various time intervals were then analysed.

(ii) Oxidation polymerization: - The arrangement of the experiment was the same as above except that air was bubbled through the oil instead of carbon dioxide. Air
from a compressor was dried by passing through sulphuric acid tower and then bubbled through the oil. The flow was controlled by a needle valve. The samples were drawn as usual. Temperature of the oil was maintained within the range of $\pm 5^\circ C$. Samples were drawn at interval of time mentioned in the individual experiments after which the samples were preserved in an atmosphere of carbon dioxide and analysed.

(c) **Polymerization of Methyl Esters**

Some of the dehydrated castor oil samples were converted into corresponding methyl esters and their polymerization was studied.

(i) **Preparation of Methyl Ester** :- 200 grams of DCO were saponified by 60 grams of potassium hydroxide in one litre of alcohol and the corresponding fatty acids were obtained.

140 grams of fatty acids were mixed with 250 c.c. of methyl alcohol. 6% by weight of concentrated sulphuric acid and 4 c.c. benzene were added to the mixture as catalyst and the whole mixture was refluxed for three hours on a hot plate at about 70$^\circ C$. The mixture was then cooled and transferred to a separating funnel. The lower layer of methyl ester was separated from the alcoholic layer. The crude ester was washed with water, then
with 2% sodium bicarbonate and finally with water again. The methyl esters were dried over anhydrous sodium sulphate. The yield of methyl esters was from 92 to 95 per cent. The methyl esters were stored in bottles in an atmosphere of carbon dioxide.

(ii) Polymerization of Methyl Esters: - The procedure for thermal polymerization of methyl esters was the same as was adopted for the polymerization of dehydrated castor oil (loc. cit.). The polymerization was carried out at 280°C. After eleven hours' polymerization the reaction was stopped and started again on the next day. Time required for cooling and regaining the temperature was noted and converted into the time equivalent at 280°C.

Alkyd Resins

As stated before, DCO prepared under different conditions, showed some differences in the mode and the rate of polymerization. To study the cause of these differences, in more details, alkyd resins are prepared by using fatty acids from different DCO samples and the properties of alkyds are investigated. In these experiments, all conditions, such as temperature, percentage of other ingredients and time of heating are kept constant.

DCO samples used for the preparation of alkyds were prepared by using the following catalysts:
(1) Phosphoric acid.
(2) Sulphuric acid.
(3) Sodium bisulphate
(4) Benzene sulphonlic acid.
(5) Benzene m-di sulphonic acid.
(6) p-toluene sulphonlic acid.
(7) phenol tri sulphonlic acid.
(8) m-Sulpho benzoic acid.
(9) Sulpho salicylic acid.
(10) Methane sulphonlic acid.
(11) Phospho tungstic acid.

DCO, instead of using as such was converted into free fatty acids before condensing into alkyd resins. This particular procedure enabled us to investigate whether there exists any difference in the composition of fatty acids from different DCO samples.

The experimental procedure included the following steps:

(a) Preparation of fatty acids from the DCO.
(b) Preparation of alkyd resins.
(c) Studying the properties of the alkyd formed.

(a) Fatty acids were prepared by the usual procedure of saponification of oil by alcoholic potassium hydroxide. 100 gms. of oil were hydrolysed by 30 gms. of potassium
hydroxide in 500 c.c. alcohol. After distilling off the alcohol resulting soap was hydrolysed by mineral acid. The total fatty acids were extracted with ether, washed free from mineral acid, dried and finally the ether was removed from the fatty acids.

(b) The alkyd resin was prepared by condensing together glycerol phthalic anhydride and the total fatty acids from the BGO in the following proportion:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>21.8%</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>31.2%</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>17.0%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.0%</strong></td>
</tr>
</tbody>
</table>

The mixture was heated at first at 180°C. for 30 minutes. The temperature was then raised to 220°C. and heating was continued for 2.5 hours. This mode of heating reduced the loss of phthalic anhydride during condensation. (The quality of phthalic anhydride sublimed during the course of reaction amounted to about 5% of the quantity originally added). The whole mass was kept stirring and the reaction was carried out in an atmosphere of carbon dioxide. Samples from the reaction mixture were drawn at an interval of thirty minutes and the acid value of the mixture was determined at various stages of reaction. The sample that was withdrawn was dissolved in 20 c.c. of
mixture of xylene and alcohol (1:2) and acid value was found out by titrating against N/10 alcoholic potassium hydroxide using phenolphthlein as indicator.

