

ENCLOSURE (B) 13

STUDIES OF PRELIMINARY PURIFICATION
OF DRY DISTILLATE FROM SODA SOAP

by

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|------|-------|-------|-------|--------|-------------|
| NAV. | CHEM. | ENG. | CAPT. | DR. | I. KAGEHIRA |
| | NAV. | CHEM. | ENG. | | M. MATSUI |
| NAV. | CHEM. | ENG. | LT. | COLR. | A. WAKANA |
| NAV. | CHEM. | ENG. | SUB | LIEUT. | M. DEHARA |

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ENCLOSURE (B)13

LIST OF TABLES
AND ILLUSTRATIONS

| | | |
|-----------------|---|----------|
| Table I(B)13 | Alkali Treatment | Page 169 |
| Table II(B)13 | Alkali-Distillation | Page 169 |
| Table III(B)13 | Alkali Distillation after Treatment with Alkali | Page 170 |
| Table IV(B)13 | Alkali-Distillation after Alkali-Treatment Using Water Trap | Page 170 |
| Table V(B)13 | Influence of Time | Page 171 |
| Table VI(B)13 | Influence of the Kinds of Purifying Agents | Page 171 |
| Table VII(B)13 | Calculated Carbonyl Value of Pure Ketones | Page 172 |
| Table VIII(B)13 | Carbonyl Value of Various Fractions | Page 172 |
| Table IX(B)13 | Calculated Carbonyl Content | Page 172 |
| Figure 1(B)13 | Effect of Time of Reaction on Carbonyl Value and Water Formed | Page 173 |
| Figure 2(B)13 | Apparatus for Pretreatment of Alkali-Distillation | Page 174 |

ENCLOSURE (B) 13

SUMMARY

Subjecting the sodium soap of a fatty acid to dry distillation, an oil which is thought to be composed of olefinic hydrocarbons with some impurities was obtained. This oil was purified by alkali distillation with 10% caustic soda and could be polymerized with no less than 10% of $AlCl_3$. The necessity of using this high quantity of $AlCl_3$ offers economic disadvantages. For instance, in order to obtain a #120 aeroengine oil with a yield of 15% of coconut oil, the quantity of $AlCl_3$ necessary for polymerization is more than 10% of the dry-distilled oil after treatment by alkali distillation. The impurities of the dry-distilled oil were also studied to find a better method of purification than alkali distillation.

The mechanism of dry distillation of sodium soaps was studied and carbonyl compounds were found in the dry-distilled oil as impurities. Efforts were made to get rid of these carbonyl compounds by distillation after condensing with 1% of caustic soda, since the condensed products of the carbonyl compounds will remain as residual matter.

It was found that the best method is to heat the dry-distilled oil at about $150^\circ C$ for 7 hours with 1% of caustic soda, attaching a water trap between the reflux condenser and the reaction vessel. It was then observed that the oil treated by the above method had a much lower carbonyl value than the oil treated by alkali distillation with 10% of caustic soda.

When carbonyl compounds are condensed in the presence of anhydrous $AlCl_3$, they split out water which diminishes the activity of $AlCl_3$ for the polymerization of olefinic hydrocarbons. Therefore, it is also necessary to determine the allowable maximum of the carbonyl value for the dry-distilled oil from fatty acid soaps in order to prepare aeroengine oil from it economically.

I. INTRODUCTIONA. History of Project

About twenty years ago efforts were made to obtain lamp oil from the sodium soaps of fatty acids by dry distillation. During the war, more efforts were made to get an aeroengine oil from these dry distilled oils of soda soaps. The amount of $AlCl_3$ required for the polymerization of dry-distilled oil was comparatively large due to impurities of the oil, and it has been reported that the best method of purification is by alkali distillation. There are two reactions in the dry distillation of soaps, namely:

1. $2R.COOM \rightarrow H_2O + M_2CO_3 + CO$ $M = Na, K.$
2. $(2R.CO)M \rightarrow R.CO_2 \cdot M.CO_2$ $M = Ca, Ba, Mg, \text{ etc.}$

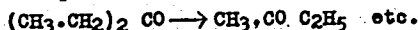
ENCLOSURE (B)13

According to M. SAITO's* studies, ketones are formed in Reaction 1 during the dry-distillation of sodium soaps, and, subsequently, olefines are formed by thermal cracking of these ketones.

