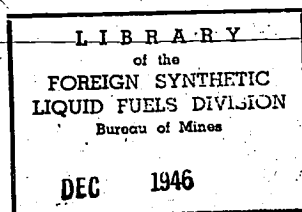
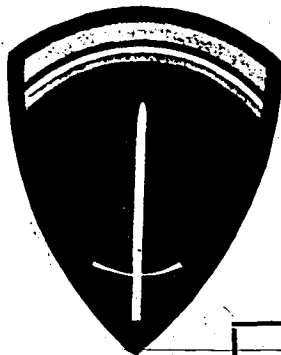


Copy 1

FIAT FINAL REPORT NO. 905

**DETERMINATION OF SUITABILITY OF
PARAFFIN MIXTURES FOR CONVERSION TO
FATTY ACIDS BY CATALYTIC OXIDATION**

Boith, H. S., and Robitchek, J. O.



OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIELD INFORMATION AGENCY, TECHNICAL

OFFICE OF MILITARY GOVERNMENT FOR GERMANY (US)

FIAT FINAL REPORT NO.905

SEPTEMBER 3, 1946

**DETERMINATION OF SUITABILITY OF
PARAFFIN MIXTURES FOR CONVERSION TO
FATTY ACIDS BY CATALYTIC OXIDATION**

BY

H. S. COITH and F. O. ROBITSCHKE

TECHNICAL INDUSTRIAL INTELLIGENCE DIVISION

U. S. DEPARTMENT OF COMMERCE

**THIS REPORT IS ISSUED WITH THE WARNING THAT IF
THE SUBJECT MATTER SHOULD BE PROTECTED BY
U.S. PATENTS OR PATENT APPLICATION, THIS PUBLI-
CATION CANNOT BE HELD TO GIVE ANY PROTECTION
AGAINST ACTION FOR INFRINGEMENT.**

FIELD INFORMATION AGENCY, TECHNICAL

ABSTRACT

Since the successful carrying out of the catalytic oxidation of paraffins to fatty acids is so dependent on the characteristics of the raw material, small scale tests for evaluating proposed raw materials are important. A description of two such tests is given. By way of showing how the tests compare with the actual production procedure, the latter is briefly reviewed.

TABLE OF CONTENTS

Subject	Page No.
Introduction	5
Brief review of the production of Synthetic Fatty Acids through Paraffin Oxidation	5
Tabulation of Fatty Acid Yields from Plant Operation	6
Testing Gatsch for the Fatty Acid Process	7
Appendix 1 List of German Personnel Interviewed	9
Appendix 2 German Target Visited	9
Appendix 3 Bibliography	9

INTRODUCTION

Objective:

The original purpose of this study was to review the German practice for converting paraffins to fatty acids. Previous investigations had shown the method, as carried out on a production scale, to be too expensive to be of interest under conditions normally prevailing in the United States. It was hoped, however, that during the war years further laboratory research, which still had not been applied to plant operation, might have resulted in developments which could give some promise of making the process of interest. With this in mind, the present trip was made to the research laboratories of Henkel & Co. in Düsseldorf, where research for the Deutsche Fettsäurewerke is carried out.

Evaluation:

No new developments were uncovered which made the situation different than previous investigators had reported it. There were found however, two small-scale techniques for evaluating raw materials for paraffin oxidation which may prove of interest to future research workers carrying out further laboratory studies on the problem.

Guide to the Reader:

Several references to material on the production and uses of the synthetic fatty acids are given in Appendix No. 3.

BRIEF REVIEW OF THE PRODUCTION OF SYNTHETIC FATTY ACIDS THROUGH PARAFFIN OXIDATION

In its essentials, the process of oxidizing paraffins to fatty acids consists in blowing air through the heated paraffins, using potassium permanganate as a catalyst. The procedure is not to be confused with the Oxo process for fatty acids, which consists in treating unsaturated paraffins with a mixture of carbon monoxide and hydrogen to form an aldehyde, and subsequently oxidizing the latter to a fatty acid.

The steps in the paraffin oxidation process are as follows:

- (1) A paraffin mixture boiling between 320° C. and 450° C. (Fischer Tropsch Gatsch) is oxidized by blowing air through it in the presence of permanganate which serves as a catalyst. The oxidation is allowed to progress until about one third of the paraffin is converted to fatty acid.
- (2) The resultant mixture of fatty acids and unreacted paraffins is given a counter current water-wash which removes water soluble fatty acids.

