

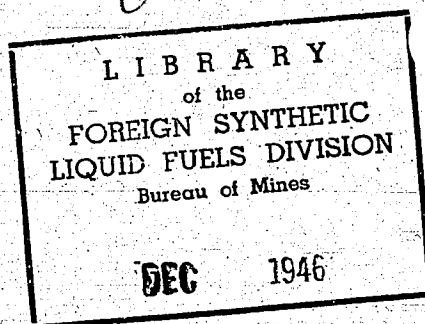
Copy 1

B.I.O.S. FINAL REPORT No. 748
ITEM No. 22

MANUFACTURE OF FATTY ACIDS BY OXIDATION OF PARAFFINS, HYDROGENATION OF THE FATTY ACIDS

at I.G. Ludwigshafen - Oppau

Lanning, H. J. + Clark, J. G.



This report is issued with the warning that, if the subject matter should be protected by British Patents or Patent applications, this publication cannot be held to give any protection against action for infringement.

BRITISH INTELLIGENCE OBJECTIVES SUB-COMMITTEE

MANUFACTURE OF FATTY ACIDS
BY OXIDATION OF PARAFFINS,
HYDROGENATION OF THE FATTY ACIDS.
AT I.G. LUDWIGSHAFEN - OPPAU.

Reported by:

H. J. Lanning

G. C. Clark

BIOS Trip No: 1124

BIOS Target Number: 22/1(f).

British Intelligence Objectives Sub-Committee,

32, Bryanston Square, W. 1.

TABLE OF CONTENTS.Subject.Page No.Manufacture of Fatty Acids.

Raw Materials	3.
Purification	3.
Oxidation	3.
Distillation	4.
Consumption of Raw Materials	5.
Application of the Products.	6.

Hydrogenation of Fatty Acids, Oppau.

Process and Plant for Low Boiling Acids	7.
Catalyst	9.
Hydrogen and Purity of Product	10.
Process for Soap Acids	11.
Process for High Boiling Acids.	12.

Hydrogenation of Soap Acids, Ludwigshafen.

Process, Plant, Catalyst.	13.
Hydrogen and Purification of Product	14.
Discontinuous Process	15.

Appendices.

"A" Flow Sheet for oxidation of the paraffins.	
"B" Flow Sheet for saponification, separation of unsaponifiable and splitting of the soap.	
"C" Flow Sheet for distillation of the fatty acids.	
"D" Flow Sheet of Fatty Alcohols Plant.	

Composition of Team.

Lanning M.O.S.
Clark M.O.S.

Manufacture of fatty acids by oxidation of
paraffins at I.G. Farbenindustrie,
Oppau works.

The following information was supplied by Dr. Wietzel, at Oppau, Ludwigshafen on Rhine.

Raw Materials: Synthetic paraffins obtained from hydrogenation of carbon monoxide (Fischer-Tropsch process) or from low temperature carbonisation of lignite. The average melting point of the paraffins is 30-50°C, and the average chain length C₁₈ to C₃₀.

Purification: The paraffins are treated in the cold with aluminium chloride, followed by Tonsil. With some poor quality paraffins, a little sodium carbonate is also added.

Oxidation: Potassium permanganate (0.15% calculated on the paraffin) is added in aqueous solution to the paraffins, and the water is evaporated off. This procedure gives good dispersion of the permanganate. The treated paraffin is passed to one of four vertical cylindrical reaction vessels of aluminium, 12 m height x 2.6 m diameter. The charge of each of these four vessels is 30 tons. The portions of the towers which are above the liquid level are constructed of stainless steel, to resist corrosion by the low molecular weight acids formed. The towers are each provided with 12 circular plates arranged in the base - each plate being about 30 cm diameter and consisting of porous ceramic material (Fritten) through which the air for oxidation passes. Although on the laboratory scale the pore size is of considerable importance, this is not found to be the case on a works scale. The oxidation reaction is exothermic and the temperature is maintained at 100-120°C by means of water circulation through the jacket provided. The gases formed during oxidation are in part condensed, the uncondensed portions passing through a tower where they are sprayed with a mixture of water and the oily condensate. The evil-smelling washed gases are burnt.