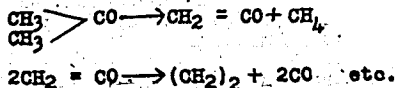
If it is assumed that this mechanism is correct, the thermocracking of ketones suggested by S. ARAKI** can be applied and accordingly asymmetric alkyl ketones would be formed in the dry-distilled oil to some extent.

By qualitative analysis it was found that this assumption was correct, since some carbonyl compounds were present in the dry-distilled oil. Thus, to exclude the carbonyl compounds from the dry-distilled oil in order to decrease the amount of $AlCl_3$ needed for polymerization, studies were conducted concerning the purification of dry-distilled oil.

Main reaction of this cracking is the thermocracking of alkyl-radicals:



Side reactions are:



II. DETAILED DESCRIPTION

To determine the quantity of carbonyl compounds in the oil, the method reported by HATAYAMA,*** using hydroxylamine hydrogen chloride, was used, and the carbonyl value was expressed as the mg of CO in 1 gm of sample. In this method an alcoholic solution of hydroxylamine hydrogen chloride in an excess KOH containing a drop of bromphenol blue indicator was prepared. This solution was poured into the sample and, after the reaction was complete, was titrated with 0.1 N HCl solution until excess alkali was neutralized. The carbonyl value was calculated as follows:

$$CO \text{ value} = \frac{28.02 \times (CO \text{ 0.1 N HCl for blank} - CO \text{ 0.1 N HCl for sample})}{10 \times \text{gm of sample}}$$

In this reaction oximes are produced in the following manner.



A. Treating with Alkali

Caustic soda was powdered and gradually added to a three-necked flask such as was used for the polymerization of oils. It was allowed to settle several hours. After filtering this precipitate, the filtrate was distilled from the first drop to $300^\circ C$, the distillate was washed with water, dehydrated by acid clay, and its carbonyl value measured. Using 1% of caustic soda, the effects of temperature and concentration of caustic soda solution and sodium metal were examined. The results are given in Table I(B)13.

- * J. Soc. Chem. Ind. Japan, 30(1927) 265
The mechanism of thermo-cracking of Stearin-soda.
- ** J. Chem. Soc. of Japan. (1930) 560
Thermo-cracking of ketones.
- *** Report of Nippon-Tsui Research Committee. p64 March, 1944.
HATAYAMA, "Qualitative Analysis of Carbonyl Compounds in Hydrocarbonar"

ENCLOSURE (B) 13

From these results it may be concluded as follows:

1. The influence of temperature is not appreciable.
2. The more solid caustic soda used, the further the polymerization proceeds, and the more the carbonyl value will be lowered.
3. When an aqueous caustic soda solution is used, the condensation of carbonyl compounds does not proceed to any great extent.

From these facts it was observed that water acts as a poison in the polymerization of carbonyl compounds with caustic soda and it can also be concluded that solid alkali serves to promote the polymerization of carbonyl compounds. The sixth experiment is of interest since it gives the lowest carbonyl value. This can be explained by the fact that some of the sodium metal first becomes caustic soda because of traces of water and further water produced from the reaction catalyzed by the caustic soda also reacts immediately with sodium metal and is removed. Hence, no poisonous influence of water on the polymerization occurs.

B. Alkali Distillation

Alkali distillation has been said to be the best method for the preliminary purification of dry-distilled oil and to give lower carbonyl values. This may be explained as follows:

1. In the alkali-distillation the polymerizing reaction of carbonyl compounds proceeds smoothly because the water is removed from the reaction zone as soon as produced. The presence of water in the alkali-distilled oil can easily be recognized by the turbidity.
2. Caustic soda remains undistilled and its concentration increases as the reaction proceeds.