After heating for requisite time the mixture was allowed to cool to about 100°C. It was then filtered through a 100 mesh copper wire-gauge. The alkyd resin so formed was diluted by xylene to 50% non-volatile and kept for aging for eight days. 0.04% cobalt as naphthenate was added as a drier.

(c) After aging the alkyd films were applied on glass plates. Properties of the films before and after baking were studied. In the latter case the films were baked at 120°C for 90 minutes. The following film properties were investigated:

(1) Drying time
(2) Hardness
(3) Elasticity
(4) Water resistance
(5) Alkali resistance
(6) Resistance to solvents such as acetone, benzene, ether and alcohol.

(d) Additional study of two typical DCO samples: In general the polymerization of DCO samples showed two types of polymerization reactions; one is intermolecular polymerization and the other is intra-molecular condensa-
The following two catalysts, representing these types, were selected and were studied as mentioned below:

The catalysts used for the dehydration of castor oil are:

(A) Sodium bisulphate (Sample - S.B.)
(B) Benzene sulphonic acid (Sample B.S.A.).

The conditions of dehydration are the same as shown in Table B. The rate of change of (i) iodine value, (ii) acid value (iii) refractive index and (iv) conjugation during the dehydration of oil in presence of above two catalysts is summarised in Table (No 32).

**Velocity of dehydration**

The dehydration of oil was carried out by changing the concentration of the catalyst. In the case of sodium bisulphate (A) 0.5, 1.0 and 2.0 per cent catalyst was used while in the case of benzene sulphonic acid (B) 0.2, 0.4 and 0.8 per cent catalyst was taken for dehydration of castor oil. In all the experiments the temperature was maintained at 250 ± 1°C. The time required for heating the oil to 250°C was noted and converted into the corresponding time at 250°C by the formula:

\[ H = \frac{1.44D}{C} \]

**H** = Time in minutes.
**D** = Doubling interval (26.7)
**C** = Heating rate in degrees F. per minute.

(J.D. von Mikusch. Ind. Eng. Chem. 32, 1061-9; 1940).
Taking into account the time required for attaining the temperature, the samples were drawn at an interval of 10 minutes and the iodine values (I.V.) of the sample was determined.

Taking the final value of DCO when complete dehydration would take place, as 155 (theoretical) = \( a \); and the initial value of the sample as 89 the velocity constant \( K \) was calculated by the formula

\[
K = \frac{2.3}{\log \frac{a}{\text{C.t.}}} - \frac{a - x}{\text{C.t.}}
\]

(\( x = \text{Actual I.V.} - 89 \) \( c = \text{concentration} \))

All iodine values are determined by Woburn method.

Polymerization of DCO.

The polymerization was carried out at three temperatures viz. 150 ± 5°, 250 ± 5° and 280 ± 5°C. The samples were drawn at time intervals given in the individual experiments and were analysed.

Fractionation of polymerized oil by solvent

DCO was polymerized at 280°C. for six hours in an atmosphere of carbon dioxide (loc. cit.). The polymerized oil was fractionated into two fractions by means of isopropyl
alcohol. The oil was mixed with six times its weight of isopropyl alcohol and the mixture was allowed to stand in a separating funnel at 30°C. for three hours. A part of the oil insoluble in the solvent at that temperature was thrown out of the mixture in the form of a separate layer. The two fractions were collected separately in tared flasks and the solvent was removed by distillation, last traces of solvent being removed under vacuum. The two fractions were weighed and were analysed.