When approximately one third of the paraffin charge has been oxidised, the latter is passed to a steel tank where it is saponified. This stage is reached in 16-36 hours (average 24 hours) - depending on the quality of the paraffin

used. The acid value of the partially oxidised mass is 60-65. The soap is pumped to a 30 cbm autoclave where it is heated to 150°C by means of a heat-exchanger. Part of the unsaponifiable separates and is returned via a wash tower to the original paraffin stock tank. The remainder of the material, which contains sodium soaps and further unsaponifiable goes to a coil consisting of a number of hair-pin turns, where it is heated to 270-300°C under a pressure of 80-120-atms. Oxyacids are partly converted to unsaturated acids at this stage. The pressure is then released, the temperature falling to 150°C, and the material is passed through a coil of similar construction where it is reheated to 330-360°C under atmospheric pressure. The coils in both the high and low pressure systems are 90 mm internal x 127 mm external diameter, and the loops are each 7 meters high. The high pressure side has 28 turns and the low pressure side 9 turns. The heating of both systems is by hot gas circulation (Umwalzgebläse).

After the low pressure heating, the remainder of the unsaponifiable distils off in steam and returns via a spray to the paraffin store tank. The soap issues in molten form to a tank where it is dissolved in water and passes to a tiled tank provided with a lead-covered stirrer where it is acidified with sulphuric acid. The aqueous layer is discarded and the crude fatty acid, after passing a wash tower, is distilled.

Distillation: The crude acids pass through a meter to a pre-heater, and thence to four or more stills in series, where they are distilled under 4 mm pressure. The stills are each 8 m x 2.2 m diameter, and are heated by high pressure steam or hot water. The columns, which are packed with Raschig rings measure:-

	Col.1	Col.2	Col.3 and subsequent
Height	3.4 m	4.0 m	3.6 m
Diameter	2.2	1.8	1.0

The fractions obtained are as follows:-

Vorlauf I	C ₄ - C ₆)	about 10% of original paraffin.			
" II	C ₇ - C ₉)				
Hauptlauf	C ₁₀ - C ₁₈	" 50%	"	"	"
Nachlauf I	C ₁₈ - C ₂₀)	" 5%	"	"	"
" II	C ₂₀ - C ₂₅)	" 10%	"	"	"
Residue					

The total yield is 75-80% of the original paraffin, the remainder being lost as gas, entrained oily materials and $C_1 - C_4$ acids in the various washes. It was intended to extract these latter with petrol, but this was never carried out. The brine cooling arrangement in the flow sheet for the distillation was intended to remove mists, but did not prove very satisfactory. In general the Hauptlauf and Nachlauf I were united.

The oxidation is carried out batchwise but all the subsequent operations - saponification, separation, splitting and distillation - are continuous.

Consumption of Raw Materials: Some figures for raw material consumption and yields are given below for what is described as a typical run (from 1st August to 1st September 1941). These figures were not given by Dr. Wietzel but were taken from correspondence filed elsewhere. It will be seen that some figures - particularly those for the yield - differ greatly from the figures given by Dr. Wietzel. This may possibly be explained by the fact that the correspondence in question was concerned with tracing the reasons for a very great loss made by the Oppau works - 2.2 million Reichsmark for a period not stated.

<u>Material</u>	<u>Kg used</u>	<u>Reichsmark per 100 kg</u>
Crude paraffins	1,406,319	28.30
Tonsil	14,500	18.20
Potassium permanganate	4,720	54.22
Aluminium chloride	25,900	30.96
Soda Ash	3,160	5.21
Caustic soda	384,614	8.75
Sulphuric acid	399,048	4.65

The chief costs for the above quantities were:-

Labour - Reichsmark	49,051
Power - "	47,624
Repairs - "	50,000

Yields:-

Seifenfettsäure	457,697 kg
Nachlauffettsäure	41,689
Vorlauffettsäure	42,557
Primärseife	2,910

Comments: No satisfactory explanation was forthcoming from Dr. Wietzel for the high pressure heating of the crude soaps in the coil system. He indicated that this was not carried out at some other factories, and this seems to be borne out by reports by other investigators on the I.G. Leuna works and on the Deutsche Fettsäurewerke, Witten/Rhur. On the other hand Dr. Wietzel stated that I.G. Heydebreck used the Oppau system. Each of these latter factories had a capacity capable of treating 20,000 tons paraffins per annum.

Applications of the Products:

Hauptlauf: Chiefly used for soap making, and for preparation of Igepon wetting agents and sulphonated fatty acids. The conversion into edible fats had reached the experimental stage only, at Oppau. Some of these acids were hydrogenated to alcohols for sulphonation to detergents.