There are some interesting relations between the alkali-distillation method and the carbonyl values of the product:

1. No great difference of effect can be observed when 1% or 10% of caustic soda is used although the latter gives a slightly lower carbonyl value.
2. Distilling the oil twice with 1% caustic soda, the same result was obtained as when 10% caustic soda was used.

From the results shown in Table II(B)13, the following two conclusions may be drawn:

1. Caustic soda acts as a catalyst, and the reaction depends more upon its catalytic condition than its quantity.
2. Polymerization of carbonyl compounds occurs during a comparatively long time, yet in the case of alkali-distillation, the time of distillation is not constant and the time is not adequate.

Therefore, with the same quantity of caustic soda the carbonyl values of the product will vary.

For these reasons it was intended to polymerize carbonyl compounds with caustic soda before alkali distillation.

ENCLOSURE (B)13

C. Alkali Distillation after Treating with Alkali

The dry-distilled oil was treated with 1% of caustic soda by the same method as for the alkali treatment and was distilled. The results are given in Table III(B)13.

Comparing the results of Table III(B)13 with Table I(B)13, the following points will be observed:

1. Method (C) is better than (A) but almost the same as (B).
2. Hardly any influence of pretreatment of alkali is observed.
3. When a dehydrating agent such as CaO is present, the results are slightly better.

These results showed that water was very injurious to the activity of caustic soda in the polymerization of carbonyl compounds. To eliminate the water from the reaction zone the following methods might be adopted.

1. To use chemical dehydrating agents in the reaction flask.
2. To use a means of removing the water formed during the reaction.

In the first method, the dehydrating agent must be stable towards heat and not react with olefinic hydrocarbons. For this purpose some alkali metals would be suitable.

In the second method a water reflux trap was used, and its behavior was studied.

D. Alkali-Distillation Using a Water Trap

Dry-distilled oil was heated with 1% caustic soda in a flask fitted with a reflux condenser and a reflux water trap. After refluxing, the oil was distilled. Detailed procedure was as follows:

A 200 gm sample was heated without caustic soda and 0.08cc of water was found in the water trap. When 1% of solid caustic soda and some pieces of boiling stones were added to the oil, and heated to 140-180°C, the water was distilled out gradually and after 5 hrs an additional 1.92cc of water was caught in the water trap. The oil was then distilled from the flask. The carbonyl value was determined as 11.6 after the distilled oil had been washed with water and dehydrated by acid clay. This carbonyl value was lower than that of any of the alkali-distilled oils with 1% of caustic soda. On this basis, this apparatus was adopted for use in further alkali-purification studies. The results are tabulated in Table IV(B)13.

E. Influence of Heating Time When Using a Water Receiver

Treating dry-distilled oil with 1% of caustic soda with the same apparatus as used in experiment (D), studies were carried out to determine the suitable treating time and the correlation between water formed and carbonyl-value. The results were as shown in Table V(B)13 and Figure 1(B)13.

1. The sample used was a fraction boiling up to 300°C of dry-distilled oil from sodium soap of coconut oil having the following properties:

ENCLOSURE (B) 3

| | |
|----------------------------|--------|
| Density | 0.7770 |
| Saponification value | 0.66 |
| Iodine value | 120.5 |
| Acid value | 0.29 |
| Carbonyl value | 33.0 |

Distilling Characteristics

| | |
|------------------|-------|
| First drop | 72°C |
| 10% | 103°C |
| 20% | 137°C |
| 30% | 153°C |
| 40% | 172°C |
| 50% | 182°C |
| 60% | 200°C |
| 70% | 240°C |
| 80% | 252°C |
| 90% | 274°C |
| 95% | 284°C |
| Dry point | 298°C |

2. Influence of Time of Reaction on Carbonyl Value. A plot of the carbonyl value showed that it decreased rapidly during the first hour of refluxing and reached a sufficiently low carbonyl value after 7 or 8 hours, using 1% of caustic soda. From this experiment, it appears that alkali distillation is not suitable for the purpose of polymerizing carbonyl compounds from the standpoint of reaction time.