**Fractional distillation of Methyl esters obtained from polymerized oils**

The above mentioned polymerized oils were saponified and converted into corresponding fatty acids. The fatty acids were then converted into methyl esters. The methyl esters were distilled under vacuum (Pressure 10 mm.) and separated into several fractions. The fractions were collected under vacuum, by using Perkin's triangle for the collection of fraction. The conditions under which the fractions were collected together with the analysis of the individual fractions are given in Table Nos. 39-40.

**Fractionation of fatty acids from polymerized oils by Urea-adduct method**

The polymerized samples were first converted into corresponding fatty acids. 10 grams of fatty acids were mixed with 40 grams of urea and 40 c.c. methyl alcohol. The mixture
was refluxed at 55°C. for half an hour and then kept at room temperature overnight. The adduct formed, was separated from the raffinate and washed with 200-300 c.c. of saturated solution of urea in methanol. The filtrates were added to the raffinate. The adduct as well as raffinate after distilling off methanol, were boiled with excess of water and a small quantity of hydrochloric acid. The liberated fatty acids were extracted with ether, dried over anhydrous sodium sulphate and ether was removed under vacuum.

In the case of Sample B.S.A. the fatty acids of polymerized oil showed a peculiar behaviour; part of fatty acids were insoluble in methanol. Also part of them was incapable of forming urea-adduct. This part was separated as a separate fraction. Analysis of all the fractions is summarized in Table No. 41. The process of fractionation and of removal of traces of solvent from the fractions incurred a loss of about 2 to 5% fatty acids. The fatty acid of sample B5A were also fractionated by methyl alcohol as a solvent.

The fatty acids and methanol were mixed in the ratio of 1:4 and the mixture was placed in a separating funnel. The fatty acids were separated into three fractions as follows:

1. Fraction insoluble at 30°C.
2. Fraction insoluble at 0°C. and
3. Fraction soluble at 0°C.

These fractions were purified by removing the last traces of the solvent under vacuum, and were analysed. The results are summarized in Table Nos. 41-43.
(f) Study of films of polymerized DCO samples

Film properties of polymerized DCO samples were studied in order to investigate the effect of intramolecular reaction on the film forming capacity of the oil. The films were studied with respect to the drying property, tack hardness and resistance to various reagents. Tack of the films was recorded on a modified Gardner tackmeter. In this instrument, the tack could be measured in terms of grams required to separate a standard circular disc pressed against the film.

(The detailed description of the tack-meter and the hardness-tester appears in the M.Sc. Thesis of Mr. Deshpande P., which is being submitted to the University of Poona in Feb., 1958).

Preparation of Films of Uniform Thickness


The polymerized oil was thinned down by a weight of vegetable turpentine. 0.04% cobalt and 0.1% (as naphthenate) on the weight of the oil was added to the mixture, which was then heated for 5 minutes at 120°C to ensure thorough mixing. Cellotape was applied to glass plates (6" x 3") at the two parallel borders. The oil was placed on the glass plate in the gap produced by the tap and excess of oil was scraped off by means of a doctor blade. Thickness of the film in wet condition was equal to that of cellophane tape and remained uniform even after drying. The films were tested for the following properties.
(1) Appearance of the film.
(2) Tack.
(3) Hardness (scratch)
(4) Resistance to cold water.
(5) Resistance to 1% alkali.
(6) Resistance to benzene.
(7) Drying time.

For measuring scratch hardness the films were applied on 6" by 4" stainless steel plates, instead of glass plates, by the same procedure as in glass plates and the hardness was measured on the hardness tester. The needle of the hardness tester was 1 mm. thick with a spherical point. The hardness was measured in grams, required to break the film, when the blunt point of the needle was scratched over the film under that particular pressure, created by the weights added in the pan. Tack was recorded on tack-meter (loc. cit.)

(g) Determination of Characteristic Values of Oils

(1) **Iodine value (I.V.)** :- The iodine value of the samples was determined by Woburn Method, using 0.32N iodine bromide solution in acetic acid. The solution was kept in contact with oil, to be tested, for one hour after which the quantity of iodine - bromide absorbed was estimated and expressed in terms of iodine. Since dehydrated castor oil contains both conjugated and non-conjugated
isomers of linoleic acid, iodine values by standard Wijs method yield lower results. Woburn method (J.D. von Mikusich and Charles Frazier. Ind. Eng. Chem. Ana. 3dn. vol. 12, 782; 1941) was found satisfactory.