- (3) The paraffin-fatty acid mixture from the water washing is saponified with sodium carbonate and sodium hydroxide.
- (4) The resulting paraffin-soap mixture is autoclaved, during which some of the unreacted paraffin is separated out by gravity. This is returned to the original oxidation vessel.
- (5) The paraffin-soap mixture from the above step is steam distilled to remove the remaining paraffin, which is also returned to the original oxidizing vessel.
- (6) The residual soap from the above process is acidified with sulphuric acid.
- (7) The liberated fatty acids are given a counter current water-wash.
- (8) The washed fatty acids are fractionally distilled.

Three plants were actually engaged in converting paraffin to fatty acids by this method. They were the I. C. plants at Oppau and at Heydebreck, each with a capacity of 20,000 tons per year, and the Deutsche Fettsäurewerke at Witten with a capacity of 40,000 tons per year.

A tabulation of the results of a year's operation of the Deutsche Fettfabrikswerke, at Witten is given below:
 Yields obtained in the Witten Operation from working up 40,000 tons of Catch per year

	Amount from various steps ex- pressed in tons.	Yield in tons expressed in 100% fatty acid or re- sidual paraffin.	Percentage yield by weight based on 100 parts of catch *	Yield based on carbon content.
Crude fatty acid	31,000	31,000	78 — 80	66
"Cooler oil" **	2,000	2,000	5 — 8	4
"Cooler water" **	11,000	3,500	(28) 6	5
Oxidate wash water	8,000	1,200	(20) 3	4
Acid waste water	100,000	3,000	(250) 7.5	6
Exhaust air	180 millions m ³			10
Loss				5
				100
Fatty Acid Distilling				
First cut (C ₄ —C ₉)	5,400		13.5	10.2
Main cut (C ₁₀ —C ₂₀)	22,200		55.5	48.0
Heavy cut (Over C ₂₀)	2,000		5.0	
Still residue	3,000		7.5	7.4
Total	32,600			

* Percentages, of course, total over 100 because of weight gain resulting from oxidation.

** Separated by condensation from the exhaust air leaving the oxidator.

TESTING GATSCH FOR THE FATTY ACID PROCESS

Of prime importance to the success of paraffin oxidation is the quality of the hydrocarbon used as a starting material. The only tests which have been devised for evaluating such a raw material are actual small scale oxidation tests. An outline of the two finally adopted is given below.

1. One apparatus for such a test, capable of being used with 2 kgs. of raw material appears as Appendix 4. In this test the steps of the actual plant procedure, tabulated on page 6, are reproduced on a miniature scale. The procedure is as follows:

A. Four grams of potassium permanganate are dissolved in a small quantity of water and this solution is slowly added, while stirring, to a beaker containing 200 grams of gatsch at a temperature of 120° C. As soon as the water is evaporated off, the temperature is slowly raised to 150° C. The contents of the beaker are then added to 1,800 grams of gatsch previously introduced into the reaction chamber of the apparatus.

The temperature of the mass in the reaction chamber is then brought to 105–110° C. and air is passed through at a rate of 100 to 150 liters per hour (50 to 75 liters per kilogram). The blowing of air through the mass is continued until a saponification value of about 140 is reached, or until the rise in saponification value ceases. (The foregoing air blowing duplicates step (1) of the plant operation.)

The material condensed and collected from the two condensers separates into two layers and corresponds to the "cooler oil" and "cooler water" of the full scale process.

The material remaining in the oxidation vessel, designated as "crude oxidate", is water washed in a separatory funnel and yields "washed oxidate" and "oxidate wash water". This procedure corresponds to step (2) of the plant procedure as outlined.

The "washed oxidate" is then saponified with the calculated quantity of sodium hydroxide (37% NaOH solution), and the material is again allowed to separate into two layers. The upper or oily layer corresponds to the "mechanical gatsch" of the larger scale process and the lower or watery layer to the "crude soap". This procedure is analogous to steps (3) and (4) outlined on page 2.

The "crude soap" is hot extracted eight times with benzine, the latter being subsequently evaporated off and yielding a benzine extracted "return gatsch". This corresponds to step (5) on page 2. In plant practice the gatsch is separated by distillation instead of extraction and is known as "distillation gatsch".

The benzine washed "crude soap" is acidified with sulphuric acid to liberate the fatty acid (analogous to step 6) which is subsequently water-washed (step 7).

The washed fatty acids are then distilled (corresponding to step 8) at a pressure of 4 mm., the distillate being separated into "light cut" and "middle cut". The portion, which would in a large-scale operation be taken off as a "heavy cut" is allowed to remain in the distillation flask with the residue. An example of data from a run in this apparatus appears on the following sheet:—

Example of an Oxidation Test on Fischer-Tropsch Gatsch in the 2 Kilogram Apparatus.