3. Correlation Between the Amount of Water Formed and Carbonyl Value. Even though the dehydrating polymerization of the carbonyl compounds seemed to be the same as in the aldol-condensation, it is necessary to correct the assumption that all oxygen atoms of carbonyl-radicals are converted to water. The time necessary for the purification can be estimated from the water producing curve, which approaches a maximum as the carbonyl value approaches a minimum.

This fact would be of value in commercial practice. The end point of the purifying reaction is the point where differential of the water in respect to time first becomes zero, namely $\frac{dV}{dt} = 0$; where V=volume of the water formed, t=time. If Q cc of oil is treated and the original carbonyl value "a" is decreased to "b" the correlation formula will be as follows:

$$\int dV = (a-b) \times \frac{16}{18} \times \frac{18}{16} \times \frac{Q}{1000} \dots\dots\dots(1)$$

$$\therefore b = a - \frac{14000}{9} \left(\frac{dV}{Q} \right) \dots\dots\dots(2)$$

For instance, taking as an example a treating time of 7 hrs from Table I(B)13, "t" is 7, a is 33.0 and b is 94. Substituting these values in formula (2), a calculated value of water formed will be obtained as follows:

$$\left(\frac{dV}{Q} \right) \times 100 = 1.57ae$$

In this experiment, the water formed was 1.60cc. This agreement shows that formula (2) can be applied for determining carbonyl values instead of chemical analysis.

ENCLOSURE (B) 13F. Influence of the Kinds of Purifying Agents

The influence of the quantity of caustic soda and the effect of using caustic-potash, sodium carbonate and a sodium carbonate-calcium oxide-water mixture were studied, and the following results were obtained:

1. Sample: A redistilled oil of the dry-distillation product from the sodium soap of cocconut oil having the following properties was used:

Carbonyl value = 45.6, time of treatment = 8 hr.

2. The results are tabulated in Table VI(B)13. From these results the following conclusions can be drawn:

- a. The necessary quantity of caustic soda is 1%.
- b. Caustic soda is better than caustic-potash as a purifying agent.
- c. Purification can be accomplished by using a comparatively large quantity of sodium carbonate.

G. Correlation Between Carbonyl Value and the Carbonyl Compounds in Any Fraction

To judge the degree of purification from the lowering of the carbonyl value, it is necessary to investigate the concept of carbonyl values. Real correlation between carbonyl value and a carbonyl compound in any fraction can be judged by comparing the carbonyl value with the amount of pure ketones contained. Previously, it has been considered that the fraction below 300°C is composed of olefines and the higher boiling fraction is composed of ketones.

The carbonyl value of pure ketones distilled between 250°-300°C is 50-100 and that of the fraction of dry-distilled oil from the soda soap of cocconut-oil is 64.7. This fraction may be considered to consist mainly of ketones. After purification the carbonyl value of this fraction is 9.7, and it consists mainly of olefines.

Carbonyl values of some pure ketones can be calculated as in Table VII(B)13.

Various fractions of dry-distilled oil were treated twice with 1% of caustic soda using a reflux and water trap. They were redistilled from an Engler-flask and the same fractions were obtained. The carbonyl value of these fractions were determined and compared with the previous values. The results are recorded in Table VIII(B)13.

The difference of carbonyl value between fractions for both the crude oil and the refined oil was small, and the content of carbonyl compounds in each fraction was calculated using the H. W. of the pure carbonyl compounds boiling within the prescribed boiling range. (Table VIII(B)13)

III. CONCLUSIONS

The necessity of preliminary purification before alkali-distillation in the manufacturing of aero-engine oil from vegetable oils was determined. This preliminary purification acts as a process to exclude the harmful effects of carbonyl compounds on the polymerization of olefines with $AlCl_3$ by condensing the carbonyl-containing compounds. The carbonyl value should always be considered, and should be kept at a minimum in the re-purification process. An

ENCLOSURE (B)13

apparatus suitable for the pretreatment of alkali-distillation is suggested in Figure 2(B)13.