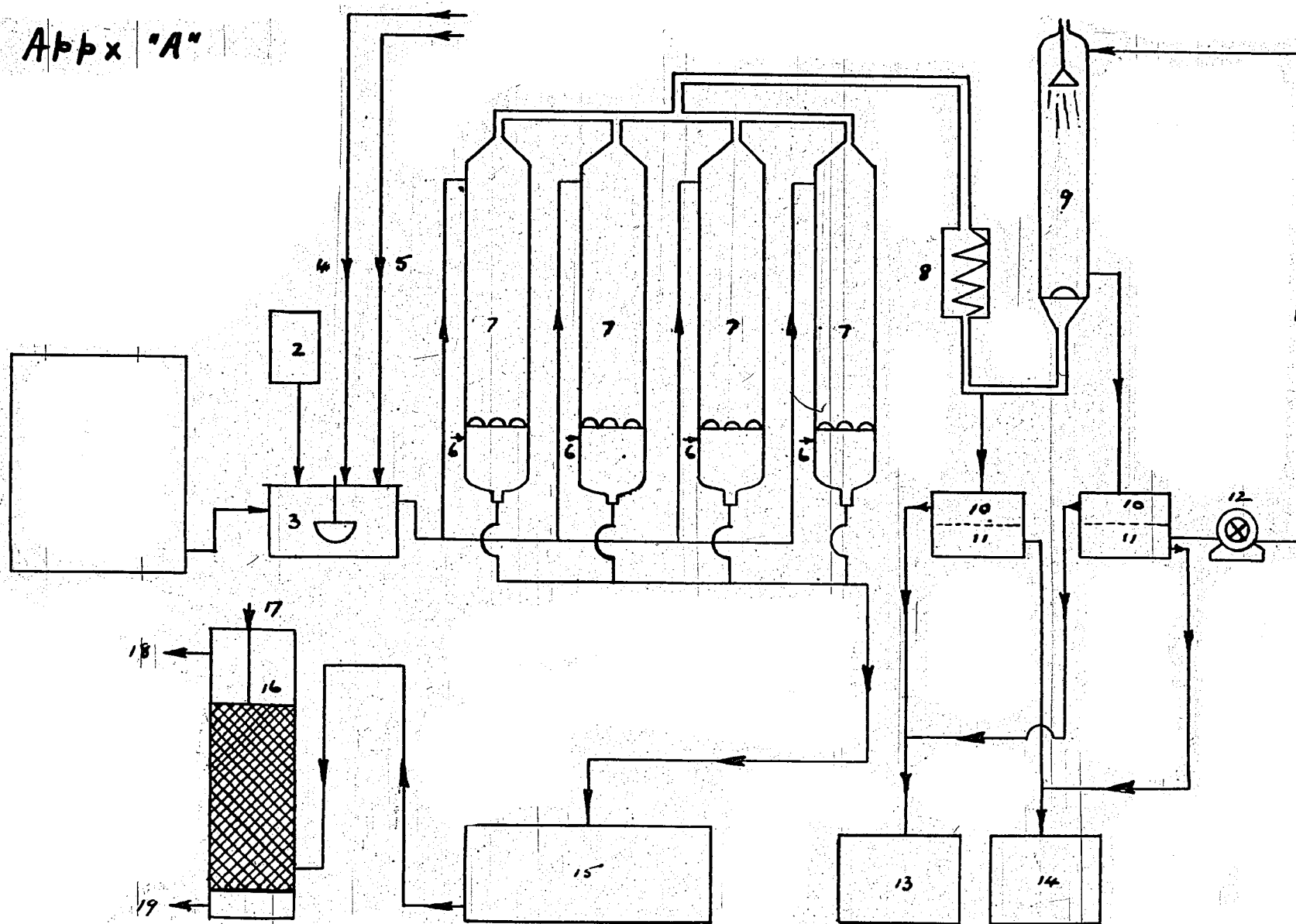
Vorlauf I: Mostly combined with Vorlauf II and hydrogenated to alcohols which are then split into $C_4 - C_6$ and $C_7 - C_9$ alcohols. These two groups are esterified with phthalic anhydride, yielding plasticisers - Palatinsols HS and F respectively.

Vorlauf II: Partly ketonised for wetting agents.

Nachlauf II: converted to sodium soaps for use as lubricating greases.

Residue: Mostly used for stoving enamels. Part hydrogenated and sulphonated.

