

## Report 8. Interrogation of Dr. Velde

Subject: Oxidation and Chlorination of Fischer-Tropsch Waxes.

Location and Date: Nienburg, May 11 and 12, 1945

Interrogation conducted by: Major D. Morten, British,  
Ministry of Fuel and Power.

Reported by: Major D. Morten.

### General

Dr. Velde, aged 40, educated at Frankfurt-on-Main, was in charge of one of the Ruhrchemie research laboratories at Oberhausen Holten. He was evacuated, and was going to continue his research work at the W.I.F.O. depot at Schaefferhof, five kilometres from Nienburg. He had practically no documents with him, as all his effects and papers had been lost on the railway, but he was quite willing to talk and has made a personal report of his recent work and proposals for future work, which is attached as an appendix to this Report.

The bulk of the work on further processing of Fischer-Tropsch waxes was designed to produce materials which are in short supply, but does not seem to have been pushed with particularly great activity, and, in accordance with general Ruhrchemie practice, seems to have been very departmentalised.

### Oxidation of Waxes

The general purpose was to produce a Montan wax substitute, as Montan wax was in short supply. Such material would be used as an emulsifier, but only gives emulsions of the solid type such as boot-polish, hand-cream, etc. and waterproofing agents for the textile industry. It could also be used to help out the supply of low water-soluble industrial fats. Work would have continued on the separation of the acids with solvents, to find more applications. The process of manufacture was as follows:- The feed material was a residual hard wax of 90°C. melting point. Lighter distilled grades, melting point 30°/35° and 50°C. were used to meet normal wax requirements. This residual wax had a molecular weight of 600, which means a carbon chain length of about 40, almost all of which was in straight chain form.

The wax is melted and heated to 125°C. and stirred with concentrated nitrosyl sulphuric acid, the proportions being 75 kilos of wax, 15 litres of acid, for a period of 8 to 12 hours. The best material for conducting this reaction is enamelled cast iron. During the process of the reaction, nitrous gases, produced from ammonia oxidation and containing about 8% of  $\text{NO}_2$ , are bubbled through the mixture. This gives a material of mixed molecular weight, but approximately  $\text{C}_{20}$ , of an acid value of 60/70 or even higher. The mixture is neutralised with KOH, using a solution of about 30/40% concentration, and the unreacted paraffins are extracted with S.B.P., boiling point about 90°C. It was stated that 100 kilograms of wax would give a yield of 80 kilograms of pure acid, of acid value 140/150. This was obtained by recycling the unchanged wax.

The research started in 1940/41, but although the process appeared to have been successful it was never put into large-scale production. The experimental plant produced about 3 tons of raw acid per month, known as OP.3; the purified form was known as OP.32. The acids were yellow in colour and could be purified with sodium dichromate, though both the pure and impure form had a nitrogen content of about 0.5%  $\text{N}_2$ . No work had been done by Velde on the production of edible fats or soaps from these acids.

### Chlorination of Wax

The feed material here was a range of Fischer-Tropsch waxes from 30° to 90°C. melting point. Apparently there was no interest in the chlorinated material as such, and this step in the process was merely used to produce olefins which could either be oxidised with dichromate, or sulphated, or alternatively used for the production of synthetic lubricating oils. Velde had done some work on this latter process, but this was apparently unknown to Clar, who was interviewed later and was working on synthetic lubricating oils. Velde had started with a wax of about 30° melting point, and produced therefrom by chlorination and dechlorination olefines of the same boiling range, i.e. 300°/400°C. These had been polymerised with aluminium chloride to give an oil of an average viscosity of 50°Engler at 50°C., with a viscosity index, given by a Pole height of 1.6, equivalent to 110+.

For the chlorination process, using a distilled wax of boiling point  $300^{\circ}/400^{\circ}\text{C.}$ , the wax was melted and heated to  $50^{\circ}/80^{\circ}\text{C.}$  and chlorine passed-in in the dark. Only glass apparatus was used on a scale of 5 litres. The olefin was prepared from this, using a vapour-phase process at a temperature of about  $350^{\circ}\text{C.}$  Two types of catalyst were available: (a) natural, Stuttgarten Masse; (b) artificial, highly heated aluminium silicate. It was stated that this catalyst was prepared at a temperature of  $1,000^{\circ}\text{C.}$  and must be sintered. It was finally prepared in small lumps of 2 to 3 mm. size.

The olefins produced would be of the  $\text{C}_{16}/\text{C}_{27}$  range, and were sulphated with 96% sulphuric acid. Dr. Valde does not know the exact proportions of the yields owing to the absence of his notes. The work was not finished, and sulphation experiments were in hand at various temperatures from below  $0^{\circ}\text{C.}$  to  $35^{\circ}\text{C.}$ , to determine the best reaction conditions. The sulphated mixture was neutralised with caustic potash or soda and the unsulphonated material extracted with petroleum ether. The finished materials were both oil and water soluble, and gave good emulsions for cutting and soluble oils without the addition of any other emulsifiers such as alcohols or fatty acid.

Nothing had been started in the way of research on the production of higher alcohols, but this was one of the projects planned for the work at Nienburg.