(2) Hydroxyl value: Hydroxyl value was determined by the method proposed by Marks S. and Morrell, R.S. using pyridine-acetic anhydride mixture as a reagent (Analyst 56, 428; 1931).

(3) Acid value: 5 grams of oil were warmed with 25 c.c. alcohol, the mixture cooled and titrated against N/10 potassium hydroxide using phenolphthalein as an indicator. Acid value is expressed as milligrams of potassium hydroxide required per gram of oil. In the case of very dark coloured samples the following modified procedure was used. 5 grams of oil were weighed in a flask then washed with warm alcohol and alcoholic layer was separated from the oil. The process was repeated several times. All the washings were collected together and titrated against N/10 potassium hydroxide. The acid value was calculated as above.

(4) Molecular weight: Molecular weights of samples were determined cryoscopically, by observing the depression in freezing point of benzene caused by dissolving known amount of oil (c. 1 gm.) in 25 c.c. benzene. Extra pure benzene, special for molecular weight determination, was used for this purpose. The molecular weight was calculated by the formula:
g - Weight of the oil in grams.

d - Depression in freezing point.

k - Constant for benzene (51.2)

l - Weight of 25 c.c. benzene (21.2).

In the case of highly polymerized sample, small part of it remained undissolved in benzene and the molecular weight in such case was slightly higher than the actual one. These results are marked with an asterisk (*).

(5) **Refractive index** :- Refractive index of samples was determined at 40°C. on Abbes' Refractometer.

(6) **Viscosity** :- Viscosity was found out by comparing the time required to empty a 5 c.c. pipette, a definite volume between two marks. Liquid paraffin was taken as a standard for comparison. Viscosity of liquid paraffin was first determined very accurately at different temperatures from 20°C to 30°C. by comparing it with that of water. Viscosity of paraffin when plotted against temperature showed a linear relationship and a straight line graph was obtained. Viscosity of paraffin at 25°C. was 0.8 poises.

The viscosity of oil was determined by finding out the time required for the sample for emptying the pipette between two marks, and comparing it with the time required for paraffin, by the formula

\[ M = \frac{100 \, g \, k}{d \, l} \]
\[
\frac{t_1}{t_2} = \frac{n_1d_1}{n_2d_2}
\]

\( t_1 \) - Time required for oil sample to evacuate
\( t_2 \) - Time required for paraffin to evacuate the same vol.
\( d_1 \) - Density of oil (Average 0.935).
\( d_2 \) - Density of paraffin (0.778)
\( n_1 \) - Viscosity of the oil. (at 25°C)
\( n_2 \) - Viscosity of paraffin (0.8 poises at 25°C.)

(7) Peroxide value (Analyst 70, 403; 1945).

(C.B.Stuffins and H. Weatherall)
Peroxide value is expressed as c.cs. of N/500 sodium thiosulphate required to react with iodine liberated from potassium iodide by one gram of fat.

Reagents:

(i) Solvent - Two volumes of acetic acid and one vol. of chloroform.

(ii) N/500 sodium thiosulphate made every day fresh.
(from N/10 sodium thiosulphate).

(iii) Freshly prepared saturated solution of potassium iodide.

(iv) Starch solution.

(v) Carbon dioxide.

Procedure:

About 1 gram of oil is weighed accurately in a 100
c.c. flask and dissolved in 20 c.c. of the solvent mixture. 1 c.c. of saturated potassium iodide is added and the reaction is allowed to occur for one hour in an atmosphere of carbon dioxide. The mixture is then poured in a 250 c.c. flask. The mixture and washings are titrated against N/500 sodium thiosulphate using starch as an indicator (added at the end point).

\[ \text{Peroxide value (P.V.)} = \frac{\text{c.c. of N/500 sodium thiosulphate}}{\text{Weight of the oil taken}}. \]

(8) **Acetone number** :- Acetone number is quantity of acetone, in grams per 100 grams of oil, required to produce permanent cloudiness in the oil. (O. Grummith; A.A. Arters and J. Starns, J. Am. Oil. Chem. Soc. Vol. 28, 141-145; 1951).

