

Table 58.

Preparation of Ester Oils, Ruhrchemie

	Crude Aldehydes	Product after alkali treatment and acidification	Esters
d_{20}	0.810	-	0.870
Acid No.	3	110	0
Sap. No.	3	119	138
Hydroxyl No.	5	119	5
Carbonyl No.	140	5	1
mg. CO/g.	-	-	1.4500
n_D^{20}	-	-	-65°C.
Setting point	-	-	-

Synthetic Fatty Acids and DetergentsThe Wax Oxidation Process.

According to Henkel the ideal raw material would consist entirely of straight-chain paraffins. Branched-chain paraffins gave rise to branched-chain fatty acids which were definitely dangerous as constituents of edible fat and gave soaps of poor detergency and unpleasant odour. Lower yields of the desired fatty acids were also obtained. If olefines were present the rate of oxidation was lower, the products were dark in colour, and the yield of the main fraction of fatty acids was less. Naphthenes gave rise to naphthenic acids which gave poor soaps and if aromatics were present there was a danger of producing carcinogenic substances. Iso-paraffins, olefines and cyclics gave excessive amounts of hydroxy acids, as shown by the hydroxyl number of the distilled acids.

The best available raw material was Fischer-Tropsch gatsch from the normal-pressure cobalt catalyst process. Gatsch from the medium-pressure process was less suitable and that from iron catalyst synthesis was the least suitable of the Fischer waxes.

The next best raw material was "T.T.H. wax" - wax obtained from the product of the low-temperature hydrogenation of brown-coal tar. Most waxes of petroleum

origin were less suitable than the above.

Henkel did not consider that it would be economic to attempt to improve an unsuitable wax by refining treatment, and up to the present have had no success in this direction even on the laboratory scale. They doubt whether it is possible to produce suitable oxidation gatsch by mild thermal cracking of Ruhrchemie hard wax.

They have not tried the I.G. method for determining the proportion of branched-chain hydrocarbons in waxes, using $SbCl_5$, but doubt its reliability. They believe that while pure normal paraffins do not react with this reagent they do so when mixed with iso-hydrocarbons. They consider that the only reliable test of the suitability of a wax for production of the fatty acids is by means of a test oxidation. The most suitable wax is one giving the maximum yield of C_{10} - C_{20} acids of highest melting point and palest colour. They stated, however, that the results of such test oxidations agreed with I.G. figures for the proportion of branched-chains, (the higher the content of iso-paraffins the less suitable the wax). They had not carried out test oxidations with pure branched-chain paraffins.

The following is a short summary of a document prepared by Henkel on the testing of waxes for the oxidation process.

"The suitability of a gatsch as starting material for the preparation of fatty acids is decided by its characteristics and by test oxidations. A good gatsch should have a low iodine number, and should boil mainly (ca. 90%) between $320^{\circ}C$. and $460^{\circ}C$. at 700 mm. as determined by distillation at 15 mm. Oxidation tests are carried out at $105 - 110^{\circ}C$., with an air rate of ca. 10 litres/100 g.wax/h., to a final saponification number of 135 - 140. Several tests on a 100 g. scale in glass reaction tubes, carried out simultaneously (in the same heating bath), serve to determine the best reaction conditions (time, temperature, amount of catalyst). The colour of the reaction product for a suitable material should not be darker than orange-yellow. A 2 kg. scale test in an electrically heated aluminium tube, 120 cm. long and fitted with a filter candle for distributing the air stream, is then carried out to permit determination of the yield and quality of the products. Working up is similar to the technical scale method but the unsaponifiable material (U.S.I.) is separated by solvent extraction instead of distillation. A second 2 kg. scale test, in which the

unsaponifiable material from the first is incorporated in the starting material, is required for a complete estimation of the suitability of a gatsch".

The fatty acid plant of Deutsche Fettsäurewerke Witten used only Fischer-Tropsch wax as raw material, but the I.G. plant at Oppau used a variety of raw materials, the principal one being T.T.H. brown-coal tar wax. Dr. Kürzinger, the manager of this plant, gave the following information:- During the war years T.T.H. wax formed 80% of the total wax oxidised, Fischer-Tropsch gatsch (from Erabag, Schaffgotsch and Krupp Treibstoffwerk) formed 10%, and 'Nerag' gatsch (petroleum wax from the dewaxing of spindle oil) the remaining 10%.