Work had been carried out on the oxidation of olefines by a mixture of sodium chromate and sulphuric acid, but it appeared that the lack of electrolytic apparatus for the recovery of the chrome sulphate had proved too much of a difficulty for much progress to be made.

The other problems on which work was to be carried out at Nienburg were :-

- (1) Separation of raw wax by selective solvent treatment instead of by distillation.
- (2) Further study of the oxidation of wax to cover the full range of waxes and to be extended to the Fischer-Tropsch diesel oil fraction.

- (3) Production of lubricating oils and cutting oils from soft paraffin by chlorination/dechlorination and either polymerisation or sulphonation.
- (4) Further work on the Fischer-Tropsch synthesis, using pressures up to 6 atmospheres, particularly the effect of methane in the synthesis gas. This seemed to be of the nature of the further understanding of the general mechanism of the reaction with a view to improving the yield, reduction of methane, etc., but carried out independently of the catalyst. It was proposed to use the normal cobalt/magnesium/thorium catalyst.
- (5) Work on the waste water from the Fischer-Tropsch plants, which causes considerable corrosion difficulties.
- (6) Development of apparatus for measuring vapour-lock tendency.

## Appendix to Report 8

(Translation of a Report Prepared by Dr. Valde)

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13th May, 1945.

### A Report on the Work carried out in the Research Section of the Plant Laboratory K.W.

#### Oxidation of Paraffin Wax

The oxidation of paraffin wax was carried out by us to provide both emulsifiers and a softening material for I.G. waxes and Montan wax which could no longer completely satisfy the increasing demand for wax acids owing to the shortage of natural waxes.

The starting material for the experiments was R.B. hard wax with a melting point of about  $90^{\circ}$ , slab paraffin with a melting point of  $50/52^{\circ}$  and to a small extent also, soft paraffin, but since the particularly required high molecular weight acids could only be derived from R.B. hard wax the tests on these two materials were carried out only to a small extent and the R.B. hard wax was preferred as the starting material. The following results apply mainly to this product.

As an oxidising agent we used not air, in spite of its wide availability but chemical means so that the first tests were carried out with a mixture of sodium bi-chromate and sulphuric acid. We succeeded in converting hard paraffin wax into fatty acids by repeated treatment at a temperature between  $100/105^{\circ}$  with mixtures of bi-chromate and sulphuric acid in fixed amounts. The results of these tests were nevertheless unsatisfactory. The acid value obtained after 5-fold oxidation amounted only to 35.

Improved results were obtained when the paraffin wax was first chlorinated to a chlorine content of about 5/6%; then the chlorine was split off by thermal treatment at  $350^{\circ}$  and the resulting mixture of olefines underwent oxidation with chrom-sulphuric acid in the same way as was applied to the

paraffin wax. By this we obtained with only a 2-fold oxidation an acid value of the order of magnitude of 80/90. The paraffin wax was in this test converted to the extent of about 50% into acids.

In the oxidation with chrom-sulphuric acid the bi-chromate added produces chromium sulphate which can be further converted to bi-chromate by anodic oxidation. This oxidation can be smoothly carried out.

However, since it was extremely difficult to obtain the necessary equipment for the anodic oxidation of chromium sulphate, other methods of oxidising the paraffin wax were investigated. Satisfactory results were thus obtained by oxidation with nitrous vitriol. The nitrogen dioxide can be obtained either pure or in the concentration resulting from the oxidation of ammonia, viz: about 8/9%.

The oxidation was carried out in the following way:- In a large agitator capable of being heated, 75 kilograms of paraffin wax were melted and the factory nitrous vitriol introduced. Then with continuous stirring and introduction of nitrous vitriol, 15 litres of nitrosyl sulphuric acid were added. After circulation for about ten hours the process is stopped and the reaction products drawn off. After separation of the nitrosyl sulphuric acid, washing of the acid residues remaining in the reaction products and drying, 70/71 kilograms of crude acids with an acid value of 70/75 remain. These crude acids, reference OP.3, still contain about 50% of paraffin wax. For the preparation of the pure acids the crude acids are saponified with high concentration alkali, the resulting soaps dried, purified and the unaltered paraffin wax removed by extraction with a benzene fraction with a boiling point of about 90°. Since the paraffin wax obtained by extraction practically corresponds to the starting material it can be further submitted to oxidation. By this means from 100 kilograms of paraffin wax about 80 kilograms of pure acids were prepared with an acid value of about 140/150. The pure acids contain about 0.5% of nitrogen. Just as the starting material is not a simple product but has an average carbon number of 40/45 corresponding to a molecular weight of 600, so the acids consist of a

whole number of fatty acids of which the acids with carbon numbers over 20 predominate. The pure acids have a melting point of 80/85°.

Fields of application for the acids are inter alia consistent fats with very special properties, for example these fats are particularly water insoluble impregnants for the textile industry for the preparation of water resistant fabrics, printing colours, etc.

By partial saponification we succeeded in preparing very effective emulsifiers which enabled the preparation of solid and semi-solid emulsions. Besides oil, benzine, diesel oil and paraffin can be emulsified with water. Fields of application for the emulsions are, for example, emulsified shoe creams or emulsified floor creams, emulsion lubricants, drilling lubricants. Some of the products mentioned can also be produced with the crude fatty acids previously referred to as OP.3.

