

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

quality toilet soap. The soap is perfectly satisfactory for laundry purposes. No odour is left on textiles even with soap made entirely from the synthetic acids. They can also be used in soap powders because of the stabilising effect of the excess alkali present. Repeated recrystallisation of the main fraction of fatty acids removed the property causing unpleasant smell but Henkel did not consider this to be of more than academic interest.

The views of Dr. Kürzinger of I.G. Farben, Oppau, on this subject were sought. He considered that the odour of synthetic soap was due to three causes:-

1. The presence of unsaponifiable matter.
2. The presence of lactones.
3. The presence of branched-chain fatty acids.

The first two are a function of the oxidation and purification processes, and the third, a function of the raw material. Dr. Weiss (who unfortunately was not available for interrogation) of the Ammonia Laboratory had prepared a number of pure branched-chain fatty acids, some of which had unpleasant odours. He definitely proved that branched-chain paraffins give rise to branched-chain acids on oxidation.

Dr. Kürzinger had oxidised a synthetic C₂₀ straight-chain paraffin. The main fraction of acids with 3% unsaponifiable matter and an ester number of 20 - 30 gave a soap which had an unpleasant odour but not so pronounced as the technical synthetic acids of ester number 5 - 10, U.S.M. 2 - 4%. After further refining, the ester number was reduced to 5 and the U.S.M. to 1% and the resulting soap was completely without odour. Dr. Kürzinger also oxidised two fractions of a Fischer gatsch which by distillation and solvent extraction had been split into straight-chain and branched-chain concentrates. The soap prepared from the straight-chain concentrate had much less odour than that from the branched-chain material, although both samples of acids had the same ester number.

It is therefore clear that the odour of synthetic soaps is due to the presence of unsaponifiable matter and lactones. Soap substantially free from these impurities gives no immediate odour. The smell which develops on the skin after washing is due to the branched-chain fatty acids set free by the acids of the sweat. He did not postulate the enzyme action referred to

by Henkel and, indeed, as certain free synthetic acids themselves have an objectionable odour this does not appear to be necessary to the argument.

Dr. Rossow, chief chemist of Deutsche Fettsäurewerke, did not consider that branched-chain acids were responsible for the odour phenomenon exhibited by synthetic soaps, but believed it was due to the lactones of hydroxy-acids. His evidence was as follows.

If a sample of the main $C_{10} - C_{20}$ fraction of fatty acids is steam distilled in vacuo in the presence of excess caustic soda, an oily distillate of foul odour is obtained. This material is neutral but has a high saponification value. The residual soap after this treatment has very much less odour. He considers that, in the soap solution, lactones are present as unstable salts which are broken down in the steam treatment and the free lactones distil off. He stated that it was known that lactones have a strong affinity for the skin and pointed out that large-ring ketones usually have strong odours.

He claimed, further, that they had oxidised a wax, obtained from Dr. Fichler of the K.W.I., Milheim, which was guaranteed to consist only of straight-chain paraffins, and that this had given evil-smelling acids. He agreed, however, that the matter was far from settled and regretted that he had not had sufficient time to make a more complete study of it.

The matter is complicated by the fact that it is not always clear precisely what odour was being referred to by the persons interrogated - the odour of the free acids, the odour of the dry soap, the odour which arises when washing or the odour which gradually develops on the skin after washing. The questions put by the authors of this report related to the last of these, which in their view is the most important, because it cannot be masked by the presence of perfume in the soap.

Dr. Herbert, of Lurgi, said that one could wash with soap containing synthetic fatty acids for the first two weeks without undue discomfort but that after that, with continued use of the soap, the smell on the skin became intolerable.

The Iodine Number of Synthetic Fatty Acids.

Questions were put concerning the cause of the increase in the iodine number of synthetic fatty acids with increase in time of contact between iodine solution and the acids, whereas no such increase takes place under similar conditions with the natural fatty acids. Henkel considered that it was probably due to the substitution in the side chains of the iso-fatty acids and stated that the phenomenon was more marked with products obtained from the oxidation of petroleum gatsch than with those from Rissger gatsch. Dr. Rossow of Witten considered that when ^{oil} solution is used, the strong acetic acid may cause dehydration of hydroxy-acids to form olefines and hence cause increased iodine absorption.