Procedure :- 10 grams of oil were weighed in a 250 c.c. dry flask. The flask and the reagent (dry acetone) were kept at 30°C. in an air thermostat. Acetone was added by burette till there was persistent cloudiness in the oil.

\[ \text{Acetone Number} = \frac{\text{c.c. of acetone} \times \text{sp. gravity of acetone} \times 100}{\text{Weight of the oil}}. \]

(9) **Unsaponifiable matter** (Analyst 58, 203; 1933).

(Report of the Sub-Committee) 2 to 2.5 grams of oil were weighed accurately and
saponified by boiling with 25 c.c. of N/2 alcoholic potassium hydroxide with occasional stirring under reflux condenser. After saponification the contents were washed with 50 c.c. water and transferred to a separating funnel. The soap solution was extracted three times with 50 c.c. ether sulphuric. The ethereal extract was washed with N/2 alkali and finally with water. The washed ethreal layer was transferred to a tared flask and the ether distilled off. The residue was heated at 80°C. until constant weight was obtained. The results are expressed as percentage of unsaponifiable matter in oil.

**Study of absorption of oils in Ultraviolet Region**

When there are conjugated double bonds present in oil, absorption takes place at specific bands; for conjugated dienes there is absorption peak at 2320-2340 Å and for conjugated trienes absorption band appears at 2670-2680 Å. Moreover, it is reported that peaks appear in the far ultraviolet region (2050 to 2200 Å) when specific structures such as naphthalene-ring etc. are present in the sample. In the case of DCO only conjugated dienes are present and so in calculating the conjugated isomer it is customary to find out extinction coefficient of the sample at 2320-2330 Å and compared it with pure trans-trans diene and multiply the result by 100. Different E-values are reported for 9-11 linoleic acid, which fall in the range of 1150-1200 (for \( E_{1%}^{1cm} \)). In the present
investigation 1200 is taken as E-value for pure trans-trans conjugated isomer.

References

5. Chemical Spectroscopy - Brode W.R.

The experimental procedure lies in finding out E-values of a substance at various wavelengths. The substance is dissolved in suitable solvent to required dilution depending upon the nature of the substance. Optical density of the substance at different wavelengths is found out and the E-values are calculated by the formula

\[ \text{E} = \frac{d}{cl} \]

\( d \) - concentration of the solute in grams/100 c.c.
\( l \) - internal cell length in centimeters.

It is a common practice to write the unit of concentration as a superscript and the unit of cell length as a subscript e.g. \( E_{0.1cm}^{1\%} \).
Determination of E-values

About 0.1 gram of oil was weighed very accurately and dissolved in the solvent. The solution was diluted to the concentration of about 0.001 grams per 100 c.c. and the absorption was determined on Beckman Spectrophotometer Model DU (with photomultiplier attachment) in the range of 2050 - 2400 Å. The solvents used were cyclohexane and ethyl alcohol; the latter solvent was used only in the case of free fatty acids. The optical density observed at various wavelength was converted into E-values and the graphs of E-value against wavelength are plotted. Conjugation in DCO is calculated by the formula

$$\% \text{ Conjugation} = \frac{E\text{-value at } 2320 \text{ Å}}{1200} \times 100$$

Both solvents were specially purified for spectroscopic use. When compared with air Cyclohexane had 64 to 87% transmission at 2320 Å. Ethyl alcohol showed 83 to 87% transmission at 2320 Å. The solvents were stored in amber coloured bottles and were redistilled before use. All the apparatus for distillation or for dilutions was pyrex glass. Two matched silica cells of internal cell length of 1.001 cm. were used for finding out the absorption.

In the present investigation, a new peak was found to appear at wavelength 2100 Å, when intramolecular condensation took place during the heat treatment of the DCO.