After bleaching OP.32 which can be effected by a mild oxidation with bichromate-sulphuric acid, a stable white product is obtained with the help of which skin cream types of emulsions can be produced.

#### Chlorination of Paraffin Wax.

As briefly mentioned in the oxidation of paraffin wax, chlorinated hard paraffin wax is an intermediate stage in the oxidation with bichromate-sulphuric acid, which is easily prepared by thermal chlorination at slightly over the melting point. In a further continuation of these tests it was ascertained that the lower molecular weight paraffins, e.g. soft paraffin, can be just as easily transformed to chlor-paraffins by thermal chlorination. The starting material is also necessary in order to obtain the products selected by us as the object of our investigations, i.e. lubricating oil with outstanding properties and cutting oils.

For these tests the starting material was a synthesis paraffin with a boiling range between 300 and 400° corresponding to C17 to about C24 or of 300/450° corresponding to C17 to about C27, the melting point of the mixture being about 30/35°. This soft paraffin was treated with gaseous chlorine at about 100° with stirring, until the chlorine

absorption amounted to about 26%, then the process was stopped and the chlorine split off later. The splitting off of chlorine can be carried out either in a purely thermal batch process at about 350° or in a continuous process by introduction of chlorine containing materials with the addition of certain catalysts. We have found of particular value in this connection SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> containing materials, e.g. the product of Stuttgarter Masse (Schuhmachersche Fabrik, Bietigheim). A particular characteristic of all the catalysts used is a definite sintering which is obtained by preheating to about 1000°.

From materials of this type we obtained on the introduction of chlorine containing products at about 350°, a mixture of olefines with extraordinarily high iodine values. The olefin mixture obtained by chlorination and dechlorination corresponds very largely in its molecular construction to the original paraffin used. Cracking and polymerisation occur only to a small extent if the dechlorination is carried out correctly.

This olefin mixture can be further converted by polymerisation with aluminium chloride into lubricating oils which have viscosities over 50°E at 50°C. and a "viscosity pole height" of about 1.6 (viscosity index not determined but over 100) or one can produce sulphonates by sulphonating with concentrated sulphuric acid and neutralisation, these permitting the manufacture of outstanding cutting oils. Tests on the cutting oils have only just been begun. The reactions involved are sulphonation, neutralisation, extraction of the unsaponifiables and drying. The fluid sulphonates obtained are oil and water soluble and produced stable emulsions capable of extreme dilution.

## Work on Benzine

### (a) Refining of Benzine

In the journal 'Öl und Kohle' Vol. 37, 1941, page 143, an article of mine appeared under the title "Methods of Refining the Primary Products of the Synthesis Process and their application to the working up of Crude Oil", in which is described a process which I developed some years ago for increasing the octane number of benzine containing olefines by



catalytic treatment which is carried out without appreciable loss of product. In this the benzine is led at a high temperature but below the cracking temperature over a bleaching earth catalyst which has the properties of causing isomerisation. Apart from a small amount of true isomerisation which leads to branching, in this process the double bonds in the olefines are displaced from the ends of the molecule to the middle whereby the octane number can be appreciably raised, thus, for example, octane number increases of 10-12 points were obtained according to the olefin content of the starting material. Also in the case of petroleum cracked benzines octane number increases of 5/6 points were obtained. Further details can be obtained from the article mentioned.

(b) Behaviour of Primary Benzine on Storage

Further investigations concern the storage stability of primary benzine and cracked benzine from primary products, in which the most important point is that an increase in peroxide content was observed without the commencement of gum formation. By the addition of inhibitors the alteration on storage can be easily prevented. A publication of mine on this subject appeared in "Öl und Kohle" 1943 under the title "On the dependence of octane number on peroxide content of synthesis benzine"

(c) Gassing of Benzine

Jointly with the Director of our Testing Station, Dr. Schaub, work was carried out on the gassing tendency of fuels and an apparatus developed in order to investigate gassing in motor spirits. A publication on this work followed in "Automobiltechnischen Zeitschrift 1941". A further publication was in preparation but could not be completed.

(d) The working up of Paraffin Wax by Distillation and Selective Extraction

At the Ruhrchemie the paraffin was divided by fractional distillation, pressing and sweating, into soft paraffin, slab paraffin and hard paraffin.

The crude paraffin produced in the synthesis process termed "oven" paraffin was first topped at 320° in a continuous distillation and by this means practically all the diesel oil components removed. The residue was subjected to a vacuum distillation

and cut at 450°. The residue was a hard paraffin with melting point 90° and from the distillates the slab paraffin components with a melting point of 50/52° were obtained by pressing and sweating. The remainder consisted of soft paraffin with melting point of 30/35°.

In my research laboratory the question was investigated as to whether it was possible to prepare hard paraffin and slab paraffin from oven paraffin without distillation, by selective extraction with solvents. As solvents the most important were acetone and benzin of different boiling ranges. The work has only just started so that no final process has yet been fixed.

(Signed) VELDE