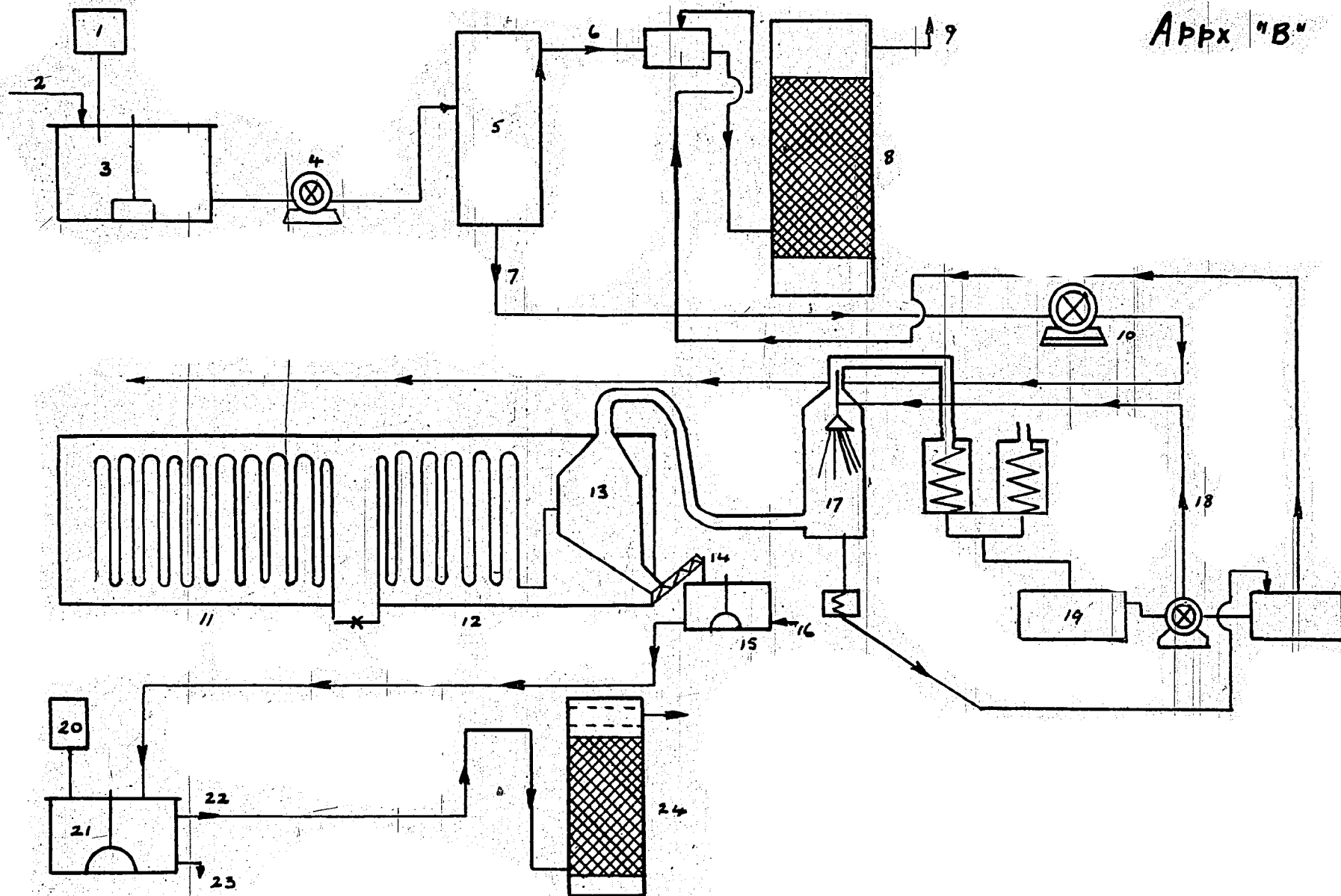
Аппарат "А"



Key to Appendix "A"

- 1 Paraffin tank
- 2 Permanganate solution
- 3 Vessel for mixing the charge
- 4 Unsaponifiable I
- 5 Unsaponifiable II
- 6 Air
- 7 Oxidation Towers
- 8 Off-gas cooler
- 9 Sprayer for off-gas
- 10 Oily condensate
- 11 Aqueous condensate
- 12 Pump
- 13 Oily condensate
- 14 Aqueous condensate
- 15 Oxidation products
- 16 Wash tower
- 17 Water
- 18 Oxidation product to saponification
- 19 Water