To avoid the harmful effect of carbonyl compounds, the dry-distilled oil of fatty acid soda soaps must be treated with caustic soda in such a manner that the water formed by the condensation of carbonyl-compounds is removed from the reaction zone. (See Figure 2(B)13.)

Table I(B)13
ALKALI TREATMENT

| No. | Purifying Agent | CO value of Sample | Temp. (°C) | Stirring Time (hr.) | Settling Time (hr.) | Yield of Purified Oil (%) | CO Value Purified Oil |
|-----|--------------------------|--------------------|------------|---------------------|---------------------|---------------------------|-----------------------|
| 1 | NaOH 1% | 40.0 | 24 | 1 | 20 | 61.2 | 22.3 |
| 2 | NaOH 1% | 40.0 | 65 | 10 | 24 | 55.3 | 27.6 |
| 3 | NaOH 1% | 40.0 | 150 | 10 | 24 | 56.0 | 27.2 |
| 4 | NaOH 10% | 40.0 | 65 | 10 | 24 | 35.2 | 24.1 |
| 5 | NaOH 10% (aq. soln. 15%) | 40.0 | 65 | 10 | 24 | 74.5 | 30.7 |
| 6 | metal Na 0.6% | 40.0 | 24 | 10 | 24 | 49.0 | 15.3 |

Table II(B)13
ALKALI-DISTILLATION

| No. | Purifying Agent | CO Value of Sample | Method of Treatment | Yield of Purified Oil (%) | Purified Oil (CO value) | Note |
|-----|-----------------|--------------------|--|---------------------------|-------------------------|--|
| 7 | NaOH 1% | 40.0 | Alkali-dist. | 67.2 | 16.8 | after the 1st Alkali-dist. CO-value was 19.9 |
| 8 | NaOH 10% | 40.0 | Alkali-dist. | 71.5 | 13.4 | |
| 9 | NaOH 2% | 40.0 | Alkali-dist. twice with 1% NaOH in each case | | 13.4 | |

ENCLOSURE (B)13

Table III(B)13
ALKALI DISTILLATION AFTER TREATMENT WITH ALKALI

| No. | Purifying Agent | CO Value of Sample | Treating Temp (°C) | Stirring Time (hr) | Settling Time (hr) | Yield of Purified Oil % | CO Value of Purified Oil |
|-----|--------------------|--------------------|--------------------|--------------------|--------------------|-------------------------|--------------------------|
| 10 | NaOH 1% | 40.0 | 24 | 5 | 10 | 90.0 | 16.1 |
| 11 | NaOH 1% CaO 10% | 40.0 | 24 | 5 | 10 | | 15.4 |
| 12 | NaOH 1% | 40.0 | 150 | 5 | 10 | 84.5 | 21.8 |

Note: Heat reflux condenser.

Table IV(B)13
ALKALI-DISTILLATION AFTER ALKALI-TREATMENT USING WATER TRAP

| No. | Purifying Agent | CO Value of Sample | Treating Temp (°C) | Treating Time (hr) | Settling Time (hr) | Yield of Purified Oil (%) | CO Value Purified Oil | Note |
|-----|---|--------------------|--------------------|--------------------|--------------------|---------------------------|-------------------------------|--------------|
| 13 | NaOH 1% | 40.0 | 140 | 5 | 20 | 77.5 | 11.6 | |
| 14 | NaOH 3% | 27.6 | 150 | 10 in each case | 0 | | 1st 9.7 2nd 5.4 3rd 4.8 | |
| 15 | Mn ₂ O ₃ 15.3% CaO 7% | 40.0 | 150 | 6 | 0 | | 14.6 | water 0.671% |
| 16 | NaOH 1% | 16.3 | 150 | 6 | 0 | 70.1 | 4.7 | water 0.861% |
| 17 | NaOH 1% | 16.3 | 150 | 6 | 0 | 79.2 | 11.4 | water 1.00% |

*three times with 1% in each.