The impression was gained that neither organisation had paid much attention or attached much significance to the phenomenon.

'Diluted' Soap.

To make toilet soap last longer, Deutsche Fettsäurewerke produced their air-blown "floating soap" which had been described in previous reports. The I.G. at Ludwigshafen - Oppau had devised another method for effecting soap economy, based on the use of a urea-formaldehyde condensation product as a "diluting" medium. Tablets of soap were produced which lathered in a satisfactory manner and yet contained only 15% of fatty acids.

The "Soap Base H.F." was prepared as follows:- 100 kg. of 30% formalin and 100 kg. of urea are heated to 45°C. for 30 minutes, caustic soda being added to maintain pH = 8 throughout this period. Then 0.4% of sodium phosphate is added as a stabiliser and to maintain the pH at 8, and the product evaporated in vacuo to sp. gr. = 1.25 at 50°C. The clear solution is then cooled with constant stirring and when cold forms a translucent paste.

To prepare the soap, the 'base' is heated to 80 - 90°C. until it becomes cloudy (10 - 15 minutes). The fatty acids and equivalent amount of caustic soda are then added with stirring and the mobile solution poured into moulds and allowed to cool.

Synthetic Edible Fat.

Contrary to statements which have been made elsewhere, Deutsche Fettsäurewerke used only natural glycerine derived from inedible fat for the production of glycerides from their synthetic fatty acids. The synthetic glycerine manufactured by I.G. at Heydebreck was not considered pure enough for the purpose.

The esterification process has been described in previous reports but the following additional details were obtained. The acids are esterified with the theoretical amount of glycerine using 1 to 1.5 parts of zinc dust per 1,000 parts of fatty acids. The temperature is 210 - 220°C. and the pressure initially 100mm. The pressure is then reduced to 20 mm., and in the last two hours, to 15 mm. The total time for a charge of 3,000 to 7,000 kg. is 8 to 10 hours. The products, with acid number 3 to 3.5, are cooled and discharged into a tank and treated with 20% sulphuric acid to dissolve the zinc. The product is then neutralised with caustic soda solution, and agitated with a mixture of active carbon and bleaching earth at 110°C. The main object of this treatment is to remove traces of soap. After filtration, the fat is heated to 250°C. under a vacuum of 2 to 3 mm. and steam, preheated to 300 - 360°C., blown through it for 13 to 18 hours. It is essential to maintain a good vacuum during this deodorising process, which was stated to be vital for obtaining good-quality fat. The fat is then cooled and again filtered.

Information concerning the suitability of these fats for human consumption was sought.

Dr. Rossow supplied a copy of a minute (16) from an official of the German Health Department to State Secretary Keppler, dated 1939, which stated that more than a thousand experiments on animals had shown that the fat made by Deutsche Fettsäurewerke was non-toxic and non-irritant and was digested, absorbed and utilised in a perfectly satisfactory manner. Experiments on 6,000 human subjects (in concentration camps) had shown that the synthetic fat was in every way a satisfactory substitute for the natural product. The German Health Department therefore approved of its use for human consumption.

The physiological experiments on synthetic fats carried out for the Reichsgesundheitsamt were under the direction of Prof. Elässner, who is now at Hemendorf, near Hannover, and is engaged in writing a comprehensive account of this work.

A rather different picture was obtained from Henkel. They considered that the presence of branched-chain fatty acids made it extremely dangerous to use the synthetic fats as human food because acids of this type could be definitely toxic (e.g. phthionic acid - a product of the tuberculosis bacillus) and they consider that permission to use the fat should never have been given. They referred to the work of Prof. Jantzen, of Freiburg, who had carried out extensive feeding trials with rats. Rats which had previously been fed on natural fat were starved for a period and then re-fed (a) with natural fats (b) with various samples of Witten fat (c) with fat prepared from pure branched-chain acids. In case (a) the rats rapidly regained their former weight. In case (b) the weight increased much more slowly and never regained the original value. In case (c) the weight continued to fall and the rats died.