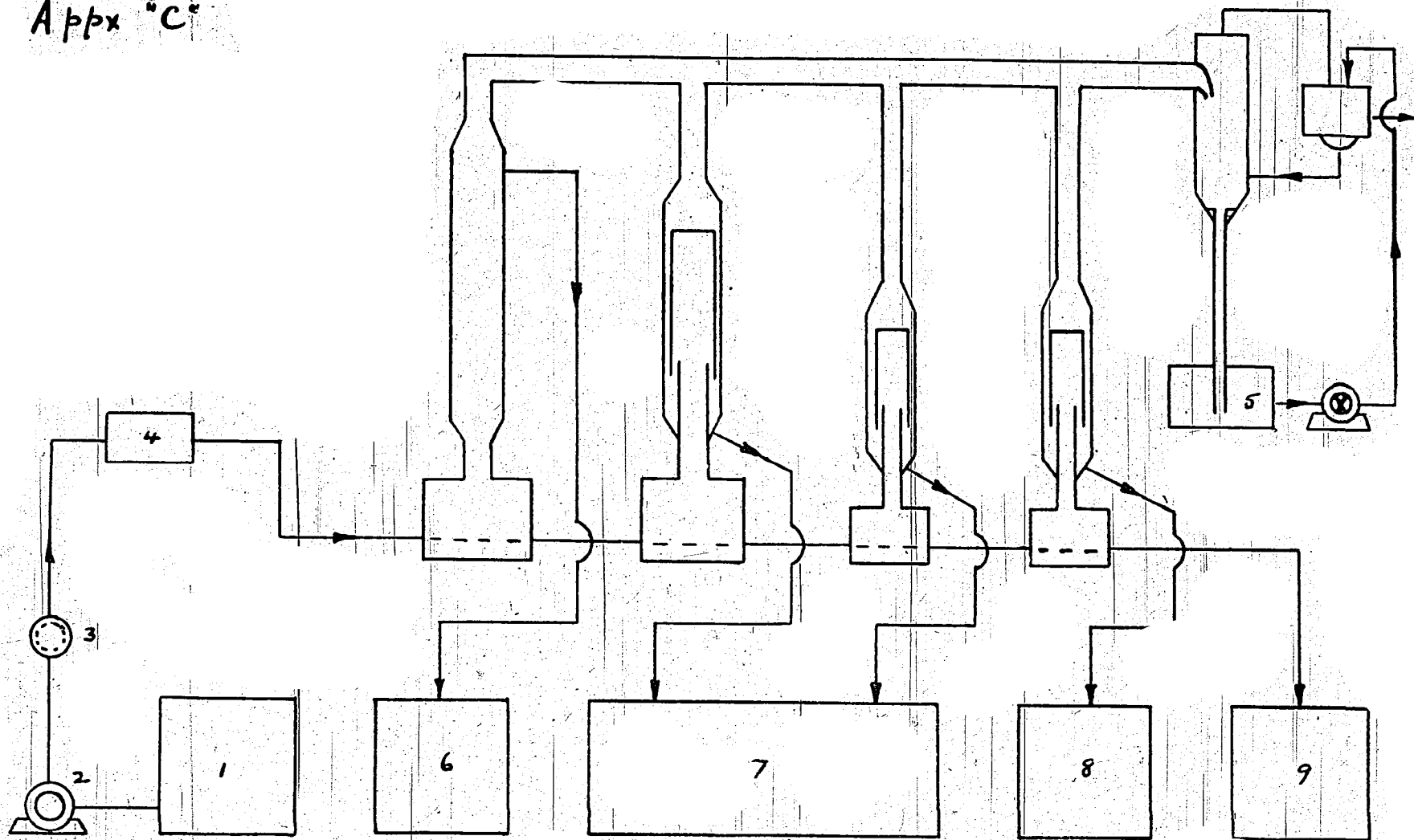
Appx "B"



Key to Appendix "B"

- 1 Caustic Soda solution
- 2 Oxidation product
- 3 Saponification tank
- 4 Pump
- 5 Autoclave
- 6 Unsaponifiable I
- 7 Crude soap solution containing unsaponifiable matter
- 8 Wash tower
- 9 Return to oxidation
- 10 High pressure pump
- 11 High pressure heating
- 12 Atmospheric pressure heating
- 13 Vapours of unsaponifiable II
- 14 Molten soap
- 15 Soap-dissolving tank
- 16 Water
- 17 Condensation of Unsaponifiable II
- 18 Part of Unsaponifiable II to the spray
- 19 Separating tank for Unsaponifiable II and water
- 20 Sulphuric acid
- 21 Soap splitting
- 22 Crude fatty acids
- 23 Sodium sulphate solution
- 24 Wash tower

Appx "C"



Key to Appendix "C"

- 1 Crude fatty acids
- 2 Pump
- 3 Meter
- 4 Pre-heater
- 5 Brine cooling tank
- 6 Vorlauf fatty acids
- 7 Hauptlauf and Nachlauf I fatty acids
- 8 Nachlauf II fatty acids
- 9 Residue from stills

I.G. Farbenindustrie, A.G., Oppau.

FATTY ACIDS HYDROGENATION

General.

The raw materials were fractions of the fatty acids produced by oxidation of paraffins. The materials were divided into three groups as follows, and were hydrogenated separately.

Low boiling	C ₄ - C ₉ acids
Soap	C ₁₀ - C ₂₀ "
High boiling	C ₂₀ - C ₃₀ " (approximately).