Charge	2 kg gatsch (fresh, no return gatsch) 4 gr potassium permanganate		
Oxidation temperature	108° C.		
Oxidation time	40 hours		
Blowing air per hour	140 liters (70 l per kg)		
Cooler oil	80 gr.		
Cooler water	300 gr.		
Crude Oxidate	1,825 gr.	Acid Val. 88	Sap. Val. 173
Water washed crude Oxidate	1,710 gr.	Acid. Val. 77	Sap. Val. 157
Saponified with 37% NaOH	515 gr.		
Mechanically separated return gatsch	590 gr.		
Benzine extracted return gatsch	295 gr.		
Washed crude fatty acid.	795 gr.		
First cut distilled fatty acid at 4 mm. pressure boiling up to 140° C.	81 gr.		Sap. Val. 430
Main cut distilled fatty acid at 4 mm. pressure boiling up to 240° C.	410 gr.		Sap. Val. 234
High molecular weight fatty acids and still residue	300 gr.		

In the example given above, the oxidation was allowed to proceed farther than normal. Usually the reaction is stopped when the crude oxidate has a saponification value between 135 and 140 (15—25 hours). Because of this over-oxidation there is more "cooler water" than normally (300 against a usual figure of 230—250). Another consequence of this over oxidation is that the resulting high molecular weight acids, which in this case are essentially oxyacids, are proportionately increased over normal operation at the expense of the "main fraction".

B. It is, of course, impossible to set limit for experimental runs on this apparatus which will show whether or not a given raw material is suitable to use on a plant run because economic conditions may be such at one time as to justify running material which under other conditions would not be practicable. A good Fischer-Tropsch gatsch when run as outlined above will give from 400—500 grams of "maincut".

The data from an experiment on the 2 kg. scale is not fully comparable to that of large scale operations. For one thing, in the larger, less air is used. Also of particular importance is the fact that in a small mass,

the separation by distillation of un-saponifiable material from the crude soap does not proceed very smoothly, therefore, the separation is carried out by means of a thorough extraction with benzine. Under such conditions the conversion of the oxyacids into unsaturated acids does not take place. For this reason the yield of fatty acids is somewhat smaller than on a large scale operation.

II. An even smaller experimental oxidation unit, capable of being used for a charge of only 100 g., is shown in Appendix 5. As in the apparatus just previously discussed, this small unit is charged with gatsch containing 0.2% of potassium permanganate in water solution. It is then brought to 108° C. by immersion in an oil bath and the oxidation is carried out by air blowing (7—10 liters per hour) until a saponification value of around 140 is reached. The oxidized mass is then water-washed and a saponification value is run on it.

This small scale apparatus is useful only for determining, in a qualitative manner, whether a given lot of gatsch is suitable for oxidation. It does not give quantitative results which can be correlated with the results of large scale operations.

APPENDIX 1
LIST OF GERMAN PERSONNEL INTERVIEWED

Name	Position	Location
Dr. Bruno Blasser	Director of Research	Henkel & Co.
Dr. Wolfgang Guendel	In charge of research on Paraffin Oxidation	Düsseldorf Henkel & Co. Düsseldorf

APPENDIX 2
GERMAN TARGET VISITED

Name	Location
Research Department of Henkel and Company	Düsseldorf

APPENDIX 3
BIBLIOGRAPHY

Copies of the reports listed below were transmitted to Washington, D. C. Inquiries should be addressed to:

Office of Publication Board,
U. S. Department of Commerce,
Washington 25, D. C.

1. Related Reports Published by Allied Intelligence Agencies:

CIOS Item No. 22, File No. XXVI-50-
Production of Synthetic Fatty Acids and Edible Fats
Deutsche Fettsäurewerke and Markische Seifenfabrik, WITTEN (Ruhr), Germany, by E. L. Balde-
schlieler, U. S., located at FIAT Records Branch,
File No. TP. 200/P 941.

FIAT Final Report No. 407
Deutsche Fettsäurewerke, WITTEN (Ruhr),
by K. S. Markley and W. H. Goss,
located at Records Branch, File No. TX. 341/P 480.

BIOS Final Report No. 86
Same title as above by same authors, but with
somewhat different type of information, located
at FIAT Records Branch, File No. TJ. 1077/P 27.
CIOS Evaluation Report No. 12
I. G. Production of Synthetic Fatty Acids,
by L. G. Bellamy and K. T. Millson, located at
FIAT Records Branch, File No. TP. 200/1083.