## The Oxidation of Hard Wax.

An emulsifier for use in the paint industry, sold under the trade name 'Parestol', was manufactured by Rheinpreussen at Moers-Meerbeck by the oxidation of crude wax, m.p. 75 - 80°C., extracted from the Fischer-Tropsch catalyst. The process was as follows:-

The wax is filtered to remove catalyst dust and then heated to 160°C. by steam coils in an aluminium vessel 2.5 m. high by 1.5 m. diameter. Air is then blown through distributors fitted in the bottom of the vessel at a rate of 100/cu.m./h./100 kg. wax. No catalyst is used, and after 1 to 2 hours induction, the reaction starts (indicated by a rise in temperature) and the steam is cut off. The oxidation then proceeds at a temperature of 120°C. with a constant rise in acid number. After 10 - 12 hours the acid number reaches 60 and after 15 hours, 75. This is the normal end point for preparing emulsifiers for use in the paint industry, but the acid number can be increased, if desired, to 120. At the specified air rate, no steam is required to maintain the temperature but at lower air rates, some steam heating must be used. From 100 kg. of wax, 105 kg.of product, acid no.75, sap. no.140, softening point 40 - 50° C., are obtained. The crude product was sold, without further treatment, to Herberts of Wuppertal and Wiegand of Oberhausen for the manufacture of oil-bound distempers and cheap camouflage paints. It can be used for the preparation of ointment bases and other pharmaceutical products. The cost of production is given as 35 Rpfg./kg. based on a cost of 30 Rpfg./kg. for the catalyst wax used as raw material. The annual production was 1,200 t.

The blow-off gases were cooled and low-boiling acids (below $C_{11}$) were recovered and sold for use in the leather industry.

According to Dr. Sauter, the catalyst wax obtained from the Brabag (Ruhland - Schwarzheide) plant was oxidised in aluminium vessels by blowing with air at 110°C. in the absence of catalysts on a scale of 5 t.per day. There was no noticeable induction period and an acid number of 50 - 60 was reached in 36 hours. The crude product was marketed under the name "Emulgierwachs P.S." by the Paraffin Verwertungsgesellschaft ( a company founded by I.G. Farben and Brabag) for use, after saponification, as a textile impregnant and constituent of ointment bases and lubricating greases. An excellent emulsion for sulphonamide ointments was obtained by blending equal parts of the saponified product, water, and the ointment base described on page 147.

This product (Emulgierwachs P.S.) must have been almost identical with the Parestol made by Rheinpreussen.

## The "O.P." Process.

As reported in early CIOS Reports, Ruhrchemie had developed to the pilot-plant stage a process for obtaining emulsifiers (similar in general properties and utility to Parestol and Emulgierwachs P.S.), in which their Hartwachs was oxidised with nitrosyl sulphuric acid. The products were designated "O.P.3", "O.P.32" etc. This work was carried out by Dr. Velde, who is no longer employed by Ruhrchemie, but a survey of his work has been prepared by Dr. Clar of Ruhrchemie and this constitutes the best account of the process yet obtained. ( 1 ).

Velde has always claimed that the fatty acids present in these products were of similar length to the original wax, but Dr. Büchner, head of the analytical laboratory, stated that Velde based this claim on the acid number etc., of the product after extracting unsaponifiable matter with heptane, but since the latter does not remove the higher hydrocarbons, his low acid number was not due to long-chain fatty acids but to hydrocarbon impurities. Büchner claims that by extraction of the crude "O.P.3" with 80% ethyl alcohol at the boiling point he removed 80% of the fatty acids present and was able to prove that these were all in the range $C_{10}$-$C_{18}$. Ruhrchemie therefore believe that the O.P. process if the most efficient way of producing soap acids by wax oxidation, as very few by-products are formed. They claim that oxidation of the hard wax by nitrosyl sulphuri acid gives a higher proportion of short-chain acids than oxidation of the "block wax", m.p. 50 - 52°C.

Catalysts were definately harmful in the oxidation of the waxes but might be of value in the oxidation of the Diesel oil. Presence of olefines was detrimental to the process.