At the time of the visit, the plant was operating on "Espenheim Gatsch", a wax extracted from low-temperature brown-coal tar obtained from the Sachsische Werke, Espenheim, and refined with liquid SO_2 . This wax is unsaturated (iodine number ca. 40) and must be hydrogenated before use. It contains some naphthenes and has a high sulphur content and was altogether less satisfactory than T.T.H. wax. They had received a consignment of 1,200 t. of this wax (of which 600 t. had been oxidised at the date of inspection) and when this had been used the plant would have to shut down. The yields of fatty acids obtained by the oxidation of 100 parts of the various waxes were stated to be as given in Table 59.

Table 59.

Fatty acids from Wax Oxidation. I.G. Farben

Wax	Fore-runnings $\text{C}_4 - \text{C}_9$ acids	Main Fraction $\text{C}_{10} - \text{C}_{20}$ acids	After runnings $\text{C}_{21} - \text{C}_{25}$ acids	Residue	Total
Fischer-Tropsch	12	50	6	7	75
T.T.H.	7.6	45.5	2.8	20.2	76.1
Nerag	(very variable, similar to but rather worse than T.T.H.)				
Espenheim	6	35	5	17	63

Dr. Kürzinger said that if the dehydration of the hydroxy-acids in the pipe still treatment has been complete, the properties of the main fractions of acids are similar in all cases (ester number 5 - 10, U.S.M. 2 - 4%) apart from the iodine number, which is higher, the higher the proportion of hydroxy-acids formed. Thus the iodine number of the main fraction was about 20 for Espeheim gatsch and about 5 for Fischer-Tropsch gatsch.

The total weight of gatsch oxidised and weights of acids obtained during the war years at Oppau are given in Table 60.

Table 60.

Oxidation of Wax, I.G. Farben, Oppau, 1941-4.

Year	Wax Oxidised t.	Patty Acids Produced				Total t.
		Fore-runnings t.	Main Fraction t.	After runnings t.	Residue t.	
1941	1,967	213	983	56	404	1,661
1942	13,001	916	6,519	231	2,239	9,905
1943	12,560	950	5,578	357	2,545	9,530
1944	6,047	429	2,499	245	1,380	4,553

Although the process and plant used, both at Witten and Oppau, have been described in previous reports, the following account of the oxidation of a good batch of T.F.H. gatsch at Oppau includes details not previously reported, and, at the risk of some duplication, appears worthy of inclusion in this report.

To a mixture of 40 t. fresh wax and 60 t. U.S.M. from a previous oxidation, 0.12 t. $KMnO_4$ in aqueous solution is added and the whole heated to $140^\circ C$. The mixture is then pumped into the oxidation vessels, and as soon as the reaction has started, the temperature is reduced to 105 to $115^\circ C$. (usually 105 - $110^\circ C$.) Air at 40 - 50 cu. ft./t. charge/hour is blown through until the acid number reaches 70 (sap. number 120 - 140). The normal period of time is 20 to 30 hours. The amount of catalyst

used depends on the quality of the grease and may range from 0.12 to 0.20%. Increase in the sulphur content and olefine content of the grease increases the amount of catalyst required. From 0.05 to 0.20% of sodium or potassium carbonate can also be added with advantage.

The oxidized product amounting to rather more than 100 t. is then washed with water at 70 - 80°C. and formic and acetic acids and manganese salts removed. The washed product 99 t. or more is then saponified with the addition of 10 t. NaOH and 24 t. water, and the 133 t. of mixture transferred to an autoclave and maintained at 140 to 150°C. under the prevailing steam pressure (about 10 atm.) for about 2 hours. The U.S.M.-II (44 t.) rises to the top of the mixture and is removed for addition to later oxidation batches.

The remaining 89 t. soap solution is then passed through a pipe still maintained at 200 - 330°C. under a pressure of 60 - 120 atm. The time of contact is about 15 - 30 mins. The pressure is then released and the solution passed through a second pipe still at 300 - 360°C. (Usually 350°C.) at atmospheric pressure, and thence into a vessel where the molten soap collects and U.S.M.-II is carried off in the steam. Amount of U.S.M.-II returned to oxidation is 16 t. The molten soap is then run into twice the weight of water and split by the addition of 95% H₂SO₄. The liberated crude fatty acids amount to 28 - 32 t. The vacuum distillation of the raw acids has been adequately described in previous reports.