Production at rate of 100-tons monthly was achieved with the low boiling acids, but due to economic reasons only 50-tons of soap and some 20/30-tons of higher acids had been worked in toto.

Some details of the process were protected in German Patent Applications -

J 71469	12 0	31.1.1942.
J 74465	12 0	12.1.1943.

Process - low boiling acids.

The basic process depends on hydrogenating esters from acids reacted with the alcohols of the corresponding group. It was considered that it would have been advantageous to have used the lower boiling fractions of the alcohols as the esterification raw material, but in fact as a general policy the total alcohols were esterified with the total acids of the same group.

The flow sheet of the plant is given in Appendix D. From this it will be seen that the steps were -

- a. esterification of acids with part of the previous production of alcohols.
- b. hydrogenation at 270°C and 250 ats. pressure in continuous plant.
- c. separation of product and return of part to esterify subsequent charge of acids.
- d. rectification of remainder of product to give C₄ - C₆ and C₇ - C₉ alcohols for use in plasticisers.

Fatty Acids Hydrogenation (Continued 1.).

Esterification.

The charge of acid and alcohol was heated in a stirred V2A vessel at atmospheric pressure, and the esterification water removed using the alcohols as entrainer. The vapourised alcohols were returned to vessel via a decanter. The temperature was finally taken to 200°C in a period of 8 hours. This stage was discontinuous.

The crude esterification product had an acid value of 30 and was used without any further treatment.

Hydrogenation.

The hydrogenation circuit consists of preheater, reactor, separator and the necessary feed and circulating pumps and storage vessels. All pipes and vessels handling acid or ester were of V2A alloy steel, but on the product side non-alloy steels were used.

Preheater.

A V2A vessel equipped with 12 atms. steam coil. Hydrogen circulated through this unit transferred all the heat needed in reactor during the heating and catalyst reduction periods. During the hydrogenation period ester and circulating gas were preheated to 250°C in this unit.

Reactor.

A well lagged steel shell fitted with a V2A liner a few millimetres thick. The liner was secured to the shell at each end.

Dimensions of shell were -

Length	12 metres (40 ft.)
Internal diameter	0.3 metre (1 ft.)

The catalyst was filled in in bulk with no cage or plates to act as support. A gangway was provided at top of reactors for this filling operation.

The remainder of the plant followed conventional lines.

Fatty Acids Hydrogenation (contd.).Catalyst.

Catalyst used was known as B.B.E. It was made at Ludwigshafen at the Catalyst Preparation Centre under Dr. Wimmer. It consists of a silica gel base impregnated with copper and chromium so that the final catalyst contained

20% copper
0.7% chromium

The impregnating solution was prepared by dissolving a precipitated basic copper carbonate in 25% NH_4OH solution and adding Hirschman salts (Ammonium Bicarbonate). The completed solution had the following characteristics.

Copper content	12.5%
Specific gravity	1.1 to 1.2
Molecular composition	$\text{Cu}(\text{NH}_3)_6$
Ratio NH_4OH	600 kg.
NH_4HCO_3	140 kg.

To this solution was added chromic acid (CrO_3) to an amount equivalent to the ratio 20 copper 0.7 chromium.

Silica gel sized 3 - 8 mm. as a support was treated with this solution three times as follows:-

Soak
Drain
Dry
Heat for 24 hours @ 100°C

After the third treatment the impregnated base was heated to 240°C for three days by which time it was free from NH_3 . The material which had somewhat disintegrated was sieved between 1 mm. and 3 mm. sieves ready for filling to reactor.

After charging the reactor the plant was swept out with nitrogen and then more of this gas added to bring pressure to 150 ats. Circulating pumps were started and preheater steam turned on. The temperature on reactor was raised to 150°C and then hydrogen added to gas stream to effect reduction of the catalyst.

Fatty Acids Hydrogenation (Contd.)Catalyst (contd.).

The reaction is exothermic and the temperature is maintained at 150° - 200°C. When no further rise in temperature was observed hydrogen was added up to the full pressure of 250 ats. and gas purged to remove nitrogen and replaced with hydrogen. The preheating and reduction took 24 hours.

One charge of 700-kg. catalyst lasted one month, during which time 100-tons of material had been hydrogenated.

Hydrogen.

The gas used was NUL gas and one analysis indicated impurities as follows:-

Nitrogen	2.6%
CO	0.001%
CH ₄	0.2%
S	2 - 10 mg. per m ³

Gas was vented to maintain impurities at a constant level. Analysis of vented gas (and therefore of circulating gas) showed

Nitrogen	4 - 10%
CH ₄	1 - 2%

Due to venting and leaks the gas used was about 50% more than theoretically required.