Ruhrchemie definitely considered that the nitrosyl sulphuric acid process was superior to the chromic acid process which they had also studied. They claimed that this opinion was not biased by the fact that they were owners of a nitric acid plant.

## Greases.

Dr. Kölbel, Rheinpreussen, had prepared in experimental quantities a product designated as "P.C.F." which was claimed to be a high grade high-pressure bearing grease. It was compounded according to the following formula:-

100 parts chlorinated catalyst wax (5 - 30% Cl)
4.4 parts sodium salt of $C_{20}$ fatty acid from oxidation of catalyst wax
10 parts calcium carbonate
1.1 parts calcium hydroxide

For hard greases, wax with a low chlorine content was used and for soft greases one of higher chlorine content.

## Fatty Acids via the OXO Process.

Ruhrchemie had investigated several methods of preparing fatty acids suitable for soap manufacture from the $C_{10}$ - $C_{17}$ Fischer-Tropsch olefines via the OXO reaction. They tried out the process of oxidizing OXO-aldehydes by air on a semi-technical scale. A batch of 80 kg. of crude OXO aldehydes is stirred in a 100 litre mixer with 20 - 25 kg. $Na_2CO_3$ in aqueous solution and air blown through the mixture for 8 hours. The product is a stiff paste containing the paraffins from the original raw material used in the OXO reaction, soap and sodium carbonate solution. It is then treated with dilute ethyl alcohol and maintained at 60 - 80°C. and $p_H$ = 9.1, when the paraffins can be separated off, the soap salted out and the fatty acids recovered by splitting with mineral acid. A cheaper process is to heat the paste in a mixer to 170°C. and distil off the paraffins and water, leaving a dry mixture of soap and soda which can be used directly as a soap powder.

They also tried the fusion of aldehydes, alcohols and esters with alkalis. The crude aldehydes are mixed with the theoretical amount of caustic soda and heated in an autoclave under 5 atm. nitrogen pressure to 320°C. The pressure rises to 50 atm. due to evolution of hydrogen. The crude soap is obtained by distilling off the hydrocarbons, but as it contains traces of catalyst from the OXO reaction, it must be split with mineral acid and the free fatty acids recovered. The yield is 80 - 85% of theory. Alkali fusion of alcohols is carried out in a similar manner but the product is inferior to that obtained from the aldehydes. The best product, however, is obtained by alkali fusion of the esters, obtained by the Cannizzaro reaction from the aldehydes, because they can be readily purified before carrying out the fusion process.

Soap can be produced by direct alkali-fusion of the high boiling fractions of primary products, obtained by synthesis with iron catalysts, as these products contain a large proportion of oxygen compounds.

The final soap in all cases is deodorised by heating the dry material in a stream of air.

The method of analysis of olefines involving oxidation with nitric acid, sp. gr. 1.25 - 1.30, devised by Dr. Rottig of Ruhrchemie, can also be applied to the preparation of fatty acids in the soap-making range. It is advisable for this purpose to use 50 - 100% excess of $HNO_3$ which, however, can be recovered.

To obtain suitable olefines for this process a method of dehydrogenation of paraffins was developed which gave a predominance of olefines with the double-bond in a mid-chain position. The method is as follows:-

Paraffins in the range $C_{20} - C_{40}$ are melted and mixed in a heated feed hopper with bromine (one mole/mole paraffin) and passed into a reaction tube containing activated alumina or aluminium silicate. The upper part of the tube, maintained at 200 - 400°C., acts mainly as a preheating zone and the lower part (at 350 - 450°C.) as the reaction zone. The reaction consists of bromination followed by de-bromination and shift of the resulting double-bond towards the centre of the chain. The throughput used is 10 - 20 volumes liquid feed per volume of catalyst per hour and an absolute pressure of 100 - 360 mm. mercury or even lower is necessary.