Prof. Thomas, formerly of Leipzig, had shown (Deutsche Medizinische Wochenschrift, 1946, May 10th, p.18) by tests on human subjects that the toleration limit for the synthetic fat was much lower than for the natural fats and that excessive amounts of dibasic acids appeared in the urine leading to kidney disorders and ultimately to decalcification of the bone structure. (A photostat copy of this paper and also of a paper dealing with synthetic fats by Kaufmann, Fette and Seifen, 1944, p.215, were obtained (7), (6).

Henkel considered it significant that the work of Profs. Jantzen and Thomas had been suppressed by the Government whereas Prof. Flässner had been allowed to publish his work (Die Ernährung, 1943, 8, 89). They also attach some significance to the fact that dogs would not eat the synthetic fat!

Dr. Kürzinger, of I.G. Farben, Oppau, stated that the fats synthesised from pure normal paraffins were quite satisfactory but those containing branched-acids were less satisfactory than natural fats. Dr. Schiller, of I.G. Farben, Ludwigshafen, Oppau, had established this by feeding tests with rats and his results were in agreement with those of Prof. Thomas, with whom he had discussed the whole problem. Dr. Kürzinger considered that the acceptance of the Witten fat by the Reichsgesundheitsamt was a political move.

By-products of the Oxidation Process.

An excellent survey of the actual and possible uses of the lower- and higher-boiling fatty acids and other by-products was published by Dr. Ludwig Mames, of Henkel, in Die Chemie,

1944, 57⁽⁶⁾ and the main object of the visit to Henkel was to obtain further information on points arising from this paper. It transpired, however, that Mannes was at the Henkel factory in the Russian Zone with all his papers and patent applications dealing with the by-product side. The staff at Düsseldorf, therefore, were not able to add much to what has been published by Mannes.

Up to the present, the foul-smelling waste air from the oxidation process has been injected into the boiler furnaces to satisfy the local authorities. They had tried scrubbing it with active carbon, but the oxygen content (11%) was sufficient to fire the carbon.

By azeotropic distillation of the aqueous condensate from the air coolers, an acid concentrate containing 79.5% formic and 8.7% acetic acids had been obtained which it was intended to use for preserving cattle food.

Although a number of uses were developed for the $C_4 - C_9$ acids, the main application was as modifiers in the manufacture of glyptal resins. Dicarboxylic acids produced by oxidation of these acids with nitric acid in the presence of vanadium pentoxide were found to be suitable for the preparation of nylon polymers, but the yields of acids so far obtained were not high enough to make the process practicable for industrial purposes. Dr. Kürzinger, of Oppau, stated that the $C_4 - C_9$ acids were being used for manufacture of plasticizers either as the acid component of esters with higher alcohols, or by hydrogenation to the corresponding alcohols and esterification with phthalic acid.

One of the main uses of the $C_{18} - C_{22}$ acids ("after runnings") was in the preparation of greases and wire drawing lubricants.

The main use of the residue from the distillation of fatty acids was in the lacquer industry. Although heating the residue to a high temperature in vacuo produced a hard, brittle resin or gum-like product, lacquer manufacturers preferred the untreated distillation residue. If the residue is dissolved or dispersed in methyl alcohol and then neutralised with caustic soda a dark coloured colloidal solution is obtained which found use as a binder for pigments in camouflage paints and was sold for this purpose to Herberts of Wuppertal.

The C₁₀ - C₁₄ fraction of acids was used by the I.G. as an emulsifier in the manufacture of Buna rubber.

The unsaponifiable matter which is separated from the oxidation product and normally is returned to the oxidation vessels, contains alcohols. Henkel had not succeeded in recovering these alcohols, but had converted them into the corresponding fatty acids by heating the crude U.S.M. with 5 - 10% excess of NaOH (based on hydroxyl number) in a closed vessel to 200 - 250°C. The product was then distilled in vacuum and the soaps obtained as a residue. It was stated that this might give better yields of soap acids than returning the material to the oxidation vessels.

At Oppau, the "U.S.M.-II" recovered from the crude soap was distilled, and the fraction distilling below 280°C., which contained 50% of alcohols and ketones was hydrogenated under pressure to convert the ketones to alcohols. The product was then esterified with phthalic acid and used as a plasticizer without separating the paraffinic material. This had been carried out on a large scale, using batches of 50-100 t.