ENCLOSURE (B)13

Table V(B)13
INFLUENCE OF TIME*

| No. | Treating Time | Water Formed (%) | CO Value of Purified Oil | Yield (%) | Calc. Quantity of Water Formed Using the Formula $\frac{9}{100} (a-b)$ |
|-----|---------------|------------------|--------------------------|-----------|--|
| 18 | 1 | 0.5 | 18.3 | 84.0 | 0.9 |
| 19 | 2 | 0.8 | 19.3 | 92.0 | 0.4 |
| 20 | 3 | 1.0 | 16.6 | 84.8 | 1.0 |
| 21 | 5 | 1.5 | 12.9 | 93.4 | 1.2 |
| 22 | 7 | 1.6 | 9.4 | 85.3 | 1.57 |
| 23 | 9 | 1.4 | 9.2 | 70.5 | 1.5 |
| 24 | 12 | | 8.8 | | 1.6 |

*Purifying agent: 1% NaOH
 Treating temp: 150°C
 Initial carbonyl value = 33.0

Table VI(B)13
INFLUENCE OF THE KINDS OF PURIFYING AGENTS
(Original CO value = 45.6)

| No. | Purifying Agent | Cono. (%) | Water Produced (cc) | Yield (%) | CO Value of Purified Oil |
|-----|--|-------------------|---------------------|-----------|--------------------------|
| 25 | NaOH | 2.0 | 2.0 | 93.5 | 11.1 |
| 26 | NaOH | 1.0 | 2.0 | 94.0 | 11.8 |
| 27 | NaOH | 0.5 | 0.5 | 88.0 | 24.6 |
| 28 | NaOH | 0.1 | 0.3 | 92.0 | 41.3 |
| 29 | KOH | 1.4 | 2.0 | 88.5 | 18.0 |
| 30 | KOH | 1.0 | 1.4 | 98.1 | 20.6 |
| 31 | Na ₂ CO ₃ | 5.0 | | | 10.6 |
| 32 | Na ₂ CO ₃ CaO H ₂ O | 1.3 0.7 5.0 | | 85 | 17.4 |

ENCLOSURE (B)23

Table VII(B)13
CALCULATED CARBONYL VALUE OR PURE KETONES

| Name | Experimental Formula | Boiling Pt (°C) | Melting Pt (°C) | CO Value |
|---------------------|----------------------|-----------------|-----------------|----------|
| Acetone | $(C_2H_2)_2CO$ | 57 | | 482.7 |
| Methyl ethyl ketone | $C_2H_5.CO.CH_3$ | 80 | | 388.8 |
| Diethyl-ketone | $(C_2H_5)_2CO$ | 101 | | 345.6 |
| Butyrene | $(C_3H_7)_2CO$ | 143 | | 245.6 |
| Valenone | $(C_4H_9)_2CO$ | | 42 | 197.1 |
| Carbronone | $(C_5H_{11})_2CO$ | 227 | 15 | 164.7 |
| Erantone | $(C_6H_{13})_2CO$ | 264 | 30 | 141.4 |
| Peralgone | $(C_8H_{17})_2CO$ | | 50 | 110.2 |
| Myristone | $(C_{13}H_{27})_2CO$ | | 76 | 71.0 |
| Palmitone | $(C_{15}H_{31})_2CO$ | | 83 | 62.2 |
| Stearone | $(C_{19}H_{35})_2CO$ | | 88 | 55.3 |

Table VIII(B)13
CARBONYL VALUE OF VARIOUS FRACTIONS

| Sample | 0-330°C | 0-150°C | 150-200°C | 200-250°C | 250-300°C |
|---|---------|---------|-----------|-----------|-----------|
| Dry-dist. oil | 45.6 | 33.2 | 34.0 | 46.3 | 64.7 |
| Purified oil | 8.2 | 8.1 | 7.0 | 5.9 | 9.7 |
| Pure alkyl ketones* | | 480-240 | 240-160 | 160-140 | 160-150 |
| Average of pure alkyl ketones taken for a scale | | 350 | 200 | 150 | 75 |

*Range of carbonyl values of ketones listed in Table VII(B)13 and boiling within each temperature range.