Product.

With a fresh catalyst the crude product had a saponification value of 3 - 5, which increased with age to 6 - 7, when catalyst was considered to be exhausted and was changed. The hydrocarbon content of the crude was 4 - 5%.

The rectified products were used for making phthalates sold as plasticisers having the following trade marks.

Phthalates of C ₄ - C ₆	alcohols	Palatinol HS
" C ₇ - C ₉	"	" F.

Fatty Acids Hydrogenation (contd.)Labour.

Each shift consisted of one charge hand and two labourers, one for hydrogenation and one for distillation and ester making. There was also supervision in conjunction with other processes.

1943 Year's Working. (i.e. last full year).

1,338-tons low boiling acids yielded.
1,103-tons alcohols.

This is 78.8% weight or 93% theoretical.

Energy requirements per ton.

8.1 tons 120 ats. steam.
1,170 m³ (40,950 cub. ft.) hydrogen.
620 m³ cooling water.
11.1 kg. B. B. E. contact.

2. Process for Soap Acids. C₁₀ - C₂₀.

The process was in the main similar to that for the lower acids. The possible production was 100 - 150 tons monthly, but only a total of 50-tons had been worked in this unit. The essential differences in process and plant were

- a. Size of Reactor - length 12 metres (40 ft.) as before.
internal diameter 0.5 metres (1.5 ft.)
- b. Alcohols for esterification. The alcohols C₄ - C₉ from low boiling acids.
- c. Reaction Temperature - 260° (i.e. 10° lower).
Catalyst, pressure, etc. were as previously reported.

Fatty Acids Hydrogenation (contd.).3. Process for high boiling acids. (Residual Acids).

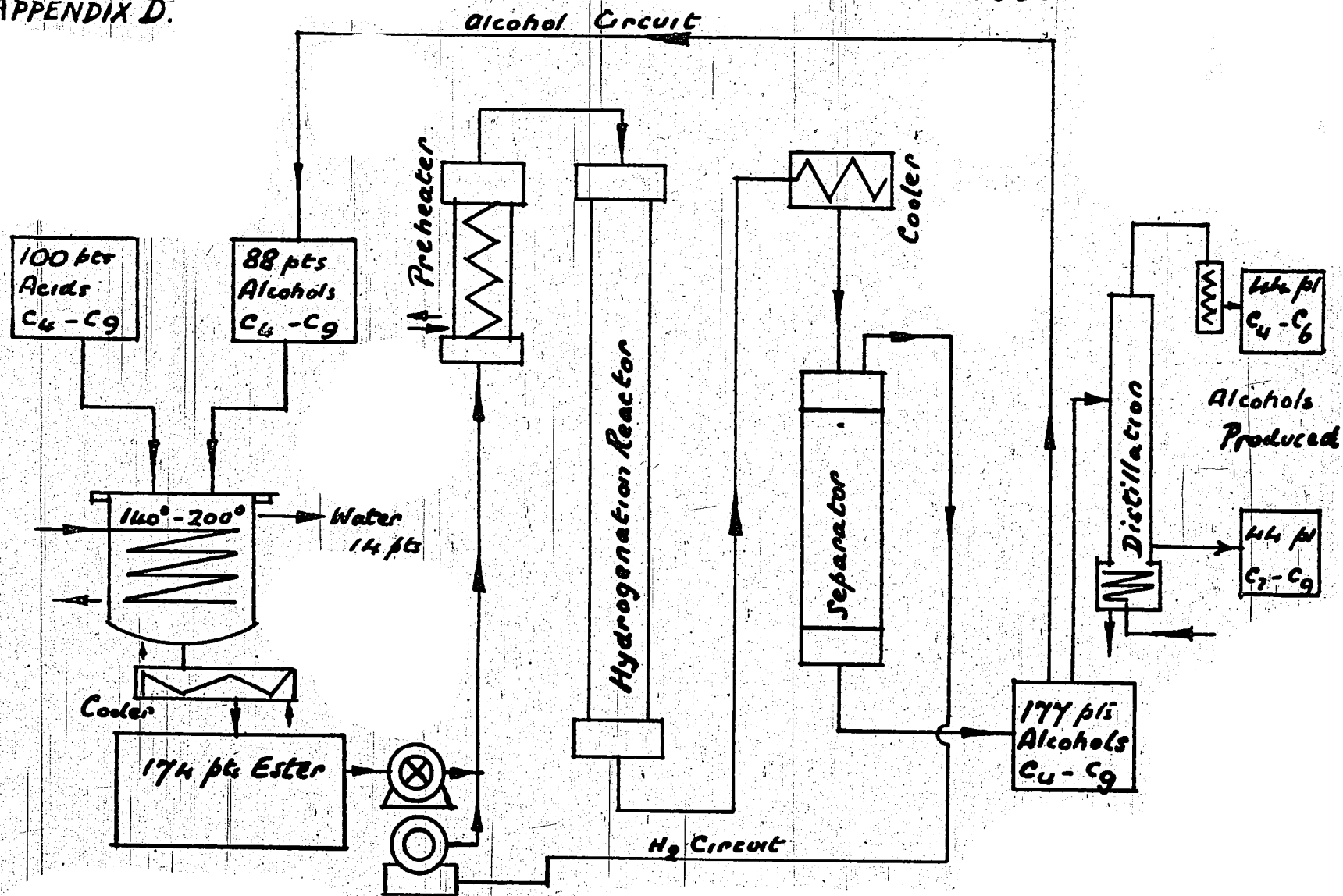
In working these materials experimental units were used - length as before but internal diameter only 0.2 metre (10inch). This was purely a matter of convenience. The residual acids and pitch from the oxidation were washed free from salts with formic acid and used in 50% solution in higher alcohols without any definite esterification step. Only 20-30 tons in all were made.