The air leaving the oxidation vessels passes through water-cooled condensers and an oil condenser known as "condenser oil" and an aqueous condenser known as "condenser water", recovered. At times the condenser oil

was worked up together with the main oxidized charge, but at times it was disposed of, without further treatment, as a by-product. The air, after leaving the condensers, still contains volatile organic matter which is lost, and other quite appreciable losses occur at later stages in the process. The nature and extent of these losses is shown in the following weight balance, given in Table 64, based on data supplied by Mr. Stein, manager of the station and amounting to

Table 61

Weight Balance for Oxidation Process

Based on Conversion of 100 Tonnes Gatsch to Fatty Acids

Product	Quantity	Amount and Nature of organic constituents	
Spent Air	36,800 cu.m.	19.5 t. low-boiling hydrocarbons, alcohols, aldehydes, ketones and fatty acids. 21.6 t. CO ₂ (equivalent to 5.9 t. C)	Lost
Condenser Oil	7.0 t.	0.21 t. aldehydes 0.28 " ketones 1.05 " alcohols 2.71 " fatty acids 2.40 " hydrocarbons 6.65 " organic matter	Recovered
Condenser Water	28.3 t.	6.70 t. of fatty acids	Recovered
Wash water from treatment of crude oxidation product	33.3 cu.m.	2.80 t. fatty acids	Lost
Gases evolved during removal of U.S.M. II in pipe still		14.5 t. of hydrocarbons as fog, CO ₂ and permanent gas.	Lost

Product	Quantity	Amount and Nature of organic constituents	
Water from washing of crude acids	137 cu.m.	2.20 t. fatty acids	Lost
Raw fatty acids	72.6 t.	72.6 t. fatty acids	Recovered
Total organic matter		=	146.5 t.
Total recovered organic matter		=	86.0 "
Loss (including CO ₂)			60.5 "
Estimated loss of hydrocarbon material		=	26 "
		=	<u>26% of Raw Material.</u>

Some data for the wax throughput, and yields and production costs for fatty acids at the Witten plant are given in Table 62. In 1943 the wax throughput reached a maximum (actually rather more than the rated throughput of 40,000 t.) and this was the best year of operation the plant had experienced. Full details were also obtained for the process costs but as these have already been reported by J.W. Vincent (BIOS Final Report No. 805) they have been omitted from this report.

Table 62.

Throughput, Yields and Costs for Wax Oxidation Plant
of Deutsche Fettsaurewerke, Witten

	1943		1944	
	Quantity, t.	Yield, % of wax input	Quantity, t.	Yield, % of wax input
Gatsch oxidised	41,159.3		27,788.1	
Raw fatty acids produced	30,425.5	73.92	19,814.3	71.30
Condenser oil produced	2,503.7	6.08	1,869.0	6.73
Distilled acids produced				
Main fraction		45.65		45.50
"After runnings"		7.69		5.19
"Fore runnings"		13.02		12.70
Residue		6.83		7.21
Condenser oil		73.19		70.60
Total Products		6.08		6.73
		79.27		77.32
Total production cost (excluding interest on capital - about 6% on 12 x 10 ⁶ RM)				
Per t. gatsch oxidised		RM. 449		RM. 493

The wax oxidation plant of the I.G. at Magdeburg, which never came into operation, was to operate the Hubbe and Farenholtz process. Some information was obtained concerning this process from the Lurgi Company who had built the plant. The process used oxidation with air at 25 atm. pressure and a temperature of 120 - 140°C. Under these conditions, no catalyst was required and the reaction time was reduced to 6 h. As the exit gases were under pressure the recovery of the volatile products was simplified, and the losses were less than those of Deutsche Fettsäurewerke, who claimed, however that their own overall efficiency was higher.

The oxidation vessels had to be made of stainless steel (instead of aluminium as at Witten and Oppau), and the capital cost of the plant was very high, viz., 60 million RM. for a plant of 50 t. wax per day throughput. The yield of the main fraction of acids was about 55% and the yield of residual acids was somewhat higher than at Witten.

The soap prepared from the Hubbe and Farenholtz acids was claimed to have a less unpleasant odour than the Witten product.

The Smell Caused by Synthetic Soaps

The main fraction of fatty acids was used primarily for soap manufacture, but an objection to their use for this purpose is the unpleasant odour which develops on the skin after washing with soap containing these acids.

According to Henkel et Cie, this property is due to the presence of branched-chain fatty acids. When the soap is used for toilet purposes, the soap is absorbed by the skin and the free fatty acids gradually liberated by the stronger acids of the sweat. Enzymes in the skin decompose the branched-chain fatty acids to lower acids which give rise to the objectionable odour. Whether or not this mechanism is correct, the production of the odour is undoubtedly associated with the human skin, and varies from individual to individual. Some people can use the soap without any unpleasantness at all - others develop the odour with soap containing only 10% of synthetic fatty acids. One of Henkels employees was exceptionally sensitive and was used by the Company for testing soap samples. For the majority of people, soap containing 20 - 25% of synthetic acids can be used without unpleasant after effects. Henkel would not, however, recommend the use of the acids in good