Table IX(B)13
CALCULATED CARBONYL CONTENT

| Sample | 0-150°C | 150-200°C | 200-250°C | 250-300°C |
|---|---------------|----------------|----------------|---------------|
| Quantity of CO contained in dry-distilled oil | 33.2/350=9.5% | 34.0/200=17.0% | 46.3/150=30.8% | 64.7/75=86.3% |
| Quantity of CO contained in purified oil | 8.1/350=2.3% | 7.0/200=3.5% | 5.9/150=3.9% | 9.7/75=12.9% |

ENCLOSURE (B) 13

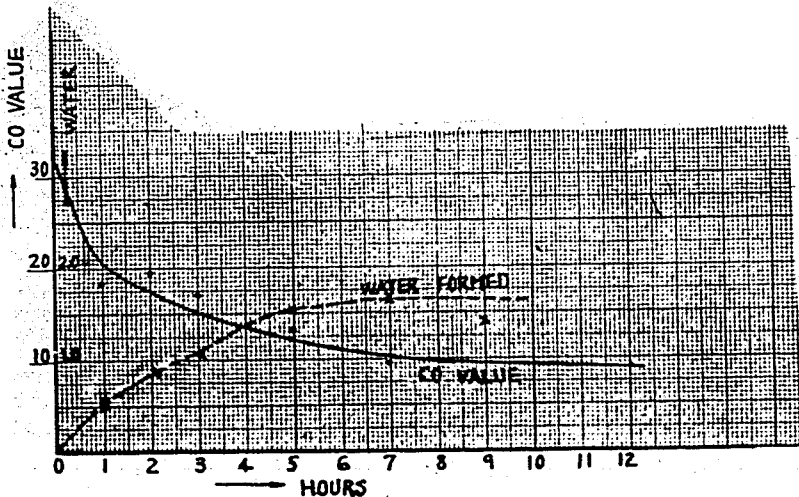


Figure 1(h) 13
EFFECT OF TIME OF REACTION ON
CARBOXYL VALUE AND WATER FORMED

ENCLOSURE (B)13

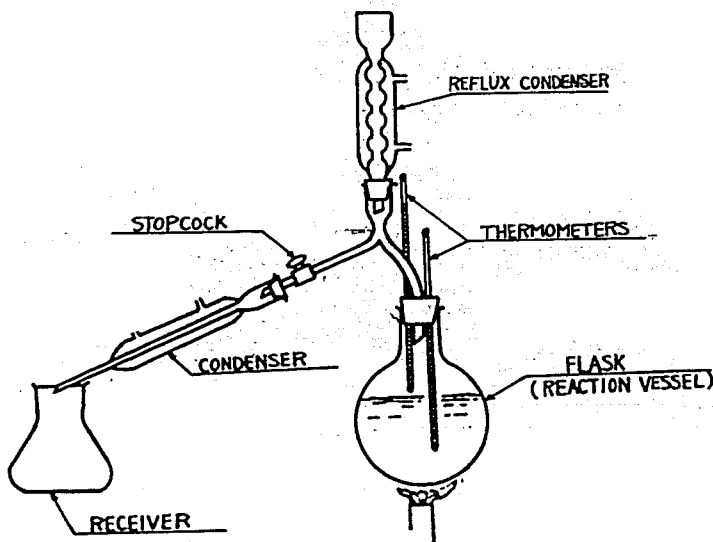


Figure 2(B)13
 APPARATUS FOR PRETREATMENT
 OF ALKALI-DISTILLATION

Figure 2(B)13

The dry distilled oil and caustic soda are put in the flask and heated for seven or eight hours at 150°C , while the stopcock is closed. The water produced is caught in the tube above the stopcock and the oil returns to the reaction vessel. Then heating is stopped and the stopcock is opened to take out the water. Heat is applied again and the purified oil is obtained in the receiver.