For equi-molar proportions of bromine and hydrocarbon the yield of olefines is 50 - 60% of theory. Using 1.5 moles bromine/mole hydrocarbon the yield rises to 70 - 80%. Unchanged paraffin and undecomposed bromo-compounds (about 5%) can be recycled and the HBr can be reconverted to bromine by oxidation with air over a tungsten catalyst. The losses of hydrocarbon material are of the order of 3 - 5%. For $C_{35} - C_{40}$ paraffins the composition of the olefines obtained was:-

60 - 75% with the double bond between $C_{16}$ and $C_{20}$
10 - 15" " " " " " $C_{12}$ " $C_{16}$
10 - 30% " " " " " $C_{1}$ " $C_{12}$

## Detergents.

The relative merits of the various methods of preparing detergents from the primary products of the Fischer-Tropsch process were discussed with the chemists of Ruhrchemie and Henkel and with Dr. Schwen of I.G. Farben., Ludwigshafen.

The sulphation of olefines was considered first, and Dr. Rottig of Ruhrchemie described the process he had used as follows. A $C_{12} - C_{18}$ fraction, containing a high proportion of $\alpha$-olefines, is treated with fuming sulphuric acid with intensive stirring at a temperature maintained between -5°and +5°C. The acid contains 5 - 10% excess $SO_3$, and a 10 - 20% excess of acid, calculated on the olefine content of the hydrocarbons, is used.

After 30 to 60 minutes, the temperature is allowed to rise to the room level and the mixture is neutralised with caustic soda (30 - 40%) to $p_H$ 10 to 10.6 taking care to maintain the temperature below 50°C. The unattacked paraffins are then extracted with hexane. Very little polymerisation takes place, if the temperature during the sulphation has been kept low, and the yield of sulphate ester should be 90 - 95% of theory.

Henkel, however, stated that the yield in this process was only 70% of theory and that the separation of the paraffins from the esters was a difficult and expensive process.

The products are esters of secondary alcohols and although their detergent properties are very good they cannot be obtained as dry, free-flowing powders, and Henkel found that they could not handle them in their filling machines for soap powders. Dr. Schwen, however, considered direct sulphation of olefines the best method of making detergents from Fischer-Tropsch oils, and that by the use of suitable machinery there was no difficulty in incorporating the products in soap powders.

Ruhrchemie considered that a disadvantage of the sulphated olefines was the high $p_H$ (10) at which they must be used.

OXO alcohol sulphates are also excellent detergents. The OXO alcohols are primary ones and give sulphate esters which are obtainable as dry powders and can be used at $p_H$ 7 and are therefore suitable for the washing of delicate fabrics. Ruhrchemie consider that the OXO product was superior to that derived from natural alcohols due to the greater range of chain length. Primary alcohol sulphates are more stable to heating than the secondary alcohol product, but should not be used at temperatures much in excess of 60°C. Both Ruhrchemie and Henkel considered that, starting from olefines, the production of alcohols by the OXO process and their conversion to sulphates was a more economic process than the direct sulphation of the olefines, in view of the greater value of the product.

The hydrocarbon sulphonates prepared by the Mersol process were inferior washing agents to the alcohol sulphates, were not obtainable as dry powders and work only in alkaline solution. They are, however, stable at 100°C. and can therefore be used in boiling solutions and are cheap to produce. The latest type ( ersol H), prepared by stopping the sulpho-chlorination after 30 - 40% conversion, is an improvement over the early types whose washing efficiency was impaired by presence of di- and poly-sulphonates. Even with the improved product, the washing efficiency is low compared with other sulphonate detergents such as Igepals, because the $SO_3H$ group occurs at random along the chain and is not restricted to the desired terminal position.

In general, Dr. Schwen stated that none of these detergents could be used in tablet soap and although they could be used satisfactorily for many purposes in laundry work they were unsuitable for washing cotton goods. Repeated use of any of these products, even the sulphonated primary alcohols, caused a grey colour to develop on cotton due to the absence of colloidal matter to "float-off" the dirt. This could be partly, but not entirely, overcome by adding 2% of Tylose to the washing powder.

Finally a diagram prepared by Ruhrchemie, which summarises the various methods of preparing fatty acids and detergents from the primary products of the Fischer-Tropsch process, is reproduced in Fig. 9.

## Summarizing Flow-Sheet of the Rheinpreussen Works.

In conclusion, as an example of how the synthesis may be conducted and the primary products worked up to readily marketable secondary products, the complete flowsheet for the Rheinpreussen synthesis works is given in Figure 10.