Catalyst, pressure as before and temperature as with soap acids.

Unsaponifiable products, ketones etc. from the oxidation were also worked up in this unit.

APPENDIX D.

Flow Sheet



I.G. Farbenindustrie, LUDWIGSHAFEN.

FATTY ALCOHOLS PROCESS.

The continuous process was in many points similar to that worked at Oppau. Only soap acids were used, and these came from Oppau or from Henkel (Dusseldorf). The production amounted to 25/30-tons month.

Process.

Esterification, hydrogenation and rectification of alcohols with return of low boiling fraction to esterification unit.

Esterification.

The soap acids were esterified with Butyl Alcohol using KHSO_4 as catalyst. The salts were washed out with water and the material dried under vacuum ready for hydrogenation.

Plant.

Smaller tubes than at Oppau. The dimensions were -

Length	8 metres (26 ft.)
Internal Diameter	0.2 metre (10 inches)

Pipes and heat exchanger were V2A or copper manganese bronze. Liner of reaction shell was copper but difficulties had arisen with distortion of liner when pressure was released.

Reactor space was 360 litres (12.6 cub. ft.).

In this plant the reactor and connecting pipes were jacketted to allow of heating by means of hot water at 250 atmospheres, as heating media. The water was circulated by means of a valve box and oscillating columns of cold water actuated by a reciprocating pump.

Catalyst.

B. B. E. - for preparation see Oppau report.

Fatty Alcohols Process (contd.)Preheating.

In this plant the ester and hydrogen were preheated separately, using pipes jacketted and supplied with 250 ats. hot water. The material was mixed at top of reactor. The reaction temperature was 250° - 270°C.

Hydrogen.

Alternatively electrolysis or NUL gas was used. The circulation was 20 m³ (700 cub. ft.) compressed gas at 250 ats. per hour.

Product.

The crude product, acid and saponification value of 1 - 5, was distilled, and the residue amounting to 10% was treated with Tonsil or active carbon and sold as a lubricant.

The distillate was rectified under reduced pressure in batch plant.

Boiler	3 m ³ (660-gallons).
Column	24 plates.
Pressure	5 mm. at top of column.
Fractions	

1. Butyl Alcohol - returned.
2. Alcohols C10 - C14
3. Alcohols over C14
4. Residues.

Discontinuous Process.

Prior to 1940 a discontinuous process had also been operated. The essential conditions were:-

Fatty Alcohols Process (Contd.).

Capacity of plant	3 m ³ (660-gallons).
Pressure	200 ats.
Charge	800/1000 kg. free acids.
Heating	250 ats. hot water.
Temperature	280° - 300°C.
Catalyst	P.H. 86 (Copper Carbonate activated with Ba, Cr and Zn)
Reaction time	6 - 8 hours.
Product	Sap. value 10 - 20.

At end of reaction, catalyst was filtered off after adding KHSO_4 to break emulsion - salts washed out and distilled. To the distilled product KOH added before rectification, in order to saponify and fix any esters and residual acids.

Document

Schema zur Fettsaure - Fabrikation I, II, III,
(Appendices A, B, & C of the Report) has been lodged with:-

Board of Trade,
German Division (Documents Unit),
Lansdowne House,
Berkeley Square, W.1.

Telephone : Grosvenor 4060, Ext: 2923.

Applicants for permission to view the Document should quote the following BIOS Reference Number: BIOS/Docs/1124/1110.